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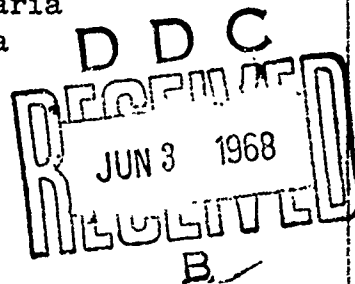
DEFENSIVE SECRETIONS OF ARTHROPODA

Final Technical Report

By

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DEFENSIVE SECRETIONS OF ARTHROPODA
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PART I - INTRODUCTION.

Chap. 1 - Aims.

In this study we intend to set out data and considerations regarding Arthropoda defensive secretions and the chemically well defined substances of which they are composed.

Biological and chemical researches are part of the study of Arthropoda defensive secretions. The sector where researches were most advanced in the past was biology, whereas chemistry had made little progress until about twenty years ago.

We now believe the situation to be the following; biological studies have made clear that the offensive and defensive function of particular substances is very widespread in the large group of Arthropoda; the chief zoological groups comprising interesting species are known, and, for the most part, the organs which produce the defensive substances; physiological activity tests have also been made in many cases with isolated substances or with variously purified extracts. This opened an extremely vast field of work for chemists, but chemical researches were undertaken late compared with the development from biological investigations. In fact only in the last twenty years have chemists turned once more with renewed and deepening interest to this kind of study. There are many reasons for this. The biological observation regarding the production and the employment of defensive secretions and anatomical research of productive organs precede the chemical study of the secretions themselves; the initial phase of research is much easier than collecting a sufficient mass of animals, and above all than the subsequent extraction of substances for chemical studies. This second part also implies a close and intense collaboration between biologists and chemists which is not easy, and the availability of huge sums for financing the mass of work necessary to complete chemical researches; in fact these generally require enormous quantities of

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material and long, complicated extractions followed by difficult structural studies.

Over the last twenty years the technique of chemical research has made such great strides as to allow for definite results with smaller quantities of material, sometimes with just a few specimens of an insect species; this progress is of fundamental importance for the development of the present phase of research. New chemical research conditions make collaboration between biologist and chemist easier, as indispensable as always. These facts and the interest shown in results already obtained explain the recent increase in researches also in the chemical field.

For the above reasons, a comparison between the mass of important work revealing new and significant facts in various biological fields (morphology, anatomy, physiology, ecology) - and that of equal value carried out in chemistry - would certainly show that the biological publications are much more numerous than those of a strictly chemical nature. This means that chemists ^{have} a wealth of preliminary indications regarding materials and subjects not yet exploited.

If one makes a comparison between the chemical studies of Arthropoda and vegetable venoms quite different results are revealed: we have a sufficient knowledge of a relatively small number of the vegetable species known (numbering about 330.000) whereas our knowledge is very limited regarding a large number of known Arthropoda species (about 884.944 species). The reasons for this can easily be divined.

In my part of the research, begun in 1947 and carried on with various and invaluable collaborators, the following 15 new natural substances were found and isolated for the first time:

1. iridomyrmecin (1947) from the worker and queen of Iridomyrmex humilis Mayr (Hymenoptera Formicidae);

The isoiridomyrmecin, chemically obtained (1948) from the iridomyrmecin in the research with Fusco, Trave and Vercellone (bibl. 232,

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- 230, 128, 129) has been found as a natural products in ants by Cavill and Co. 1956 (60).
2. pederin (1963) from the adult beetle Paederus fuscipes Curt. (Coleoptera Staphylinidae);
 3. iridodial (1956) from the workers of Tapinoma nigerrimum Nyl. (in the researches by Trave and Pavan (339)) and from workers of the genera Dolichoderus and Iridomyrmex in the contemporaneous researches by Cavill and Co., (60) (Hym. Formic.);
 4. dendrolasin (1966) from the worker of Lasius (Dendrolasius) fuliginosus Latr. (Hym. Formic.);
 5. pseudopederin (1961) from the adult beetle Paederus fuscipes Curt. (Coleopt. Staph.);
 6. pederone (1967) from the adult beetle Paederus fuscipes Curt. (Coleopt. Staph.);
 7. cossin A (1966) from the larva of Cossus cossus L. (Lepidoptera, Cossidae);
 8. cossin B " " " " " "
 9. cossin C " " " " " "
 10. cossin 1 " " " " " "
 11. cossin 2 " " " " " "
 12. cossin 3 " " " " " "
 13. cossin B₁ " " " " " "
 14. cossin C₁ " " " " " "
 15. zeuzerina (1967) from the larva of Zeuzera pyrina L. (Lepidopt. Cossidae):

In analogous researches carried out by other authors the following new substances were isolated as natural defensive products:

16. dolichodial (1960) from the worker of Dolichoderus (Hymenoptera Formicidae);
- 17.-18. cybisterone and 6-dihydrocybisterone (1967) from genera Cybister (Coleopt. Carabidae).

Chemical and biological investigations were carried out on these products new to chemical literature. There derived therefrom studies and practical results in the field of synthesis of analogous products (for example, isoiridomyrmecin, periidrodendrolasin, etc.).

These considerations induced me to make an inventory of the zoological area hitherto exploited and the results obtained in the chemical sector. Therefore, in this paper, after introducing the subject and placing the Arthropoda group in the animal kingdom (Chap. 5-9), I shall give a list of the composition of the defensive secretion for each animal species (Chap. 10-17), and then, for each substance defined, a list of the animal species in whose secretions, it has been found (Chap. 18-20).

I also thought it opportune to devote a special chapter to each of the new substances, or groups of similar new substances, in which I have collected and arranged the available data (Chap. 21-28).

Lastly, in the concluding chapter, I have tried to see the subject of Arthropoda defensive secretions in the light of comparative, chemical, biological, biochemical and ecological findings, as might be seen by a naturalist considering the chemical aspects of these problems as primary factor of our knowledge of living beings generally and particularly of defensive secretions.

Chap. 2 -Precedents.

There are already remarkable works, both partial and comprehensive, on the subject of this paper. Among the most recent papers on chemical and biological synthesis I will mention that by Kaiser and Michl (1958), two of my notes (1958) and that by Eisner and Roth (1962), and the recent note of Weatherston 1967. It is not possible to quote here all the contemporary researchers who have made remarkable contributions in this sector: I shall refer to them in the literature. I shall only mention, among the most active groups of researchers generally, those of Blum and Coll., Cardani and Coll., Casnati and Coll.; Cavill and Coll.; Eisner and Coll., Fusco, Trave and Coll.; Korte and Coll.; Quilico and

Coll.; Schildknecht and Coll.

Many important synthetic studies on the subject can be found in biological literature, amongst which for example Phisalix (1922), Fredericq 1924, Pawlowsky 1927, Deegener 1928, Maas 1937. A volume of literatura on animal venoms was published by Harmon and Pollard, 1948.

Recently meetings and international congresses have taken place on animal venoms where the sector regarding Arthropoda was granted an important or exclusive part (Venoms, 1956; XI International Congress of Entomology, Vienna 1960, Symposia no. 3 and 4; International Symposium on Animal Venoms, Sao Paulo 1966: First Int. Symposium on Animal Toxins, Atlantic City 1966).

Chap. 3 - Remarks.

Frequent mention is made in the literature on defensive secretions of Arthropoda of substances contained in secretions which are chemically defined but where solid documentation is lacking. Also Roth and Eisner 1962 show this. It is quite clear we cannot take such data into consideration in our synthesis; they might, however, serve to show a field of work to be considered anew. A typical example is that of the toxic substance of Coleoptera Staphylinidae of the Paederus genus, which several authors have first supposed to be identical with cantharidin; others then claimed it was identical (a fact which was repeated for several decades in world literature), whereas it was a product which we proved to be new and which we called pederin, with physical and biological properties quite different from those of cantharidin and an entirely different structure. Another example is that of the odorous products of the anal glands of the Dolichoderinae ants (for example Tapinoma) which in the literature are referred to as amylic and butyric esters, a smell of rancid butter, etc. whereas research by other authors and ourselves have shown it to be methyleptenon, propylisobutylketone, etc.

Throughout this paper we shall frequently refer to the zoological systematics summarized in Tables 1-4. When I refer to the Myriapo-

da group I intend the entire Pauropoda, Diplopoda, Chilopoda and Symphyla.

Chap. 4 - Acknowledgments.

My interest in the studies on insect defensive secretions goes back to 1947 when I discovered and isolated iridomyrmecin. Since then - as we have seen - various other new natural substances are derived from the development of my researches. These have been carried out contemporarily as activity of the Istituto di Anatomia Comparata dell'Università di Pavia, directed by Prof. M. Vialli, and of the Istituto di Entomologia Agraria dell'Università di Pavia, of which I am the Director. In the course of these researches, which are still being developed, I have had invaluable collaborators from the University of Pavia and other Italian and foreign universities. I found the help of my assistants in the Institute under my direction to be precious: Dr. A. Baggini, Dr. A. Gabba, Dr. M. Valcurone. I should particularly like to mention my colleagues prof. G. Bo, A. Nascimbene and E. Testori, for their kind collaboration during the first years of research. The Italian Company (Soc. Montecatini, Soc. Montedison, Soc. Farmitalia) and the Consiglio Nazionale delle Ricerche have furnished me with basic equipment.

The Muséum National d'Histoire Naturelle of Paris helped me in facilitating my stay at the Station Experimentale de La Maboké (Boukoko, République Centrafricaine); the Institut National pour l'étude Agronomique du Congo (Kinshasa) allowed me to carry out profitable study in the laboratories of Yangambi (Kisangani); the Universidad Central de Venezuela, granted me a sojourn at the laboratories of the Facultad de Agronomía de Maracay at Rancho Grande.

Particular importance must be given to the aid received from European Research Office of the United States Government, which allowed me to make invaluable progress.

Important studies have been devoted to the materials deriving from my researches at the Laboratorio medico-micrografico della Provincia di Pavia, directed by prof. L. Bianchi, and at the following Institutes and University Faculties:

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- Istituto di Chimica del Politecnico di Milano, directed by prof. A. Quilico.
- Istituto di Chimica Industriale dell'Università di Milano, directed by prof. R. Fusco.
- Cattedra di Chimica del Politecnico di Milano, directed by prof. C. Cardani.
- Istituto di Chimica dell'Università di Sassari, directed by prof. R. Trave.
- Istituto di Chimica Organica dell'Università di Pavia, directed by prof. P. Grünanger.
- Cattedra di Chimica Biologica dell'Università di Pavia, directed by prof. A. Castellani.
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- Istituto di Microbiologia dell'Università di Milano, directed by prof. R. Deotto.
- Istituto di Patologia e Clinica Medica Veterinaria dell'Università di Parma, directed by prof. I. Vaccari.

PART II - ARTHROPODA: PRODUCERS OF DEFENSIVE SECRETIONS AS CONSIDERED
IN THE WHOLE OF THE ANIMAL KINGDOM.

Chap. 5 - Arthropoda: producers of secretions in the animal kingdom.

In the Animal Kingdom 1.200.000 species have hitherto been counted and systematically described, distributed into 22 Types.

The Type Arthropoda is the most numerous with about 884.944 species described, distributed into 12 Classes:

1. <u>Onychophora</u>	73 species	7. <u>Crustacea</u>	25.000 species
2. <u>Paupoda</u>	50 "	8. <u>Merostomata</u>	5 "
3. <u>Diplopoda</u>	7.000 "	9. <u>Arachnida</u>	33.873 "
4. <u>Chilopoda</u>	2.350 "	10. <u>Pycnogonida</u>	440 "
5. <u>Symphyla</u>	50 "	11. <u>Pentastomida</u>	60 "
6. <u>Insecta</u>	815.763 "	12. <u>Tardigrada</u>	280 "

According to present evaluation, it is presumed that the number of existing Arthropoda species, not yet scientifically described, may be 5-10 times greater than those known at present.

Of this number of species of the Arthropoda Type, less than 10% of those described may be considered producers of defensive secretions, which means at least 82.538 species.

Literature data available show that hitherto chemical definition of certain defensive secretion components has been made for only 426 species of Arthropoda. Naturally, on the other hand, there is a very large number of species which have been ascertained as producers of defensive substances, but about which we have no definite chemical data.

In Table 1 the quantitative data of the species presumed to produce defensive secretions have been comparatively summarized, and also of those for which there are precise chemical data of the secretion components themselves.

Table 1 - Species of Arthropoda described (2), species presumably producers of defensive secretions (3) and species with chemically known secretion components (4).

1. T y p e A R T H R O P O D A	2. presumed no. of species described	3. presumed no. of species produ- cing defensive secretions	4. no. of species with known che- mically defined defensive secre- tions
C l a s s e s			
1. <u>Onychophora</u>	73		
2. <u>Pauropoda</u>	50	] 8.000	
3. <u>Diplopoda</u>	7.000		43
4. <u>Chilopoda</u>	2.350		2
5. <u>Symphyla</u>	50		
6. <u>Insecta</u>	815.763	50.000	342
7. <u>Crustacea</u>	25.000	1.000	2
8. <u>Merostomata</u>	5		
9. <u>Arachnida</u>	33.873	23.538	37
10. <u>Pycnogonida</u>	440		
11. <u>Pentastomida</u>	60		
12. <u>Tardigrada</u>	280		
Totali	884.944	82.538	426

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From the ecological point of view, the 884.944 species of Arthropoda hitherto known are arrangeable in land species and water species. To be precise these are:

- land: Onychophora, Tardigrada, Myriapoda, Arachnida (with the exception of a few limnobioid species of Araneae and Acara), part of Crustacea Isopoda, most the Insecta (with the exception of a few thousands of Coleoptera and Heteroptera): in all at least 860.000 species;
- water (marine or limnobioid): almost all the Crustacea (with the exception of some Isopoda) Pycnogonida, Pentatomida, Merostomata and a few thousands species of Insecta (especially Coleoptera and Heteroptera): in all about 25.000 species.

The species of Arthropoda whose poisonous substances are chemically known, belong mostly to the land species (Insecta, Myriapoda, Arachnida). Of the water species only five species belonging to Coleoptera Dytiscidae have chemically defined defensive substances.

PART III - THE DEVELOPMENT OF CHEMICAL RESEARCHES ON THE DEFENSIVE SECRETIONS OF VARIOUS ARTHROPODA GROUPS.

Chemical research of Arthropoda defensive secretions has taken differing developments according to the various groups. This is in relation to varying frequency of interesting species in various groups, to the degree of importance of defensive phenomena, to the varying possibilities of procuring species for researches. The lines these surveys took are summarized in the following chapters.

Chap. 6 - Chemical research on Diplopoda and Chilopoda poisons.

The Onychophora and Pauropoda are small land animals which are not generally considered to produce poisonous substances.

The Diplopoda (Chap. 10) include the order of Glomerida of which only four species have been chemically studied. Presumably all Glomerida possess active poisonous organs, as certainly do the various European species of the Glomeris genus which we have examined. Polydesmida produce interesting defensive substances which have hitherto been studied in American, African and European species. During our orientative researches of European and African fauna, we have determined at least fifty species producing defensive secretions. Research was carried out as far as defining the venom components of three of these species (Polydesmus collaris collaris Koch, Gomphodesmus pavani Dem., Orthomorpha coarctata Sauss.). Presumably 6.500 species of Diplopoda produce defensive substances.

The group of Juliformia (Chap. 10) which include the Orders Julida, Spirobolida, Spirostreptida and Cambalida, has at least 2.000 species which may practically be numbered among the producers of defensive venoms. From studies carried out hitherto on 26 species it appears that the defensive secretions are mostly composed of quinones. Full research defining the various components was carried out on one of these species (Archilulus (Schizophyllum) sabulosus L.). We have also

ascertained the production of quinonic poisons in 40 species of European, American and African fauna.

Chilopoda (Chap. 10) of which about 2.350 species are known, partially produce poisonous substances which they inject into their prey by biting. The sting of numerous species is also feared by man due to the local effects it produces. The chemistry of such poisons in two species has been studied but research appears to be not yet complete.

Chap. 7 - Chemical research on Insecta poisons.

Of the 31 Orders into which the Insecta are divided (comprising 815.763 species described), the chemical composition of defensive secretions has been studied in 10 Orders, in all 342 species. The Orders in which research has been more profound are: Coleoptera (146 species), Hymenoptera (96 species), Heteroptera (44 species).

Of about the 300.000 species of Coleoptera known, 146 (Chap. 14) have been studied up to date. It is estimated that at least 10.000 species produce defensive substances. Of these we may mention certain of the Staphylinidae (in which, from various species of the genus Paederus, pederin, pseudopederin, pederone have been extracted), as well as Carabidae, Tenebrionidae, and Meloidae which, in this order, have hitherto furnished most of the known data on defensive secretions.

Heteroptera (Chap. 12) comprising 31.000 known species, offer many interesting aspects: in fact, besides the adults with various types of glands producing defensive substances, also the younger forms produce defensive venoms in many species. Reduviidae, too, produce poisonous substances to be injected into their prey by means of the oral apparatus, substances which have been studied as far as the definition of some components only in one case (Platymeris). Also Corixoidea produce poisonous substances injected into the prey by means of the oral apparatus, but these have not yet been studied.

Heteroptera species probably producing toxin secretions, are 26.000.

Hitherto data have been collected from 44 species of Heteroptera permitting us to chemically identify certain components of the defensive secretions.

In the order of Hymenoptera 96 species have been studied out of 200.000 known (Chap. 15); most of these are Formicidae. The venom of Apidae has been studied (especially of Apis mellifera), but presents certain important aspects not yet clarified. Few precise chemical data are known about Vespidae venoms, which are also extremely interesting. The number of species which probably produce poisonous secretions is estimated to be 10.000.

Chap. 8 - Chemical research on Crustacea Isopoda poisons.

The Class of Crustacea (Chap. 16) with 25.000 species described, almost totally water species, includes only two land species of the Isopoda order, whose defensive secretions have been studied. The Isopoda comprise 4.000 species of which numerous land species (perhaps 1.000) producing defensive substances with a complex structure. The defensive secretions of the water species, both lymnobia and marine, are not known.

Chap. 9 - Chemical research on Arachnida poisons.

The Arachnida class (Chap. 17) comprising about 34.000 described species, mostly land dwellers (with the exception of a few Araneae species and part of the Acari), includes at least 23.000 species which are presumably producers of poisonous substances. The two orders with the most interesting venoms are Scorpiones (600 species) and Araneae (20.000 species). The number of species hitherto studied

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is small compared with such vast quantity of material available (37 in all, mainly Scorpiones and Araneae) and precise chemical data on the composition of their venoms are scarce. This is due to the difficulties inherent in the proteic nature of the toxic principles present in the venoms. The study of Arachnida venoms is also interesting from a practical point of view because of the numerous and occasionally serious cases of poisoning in man caused by the sting of Scorpiones and Araneae.

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Table 2 - Number of Arthropoda Onychophora and Myriapoda (Pauro-
poda, Diplopoda, Chilopoda, Symphyla) species described
(2), of the species presumed to produce defensive secre-
tions (3.), and of the species producing chemically defi-
ned defensive substances (4.).

1. Type <u>A R T H R O P O D A</u>	2. presumed no. of species described	3. presumed no. of species producing de fensive se- cretions	4. no. of species with known che mically defi- ned defensive secretions
Cl. <u>ONYCHOPHORA</u>	<u>73</u>		
(<u>M Y R I A P O D A</u>)....	(<u>9.450</u>)	(<u>7.550</u>)	(<u>45</u>)
Cl. <u>PAUROPODA</u>	<u>50</u>	<u>0</u>	
Cl. <u>DIPLOPODA</u>	<u>7.000</u>	<u>6.500</u>	<u>43</u>
Ord. <u>Polyxenida</u>			
<u>Glomerida</u>	500	500	4
<u>Glomeridesmida</u>			
<u>Chordeumida</u>			1
<u>Polydesmida</u>	2.500	2.500	12
Juliformia [<u>Julida</u>	2.000	2.000	4
<u>Spirobolida</u>			9
<u>Spirostreptida</u>			12
<u>Cambalida</u>			1
Sup.Ord. <u>Colobognatha</u>			
Cl. <u>CHILOPODA</u>	<u>2.350</u>	<u>1.000</u>	<u>2</u>
Ord. <u>Geophilomorpha</u>			
<u>Scolopendromorpha</u>	420		2
<u>Lithobiomorpha</u>			
<u>Scutigermorpha</u>			
Cl. <u>SYMPHILA</u>	<u>50</u>	<u>50</u>	

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Table 3 - Number of Insecta species described (2.), of the species presumed to produce defensive secretions (3.), and of the species producing chemically defined defensive substances (4.).

1. Type <u>A R T H R O P O D A</u> Class <u>I N S E C T A</u>	2. presumed no. of species described	3. presumed no. of species producing de fensive se- cretions	4. no. of species with known che mically defi- ned defensive secretions
Ord. 1. <u>Collembola</u>	2.000		
2. <u>Protura</u>	90		
3. <u>Diplura</u>	380		
4. <u>Thysanura</u>	350		
5. <u>Ephemeroptera</u>	1.500		
6. <u>Odonata</u>	4.870		
7. <u>Blattodea</u>	2.500	100	15
8. <u>Mantodea</u>	1.800		
9. <u>Isoptera</u>	2.000	150	4
10. <u>Zoraptera</u>	19		
11. <u>Plecoptera</u>	1.490		
12. <u>Embioptera</u>	149		
13. <u>Grylloblattodea</u>	5		
14. <u>Dermaptera</u>	1.100	150	1
15. <u>Phasmida</u>	2.000	100	1
16. <u>Orthoptera</u>	15.000	500	1
17. <u>Psocoptera</u>	1.000		
18. <u>Mallophaga</u>	2.675		
19. <u>Siphunculata</u>	400		
20. <u>Thysanoptera</u>	3.170		
21. <u>Heteroptera</u>	31.000	26.000	44
22. <u>Homoptera</u>	26.500		
23. <u>Neuroptera</u>	4.670		
24. <u>Mecoptera</u>	350		
25. <u>Trichoptera</u>	4.470		
26. <u>Lepidoptera</u>	120.000	2.000	28
27. <u>Diptera</u>	85.000	1.000	6
28. <u>Siphonaptera</u>	1.100		
29. <u>Coleoptera</u>	300.000	10.000	146
30. <u>Strepsiptera</u>	175		
31. <u>Hymenoptera</u>	200.000	10.000	96
Class <u>I N S E C T A</u>	815.763	50.000	342

Table 4 - Number of Crustacea, Merostomata, Arachnida, Pycnogonida, Pentastomida species described (2.), of the species presumed to produce defensive secretions (3.), and of the species producing chemically defined defensive substances (4.).

1. Type <u>A R T H R O P O D A</u>	2. presumed no. of species described	3. presumed no. of species producing de fensive se- cretions	4. no. of species with known che mically defi- ned defensive secretions
Cl. <u>CRUSTACEA</u> (*)..... (35 Orders)	<u>25.000</u>	<u>1.000</u>	<u>2</u>
Ord. <u>Isopoda</u>	4.000	1.000	2
Cl. <u>MEROSTOMATA</u>	<u>5</u>		
Cl. <u>ARACHNIDA</u>	<u>33.873</u>	<u>23.538</u>	<u>37</u>
Ord. <u>Scorpiones</u>	600	600	16
<u>Pseudoscorpiones</u>	1.000	500	
Pedi- <u>Uropygi</u>	98	98	1
palpi <u>Amblypigi</u>	60		
<u>Palpigradi</u>	20		
<u>Ricinulei</u>	15		
<u>Solifugae</u>	600		
<u>Opiliones</u>	2.340	2.340	1
<u>Araneae</u>	20.000	20.000	19
<u>Acari</u>	9.140		
Cl. <u>PYCNOGONIDA</u>	<u>440</u>		
Cl. <u>PENTASTOMIDA</u>	<u>60</u>		
Cl. <u>TARDIGRADA</u>	<u>280</u>		

(*) A list of the Crustacea Order, mostly formed by water animals (marine or lymnobiis) for which there are no known defensive venoms, is omitted with the exception of the Order Isopoda.

PART IV - THE ARTHROPODA SPECIES PRODUCERS OF DEFENSIVE SECRETIONS
AND CHEMICALLY DEFINED SUBSTANCES.

In Chapters 10-17 I have given a list of the Orders and the Families systematically arranged and, in alphabetical order, the species of Arthropoda producing defensive secretions with one or more chemically known components. The indication of known products is followed by the number or numbers corresponding to the publications listed in Part VIII, Bibliography.

Cap. 10 - Myriapoda Diplopoda and Chilopoda and chemically defined substances of defensive secretions.

(M Y R I A P O D A)

Cl. D I P L O P O D A

Ord. GLOMERIDA

Fam. Glomeridae

Glomeris marginata Vill.

glomerin: 315, 317; glomerin and omoglomerin: 191, 302, 316.

Glomeris conspersa Koch

glomerin, omoglomerin: 302.

Glomeris hexasticha Brandt

glomerin, omoglomerin: 302.

Loboglomeris rugifera Verh.

glomerin: 302.

Ord. CHORDEUMIDA

Fam. Chordeumidae

Abacion magnum Loomis

p-cresol (= p-methyl-phenol): 107, 348B, 363; phenol: 103, 106.

- IV 2 -

Ord. POLYDESMIDA

Fam. StrongilosomidaeOrthomorpha coarctata Sauss (= O. coarctata Sch.)

benzaldehyde, phenol, guaiacol, hydrocyanic acid, benzoic acid:
199.

Orthomorpha gracilis Koch (= Fontaria gracilis Koch, Paradesmus (Fontaria) gracilis Koch, Oxydus gracilis Koch)

hydrocyanic acid: 50, 93, 104, 140, 157, 179, 199, 348 B, 349, 363; benzaldehyde, hydrocyanic acid: 50, 125, 180, 265, 354.

Fam. EurydesmidaeApheloria corrugata Wood

hydrocyanic acid, benzaldehyde: 50, 348 B; benzaldehyde, hydrocyanic acid, mandelonitrile: 104, 105, 108, 118, 157, 363; hydrocyanic acid: 278.

Cherokia georgiana Bollman

hydrocyanic acid: 50, 104, 157, 348 B.

Leptodesmus haydenianus Wood

hydrocyanic acid: 77.

Nannaria sp.

hydrocyanic acid: 50, 104, 157, 278, 348 B.

Pachydesmus crassicutis (Wood)

β -glucosidase + cyanogenic glucoside $\longrightarrow$ hydrocyanic acid, benzaldehyde, glucose, a disaccharide: 32, 363, 363; hydrocyanic acid, benzaldehyde, sugars: 50.

Rhysodesmus vicinus Sauss. (= Polydesmus vicinus Sauss., Pclydesmus (Fontaria) vicinus Sauss.)

glucoside of p-isopropyl mandelic nitrile $\longrightarrow$ hydrocyanic acid, glucose, cuminaldehyde: 32, 104, 218, 363; hydrocyanic acid, glucoside of p-isopropyl mandelic nitrile: 50; hydrocyanic acid, cuminaldehyde: 348 B.

- IV 3 -

Fam. PolydesmidaeGomphodesmus pavani Dem.

D-(+)-mandelic nitrile, benzoic acid, benzaldehyde, hydrocyanic acid, mandelonitrile benzoate: 7.

Polydesmus virginiensis Drury (= Polydesmus (Fontaria) virginiensis Drury, Fontaria virginiensis Drury)

hydrocyanic acid: 61, 179, 180, 195, 199, 265, 354, 363.

Polydesmus collaris collaris Koch

mandelonitrile benzoate, benzaldehyde, hydrocyanic acid: 50, 157, 363, benzoic acid, hydrocyanic acid, benzaldehyde, mandelonitrile benzoate: 4 A; benzaldehyde, hydrocyanic acid: 348 B.

Pseudopolydesmus serratus (Say)

hydrocyanic acid, undetermined components in a mixture: 278, hydrocyanic acid: 50, 104, 157, 348 B, 363.

(JULIFORMIA)

Ord. JULIDA

Archiulus (Schizophyllum) sabulosus L. (= Archiulus sabulosus L., Schizophyllum sabulosum L.)

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 9, 198, 199, 245, 246, 248, 278, 310, 348 B, 355, 363; 1,4-benzoquinone, quinones and their methyl derivatives: 199, 2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone, 2-methyl-hydroquinone, 2-methyl-3-methoxy-hydroquinone: 157, 301.

Brachyulus unilineatus Koch

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 157, 293, 299, 310, 348 B;

Cylindroiulus teutonicus Pocock

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 157, 293, 299, 310, 348 B.

- IV 4 -

Schizophyllum mediterraneum (= Julus terrestris L.)

1,4-benzoquinone: 10, 13, 41, 50, 125, 177, 179, 201, 245, 246, 263, 265, 276, 278, 310, 333 B, 335, 348 B, 363, 1,4-benzoquinone, other quinones and their methyl derivatives: 199.

Ord. SPIROBOLIDA

Chicobolus spinigerus Wood

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 50, 157, 193, 278, 348 B, 363.

Floridobolus penneri Causey

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 50, 157, 198, 278, 348 B, 363.

Narceus annularis Raf.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 50, 175, 198, 278, 348 B, 363.

Narceus gordanus Chamb.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 50, 175, 198, 278, 348 B, 363.

Orthocricus arboreus (Sauss.)

quinones: 363.

Pachybolus laminatus Cook

1,4-benzoquinone, other quinones and their methyl derivatives: 199; 2-methyl-1,4-benzoquinone: 8, 10, 15, 50, 245, 246, 278, 310, 335, 348 B, 363.

Orthocricus sp.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone: 157, 293, 299, 310; 2-methyl-hydroquinone, 2-methyl-3-methoxy-hydroquinone: 294.

Rhinocricus insulatus (Chamberlin)

trans-2-dodecenal, 2-methyl-1,4-benzoquinone: 157, 348 B, 355, 363.

- IV 5 -

Trigonoiulus lumbricinus Gerst.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone:
50, 157, 198, 278, 348 B, 363.

Ord. SPIROSTREPTIDA

Aulonopygus aculeatus Attems

2-methyl-1,4-benzoquinone: 8.

Aulonopygus aculeatus barbieri

2-methyl-1,4-benzoquinone: 8.

Doratoronus annulipes Carl

2-methyl-1,4-benzoquinone, 3-methoxy-2-methyl-1,4-benzoquinone:
106, 348 B.

Orthoporus conifer (Attems)

3-methoxy-2-methyl-1,4-benzoquinone: 106, 348 B.

Orthoporus flavior Chamberlin e Mulaik

2-methyl-1,4-benzoquinone, 3-methoxy-2-methyl-1,4-benzoquinone:
106, 348 B.

Orthoporus punctilliger Chamberlin

2-methyl-1,4-benzoquinone, 3-methoxy-2-methyl-1,4-benzoquinone:
106, 348 B.

Spirostreptus sp.

2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone:
293.

Spirostreptus castaneus Attems

1,4-benzoquinone, other quinones and their methyl derivatives:
199; 1,4-benzoquinone: 8, 10, 50, 106, 245, 246, 278, 310, 333B,
335, 348 B, 363.

Spirostreptus multisulcatus Dem.

2-methyl-1,4-benzoquinone: 8.

Spirostreptus virgator Silv.

2-methyl-1,4-benzoquinone: 8, 106, 348 B; 1,4-benzoquinone, o
ther qui,ones and their methyl derivatives: 10, 50, 199, 245,
278, 310, 355, 363.

- IV 6 -

Fam. OdontopygidaePeridontopyge aberrans Attems

2-methyl-1,4-benzoquinone: 8

Peridontopyge vachoni

2-methyl-1,4-benzoquinone: 8

Ord. CAMBALIDA

Cambala hubrichti Hoffman2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone:
106, 348 B.

Cl. CHILOPODA

Ord. SCOLOPENDROMORPHA

Ethmostigmus spinosus (*)lysins, anti-coagulin, diastase, invertase, proteolytic enzymes:
78.Scolopendra viridicornis Newport

5-hydroxytryptamine: 352, 353.

(*) Salivary glands and the third pair of glands mixed with a minimum of fat body and pigmented body: 78.

Chap. 11 - Insecta Blattodea, Isoptera, Dermaptera, Phasmida, Orthoptera and chemically defined substances of defensive secretions.

Ord. BLATTODEA (= DYCTIOPTERA)

Fam. Diplopteridae

Diploptera punctata (Eschscholtz)

glucoside which contains benzoquinone + β -glucosidase $\longrightarrow$ p. benzoquinones: 19, 32, 133, 325; 1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone, undetermined components in a mixture: 278; 1,4-benzoquinone and two derivatives: 99, 109; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 33, 80, 133, 245, 246, 333 B, 335, 348 A, 348 B; quinones: 134, 355 B.

Fam. Blattidae

Cutulia sororor (Brunner)

trans-hex-2-enal: 70, 83 A, 278, 348 A, 348 B.

Eurycotis biolleyi Rehn

water, D-gluconic acid, γ -gluconolactone, δ -gluconolactone, 2-hexenal: 83 A.

Eurycotis decipiens (Kirby)

D-gluconic acid, 2-hexenal, water, γ -gluconolactone, δ -gluconolactone: 83, 83 A, 348 A.

Eurycotis floridana Walk.

trans-hex-2-enal: 15, 18, 19, 24, 28, 44, 80, 109, 111, 131, 133, 156, 163, 220, 247, 277, 278, 280, 347, 348 A, 348 B; D-gluconic acid, 2-hexenal: 83 A.

Pelmatosilpha coriacea Rehn

trans-hex-2-enal: 19, 83 A, 157, 348 A, 348 B.

Platyzosteria armata Tepper

unbranched unsaturated aldehyds: 348 A.

Platyzosteria castanea Brunner

2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (traces), 2-methylene pentanal (traces), 2-methyl butanol, 2-methylene butyric acid:
348 A.

Platyzosteria coolgardiensis Tepper

unbranched insaturated aldehyds: 348 A.

Platyzosteria jungii (Tepper)

2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (traces), 2-methylene pentanal (traces), 2-methyl butanol, 2-methylene butyric acid:
348 A.

Platyzosteria morosa Shelford

2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (traces), 2-methylene pentanal (traces), 2-methyl butanol, 2-methylene butyric acid:
348 A.

Platyzosteria novae seelandiae Brunner

trans-hex-2-enal, undeterminated compounds in a mixture: 278;
trans-hex-2-enal: 348 A, 348 B.

Platyzosteria ruficeps Shelford

2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (traces), 2-methylene pentanal (traces), 2-methyl butanol, 2-methylene butyric acid:
348 A.

Platyzosteria scabra Brunner

unbranched unsaturated aldehydes: 348 A.

Platyzosteria scabrella Tepper

unbranched unsaturated aldehydes: 348 A.

Ord. ISOPTERA

Fam. TermitidaeNasutitermes sp. (soldiers)

24-methylene cholesterol: 292; α -pinene, β -pinene: 134, 358.

Nasutitermes hexitiosus (Hill)

α -pinene, β -pinene and/or other monoterpenoid hydrocarbons: 200, 348 B.

Nasutitermes graveolus (Hill)

α -pinene, β -pinene and/or other monoterpenoid hydrocarbons: 200, 348 B.

Nasutitermes walkeri (Hill)

α -pinene, β -pinene and/or other monoterpenoid hydrocarbons: 200, 348 B.

Ord. DERMAPTERA

Fam. ForficulidaeForficula auricularia L.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 100, 138, 278, 307, 348 B; 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, hydroquinones: 299; 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, 2-methyl-hydroquinone, 2-ethyl-hydroquinone: 157, 301.

Ord. PHASMIDA

Fam. PseudophasmidaeAnisomorpha buprestoides (Stoll)

anisomorphal: 66, 101, 111, 157, 187, 189, 348 B, 67 C, 274 A.
(anisomorphal = dolichodial)

Ord. ORTHOPTERA

Fam. AcrididaePoekilocerus bufonius Klug

histamine: 282; histamine, digitalis-like compound: 111, 221;
histamine, calotropin, calactin: 118, 283.

Chap. 12 - Insecta Heteroptera and chemically defined substances
of defensive secretions.

Ord. HETEROPTERA

Fam. Corixidae

Corixa dentipes Thoms

4-keto-trans-hex-2-enal: 4 A, 266.

Sigara falleni (Fieb)

4-keto-trans-hex-2-enal: 4 A, 157, 266, 348 B.

Fam. Belostomatidae

Lethocerus indicus Lep.

trans-hex-2-enyl-butyrate: 4 A, 92; trans-hex-2-enyl-acetate:
4 A, 24, 44, 80, 156, 220, 266, 278.

Fam. Reduviidae

Platyeris rhadamanthus Gaerst.

six, eight proteins, three proteolytic fractions: alkaline endo-
peptidase, hyaluronidase, protease, phospholipase: 97; six protein
fractions: three with trypsin-like proteolytic activity, one with
strong hyaluronidase activity and one with weak phospholipase acti-
vity, histamine ?, neurotoxic activity: 11, 96, 111, 278.

Cimex lectularius L.

trans-hex-2-enal, trans-oct-2-enal: 4 A, 299; hyaluronidase, hista-
mine: 193; hyaluronidase, histamine and substance which contracts
muscle: 11, 163.

Fam. Coreidae

Acanthocephala femorata Fabr.

trans-hex-2-enal: 4 A, 24, 80, 157, 348 B.

Acanthocoris sordidus (Thunberg)

trans-hex-2-enal, n-hexanal, unidentified carbonyl compound:
4 A, 364.

Agriopocoris froggatti Miller

acetic acid (trace), n-hexanal (°), n-hexanol, n-hexyl-acetate:

4 A: 348; n-hexanal: 348 B.

(°) In one sample of aged bugs the scent consisted entirely of hexanal.

Amorbus alternatus Dallas

acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348, n-hexanal: 348 B.

Amorbus rhombifer (§) Westwood

acetic acid, (*) n-hexanal, n-hexanol, n-butyl butyrate, n-hexyl acetate: 4 A; 348; n-hexanale: 348 B.

(§) One sample contained a compound believed to be butyric acid: 348.

(*) This fraction from the gas chromatograph contained a high concentration of n-butanal: 348.

Amorbus rubiginosus Guérin

n-hexanal, undetermined compounds in a mixture: 278; n-hexanal: 347, 348 B; acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348.

Aulacosternum nigrorubrum Dallas

acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348; n-hexanal: 348 B.

Hygia opaca (Uhler)

n-hexanal: 4 A, 364.

Leptocoris apicalis Westw.

trans-oct-2-enal, trans-dec-2-enal, n-octyl acetate: 4 A.

Mictis caja Stål.

acetic acid, n-hexanal, n-hexanol, n-butyl butyrate, n-hexyl acetate: 4 A, 348; n-hexanal: 348 B.

Mictis profana Fabr.

n-hexanal, undetermined compounds in a mixture: 278; acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348; n-hexanal: 347, 348 B.

Pachycolpura manca Breddin

acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348; n-hexanal: 348 B.

Plinachtus bicoloripes Scott

n-hexanal: 4 A, 364.

Riptortus clavatus (Thunberg)

n-butanal: 4 A, 364.

Fam. HyocephalidaeHyocephalus sp.

acetic acid (trace), n-hexanal, n-hexanol, n-hexyl acetate (traces?): 4 A, 348; n-hexanal: 348 B.

Fam. PentatomidaeAelia fieberi Scott

trans-dec-2-enal, trans-oct-2-enal: 4 A, 364.

Biprorulus bibax

n-tridecane, n-dodecane, trans-dec-2-enal, trans-dec-2-henyl acetate: 4 A, 132, 220.

Brachymena quadripustulata Fabr.

trans-hex-2-enal: 4 A, 18, 132, 278, 348 B.

Carpocoris purpureipennis (De Geer)

n-tridecane: 4 A, 274.

Dolychoris baccarum L.

trans-hex-2-enal, trans-oct-2-enal, trans-dec-2-enal, two carbonyl products (20% + 2%): 4 A, 132, 157, 294, 299, 314; trans-hex-2-enal, trans-oct-2-enal, trans-dec-2-enal: 348 B.

Eurygaster sp.

trans-hex-2-enal, trans-oct-2-enal, 20% of undetermined carbonyl compounds: 4 A, 132, 299.

Euschistus servus Say

According to Blum e Traynham, 1960, the gross chemistry of the secretion from scent glands is very similar to that of Oebalus pugnax (F.).

Graphosoma rubrolineatum (Westwood)

trans-dec-2-enal, n-hexanal: 4 A, 364.

Menida Scotti (Puton)

trans-dec-2-enal, unidentified carbonyl compound: 4 A, 364.

Musgraveia sulciiventris Stål

n-tridecane, n-dodecane, trans-oct-2-enal, trans-dec-2-enal, trans-hex-2-enal (traces), trans-oct-2-enyl acetate, three very minor constituents: 132.

Nezara antennata Scott

trans-dec-2-enal: 4 A, 364.

Nezara viridula L.

4-keto-hex-2-enal: 134; trans-dec-2-enal, unidentified carbonyl compound: 4 A, 364; according to Blum and Traynham, 1960, the gross chemistry of the secretion from scent glands is very similar to that of Oebalus pugnax (F.); trans-hex-2-enal, trans-hept-2-enal, trans-dec-2-enal; 4-keto-trans-hex-2-enal, n-tridecane: 348 B.

Nezara viridula L. var. smaragdula F.

trans-hex-2-enal, trans-dec-2-enal, one dicarbonyl compound, tri-decane: 4 A, 132, 347; propenal, trans-but-2-enal, methyl-ethyl-ketone, ethyl-propyl-ketone, 4-keto-hex-2-ene, trans-hex-2-enal, 4-keto-trans-hex-2-enal, trans-hex-2-enyl acetate, trans-oct-2-enal, methyl-heptyl-ketone (traces), n-undecane, 4-keto-trans-oct-2-enal, trans-oct-2-enyl acetate, n-dodecane, trans-dec-2-enal, cis-dec-2-enal (traces), n-tridecane, trans-dec-2-enyl acetate: 4 A, 132; trans-hex-2-enal, dec-2-enal, tridecane, undetermined compounds in a mixture: 278; thirteen volatile components including: n-tridecane, n-dec-2-enal, trans-hex-2-enal, an α - β dicarbonyl compound: 4 A, 132, 135.

Oebalus pugnax F.

trans-hept-2-enal, n-tridecane, six components including: an unsaturated dicarbonyl, a monocarbonyl, an alcohol, an acid: 4 A, 27, 132; n-tridecane, trans-hept-2-enal, dicarbonyl compound: 4 A, 13, 28, 132; 2-heptenal, n-tridecane: 80; trans-hept-2-enal, n-tridecane, undetermined components in a mixture: 278.

Palomena viridissima P.

trans-hex-2-enal, trans-oct-2-enal, trans-dec-2-enal, unknown carbonyl compounds: 4 A, 132, 299.

Poecilometis strigatus Westw.

trans-hex-2-enal, trans-oct-2-enal, a dicarbonyl compound: 4 A, 132, 347; trans-hex-2-enal, 2-octenal, undetermined components in a mixture: 278; trans-hex-2-enal, trans-oct-2-enal: 348 B.

Rhoecocoris sulciventris Stål

trans-hex-2-enal, trans-oct-2-enal, a dicarbonyl compound, n-tri-decane: 4 A, 347; n-tridecane, trans-oct-2-enal, trans-oct-2-enyl acetate, n-dodecane, trans-dec-2-enal, trans-hex-2-enal (traces), three very minor constituents: 4 A, 220; trans-hex-2-enal, 2-octenal, n-tridecane, undetermined components in a mixture: 278; trans-hex-2-enal, trans-oct-2-enal: 348 B.

Tessaratomia aethiops Dist.

adults: trans-hex-2-enal, trans-oct-2-enal, 4-keto-trans-hex-2-enal, trans-oct-2-enyl-acetate, n-tridecane: 4 A.

larvae: trans-oct-2-enal, 4-keto-trans-hex-2-enal, n-tridecane: 4 A.

Scotinophara lurida Burmeister

trans-dec-2-enal, trans-oct-2-enal, trans-hex-2-enal, unidentified carbonyl compound: 4 A, 364.

Fam. PlataspidaeCeratocoris cephalicus Mont.

n-tridecane: 4 A.

Fam. CydnidaeMacroscytus sp.

4-keto-trans-hex-2-enal, trans-oct-2-enyl acetate, trans-dec-2-enyl acetate, n-dodecane, n-tridecane: 4 A.

Scaptocoris divergens Froeschner

propenal, propanal, trans-but-2-enal, trans-hex-2-enal, pentenal, trans-hept-2-enal, trans-oct-2-enal, furan, methyl-furan, 2-me

thyl-1,4-benzoquinone, unidentified quinone: 4 A, 132, 157, 277;
trans-hex-2-enal, trans-hept-2-enal, trans-oct-2-enal: 348 B.

Cap. 13 - Insecta Lepidoptera and Diptera and chemically defined
 substances of defensive secretions.

Ord. LEPIDOPTERA

Fam. Cossidae

Cossus cossus L.

cossin A, cossin B, cossin C: 248, 250, 396, 338, cossin 1, cos
cossin 3,
 sin 2, cossin A, cossin B, cossin C, cossin B₁, cossin C₁: 334.

Zeuzera pyrina L.

zeuzerina:

Fam. Anthroceridae

Procris geryon (Hueb)

hydrocyanic acid: 161.

Zygaena filipendulae (L.)

hydrocyanic acid: 161; acetylcholine: 321 B.

Zygaena lonicerae (von Sch.)

histamine: 124, 161; hydrocyanic acid: 161; acetylcholine: 321 B.

Fam. Pyrallidae

Eurrhynx hostulata L.

histamine: 124.

Fam. Geometridae

Abraxas grossulariata (L.)

histamine: 124.

Fam. Notodontidae

Cerura vinula L. (= Dicranura vinula L.)

larvae: formic acid, undetermined components in a mixture: 278;
 larvae: formic acid: 36, 91, 125, 137, 172, 180, 193, 217, 245,
 263, 341, 348 B, 355 B; larvae: acetic acid, formic acid, metha
 crylic acid, tiglic acid: 134; larvae: formic acid, aminoacids:
 303.

Datana ministra

larvae: formic acid: 149.

Dicranura furcula

larvae: formic acid: 180.

Schizura concinna (Abb. e Smith) (= Notodonta concinna Abb. e Smith)

larvae: hydrochloric acid: 36, 90, 91, 193, 245, 341; formic acid: 149.

Schizura leptinoides Grote

formic acid: 278, 348 B.

Fam. Lymantriidae

Euproctis flava Brem.

hairs: histamine or histamine-like substances, pharmacologically active proteins: 163.

Porthesia sp.

hairs: formic acid, organic base, enzyme (probably): 125.

Fam. Arctiidae

Arctia caja L.

imago: choline ester, non dialyzable heat-labile toxic substance: 16; choline ester (β,β -dimethylacrylyl-choline): 17, 278, 281, 283, 355 B; choline ester (β,β -dimethylacrylyl-choline), histamine (traces): 124; methanol (probably): 281.

Hypocrita jacobaeae L.

histamine: 124.

Spilosoma lubricipeda L.

imago: histamine: 124, 281.

Fam. Thaumetopocidae

Cnethocampa sp.

hairs: larvae: formic acid: 173.

Thaumetopoea pityocampa Schiff. (Cnethocampa pityocampa)

larvae, hairs: histamine or histamine-like substances, pharmacologically active proteins: 163; larvae, hairs: histamine (probably): 355 B; larvae: formic acid: 263.

Fam. SaturniidaeAutomeris sp.

hairs, larvae: 5-hydroxytryptamine: 352.

Automeris (illustris ?)

hairs: 5-hydroxytryptamine: 353.

Dirphia sp.

hairs: histamine: 11, 340; hairs: histamine, pharmacologically active proteins: 163.

Fam. LasiocampidaeDendrolimus spectabilis Btlr.

hairs: histamine or histamine-like substances, pharmacologically active proteins: 163.

Dendrolimus undans Walk.

hairs: histamine or histamine-like substances, pharmacologically active proteins: 163.

Fam. PapilionidaePapilio machaon L.

larvae: isobutyric acid, 2-methylbutyric acid: 110, 111, 348 B.

Fam. DanaidaeDanaus plexippus L.

pupae and adults: digitalis-like toxin: 222; imago tissue: two heart poisons: 283.

Fam. MegalopygidaeMegalopyge sp.

hairs: histamine, pharmacologically active proteins: 163; hairs: histamine: 11, 340.

Megalopyge urens Berg.

hairs: globuline: 117.

Ord. DIPTERA

Fam. FungivoridaeCeroplatus sp.

oxalic acid: 80.

Ceroplatatus lineatus F.

oxalic acid: 181, 245.

Platyura sp.

oxalic acid: 80.

Platyura discoloria Mg.

oxalic acid: 181, 245.

Platyura fasciata

oxalic acid: 181, 245.

Platyura nigricornis F.

oxalic acid: 181, 245.

Cap. 14 - Insecta Coleoptera and chemically defined substances of
defensive secretions.

Ord. COLEOPTERA

Fam. CarabidaeAbax ater Villers

methacrylic acid, tiglic acid: 157, 299, 311.

Abax ovalis Dftsch.

methacrylic acid, tiglic acid: 157, 299, 311.

Abax parallelus Dftsch.

methacrylic acid, tiglic acid: 157, 299, 311.

Acinopus sp.

formic acid: 111, 299, 348 B.

Apotomopterus albr. Esakii Mor.

methacrylic acid, tiglic acid: 299, 311.

Apotomopterus insulicula Chaud.

methacrylic acid, tiglic acid: 157, 299, 311.

Brachynus sp.

nitrogen oxides: 91, 341.

Brachynus crepitans L.quinones (phenolic precursors + H_2O_2): 108; hydroquinone, 2-me

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thyl hydroquinone + $H_2O_2 \longrightarrow$ 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, $H_2O + O_2$: 8, 9, 39, 80, 98, 133, 156, 245, 246, 278, 290, 298, 335, 348 B, 355 B; nitrogen oxides, nitrous acid: 125.

Brachynus explodens Duft.

hydroquinone, 2-methyl-hydroquinone + $H_2O_2 \longrightarrow$ 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, $H_2O + O_2$: 133, 278, 298, 348 B.

Brachynus sclopeta Fabr.

hydroquinone, 2-methyl-hydroquinone + $H_2O_2 \longrightarrow$ 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, $H_2O + O_2$: 133, 278, 298, 348 B.

Calathus sp.

formic acid: 111, 299, 348 B.

Calosoma prominens Lec.

salicylaldehyde: 107, 111, 114, 134, 157, 348 B.

Calosoma sycophanta L.

salicylaldehyde, metacrylic acid, tiglic acid: 51, 138.

Carabus sp.

butyric acid: 91, 125, 217, 341.

Carabus auratus L.

metacrylic acid, tiglic acid: 157, 299, 311.

Carabus auronitens Fbr.

metacrylic acid, tiglic acid: 157, 299, 311.

Carabus cancellatus Illig.

metacrylic acid, tiglic acid: 299, 311.

Carabus convexus Fbr.

metacrylic acid, tiglic acid: 157, 299, 311.

Carabus coriaceus L.

metacrylic acid, tiglic acid: 157, 299, 311.

Carabus cyaneus F.

metacrylic acid, tiglic acid: 299, 311.

Carabus granulatus L.

metacrylic acid, tiglic acid: 157, 299, 311.

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Carabus irregularis Fbr.

methacrylic acid, tiglic acid: 157, 299, 311.

Carabus procerulus Chaud.

methacrylic acid: 157, 299, 311.

Carabus Ullrichi Germ.

methacrylic acid, tiglic acid: 157, 299, 311.

Carabus violaceus L.

methacrylic acid, tiglic acid: 157, 299, 311.

Carterus sp.

formic acid: 111, 299.

Chlaenius cordicollis Kirbym-cresol: 107, 111, 348 B.Cychrus sp.

butyric acid: 217.

Cychrus rostratus Lin.

methacrylic acid: 111, 299, 311.

Damaster oxuroides Schaum

methacrylic acid: 111, 157, 299, 311.

Harpalus dimidiatus Rossi

formic acid: 293, 299.

Pheropsophus africanus Dej.

nitrous acid: 131, 245; nitrous acid or nitrites: 137, 278, 341, 342.

Pheropsophus agnatus

formic acid: 125.

Pheropsophus catoirei Dej.

1,4-benzoquinone, 2-methyl-1,4-benzoquinone: 278, 298, 348 B.

Pseudophonus griseus Panz.

formic acid: 107, 157, 293, 299, 309, 348 B.

Pseudophonus pubescens Mull.

formic acid: 107, 293, 299, 309, 348 B.

Pterostichus metallicus Fbr.

methacrylic acid, tiglic acid: 157, 299, 311.

Pterostichus niger Schall.

methacrylic acid, tiglic acid: 157, 299, 311.

Pterostichus vulgaris L.

methacrylic acid, tiglic acid: 157, 299, 311.

Fam. DytiscidaeAcilius sulcatus L.

cortexone, cybisterone, 6-dihydrocybisterone: 300 A; cortexone, 6-dehydrocortexone, cybisterone, 6-dihydrocybisterone, 6-dehydro progesterone: 300 B.

Cybister lateralimarginalis De Geer

p-hydroxybenzaldehyde, methyl-p-hydroxy-benzoate, stilbene unknown carboxylic acid: 299; cybisterone: 300 A, 305; p-hydroxybenzaldehyde, methyl-p-hydroxy-benzoate: 348 B.

Dytiscus latissimus L.

p-hydroxybenzaldehyde, methyl-p-hydroxy-benzoate, benzoic acid: 299, 348 B.

Dytiscus marginalis L.

benzoic acid, p-hydroxybenzaldehyde: 293; benzoic acid, p-hydroxybenzaldehyde, methyl-p-hydroxy-benzoate: 157, 294, 299, 312, 348 B; benzoic acid: 300; unidentified aliphatic α - β -unsaturated ketone: 297, 347; 11-desoxycorticosterone: 295 A, 304, 305; 11-desoxycorticosterone, benzoic acid, methyl-p-hydroxy-benzoate, p-hydroxybenzaldehyde: 295; cortexone, 6-dihydrocybisterone, cybisterone: 300 A.

Hydroporus palustris L.

p-hydroxybenzaldehyde: 299, 348 B.

Ilybius fenestratus Fabr.

testosterone: 296.

Ilybius fuliginosus Fabr.

testosterone: 296.

Fam. SilphidaePhosphuga atrata L.

ammonia (4,5% solut.): 157, 313.

Silpha obscura L.

ammonia (4,5% solut.): 157, 313.

Oeceoptoma thoracicum L. (O. thorcica L.)

ammonia (4,5% solut.): 157, 313.

Fam. StaphylinidaePaederus columbinus Lap.

pederin, pederone: 49.

Paederus fuscipes Curt.

pederin, pseudopederin: 46, 47, 48: pederin: 5, 45, 80, 131,
 133, 150, 156, 163, 169, 184, 235, 236, 238, 240, 242, 244,
 245, 246, 251, 253, 278, 319, 323, 348 B, 355 B; pederin, pseu
 dopederin, pederone: 49

Paederus melanurus Arag.

pederin: 45; pederin, pederone: 49.

Paederus litoralis Gravh.

pederin: 45.

Paederus rubrothoracicus Goeze

pederin: 45.

Paederus rufocyaneus Bernh.

pederin: 45.

(*)

(*) According to Stepanova e Coll., 1961 (Farm.Zhur., Kiev), 16:
 156ⁱⁿ, Paederus caligatus Erichs there is cantharidin. In all the
 similar species of Paederus we never found cantharidin.

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Fam. MeloidaeCissites cephalotes Oliv. (C. axillosa)

cantharidin: 94, 163.

Cyaneolytta gigas F. (Lytta gigas)

cantharidin: 94.

Cyaneolytta violacea Brandt (Lytta violacea)

cantharidin: 94.

Decapotama lunata Pall. (Mylabris lunata)

cantharidin: 94.

Eletica wahlbergia Fahr.

cantharidin: 94.

Epicauta adspersa Klug (Lytta adspersa Klug)

cantharidin: 94, 125, 137, 163.

Epicauta femoralis Er. (Cantharis femoralis)

cantharidin: 94.

Epicauta gorhami Mars.

cantharidin: 94, 163.

Epicauta hirticornis Haag (Cantharis hirticornis)

cantharidin: 94.

Epicauta pennsylvanica Deg. (Lytta atrata)

cantharidin: 94.

Epicauta ruficeps Ill. (Lytta ruficeps)

cantharidin: 94, 163.

Epicauta velata Gerst. (Cantharis velata)

cantharidin: 94.

Epicauta vittata F. (Lytta vittata, Cantharis vittata)

cantharidin: 82, 94, 125, 137, 163, 263.

Horia debyi Fairm.

cantharidin: 94, 163.

Lydus trimaculatus Fischer

cantharidin: 94.

Lytta conspicua Waterh. (Mylabris conspicua)

cantharidin: 94.

Lytta sanguinea Haag (Huechys sanguinea)

cantharidin: 94.

Lytta vesicatoria L. (Cantharis vesicatoria)

cantharidin: 5, 88, 94, 125, 136, 137, 163, 169, 240, 263, 319,
342, 344, 351, 355 B.

Macrobasis albida Say.

cantharidin: 94, 163, 344.

Macrobasis cinerea F. (Lytta cinerea)

cantharidin: 94.

Meloe sp.

cantharidin: 125, 131, 186, 236, 278.

Meloe angusticollis Say

cantharidin: 94.

Meloe majalis L.

cantharidin: 94, 125.

Meloe proscarabeus L.

cantharidin: 94, 157.

Meloe variegatus Donovan. (Mylabris variegata)

cantharidin: 94.

Meloe violaceus Marsch.

cantharidin: 94.

Mylabris balteata Pall. (Mylabris punctum Duges)

cantharidin: 79, 94, 163.

Mylabris bifasciata De Geer (Zonabris bifasciata De Geer)

cantharidin: 94, 163. (confirmed by personal researches)

Mylabris calida Pall. (Mylabris maculata)

cantharidin: 94.

Mylabris cichorii L. (Zonabris cichorii L.)

cantharidin: 94, 125, 136, 163, 263, 344.

Mylabris colligata Redt.

cantharidin: 94.

Mylabris crocata Pall. (Mylabris duodecimpunctata)

cantharidin: 94.

Mylabris dicincta Bertol.

cantharidin: 94 (confirmed by personal researches)

Mylabris dilloni Guer.

cantharidin: (unpublished)

Mylabris ertli Voigts

cantharidin: (unpublished)

Mylabris escherichi Voigts semireducta Pic.

cantharidin: (unpublished)

Mylabris holosericea Klug

cantharidin: 79, 94.

Mylabris macilenta Mars.

cantharidin: 94.

Mylabris oculata Thunb.

cantharidin: 94.

Mylabris phalerata Pall. (Mylabris sidae, Zonabris phalerata Pall.)

cantharidin: 94, 136, 163.

Mylabris praestans Gerst.

cantharidin: (unpublished)

Mylabris pustulata Thunb.

cantharidin: 79, 94, 163, 263.

Mylabris quadripunctata L. (Mylabris melanura)

cantharidin: 79, 94, 163.

Mylabris quatuordecimpunctata Pall.

cantharidin: 94, 125, 263.

Mylabris schoenherri Billb.

cantharidin: 163.

Mylabris tripartita Gerst.

cantharidin: 94.

Mylabris tristigma Gerst.

cantharidin: (unpublished)

Mylabris variabilis Pall.

cantharidin: 79, 94, 163, 319.

Psalydolytta castaneipennis Makel

cantharidin: (unpublished)

Fam. Tenebrionidae

Blaps gibba L.

various benzoquinones: 245, 246, 248, 335.

Blaps gigas Lap. Cast.

1,4-benzoquinone: 10, 201, 245, 246, 335; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 299; quinone or quinones: 333 B.

Blaps judaeorum Miller

quinones: 278.

Blaps lethifera Marsh.

1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 299, 308, 348 B.

Blaps mortisaga L.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 299, 308, 348 B; two benzoquinones: 306.

Blaps mucronata Latr.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 299, 308, 348 B; various benzoquinones: 245, 246, 248, 335.

Blaps nitens Cast.

quinones: 278.

Blaps requieni Sol.

various benzoquinones: 248; 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 299, 308, 348 B.

Diaperis bcleti L.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 293, 299, 348 B.

Diaperis hispilabris Say

2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone, undetermined components in a mixture: 80, 278.

Diaperis maculata Ol.

2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone: 80, 245, 246, 278, 333 B, 335, 348 B.

Eleodes hispilabris

1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 348 B.

Eleodes longicollis Le Conte

1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, caprylic acid, n-tridecane, glucose: 348 B; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, carbonyl components: 71, 111, 190, 192, 278; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, 1-tridecene, 1-undecene, 1-nonene (probably), caprylic acid, glucose: 108, 157, 188; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 102; 1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone, 1-tridecene, 1-undecene, glucose, 1-nonene (probably): 153.

Eleodes obsoleta (Say)

a quinone compound possessing alkyl groups: 33.

Gnaptor spinimanus Pall.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 278, 308, 348 B.

Helops aeneus Montrouz

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 299, 348 B.

Helops quisquilius Strm.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 293, 299, 348 B.

Latheticus oryzae Wat.

unknown quinones: 245, 246, 335; 2-ethyl-1,4-benzoquinone and/
or 2-methyl-1,4-benzoquinone: 177.

Morica planata tingitana Baudi

2-methyl-1,4-benzoquinone: 278, 308, 348 B.

Opatroides punctulatus Brull.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 299, 348 B.

Opatrum sabulosum L.

2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 293, 299,
348 B.

Pimelia confusa Sen.

2-methyl-1,4-benzoquinone: 278, 308, 348 B.

Scaurus dubius Sol.

1,4-benzoquinone: 293.

Scaurus uncinus Forst.

1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 299.

Scotobates calcaratus (Fabr.)

unknown quinones: 245, 246, 335.

Tenebrio molitor L.

2-methyl-1,4-benzoquinone: 278, 291, 299, 348 B; 2-methyl-1,4-hydroquinone: 301.

Tenebrio obscurus Fabr.

1,4-benzoquinone: 278, 308, 348 B.

Tribolium sp.

quinones: 240, 341, 355 B.

Tribolium castaneum Herbst.

quinone: 85, 86; p-benzoquinone derivatives: 168; 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone: 133, 333 B; 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone, 2-methoxy-1,4-benzoquinone: 9, 10, 80, 131, 177, 245, 246, 278, 335, 348 B.

Tribolium confusum J. du Val.

quinone: 85, 86, 279; p-benzoquinone derivatives: 168; 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone: 80, 133, 278, 348 B; 2-ethyl-1,4-benzoquinone, 2-methyl-1,4-benzoquinone, unknown quinones: 245, 246, 335.

Tribolium destructor Uytt.

unknown quinones: 245, 246, 335; cresol, unknown aromatic component: 219; 2-ethyl and/or 2-methyl-1,4-benzoquinone: 177.

Uloma impressa Melsh.

unknown quinones: 245, 246, 335.

Fam. Alleculidae

Prionychus ater Fabr.

1,4-benzoquinone: 293; 2-methyl-1,4-benzoquinone, 2-ethyl-1,4-benzoquinone: 299.

Fam. Cerambycidae

Aromia moscata L.

salicylaldehyde: 348 B.

Fam. Chrysomelidae

Blefarida evanida Baly

larvae: protein substance (probably): 163

Diamphidia simplex Peringuey (= Diamphidia locusta)

larvae: protein substance (probably): 163; larvae: toxalbumin: 163; toxic saponin: 355 B.

Melasoma populi L. (= Chrysomela populi L.)

salicylaldehyde (*): 87, 91, 114, 125, 131, 137, 156, 199, 217, 235, 236, 238, 240, 245, 246, 247, 248, 278, 341, 348 B, 355 B, 359.

(*) According to Claus (1862) there is a matter of salicylic acid. Other authors as well reported this initial observation.

Melasma saliceti Weise

salicylaldehyde (larvae): 152.

Phyllodecta vitellinae L.

salicylaldehyde: 91, 114, 133, 156, 199, 245, 278, 341, 345,
348 B.

Plagiodera sp.

salicylaldehyde: 114, 278, 348 B.

Plagiodera versicolor Laich.

larvae: salicylaldehyde: 152.

Chap. 15 - Insecta Hymenoptera and chemically defined substances
of defensive secretions.

Ord. HYMENOPTERA

Fam. BrachonidaeHabrobracon hebetor Say (= Microbracon hebetor Say)

protein, protein-like substance: 176, 352.

Fam. ApidaeApis mellifera L.

histidine, histamine, lecithin, hyaluronidase,
phospholipase A: 156, 246; histamine: 81, 176, 288, 352; apito-
xin (polypeptide): 38; lecithinase A, direct hemolytic factor:
211; lecithinase, hyaluronidase: 158; protein toxin, lecithina-
se A, spreading factors, riboflavin, histamine, magnesium,
copper: 35; formic acid, histamine, apitoxin (polypeptide - pro-
tease), riboflavin (vit. B₂), lecithinase A, 5-hydroxytryptamine
(*), kinin (*), spreading hyaluronidase-like factors: 37; alani-
ne, arginine, aspartic acid, cystine, cysteine, glutamic acid,
glycine, histidine, isoleucine, leucine, lysine, methionine,
phenylalaline, proline, serine, threonine, tryptophane, tyrosi-
ne, valine, histamine, lecithin, hyaluronidase, phospholipase
A: 163, 245, 261; tryptophane, choline, glycerol, phosphoric

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acid, palmitic acid, unsaturated fatty acid, volatile fatty acid (butyric acid?): 318; histamine, apitoxin (=polypeptide - protease): 137, 175; 5-hydroxytryptamine: 352; hyaluronidase activity: 159, 286 A; histamine, five protein fractions: 321 A; fraction I: glycine, alanine, valine, leucine, isoleucine, serine, threonine, lysine, arginine, aspartic acid, glutamic acid, tryptophane, proline; fraction II: the same aminoacids of fraction I + phenylalanine, tyrosine, histidine, methionine, cystine: 122; histamine, mellitin (containing thirteen aminoacids), phospholipase A, hyaluronidase: 169; protein substances, phospholipase A, hyaluronidase: 143, 144, 208, 214; hyaluronidase, phospholipase A, toxin, two unknown ninhydrin-positive components: 141; fraction I: direct hemolytic activity, fraction II: phospholipase A with indirect hemolytic activity: 123; histamine, protein like substance containing 8% of tryptophane, sterol-like substance, protein: 164; fraction O, fraction I (toxic), glycine, alanine, valine, leucine, isoleucine, serine, threonine, lysine, arginine, aspartic acid, glutamic acid, tryptophane, proline, Fraction II: the same aminoacids of fraction I + tyrosine, cystine, methionine, phenylalanine, histidine, phospholipase A, hyaluronidase, histamine: 11, 207; isoamyl acetate: 34, 183, 320, 358; histamine, apamin, mellitin, phospholipase A, hyaluronidase: 324; 10-hydroxy-2-decenoic acid: 320 B; water, alanine, arginine, cystine, glutamic acid, histidine, proline, asparagine (*), glycine (*), isoleucine (*), leucine (*), lysine (*), ornithine (*), phenylalanine (*), serine (*), threonine (*), tyrosine (*), valine (*), α -aminobutyric acid (*), β -isoaminobutyric acid (*), histamine, fructose, glucose, five-six lecithin-like compounds, two steroids (possibly), histapeptide (alanine, glycine, proline, alanine, gluNH₂, histamine), small peptides (probably fourteen), apamin (ten aminoacids), mellitin, enzymes including phospholipase and hyaluronidase, four antigenic proteins, eleven unidentified compounds: 212 A.

(*) traces.

- According to Fredericq 1924 (125) Apis mellifera venom contains: hydrochloric acid, phosphoric acid, organic base.
- According to Pawlowsky 1927 (263) Apis mellifera venom contains: formic acid, hydrochloric acid, phosphoric acid, protein substances, organic base, tryptophane, choline, glycerol, palmitic acid, high molecular unsaturated fatty acid (probably): 263.
- Owing to the complexity of the bibliographic data, we list the chemically determined substances from bee venom: glycerol, choline, histamine, 5-hydroxytryptamine, formic acid, butyric acid (probably), palmitic acid, 10-hydroxy-2-decenoic acid, isoamyl ^G-iso-aminobutyric acid, acetate, glycine, alanine, serine, α -aminobutyric acid, threonine, valine, aspartic acid, asparagine, leucine, isoleucine, glutamic acid, glutamine, ornithine, cysteine, cystine, methionine, lysine, arginine, proline, histidine, phenylalanine, tyrosine, tryptophane, apamin, mellitin, kinin, apitoxin (polypeptide-protease), histapeptide (alanine, glycine, proline, alanine, gluNH₂, histamine), riboflavin, lecithin, phospholipase A, hyaluronidase, lecithinase, lecithinase A, glucose, fructose.

Bombus pratorum L.

hyaluronidase: 245, 246; lecithinase, hyaluronidase: 158; hyaluronidase activity: 159.

Lestrimelitta limao (Fr. Smith)

citral: 21.

Xylocopa sp.

an organic base connected with an acid: 263.

Fam. Vespidae

Dolichovespula media De G.

5-hydroxytryptamine: 245, 246.

Polistes gallicus L.

5-hydroxytryptamine: 75, 115, 245, 246, 353.

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Polistes omissa Weyrauch

hyaluronidase, acetylcholine: 11; hyaluronidase, esterase: 286 A.

Polistes versicolor (Ol.)

5-hydroxytryptamine: 353.

Polybia occidentalis scutellaris

5-hydroxytryptamine: 353.

Synoeca surinama

5-hydroxytryptamine: 352, 353.

Vespa crabro L.

5-hydroxytryptamine: 353; 5-hydroxytryptamine, histamine, kinin: 352; acetylcholine, phospholipase B, 5-hydroxytryptamine: 245, 246; histamine, 5-hydroxytryptamine, acetylcholine, free amino acids: 66, 163, 169; hyaluronidase, histamine, acetylcholine: 11; histamine, 5-hydroxytryptamine, acetylcholine, kinin, phospholipase A, phospholipase B: 324; 5-hydroxytryptamine, acetylcholine, kinin, histamine: 287 B, acetylcholine: 321 B.

Vespula germanica Fab. (= Vespa germanica Fabr.)

histamine: 176; pipecolinic acid: 194; 245; 246; acetylcholine, cholinesterase, hyaluronidase, phospholipase B, kinin, 5-hydroxytryptamine: 182.

Vespula media

5-hydroxytryptamine: 115.

Vespula vulgaris L. (= Vespa vulgaris L.)

histamine, cholinesterase, hyaluronidase, phospholipase B, 5-hydroxytryptamine, kinin: 245, 246; histamine, kinin: 352; 5-hydroxytryptamine: 75, 209, 240, 353; 5-hydroxytryptamine, histamine, kinin: 66, 115, 151, 288, 183 A; histamine, 5-hydroxytryptamine, free amino acids: 163; histamine, 5-hydroxytryptamine, potent unidentified smooth muscle stimulant substance: 160; histamine, 2-5-hydroxytryptamine, kinin, hemolytic factor, hyaluronidase, phospholipase A, phospholipase B, cholinesterase: 169;

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cholinesterase, hyaluronidase, lecithinase: 158; hyaluronidase, 5-hydroxytryptamine, kinin, histamine: 11; hystamine, 5-hydroxytryptamine, kinin, phospholipase A, phospholipase B, hyaluronidase: 324; hyaluronidase: 286 A.

Fam. FormicidaeSubfam. PonerinaeEctatomma tuberculatum (Olivier)

proteinaceous substance: 147.

Myrmecia forficata Fabr.

hystamine, one or more histamine-like compounds: 89.

Myrmecia gulosa (Fabr.)

eight fractions: hystamine, hyaluronidase, phospholipase C, kinin-like substances, direct hemolytic factor: 66, 67, 68.

Odontomachus hematoda insularis Guerin

proteinaceous substance: 147.

Pachycondila sp.

formic acid: 213.

Pachycondila harpax

formic acid: 193; proteinaceous substance: 147.

Paltothyreus tarsatus (Fabr.)

dimethyldisulfide, dimethyltrisulfide: 53.

Paraponera clavata F.

polypeptide containing at least eleven amino acids including: aspartic acid, lysine, leucine, isoleucine, alanine, glutamic acid: 147.

Subfam. PseudomyrminaePseudomyrmex pallidus (Fr. Smith)

basic protein: 23, 333 A.

Subfam. DolichoderinaeConomyrma pyramica (Roger)

2-heptanone: 29

Dolichoderus sp.

dolichodial: 270

Dolichoderus (Acanthoclinea) clarki (Wheeler)

dolichodial, 4-methyl-2-hexanone: 30, 31, 52, 61, 66, 249, 348 B;

dolichodial: 55, 62, 63, 64, 80, 187, 249, 250.

Dolichoderus (Acanthoclinea) dentata Forel

dolichodial: 52, 55, 61, 63, 187, 249, 250, 348 B.

Dolichoderus (Diceratoclinea) scabridus (Roger)

dolichodial: 250; iridodial; 2-methyl-2-hepten-6-one, isoiridomyrmecin, dolichodial: 52, 55, 61, 63, 187, 249, 348 B.

Iridomyrmex sp.

dolichodial: 270.

Iridomyrmex conifer For.

iridodial: 59, 73, 131, 139, 185, 270, 351; iridodial, 2-methyl-2-hepten-6-one: 52, 55, 60, 61, 66, 245, 246, 261, 278, 332, 339, 348 B; iridodial, 2-methyl-2-hepten-6-one: 62, 80, 156.

Iridomyrmex detectus Sm.

2-methyl-2-hepten-6-one: 58, 163, 169; iridodial: 1 A, 59, 73, 131, 139, 185, 270, 351; 2-methyl-2-hepten-6-one, iridodial: 52, 55, 60, 61, 63, 66, 133, 241, 245, 246, 261, 278, 332, 339, 348 B; iridodial, 2-methyl-2-hepten-6-one, propyl isobutyl ketone: 62, 80, 130, 156.

Iridomyrmex gracilis Lowne

terpenoid constituents: 60.

Iridomyrmex gracilis var. rubriceps Forel

terpenoid constituents: 60.

Iridomyrmex humilis Mayr (I. pruinus Roger humilis Mayr)

iridomyrmecin: 5, 30, 40, 52, 55, 60, 61, 62, 66, 80, 128, 129,

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130, 131, 133, 134, 139, 144 A, 154, 155, 156, 163, 165, 166 A, 169, 185, 202, 204, 223, 224, 225, 226, 227, 228, 229, 230, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 245, 246, 248, 249, 250, 252, 254, 257, 258, 260, 261, 262, 264, 267, 268, 270, 271, 274 A, 275 A, 278, 319, 321, 331, 332, 332 A, 337, 339, 348 B, 351, 356, 355 B, 361.

Iridomyrmex myrmecodiae Em.

dolichodial: 52, 55, 61, 63, 130, 187, 348 B.

Iridomyrmex nitidiceps

iridodial: 270; iridodial, 2-methyl-2-hepten-6-one: 52, 55, 61, 63, 66, 348 B.

Iridomyrmex nitidus Mayr

isoiridomyrmecin: 40, 52, 55, 60, 61, 62, 63, 64, 65, 66, 72 A, 73, 130, 131, 133, 139, 156, 185, 202, 241, 245, 246, 261, 270, 332, 339, 348 A, 351, 361; isodihydronepetalactone, isoiridomyrmecin: 56.

Iridomyrmex pruinosus Roger

methyl-n-amyl-ketone: 21, 29, 30, 31, 52, 66, 320, 356, 357.

Iridomyrmex rufoniger Lowne

iridodial, 2-methyl-2-hepten-6-one, dolichodial: 55, 63, 348 B; dolichodial: 52, 61, 187; iridodial: 59; terpenoid constituents: 60.

Liometopum microcephalum Panz.

2-methyl-2-hepten-6-one, acetic acid, butyric acid, isovaleric acid, formic acid: 52, 130.

Tapinoma erraticum Latr.

2-methyl-2-hepten-6-one: 261, 332.

Tapinoma nigerrimum Nyl.

iridodial: 59, 139, 270; 2-methyl-2-hepten-6-one, propyl isobutyl ketone: 183, 359; 2-methyl-2-hepten-6-one, propyl isobutyl ketone, a dialdehyde: 350, 2-methyl-2-hepten-6-one, propyl iso

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butyl ketone, iridodial: 30, 42, 52, 55, 61, 62, 66, 80, 130, 131, 133, 156, 182, 204, 245, 246, 248, 249, 250, 278, 332, 332 A, 339, 348 B, 351, 356; propyl isobutyl ketone: 31.

Subfam. MyrmicinaeAtta sexdens rubropilosa For.

citral: 21, 42, 43, 53, 66, 80, 133, 134, 139, 182, 202, 204, 249, 250, 270, 278, 332 A, 348 B, 355 B, 356, 357, 358.

Crematogaster (Atopogyne) africana Mayr

trans-hex-2-enal: 15, 19, 30, 53, 66, 80, 132, 134, 157, 348 B.

Crematogaster lineolata (Say) clara Mayr

formic acid (traces): 193.

Crematogaster scutellaris scutellaris Oliv.

formic acid: 137, 203, 204, 205, 224, 226, 228, 231, 233, 256, 259, 264, 319.

Daceton armigerum (Latreille)

proteins: 25.

Monomorium antarcticum Wheeler

proteins and free amino acids: 20.

Monomorium pharaonis (L.)

proteins and free amino acids: 20.

Myrmica rubida Latr.

formic acid: 66, 245, 246, 328.

Myrmica ruginodis Nyl.

formic acid: 66, 245, 246, 328.

Myrmecaria natalensis Fred.

D-limonene, L-limonene: 134, 248, 278, 348 B; D-limonene, L-limonene, acetic acid, propionic acid, isovaleric acid, isobutyric acid (traces): 66, 139, 249, 250, 270.

Pheidole fallax Mayer

an indole base (probably scatole): 174.

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Pogonomyrmex badius (Latr.)

proteins and free amino acids: 148.

Solenopsis saevissima Fr.Smith

nitrogenous base: 23; amine: 26; hemolytic, non protein, alkaline principle (probably a amine): 4.

Solenopsis saevissima var. richteri For.

high molecular weight nitrogen-containing unsaturated compound (alkaloid?): 22; solenopsin: 249, 250; strongly hemolytic component. (probably a amine): 11.

Solenopsis xyloni McCook

amine: 26.

Subfam. FormicinaeAcanthomyops sp.

citronellal, citronellol: 53, 139, 249, 250, 270.

Acanthomyops claviger Roger

citronellal: 357; citronellal, citral: 21, 53, 66, 72, 111, 145, 157, 183, 189, 348 B, 356, 358: citronellal, citral, mixture of undetermined components: 278; citronellal, citral, formic acid: 134; monoterpene aldehydes: 174.

Cataglyphis bicolor (Fab.)

formic acid: 66, 163, 180, 245, 246, 327, 330, 333 A.

Camponotus aethiops Latr.

formic acid: 66, 163, 245, 246, 330.

Camponotus americanus Mayr

formic acid: 193.

Camponotus compressus F. thoracica F.

formic acid: 163.

Camponotus fumidus Roger

formic acid: 193.

Camponotus ligniperda Latr.

formic acid: 11, 66, 163, 179, 245, 246, 326, 327, 330, 332 A.

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Camponotus maculatus Fabr.

formic acid: 66, 245, 246, 301, 330, 333 A.

Camponotus maculatus Fabr. sansabeanus Bkly

formic acid: 193.

Camponotus thoracicus F.

formic acid: 66, 245, 246, 330.

Colobopsis truncata Spin.

formic acid: 66, 163, 245, 246, 330.

Lasius alienus Först.formic acid: 66, 163, 203, 204, 224, 226, 228, 231, 234, 245,
246, 256, 259, 260, 264, 330.Lasius bicornis affinis Sch.formic acid: 163, 203, 204, 205, 223, 224, 226, 228, 231, 234,
235, 255, 256, 259, 260, 264.Lasius (Chthonolasius) bicornis (Foerst.)methyl-undecyl- ketone: 30; palmitic acid, n-undecane, methyl-
n-undecyl-ketone: 53, 249, 267.Lasius (Chthonolasius) umbratus Nyl.n-undecane, methyl-n-undecyl-ketone: 66, 80, 133, 272; 332 A;
palmitic acid, n-undecane, methyl-n-undecyl-ketone: 53, 249,
267; methyl-n-undecyl-ketone: 30.Lasius (Dendrolasius) fuliginosus Latr.dendrolasin: 5, 53, 54, 69, 131, 139, 156, 163, 169, 204, 240,
242, 245, 247, 248, 249, 261, 269, 270, 270 A, 271, 272, 273,
278, 286 B, 319, 332, 332 A, 339, 348 B, 351, 355 A, 356, 357,
358, 360; formic acid, dendrolasin: 66, 80, 134, 245, 246, 250;
dendrolasin, n-undecane, palmitic acid: 249, 267; formic acid:
163, 180, 203, 204, 205, 223, 224, 226, 228, 231, 233, 235,
255, 256, 259, 260, 264, 326, 327, 330; 6-methyl-hept-5-en-2-
one (traces), perillen cis-citral, trans-citral, dendrolasin,
farnesal, two unidentified compounds: 13 A.

Lasius flavus F.

formic acid: 66, 163, 179, 245, 246, 326, 327, 330.

Lasius niger L.

formic acid: 66, 163, 203, 204, 205, 213, 224, 226, 228, 231, 234, 245, 246, 256, 259, 260, 264, 330.

Lasius niger x alienus

formic acid: 203, 204, 205, 224, 226, 228, 231, 234, 256, 259, 260, 264.

Formica cinerea Mayr

formic acid: 66, 163, 245, 246, 330.

Formica exsecta Nyl.

formic acid: 66, 163, 245, 246, 330.

Formica exsecta Nyl. pressilabris Nyl.

formic acid: 163.

Formica exsectoides Forel.

formic acid: 1 B, 58, 163, 278.

Formica fusca L.

formic acid: 66, 163, 213, 245, 246, 327, 330.

Formica fusca L. glebaria Nyl.

formic acid: 66, 163, 245, 246, 326, 330.

Formica fusca L. gnava Bkly

formic acid: 193, 213.

Formica nigricans Em.

formic acid: 165, 332 A; formic acid, ammonia: 215.

Formica picea Nyl.

formic acid: 66, 163, 245, 246, 330.

Formica polystena Först.

formic acid: 157, 165, 183, 216, 287, 332, 332 A, 333; formic acid, ammonia: 215.

Formica pratensis Retz.

formic acid: 66, 119, 137, 157, 163, 165, 169, 203, 204, 205, 224, 226, 228, 231, 234, 235, 245, 246, 256, 259, 260, 264,

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326, 327, 328, 330, 331; formic acid, ammonia: 215.

Formica pressilabris Nyl.

formic acid: 66, 245, 246, 330.

Formica rufa L.

formic acid, amino acids, odorous substances: 333, formic acid: 11, 66, 119, 137, 157, 163, 165, 167, 179, 180, 242, 245, 246, 261, 263, 278, 319, 326, 327, 329, 330, 332, 332 A, 333 A, 346, 351, 355 B; n-undecane: 267, 272, 289; formic acid, ammonia: 215.

Formica rufibarbis F.

formic acid: 66, 163, 245, 246, 326, 327, 330.

Formica sanguinea Latr.

formic acid: 66, 163, 245, 246, 326, 327, 330.

Formica truncicola Nyl.

formic acid: 66, 245, 246, 326, 327, 330.

Plagiolepis pygmaea Latr.

formic acid: 66, 163, 245, 246, 330, 332 A.

Polyergus rufescens Latr.

formic acid: 66, 163, 245, 246, 330.

Chap. 16 - Crustacea Isopoda and chemically defined substances of defensive secretions.

Cl. C R U S T A C E A

Ord. ISOPODA

Fam. Porcellionidae

Porcellio scaber (Latr.)

cis-dec-3-en-1-ol, trans-dec-3-en-1-ol, cis/trans-non-en-1-ol, nonan-1-ol, unsaturated component: 57 (1).

Fam. Armadillididae

Armadillidium sp.

octan-1-ol: 57 (1).

(1) See pag. 42.

Chap. 17 - Arachnida Scorpiones, Uropygi, Araneae and chemically defined substances of defensive secretions.

CL. A R A C H N I D A

Ord. SCORPIONES

Fam. Buthidae

Androctonus australis (L.)

neurotoxic basic proteins: 196, 197, 352; scorpamins: 212;
two toxic fractions each containing: aspartic acid, threonine, serine, glutamic acid, proline, glycine, alanine, cystine, valine, isoleucine, leucine, tyrosine, phenylalanine, lysine, histidine, arginine, tryptophane: 195.

Buthacus arenicola (E. Simon)

lecithinase, coagulase: 6.

Buthotus minax

5-hydroxytryptamine: 352, 353.

Buthus australis Hector

hyaluronidase activity: 163.

Buthus martensii Karsch

buthotoxin: 163, 169, 212.

Buthus occitanus (Am.) (= Buthus europaeus ?)

neurotoxic proteins: 196, 197, 352; scorpamin: 212; hyaluron-

- (1) The defensive action of alcohols found is only supposed and the organ producing the substances is not yet known (Cavill and Coll., 1966, 57).

The mucilaginous substances from glands of uropoda in many species of terrestrial Isopods, have probably a defensive action.

According to T. Paulucci Maccagno 1951-52 (Sul secreto delle ghiandole tegumentali lobate degli Isopodi terrestri. Bull. Ist. Mus. Zool. Univ. Torino, 3 (14): 177-184, 1951-52) Porcellio scaber and P. laevis secretions contain: proteins with indole and benzene groups, tyrosine, cystine, mucoproteins, mucins, neutral fats, chlorides, urea, uric acid.

dase activity: 159, 163; aspartic acid, threonine, serine, glutamic acid, proline, glycine, alanine, cystine, valine, isoleucine, leucine, tyrosine, phenylalanine, lysine, histidine, arginine, tryptophane: 195.

Centruroides gracilis Gervais

5-hydroxytryptamine: 353.

Centruroides sculpturatus Ewing

peptide or with peptides closely associated substance, polysaccharide (probably): 324; sixteen protein fractions: 324 A.

Isometrus maculatus (De Geer)

hyaluronidase activity: 163.

Leiurus quinquestriatus H. e E.

5-hydroxytryptamine: 3, 353; 5-hydroxytryptamine and enzymes: 286, 5-hydroxytryptamine, peptide compound or compounds: 212; two low molecular basic proteins, 5-hydroxytryptamine: 2, 352.

Tityus bahiensis Perty

a low-molecular substance attached to protein: 163, 212; protein-like substances, lysine: 169; 5-hydroxytryptamine: 353.

Tityus serrulatus Lutz e Mello

a low-molecular substance attached to protein: 163, 212; protein-like substances, lysine: 169; 5-hydroxytryptamine: 353.

Fam. Scorpionidae

Heterometrus maurus L. (= Scorpio maurus L.)

hyaluronidase activity: 159, 163; lecithinase, anticoagulase: 6.

Fam. Vejovidae

Vejovis sp.

5-hydroxytryptamine: 353.

Vejovis spinigerus

5-hydroxytryptamine: 353.

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Fam. ChactidaeEuscorpius italicus (Herbst)

adenosine triphosphatase, hyaluronidase activity: 163; hyaluronidase activity: 120.

Ord. UROPYGI

Fam. ThelyphonidaeMastigoproctus giganteus (Lucas)

acetic acid, caprylic acid, H₂O: 112, 113, 204, 249, 250, 278, 348 B.

Ord. OPILIONES

Fam. GonyleptidaeHeteropachyloidellus robustus Roewer (*)

2,3-dimethyl-1,4-benzoquinone, 2,5-dimethyl-1,4-benzoquinone, 2,3,5-trimethyl-1,4-benzoquinone: 9, 10, 80, 116, 121, 245, 246, 248 B, 278, 335.

Ord. ARANEAE

Fam. TheraphosidaeAcanthoscurria atrox Vellard

glutamic acid, β -aminobutyric acid, aspartic acid, four protein fractions: 169; 5-hydroxytryptamine: 353; four protein fractions, free amino acids: 163.

Acanthoscurria sternalis Pocock

5-hydroxytryptamine: 353.

Aphonopelma sp.

ten protein fractions: 324 A.

(*) This species is cited also as undetermined genus and species of Fam. Gonyleptidae.

Grammostola actaeon Pocock

glutamic acid, γ -aminobutyric acid, four protein fractions: 169;
four protein fractions, free amino acids: 163.

Grammostola mollicoma Ausserer

glutamic acid, γ -aminobutyric acid, four protein fractions: 169;
four protein fractions, free amino acids: 163.

Grammostola pulchripes Simon

four protein fractions, free amino acids: 163.

Lasiadora klugii Koch

glutamic acid, γ -aminobutyric acid: 169; four protein fractions,
free amino acids: 163.

Pamphobetus roseus M.-Leitao

four protein fractions, free amino acids: 163.

Pamphobeteus soracabae M.-Leitao

glutamic acid, γ -aminobutyric acid: 169; four protein fractions,
free amino acids: 163.

Pamphobeteus tetracanthus M.-Leitao

glutamic acid, γ -aminobutyric acid: 169; four protein fractions,
free amino acids: 163.

Pterinopelma vellutinum M.-Leitao

5-hydroxytryptamine: 353.

Fam. LycosidaeLycosa erythrognata Luc. (~~L.~~ raptoria Wlk.)

glutamic acid, aspartic acid, lysine, proteins, hyaluronic acid,
histamine, nitrogen, inorganic phosphates: 169; 5-hydroxy
tryptamine 353; hyaluronidase-like substance, trypsin: 162.

Scaptocosa raptoria Wlk.

proteins, free amino acids including glutamic acid, proteolytic
ferment, L-amino acid dehydrogenase, hyaluronidase: 163.

Fam. TheridiidaeLatrodectus mactans F.

five-six protein compounds: free amino acids and high content of glutamic acid: 284; twelve amino acids including glutamic acid: 285; seven protein and three non-protein fractions: 184D.

Latrodectus tredecimguttatus Rossi

six protein fractions: 14, 163; three toxic protein components: 126, 127, 184 D, 206, 343; two active protein fractions: 352, lipoprotein: 163.

Fam. ArgiopidaeAraneus diadematus Clerck

hyaluronidase: 163.

Fam. CtenidaeCtenus nigriventer Keys (= Phoneutria nigriventer Keys)

proteins, hyaluronic acid: 169; hyaluronidase like substance, trypsin: 162; proteolytic enzyme, L-amino acid dehydrogenase, hyaluronidase: 163.

Phoneutria fera Perty (= Ctenus ferus Perty) (1)

5-hydroxytryptamine: 352, 353; proteins, free amino acids including glutamic acid: 163.

(1) According to Lang K., Lehnartz E. (1960) 169, the secretion of Phoneutria fera Perty (= Ctenus nigriventer Keys) contains: glutamic acid, aspartic acid, lysine, histamine, inorganic phosphates.

PART V - CHEMICALLY DEFINED SUBSTANCES OF DEFENSIVE SECRETIONS OF
ARTHROPODA AND THE SPECIES IN WHICH THEY ARE PRESENT.

Chap. 18 - Remarks.

In this chapter I have listed the substances that we presume to be present in Arthropoda defensive secretions, including the list of the species in which it has been found for each one. The species are arranged systematically and are followed by the code of the zoological group to which they belong. The codes used are the following:

ARA	- Arachnida Araneae
BLA	- Insecta Blattodea
CHOR	- Diplopoda Chordeumida
COL	- Insecta Coleoptera
CRU	- Crustacea Isopoda
DER	- Insecta Dermaptera
DIP	- Insecta Diptera
GLO	- Diplopoda Glomerida
HET	- Insecta Heteroptera
HYM	- Insecta Hymenoptera
ISO	- Insecta Isoptera
JUL	- Diplopoda Juliformia
LEP	- Insecta Lepidoptera
OPI	- Arachnida Opiliones
ORT	- Insecta Orthoptera
PHA	- Insecta Phasmida
POL	- Diplopoda Polydesmida
SCOL	- Chilopoda Scolopendromorpha
SCORP	- Arachnida Scorpiones
URO	- Arachnida Uropygi

Chap. 10 - Organic substances.

HYDROCARBONS

n-undecane

Formica rufa L., Lasius (Chthonolasius) bicornis Foerst., L. (Ch.)
umbratus Nyl., L. (Dendrolasius) fuliginosus Latr. (HYM);
Nezara viridula L. var. smaragdula Fabr. (HET).

n-dodecane

Biprorulus bibax , Musgraveia sulciventris Stål., Nezara viridu-
la L. var. smaragdula F., Rhoecocoris sulciventris Stål, Macroscy-
tus sp. (HET).

n-tridecane

Biprorulus bibax , Carpocoris purpureipennis (De Geer), Cerato-
coris cephalicus Mont., Euschistus servus Say., Macroscytus sp.,
Mysgraveia sulciventris Stål, Nezara viridula L., N. viridula L.
var. smaragdula Fabr., Oebalus pugnax Fabr., Rhoecocoris sulciven-
tris Stål, Tessaratomia aethiops Dist. (adults and larvae) (HET);
Eleodes longicollis Le Conte (COL).

1-nonene

Eleodes longicollis Le Conte (probably) (COL).

1-undecene

Eleodes longicollis Le Conte (COL).

1-tridecene

Eleodes longicollis Le Conte (COL).

SULFIDES

dimethyldisulfide

Paltothyreus tarsatus (Fabr.) (HYM).

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dimethyltrisulfidePaltothyreus tarsatus Fabr. (HYM).ALCOHOLSmethanolArctia caja L. (LEP).glycerolApis mellifera L. (HYM).n-hexanolAgriopocoris froggatti Mill., Amorbus alternatus Dallas, A. rhombifer West., A. rubiginosus Guérin, Aulacosternum nigrorubrum Dallas, Mictis caja Stål, M. profana Fabr., Pachycolpura manca Breddin, Hyocephalus sp. (HET).2-methyl butanolPlatyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).2-methylene butanolPlatyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).ottan-1-olArmadillidium sp. (CRU).nonan-1-olPorcellio scaber (Latr.) (CRU).cis-non-3-en-1-olPorcellio scaber (Latr.) (CRU).trans-non-3-en-1-olPorcellio scaber (Latr.) (CRU).cis-dec-3-en-1-olPorcellio scaber (Latr.) (CRU).

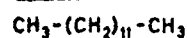
trans-dec-3-en-1-olPorcellio scaber (Latr.) (CRU).cossin 1 (*)Cossus cossus L., larvae (LEP).cossin 2 (*)Cossus cossus L., larvae (LEP).cossin 3 (*)Cossus cossus L., larvae (LEP).(*) For cossin A, cossin B, cossin C, cossin B₁, cossin C₁, see Esters.AMINES AND AMINO ALCOHOLScholineApis mellifera L. (HYM).histaminePoecillocerus bufonius Klug (ORT);Abraxas grossulariata L., Arctia caja L. (§), Dendrolimus spectabilis Btlr. (§), D. undans Walk. (§), Dirphia sp., Euproctis flava Brem. (§), Eurrhyncha hostulata L., Hypocrita jacobaeae L., Megalopyge sp., Spilosoma lubricipeda L., Thaumetopoea pityocampa Sch.(§), Zygaena lonicerae von Sch. (LEF);Cimex lectularius L., Platyeris rhadamanthus Gaerst. (§) (HET);Apis mellifera L., Myrmecia forficata Fabr., M. gulosa Fabr., Vespa crabro L., Vespula germanica Fabr., V. vulgaris L. (HYM);Lycosa erythrognata Luc. (ARA).

(§) probably.

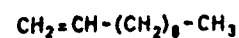
5-hydroxytryptamineScolopendra viridicornis Newport (SCOL);Automeris sp. (hairs, larvae), Automeris (illustris?) (hairs) (LEP);Apis mellifera L., Dolicovespula media De G., Polybia occidentalis scutellaris , Polistes gallicus L., P. versicolor (Ol.),

HYDROCARBONS

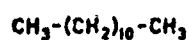
n-UNDECANE



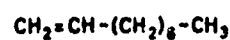
n-TRIDECANE



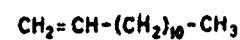
1-UNDECENE



n-DODECANE



1-NONENE



1-TRIDECENE

SULFIDESALCOHOLS

METHANOL



GLYCEROL



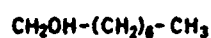
2-METHYL BUTANOL



2-METHYLENE BUTANOL



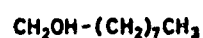
n-HEXANOL



OTTAN-1-OL



CIS, TRANS-NON-3-EN-1-OL



NONAN-1-OL



CIS, TRANS-DEC-3-EN-1-OL



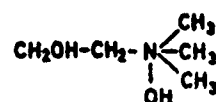
COSSIN 1



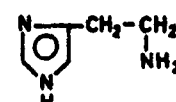
COSSIN 2



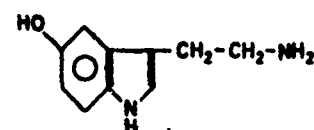
COSSIN 3

AMINES AND AMINO ALCOHOLS

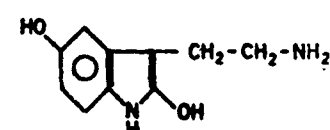
CHOLINE



HISTAMINE



5-HYDROXYTRYPTAMINE



2,5-HYDROXYTRYPTAMINE

Synoeca surinama , Vespa crabro L., Vespula germanica Fbr., V. media , V. vulgaris L. (HYM);
Buthotus minax , Centruroides gracilis Gervais, Leiurus quinque-
striatus H. et E., Tityus bahiensis Perty, T. serrulatus L.M., Ve-
jovis sp., V. spinigerus (SCORP);
Acanthoscurria atrox Vellard, A. sternalis Poc., Lycosa erythro-
gna Luc., Phoneutria fera Perty, Pterinopelma vellutinum M-Leitao
 (ARA).

2,5-hydroxytryptamine

Vespula vulgaris L. (HYM).

SATURATED ALDEHYDES

propanal

Scaptocoris divergens Froesch (HET).

n-butanal

Riptortus clavatus (Thunberg), Amorbus rhombifer West. (HET).

2-methyl-butanal

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shel-
 ford, P. ruficeps Shelford (BLA).

n-hexanal

Acanthocoris sordidus (Thunberg), Agriopocoris froggatti Miller, A-
morbus alternatus Dallas, Amorbus rhombifer West., Amorbus rubigi-
nosus Guérin, Aulacosternum nigrorubrum Dallas, Graphosoma rubroli-
neatum (Westwood), Hygia opaca (Uhler), Hyocephalus n.sp., Mictis
caja Stål, Mictis profana Fabr., Pachycolpura manca Breddin, Plina-
chtus bicoloripes Scott (HET).

UNSATURATED ALDEHYDES

trans-prop-2-enal

Nezara viridula L. var. smaragdula F., Scaptocoris divergens
 Froesch. (HET).

- V 6 -

2-methylene propanal

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

trans-but-2-enal

Nezara viridula L. var. smaragdula F., Scaptocoris divergens Froesch. (HET).

2-methylene butanal

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

2-methylene butanal dimer

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

pentenal

Scaptocoris divergens Froesch. (HET).

2-methylene pentenal

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

trans-hex-2-enal

Cutilia sororor (Brunner), Eurycotis decipiens (Kirby), E. florida-na Walk., Pelmatosilpha coriacea Rehn, Platyzosteria novae seelandiae Brunner (BLA);

Acanthocoris sordidus (Thunberg), Acantocephala femorata Fab., Brachymena quadripustulata Fabr., Cimex lectularius L., Dolychoris bac-carum L., Eurygaster sp., Musgraveia sulciventris Stål, Nezara viridula L., N. v. var. smaragdula Fabr., Palomena viridissima P., Precilometis strigatus Westwood, Rhoecocoris sulciventris Stål, Scaptocoris divergens Froeschner, Scotinophara lurida Burmeister, Tessaratoma aethiops Dist. (adults) (HET);

Crematogaster (Atopogyne) africana Mayr (HYM).

trans-hept-2-enal

Euschistus servus Say, Oebalus pugnax Fabr., Nezara viridula L.,
Scaptocoris divergens Froesch. (HET).

trans-oct-2-enal

Aelia fieberi Scott., Cimex lectularius L., Dolychoris baccarum L.,
Eurygaster sp., Leptocoris apicalis West., Musgraveia sulciventris
Stål, Nezara viridula L. var. smaragdula Fabr., Palomena viridissi-
ma P., Poecilometis strigatus Westwood, Rhoecocoris sulciventris
Stål, Scaptocoris divergens Froeschner, Scotinophara lurida Burmei-
ster, Tessaratomya aethiops Dist. (adults and larvae) (HET).

trans-dec-2-enal

Aelia fieberi Scott., Biprorulus bibax , Dolichoris baccarum L.,
Graphosoma rubrolineatum West., Leptocoris apicalis West., Menida
scotti Puton, Musgraveia sulciventris Stål, Nezara antennata Scott.,
N. viridula L., N. v. L. var. smaragdula Fabr., Palomena viridissi-
ma P., Rhoecocoris sulciventris Stål, Scotiniphara lurida Burmeister
(HET).

cis-dec-2-enal

Nezara viridula L. var. smaragdula F. (HET).

trans-dodec-2-enal

Rhinocricus insulatus Chamberlin (JUL).

AROMATIC ALDEHYDESbenzaldehyde

Apheloria corrugata Wood, Orthomorpha coarctata Sauss., O. gracilis
Koch, Pachydesmus crassicutis Wood, Polydesmus collaris collaris
Koch, Gomphodesmus pavani Dem. (POL).

p-hydroxybenzaldehyde

Cybister lateralimarginalis D.G., Dytiscus latissimus L., D. margina-
lis L., Hydroporus palustris L. (COL).

salicylaldehyde

Aromia moschata L., Calosoma prominens Lec., C. sycophanta L. (adults), Melasoma populi L., M. saliceti Weise (larvae), Phyllodecta vitellinae L., Plagioderia sp., Plagioderia versicolor Laich. (larvae) (COL).

cuminaldehyde

Rhysodesmus vicinus Sauss. (POL).

SATURATED KETONESmethyl-ethyl-ketone

Nezara viridula L. var. smaragdula F. (HET).

methyl-heptyl-ketone

Nezara viridula L. var. smaragdula F. (HET).

ethyl-propyl-ketone

Nezara viridula L. var. smaragdula F. (HET).

methyl-n-amyl-ketone

Conomyrma pyramica (Roger), Iridomyrmex pruinosus Roger (HYM).

methyl-n-undecyl-ketone

Lasius (Chthonolasius) bicornis Foerst, L. (Ch.) umbratus Nyl. (HYM).

4-methyl-2-hexanone

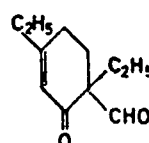
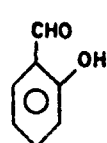
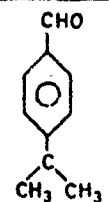
Dolichoderus (Acanthoclinea) Clarki (Wheeler) (HYM).

n-propyl-isobutyl-ketone

Iridomyrmex conifer For., Iridomyrmex detectus Sm., Tapinoma niger-rimum Nyl. (HYM).

UNSATURATED KETONES2-methyl-2-hepten-6-one

Dolichoderus (Diceratoclinea) scabridus Roger, Iridomyrmex conifer For., I. detectus Sm., I. nitidiceps Andre, I. rufoniger Lowne, Lasius (Dendrolasius) fuliginosus Latr., Liometopum microcephalum Panz., Tapinoma nigerrimum Nyl., T. erraticum Latr. (HYM).

<u>ALDEHYDES</u>			
SATURATED		$\text{CH}_3-(\text{CH}_2)_4-\text{CHO}$ n-HEXANAL	
$\text{CH}_3-\text{CH}_2-\text{CHO}$ PROPANAL	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}$ n-BUTANAL	$\text{CH}_3-\overset{\text{C}_2\text{H}_5}{\underset{ }{\text{CH}}}-\text{CHO}$ 2-METHYL-BUTANAL	
UNSATURATED			
$\text{CH}_2=\text{CH}-\text{CHO}$ TRANS-PROP-2-ENAL	$\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CHO}$ 2-METHYLENE PROPANAL	$\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$ TRANS-BUT-2-ENAL	
$\text{CH}_2=\overset{\text{C}_2\text{H}_5}{\text{C}}-\text{CHO}$ 2-METHYLENE BUTANAL	 2-METHYLENE BUTANAL DIMER	$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CHO}$ PENTENAL	
$\text{CH}_2=\overset{\text{C}_3\text{H}_7}{\text{C}}-\text{CHO}$ 2-METHYLENE PENTENAL	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CHO}$ TRANS-HEX-2-ENAL		
$\text{CH}_3-(\text{CH}_2)_3-\text{CH}=\text{CH}-\text{CHO}$ TRANS-HEPT-2-ENAL		$\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}-\text{CHO}$ TRANS-OCT-2-ENAL	
$\text{CH}_3-(\text{CH}_2)_6-\text{CH}=\text{CH}-\text{CHO}$ CIS,TRANS-DEC-2-ENAL		$\text{CH}_3-(\text{CH}_2)_8-\text{CH}=\text{CH}-\text{CHO}$ TRANS-DODEC-2-ENAL	
AROMATIC			
 BENZALDEHYDE	 p-HYDROXYBENZALDEHYDE	 SALICYLALDEHYDE	 CUMINALDEHYDE
BENZALDEHYDE p-HYDROXYBENZALDEHYDE SALICYLALDEHYDE CUMINALDEHYDE			

<u>KETONES</u>			
SATURATED		$\text{CH}_3-\text{CO}(\text{CH}_2)_6-\text{CH}_3$ METHYL-HEPTYL-KETONE	
$\text{CH}_3-\text{CH}_2-\text{CO}-\text{CH}_3$ METHYL-ETHYL-KETONE	$\text{CH}_3-(\text{CH}_2)_4-\text{COCH}_3$ METHYL-n-AMYL-KETONE	$\text{CH}_3-\text{CH}_2-\text{CO}-(\text{CH}_2)_2-\text{CH}_3$ ETHYL-PROPYL-KETONE	$\text{CH}_3-(\text{CH}_2)_{10}-\text{COCH}_3$ METHYL-n-UNDECYL-KETONE
$\text{CH}_3-\text{CO}-\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{CH}}}-\text{CH}_2-\text{CH}_3$ 4-METHYL-2-HEXANONE		$\text{H}_3\text{C} \begin{array}{l} \diagdown \\ \diagup \end{array} \text{CH}-\text{CH}_2-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CH}_3$ H_3C n-PROPYL-ISOBUTYL-KETONE	
UNSATURATED		$\text{H}_3\text{C} \begin{array}{l} \diagdown \\ \diagup \end{array} \text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CO}-\text{CH}_3$ H_3C 2-METHYL-2-HEPTEN-6-ONE	
$\text{CH}_3-\text{CH}_2-\text{CO}-\text{CH}=\text{CH}-\text{CH}_3$ 4-KETO-HEX-2-ENE			
<u>KETO ALDEHYDES</u>			
$\text{CH}_3-\text{CH}_2-\text{CO}-\text{CH}=\text{CH}-\text{CHO}$ 4-KETO-TRANS-HEX-2-ENAL		$\text{CH}_3-(\text{CH}_2)_3-\text{CO}-\text{CH}=\text{CH}-\text{CHO}$ 4-KETO-TRANS-OCT-2-ENAL	

4-keto-hex-2-ene

Nezara viridula L. var. smaragdula F. (HET).

UNSATURATED KETO ALDEHYDES4-keto-trans-hex-2-enal

Corixa dentipes Thoms, Macroscytus sp., Nezara viridula L., N. v.
L. var. smaragdula Fabr., Sigara falleni (Fieb.), Tessaratomia aethiops Dist. (adults and larvae) (HET).

4-keto-trans-oct-2-enal

Nezara viridula L. var. smaragdula F. (HET).

CARBOXYLIC ACIDSformic acid

Cerura vinula L. (larvae), Cnethocampa sp., Datana ministra (larvae), Dicranura furcula Boisduval (larvae), Portesia sp. (hairs), Schizura concinna Abbot and Smith (larvae), S. leptinoides Grote, Thaumetopoea pityocampa Sch. (larvae) (LEP);

Acinopus sp., Calathus sp., Carterus sp., Harpalus dimidiatus Rossi, Pheropsophus agnatus, Pseudophonus griseus Panz., P. pubescens Mull (COL);

Acanthomyops claviger (Roger), Apis mellifera L., Camponotus aethiops Latr., C. americanus Mayr, C. compressus F. thoracica F., C. fumidus Roger, C. ligniperda Latr., C. maculatus Fabr., C.m. sansabeanus Bkly, C. thoracicus F., Cataglyphis bicolor Fabr., Colobopsis truncata Sprin., Crematogaster lineolata clara Mayr, Cr. scutellaris scutellaris Oliv., Formica cinerea Mayr, F. exsecta Nyl., F. e. Nyl. pressilabris Nyl., F. exectoides Forel, F. fusca L., F.f. L. glebaria Nyl., F. f. L. gnava Bkly, F. nigricans Em., F. picea Nyl., F. polyctena Först., F. pratensis Retz., F. pressilabris Nyl., F. rufa L., F. rufibarbis F., F. sanguinea Latr., F. truncicola Nyl., Lasius alienus Först., L. bicornis affinis Sch., L. (Dendrolasius) fuliginosus Latr., L. flavus F., L. niger L., L. n. x alienus Först.,

Liometopum microcephalum Panz. (*), Myrmica rubida Latr., M. ruginodis Nyl., Pachycondila sp., P. harpax (Fabr.), Plagyolepis pygmaea Latr., Polyergus rufescens Latr. (HYM).

acetic acid

Agriopocoris froggatti Miller, Amorbus alternatus Dallas, A. rhombifer West., A. rubiginosus Guérin, Aulacosternum nigrorubrum Dallas, Hyocephalus sp., Mictis caja Stål, M. profana Fabr., Pachycolpura manca Breddin (HET);

Cerura vinula L. (larvae) (LEP);

Liometopum microcephalum Panz., Myrmicaria natalensis Fred. (HYM);

Mastigoproctus giganteus (Lucas) (URO).

propionic acid

Myrmicaria natalensis Fred. (HYM).

butyric acid

Carabus sp., Cychrus sp. (COL);

Apis mellifera L. (*), Liometopum microcephalum Panz. (HYM).

isobutyric acid

Papilio machaon L., (larvae) (LEP);

Myrmicaria natalensis Fred. (HYM).

2-methyl butyric acid

Papilio machaon L., (larvae) (LEP).

isovaleric acid

Liometopum microcephalum Panz., Myrmicaria natalensis Fred. (HYM).

caprylic acid

Eleodes longicollis Lec. (COL);

Mastigoproctus giganteus (Lucas) (URO).

palmitic acid

Apis mellifera L., Lasius (Chthonolasius) bicornis Foerst., L. (Ch.) umbratus Nyl., L. (Dendrolasius) fuliginosus Latr. (HYM).

(*) probably.

methacrylic acid

Cerura vinula L., (larvae)(LEP);

Abax ater Villers, A. ovalis Dftsch., A. parallelus Dftsch., Apotomopterus albrechti Esakii A. Mor., A. insulicula Chaud., Calosoma syncophanta L., Carabus auratus L., C. auronitens Fbr., C. cancellatus Illig., C. convexus Fbr., C. coriaceus L., C. cyaneus F., C. granulatus L., C. irregularis Fbr., C. procerulus Chaud., C. Ullrichi Germ., C. violaceus L., Cychrus rostratus Lin., Damaster oxuroides Schaum, Pterostichus metallicus Fbr., Pt. niger Schall., Pt. vulgaris L.(COL).

2-methylene butyric acid

Platyzosteria castanea Brunner, P. jungii (Tepper), P. morosa Shelford, P. ruficeps Shelford (BLA).

tiglic acid

Cerura vinula L., (larvae)(LEP);

Abax ater Villers, A. ovalis Dftsch., A. parallelus Dftsch., Apotomopterus albrechti Esakii A. Mor., A. insulicula Chaud., Calosoma syncophanta L., Carabus auratus L., C. auronitens Fabr., C. cancellatus Illig., C. convexus Fbr., C. coriaceus L., C. cyaneus F., C. granulatus L., C. irregularis Fbr., C. ullrichi Germ., C. violaceus L., Pterostichus metallicus Fbr., P. niger Schall., P. vulgaris L. (COL).

10-hydroxy-2-decenoic acid

Apis mellifera L. (HYM).

D-gluconic acid

Eurycotis biolleyi Rehn, E. decipiens (Kirby), E. floridana Walk.(BLA).

ascorbic acid

Chrysocoris stolli Wolf (HET).

hyaluronic acid

Ctenus nigriventer Keys, Lycosa erythrogna Luc. (ARA).

benzoic acid

Gomphodesmus pavani Dem., Orthomorpha coarctata Sauss., Polydesmus

collaris collaris Koch (POL);

Dytiscus latissimus L., D. marginalis L. (COL).

pipecolinic acid

Vespula germanica Fabr. (HYM).

oxalic acid

Ceroplatus lineatus F., Platyura discoloria Mg., Pl. fasciata Meigen,
Pl. nigricornis F., Pl. sp., Ceroplatus sp. (DIP).

PHENOLS

phenol

Abacion magnum Loomis (CHOR);

Orthomorpha coarctata Sauss. (POL).

guaiacol

Orthomorpha coarctata Sauss. (POL).

cresol

Tribolium destructor Uytt. (COL).

m-cresol

Chlaenius cordicollis Kirby (COL).

p-cresol

Abacion magnum Loomis (CHOR).

FURANS

furan

Scaptocoris divergens Froesch. (HET).

methyl furan

Scaptocoris divergens Froesch. (HET).

perillen

Lasius (Dendrolasius) fuliginosus Latr. (HYM).

dendrolasin

Lasius (Dendrolasius) fuliginosus Latr. (HYM).

ESTERSisoamyl acetate

Apis mellifera L. (HYM).

n-hexyl acetate

Agriopocoris froggatti Miller, Amorbus alternatus Dallas, A. rhombifer West., A. rubiginosus Guérin, Aulacosternum nigrorubrum Dallas, Hyocephalus sp., Mictis caja Stål, M. profana Fabr., Pachycolpura manca Breddin (HET).

n-octyl acetate

Leptocoris apicalis Westw. (HET).

trans-hex-2-enyl acetate

Lethocerus indicus (Lep. and Serv.), Nezara viridula L. var. smaragdula F. (HET).

trans-oct-2-enyl acetate

Macroscytus sp., Musgraveia sulciventris Stål., Nezara viridula L. var. smaragdula F., Rhoecocoris sulciventris Stål., Tessaratomyia aethiops Dist. (adults) (HET).

trans-dec-2-enyl acetate

Biprorulus bibax , Macroscytus sp., Nezara viridula L. var. smaragdula F. (HET).

coffin A (*)

Cossus cossus L. (larvae) (LEP).

coffin B (*)

Cossus cossus L. (larvae) (LEP).

coffin C (*)

Cossus cossus L. (larvae) (LEP).

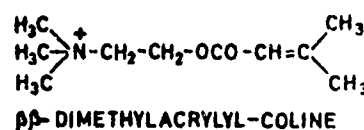
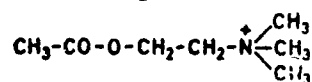
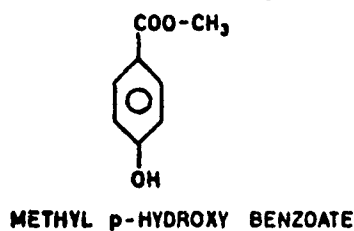
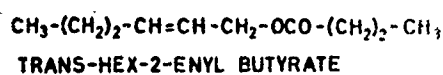
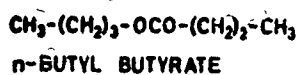
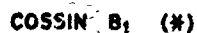
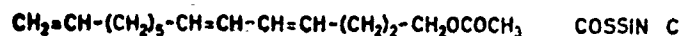
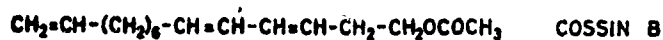
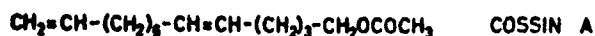
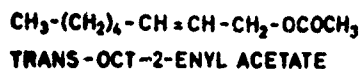
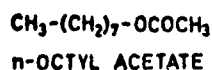
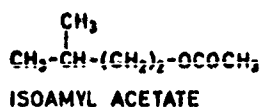
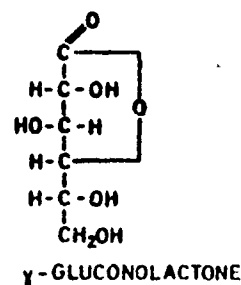
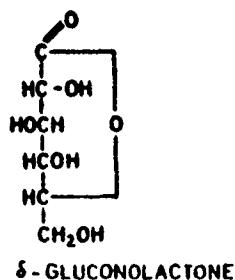
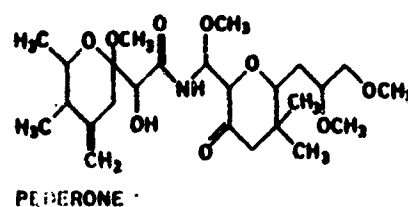
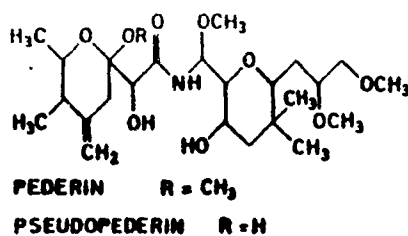
coffin B₁ (*)

Cossus cossus L. (larvae) (LEP).

(*) For coffin 1, coffin 2, coffin 3, see alcohols.

cossin C₁ (*)Cossus cossus L. (larvae) (LEP).n-butyl butyrateAmorbus rhombifer West., Mictis caja Stål. (HET).trans-hex-2-enyl butyrateLethocerus indicus (Lep. and Serv.) (HET).methyl p-hydroxy benzoateCybister lateralimarginalis D.G., Dytiscus latissimus L., D. marginalis L. (COL).acetylcholinePolistes omissa Weyrauch, Vespa crabro L., Vespula germanica Fbr. (HYM);Zygaena filipendulae L., Z. ionicerae (Von Sch.) (LEP).ε-dimethylacrylyl-cholineArctia caja L. (imago) (LEP).LACTONESγ-gluconolactoneEurycotis biolleyi Rehn, E. decipiens (Kirby) (BLA).δ-gluconolactoneEurycotis biolleyi Rehn, E. decipiens (Kirby) (BLA).AMIDESpederinPaederus columbinus Lap., P. fuscipes Curt., P. melanurus Arag., P. litoralis Gravh., P. rubrothoracicus Goeze, P. rufocyaneus Bernh. (COL).pseudopederinPaederus fuscipes Curt. (COL).

(*) For cossin 1, cossin 2, cossin 3, see alcohols.

ESTERSLACTONESAMIDES

pederone

Paederus columbinus Lap., P. fuscipes Curt., P. melanurus Arag. (COL).

NITRILEShydrocyanic acid

Apheloria corrugata Wood, Cherockia georgiana Bollman, Gomphodesmus pavani Dem., Leptodesmus (Polydesmus) haydenianus Wood, Nannaria sp., Orthomorpha coarctata Sauss., O. gracilis Koch, Pachydesmus crassicutis Wood, Polydesmus collaris collaris Koch, P. (Fontaria) virginien-sis Drury, Pseudopolydesmus serratus Say, Rhysodesmus vicinus Sauss. (POL);

Zygaena filipendulae L., Z. lonicerae (von Schev.), Procris geryon (Hueb.) (LEP).

D-(+)-mandelic nitrile

Apheloria corrugata Wood, Gomphodesmus pavani Dem. (POL).

mandelonitrile benzoate

Gomphodesmus pavani Dem., Polydesmus collaris collaris Koch (POL).

glucoside of p-isopropil mandelonitrile

Rhysodesmus vicinus Sauss. (POL).

AMINO ACIDSglycine

Apis mellifera L. (HYM).

Androctonus australis L., Buthus occitanus Am. (SCORP).

alanine

Apis mellifera L., Paraponera clavata F. (HYM);

Androctonus australis L., Buthus occitanus Am. (SCORP).

serine

Apis mellifera L. (HYM);

Androctonus australis L., Buthus occitanus Am. (SCORP).

α -aminobutyric acidApis mellifera L. (HYM). β -iso-aminobutyric acidApis mellifera L. (HYM). γ -aminobutyric acidAcanthoscurria atrox Vellard, Grammostoma actaeon Pocock, Gr. mollicoma Ausserer, Lasiadora klugii Koch, Pamphobeteus soracabae M.-Leitao, P. tetracanthus M.-Leitao (ARA).threonineApis mellifera L. (HYM);Androctonus australis L., Buthus occitanus Am. (SCORP).valineApis mellifera L. (HYM);Androctonus australis L., Buthus occitanus Am. (SCORP).aspartic acidApis mellifera L., Paraponera clavata F. (HYM);Androctonus australis L., Buthus occitanus Am. (SCORP);Acanthoscurria atrox Vellard, Lycosa erythrognata Luc. (ARA).asparagineApis mellifera L. (HYM).leucineApis mellifera L., Paraponera clavata F. (HYM);Androctonus australis L., Buthus occitanus Am. (SCORP).isoleucineApis mellifera L., Paraponera clavata F. (HYM);Androctonus australis L., Buthus occitanus Am. (SCORP).glutamic acidApis mellifera L., Paraponera clavata F. (HYM);Androctonus australis L., Buthus occitanus Am. (SCORP).

- V 17 -

Acanthoscurria atrox Vellard, Grammostoma actaeon Pocock, Grammostoma mollicoma Ausserer, Lasiadora klugii Koch, Latrodectus mactans F., Lycosa erythrognata Luc., Pamphobeteus soracabae M.-Leitao, P. tetracanthus M.-Leitao, Phoneutria fera Perty, Scaptocosa raptoria Perty (ARA).

glutamine

Apis mellifera L. (HYM).

ornithine

Apis mellifera L. (HYM).

cysteine

Apis mellifera L. (HYM).

cystine

Apis mellifera L. (HYM); Androctonus australis L., Buthus occitanus Am. (SCORP).

methionine

Apis mellifera L. (HYM).

lysine

Apis mellifera L., Paraponera clavata F. (HYM);
Androctonus australis L., Buthus occitanus Am., Tityus bahiensis Perty, T. serrulatus L. e Mello (SCORP);
Lycosa erythrognata Luc. (ARA).

arginine

Apis mellifera L. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

proline

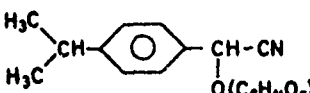
Apis mellifera L. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

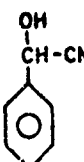
histidine

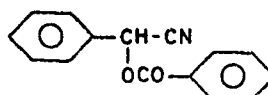
Apis mellifera L. (HYM);
Androctonus australis L., Buthus occitanus Am. (SCORP).

NITRILES

$\text{H}-\text{C}\equiv\text{N}$
HYDROCYANIC ACID


GLUCOSIDE OF p-ISOPROPYL MANDELONITRILE


D-(+)-MANDELIC NITRILE


MANDELONITRILE BENZOATE

AMINO ACIDS

COOH
 CH_2-NH_2
GLYCINE

COOH
 CHNH_2
 CH_3
ALANINE

COOH
 $\text{CH}-\text{NH}_2$
 CH_2OH
SERINE

COOH
 CHNH_2
 CH_2
 CH_3
d-AMINO BUTYRIC ACID

COOH
 CH
 H_3C CH_2NH_2
 β -ISO-AMINO BUTYRIC ACID

$\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$
 NH_2
 γ -AMINO BUTYRIC ACID

COOH
 CHNH_2
 CHOH
 CH_3
THREONINE

COOH
 $\text{CH}-\text{NH}_2$
 $\text{CH}-\text{CH}_3$
 CH_3
VALINE

COOH
 CHNH_2
 CH_2
 COOH
ASPARTIC ACID

COOH
 $\text{CH}-\text{NH}_2$
 CH_2
 $\text{CO}-\text{NH}_2$
ASPARAGINE

COOH
 $\text{CH}-\text{NH}_2$
 CH_2
 $\text{CH}-\text{CH}_3$
 CH_3
LEUCINE

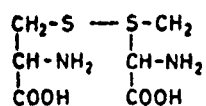
COOH
 $\text{CH}-\text{NH}_2$
 $\text{CH}-\text{CH}_3$
 CH_2
 CH_3
ISOLEUCINE

COOH
 $\text{CH}-\text{NH}_2$
 CH_2
 CH_2
 COOH
GLUTAMIC ACID

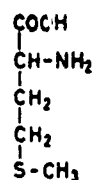
COOH
 $\text{CH}-\text{NH}_2$
 CH_2
 CH_2
 CONH_2
GLUTAMINE

COOH
 $\text{CH}-\text{NH}_2$
 CH_2
 CH_2
 CH_2-NH_2
ORNITHINE

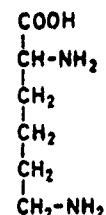
COOH
 $\text{CH}-\text{NH}_2$
 CH_2SH
CYSTEINE

AMINO ACIDS

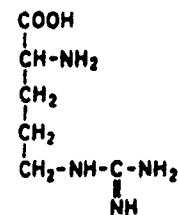
CYSTINE



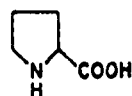
METHIONINE



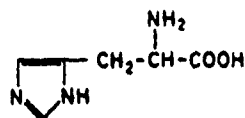
LYSINE



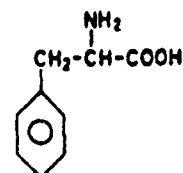
ARGININE



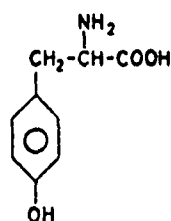
PROLINE



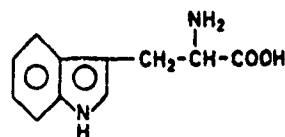
HISTIDINE



PHENYLALANINE



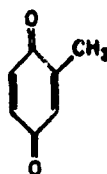
TYROSINE



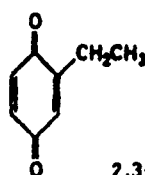
TRYPTOPHANE

QUINONES

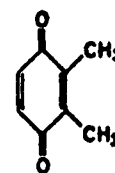
1,4-BENZOQUINONE



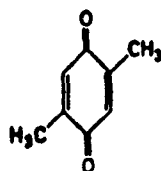
2-METHYL-1,4-BENZOQUINONE



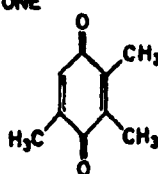
2-ETHYL-1,4-BENZOQUINONE



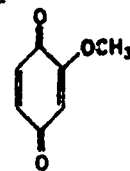
2,3-DIMETHYL-1,4-BENZOQUINONE



2,5-DIMETHYL-1,4-BENZOQUINONE



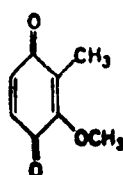
2,3,5-TRIMETHYL-1,4-BENZOQUINONE



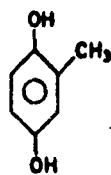
2-METHOXY-1,4-BENZOQUINONE



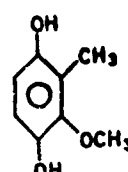
HYDROQUINONE



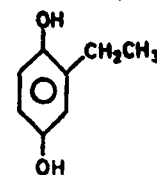
2-METHYL-3-METHOXY-1,4-BENZOQUINONE



2-METHYL-HYDROQUINONE



2-METHYL-3-METHOXY-HYDROQUINONE



2-ETHYL-HYDROQUINONE

phenylalanineApis mellifera L. (HYM);Androctonus australis L., Buthus occitanus Am. (SCORP).tyrosineApis mellifera L. (HYM);Androctonus australis L., Buthus occitanus Am. (SCORP).tryptophaneApis mellifera L. (HYM);Androctonus australis L., Buthus occitanus Am. (SCORP).QUINONES1,4-benzoquinoneArchiulus (Schizophyllum) sabulosus L., Pachybolus laminatus Cook,Schizophyllum mediterraneum , Spirostreptus castaneus Attems,Sp. virgator Silv. (JUL);Diploptera punctata (Esch.) (BLA);Blaps gigas L., Bl. lethifera Marsh., Brachynus crepitans L., B. ex-plodens Duft., B. sclopeta Fabr., Eleodes hispilabris , E. longi-collis Le Conte, Pheropsophus catoirei Dej, Prionychus ater Fabr.,Scaurus dubius Sol., S. uncinus Först., Tenebrio obscurus Fabr. (COL).2-methyl-1,4-benzoquinoneArchiulus (Schizophyllum) sabulosus L., Aulonopygus aculeatus Attems,A. aculeatus barbieri , Brachyulus unilineatus Koch, Cambala hu-brichti Hoffman, Chicobolus spinigerus Wood, Cylindrojulus teutoni-cus Pocock, Doratogonus annulipes Carl, Floridobolus pennery Causey,Narceus annularis Raf., N. gordanus Chamb., Orthoporus flavior Cham-berlin e Mulaik, Or. punctilliger Chamberlin, Pachybolus laminatusCook, Peridontopyge aberrans Attems, P. vachoni , Rhinocricussp., Rh. insulatus Chamberlin, Spirostreptus sp., Sp. multisulcatusDem., Sp. virgator Silv., Trigonojulus lumbricinus Gerst (JUL);Diploptera punctata (Esch.) (BLA);

Forficula auricularia L. (DER);

Scaptocoris divergens Froesch. (HET);

Blaps gigas L., Bl. lethifera Marsh., Bl. mortisaga L., Bl. mucronata Latr., Bl. requienii Solier, Brachynus crepitans L., Br. explosans Duft., Br. sclopeta Fabr., Diaperis boleti L., D. maculata Ol., D. hispilabris Say, Eleodes hispilabris , E. longicollis Le Conte, Gnaptor spinimanus Pall., Helops aeneus Montrouz, H. quisquilius Strm., Latheticus oryzae Wat., Morica planatatingitana Baudi, Opatroides punctulatus Brull., Opatrum sabulosum L., Pimelia confusa Sen., Pheropsophus catoirei Dej, Prionychus ater Fabr., Scaurus uncinus Först., Tenebrio molitor L., Tribolium castaneum Herbst., Tr. confusum J. du V. (COL).

2-ethyl-1,4-benzoquinone

Diploptera punctata (Esch.) (BLA);

Forficula auricularia L. (DER).

Blaps gigas L., Bl. lethifera Marsh., Bl. mortisaga L., Bl. mucronata Latr., Bl. requienii Solier, Diaperis boleti L., D. maculata Ol., D. hispilabris Say, Eleodes hispilabris , E. longicollis Le Conte, Gnaptor spinimanus Pall., Helops aeneus Montrouz, H. quisquilius Strm., Latheticus oryzae Wat., Opatroides punctulatus Brull., Opatrum sabulosus L., Prionychus ater Fabr., Scaurus uncinus Först., Tribolium castaneum Herbst, Tr. confusum J. du V., Tr. destructor Uytt. (COL).

2,3-dimethyl-1,4-benzoquinone

Heteropachyloidellus robustus Roewer (OPI).

2,5-dimethyl-1,4-benzoquinone

Heteropachyloidellus robustus Roewer (OPI).

2,3,5-trimethyl-1,4-benzoquinone

Heteropachyloidellus robustus Roewer (OPI).

2-methoxy-1,4-benzoquinone

Tribolium castaneum Herbst (COL).

- V 20 -

2-methyl-3-methoxy-1,4-benzoquinone

Archiulus (Schizophyllum) sabulosus L., Brachyulus unilineatus Koen.,
Cambala hubrichti Hoffman, Chicobolus spinigerus Wood, Cylindroiulus
teutonicus Pocock, Doratogonus annulipes Carl, Floridobolus penneri
 Causey, Narceus annularis Raf., N. gordanus Chamb., Orthoporus coni-
fer Attems, Or. flavior Chamberlin and Mulaik, Or. punctilliger Cham-
 berlin, Rhinocricus sp., Spirostreptus sp., Trigonoius lumbricinus
 Gerst. (JUL).

hydroquinone

Brachynus crepitans L., Br. explodens Duft., Br. sclopeta Fabr. (COL).

2-methyl-hydroquinone

Archiulus (Schizophyllum) sabulosus L., Rhinocricus sp. (JUL).
Forficula auricularia L. (DER);
Brachynus crepitans L., Br. explodens Duft., Br. sclopeta Fabr.,
Tenebrio molitor L. (COL).

2-ethyl-hydroquinone

Forficula auricularia L. (DER).

2-methyl-3-methoxy-hydroquinone

Archiulus (Schizophyllum) sabulosus L., Rhinocricus sp. (JUL).

SUGARSglucose

Pachydesmus crassicutis Wood, Rhysodesmus vicinus Saus. (POL);
Eleodes longicollis Lec. (COL);
Apis mellifera L. (HYM).

fructose

Apis mellifera L. (HYM).

TERPENIC DERIVATIVESHYDROCARBONSD,L-limonene

Myrmicaria natalensis Fred. (HYM).

 α , β -pinene

Nasutitermes sp. (soldiers), N. exitiosus (Hill.), N. graveolus Hill.,
N. walkeri Hill. (ISO).

ALCOHOLScitronellol

Acanthomyops sp. (HYM).

ALDEHYDEScitral

Acanthomyops claviger Roger, Atta sexdens rubropilosa For., Lasius
(Dendrolasius) fuliginosus Latr., Lestrimelitta limao (Fr. Smith)
(HYM).

citronellal

Acanthomyops sp., A. claviger Roger (HYM).

farnesal

Lasius (Dendrolasius) fuliginosus Latr. (HYM).

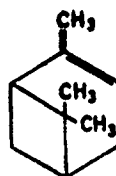
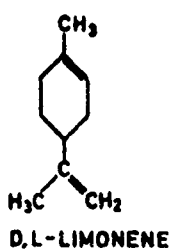
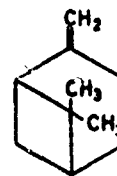
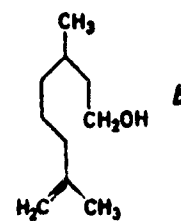
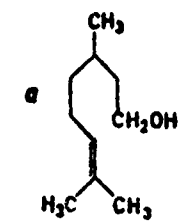
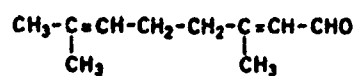
iridodial

Dolichoderus (Diceratoclinea) scabridus Roger, Iridomyrmex conifer
For., Ir. detectus Sm., Ir. nitidiceps (Andre), Ir. rufoniger Lowne,
Tapinoma nigerrimum Nyl. (HYM).

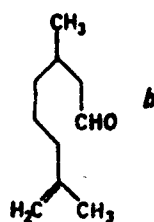
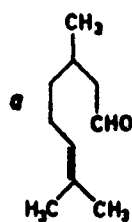
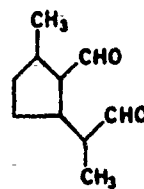
dclichodial

Anisomorpha baprestoides Stoll (PHA);

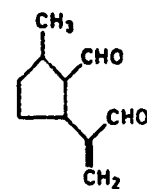
Dolichoderus sp., D. (Acanthoclinea) Clarki Wheeler, D. (Ac.) denta-
ta Forel, D. (Diceratoclinea) scabridus Roger, Iridomyrmex sp., Ir.
myrmecodiae Em., Ir. rufoniger Lowne (HYM).

TERPENIC DERIVATIVES**HYDROCARBONS** α , β - PINENE**ALCOHOLS**CITRONELLOL (MIXTURE OF *a, b*)**ALDEHYDES**

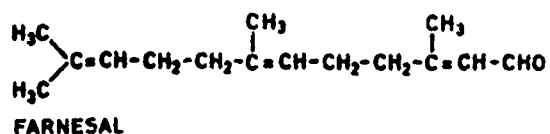
CITRAL

CITRONELLAL (MIXTURE OF *a, b*)

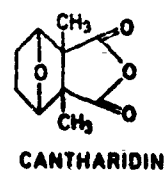
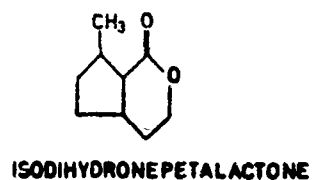
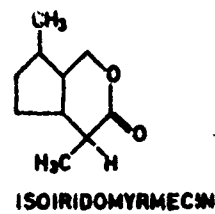
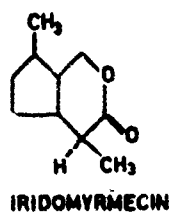
IRIDODIAL



DOLICHODIAL



FARNESAL

LACTONES, ANHYDRIDES

LACTONES, ANHYDRIDESiridomyrmecin

Iridomyrmex humilis Mayr (HYM).

isoiridomyrmecin

Dolichoderus (Diceratoclinea) scabridus Roger, Iridomyrmex nitidus Mayr (HYM).

isodihydronepetalactone

Iridomyrmex nitidus Mayr (HYM).

cantharidin

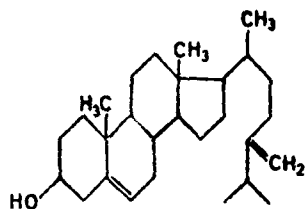
Cissites cephalotes Oliv., Cyaneolytta gigas F., C. signifrons Fahr., C. violacea Brandt, Decapotama lunata Pall., Eletica wahlbergia Fahr., Epicauta adspersa Klug, Ep. femoralis Er., Ep. gorhami Mars., Ep. hirticornis Haag, Ep. pennsylvanica Deg., Ep. ruficeps Ill., Ep. velata Gerst., Ep. vittata F., Horia debyi Fairm., Lydus trimaculatus Fischer, Lytta conspicua Waterh., L. sanguinea Haag, L. vesicatoria L., Macrobasis albida Say, M. cinerea F., Meloe sp., Me. angusticollis Say, Me. majalis L., Me. proscarabeus L., Me. variegatus Donov., Me. violaceus Marsh., Mylabris balteata Pall., My. bifasciata De Geer, My. calida Pall., My. cichorii L., My. colligata Redt., My. crocata Pall., My. dicincta Bertol., My. dilloni Guer., My. escherichi Voigts, My. ertli Voigts, My. mireducta Pic., My. holosericea Klug, My. macilenta Mars., My. oculata Thunb., My. phalerata Pall., My. praestans Gerst., My. pustulata Thunb., My. quadripunctata L., My. quatuordecimpunctata Pall., My. schoenherri Billb., My. tripartita Gerdt., My. tristigma Gerst., My. variabilis Pall., Psalydolytta castaneipennis Makel (COL).

STEROIDS24-methylene cholesterol

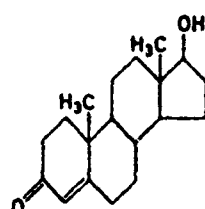
Nasutitermes sp. (soldiers) (ISO).

testosterone

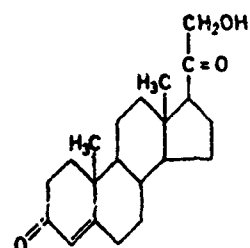
Ilybius fenestratus Fabr., Ilybius fuliginosus Fabr. (COL).

STERIODS

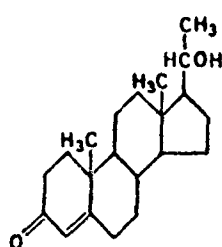
24-METHYLENE CHOLESTEROL



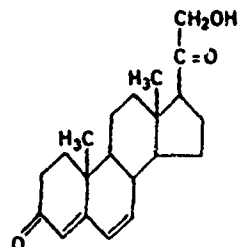
TESTOSTERONE



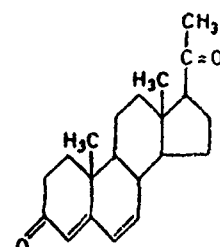
11-DESOXYCORTICOSTERONE



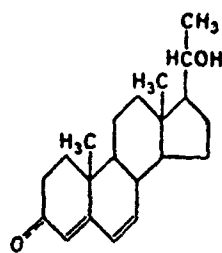
6-DIHYDROCYBISTERONE



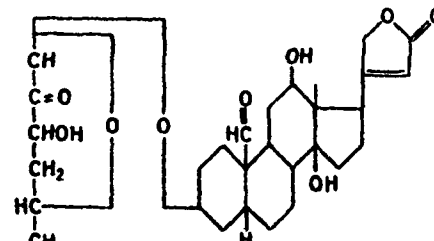
6-DEHYDROCORTXONE



6-DEHYDROPROGESTERONE



CYBISTERONE



CALOTROPIN

CALACTIN *)

- V 23 -

11-desoxycorticosteroneAcilius sulcatus , Dytiscus marginalis L. (COL).6-dihydrocybisteroneAcilius sulcatus , Dytiscus marginalis L. (COL).6-dehydrocortexoneAcilius sulcatus (COL).6-dehydroprogesteroneAcilius sulcatus (COL).cybisteroneAcilius sulcatus , Cybister lateralimarginalis De Geer, Dytiscus marginalis L. (COL).calotropinPoecillocerus bufonius Klug (ORT).calactinPoecillocerus bufonius Klug (ORT).ALKALOIDSglomerinGlomeris marginata Vill., Gl. conspersa Koch, Gl. hexasticha Brandt, Loboglomeris rugifera Verh. (GLO).omoglomerinGlomeris marginata Vill., Gl. conspersa Koch, Gl. hexasticha Brandt (GLO).FLAVOPROTEINSriboflavinApis mellifera L. (HYM).

- V 24 -

PHOSPHATIDESlecithinApis mellifera L. (HYM).ENZYMESadenosine triphosphataseEuscorpius italicus (Herbst) (SCORP).L-amino acid dehydrogenaseCtenus nigriventer Keys., Scaptocosa raptoria Walk (ARA).cholinesteraseVespula germanica Fbr., V. vulgaris L. (HYM).alkaline phosphataseChrysocoris stolli Wolf (HET).phospholipase AApis mellifera L., Vespa crabro L., Vespula vulgaris L. (HYM).phospholipase BVespa crabro L., Vespula germanica Fbr., V. vulgaris L. (HYM).phospholipase CMyrmecia gulosa (F.) (HYM). β -glucosidasePachydesmus crassicutis Wood (POL);Diploptera punctata (Escholtz) (BLA).hyaluronidaseCimex lectularius L., Platymeris rhadamanthus Gaerst. (HET);Apis mellifera L., Bombus pratorum L., Myrmecia gulosa Fabr., Polistes omissa Veyrauch, Vespa crabro L., Vespula germanica Fbr., V. vulgaris L. (HYM);Araneus diadematus Clerck, Ctenus nigriventer Keys, Scaptocosa raptoria Walk (ARA).

invertaseEthmostygmus spinosus (SCOL).trypsinCtenus nigriventer Keys., Lycosa erithrognata Luc. (ARA).Chap. 20 - Inorganic substances.

In the literature consulted the presence of inorganic substances has been found in the defensive secretions of various Arthropoda. For some of them a further and more carefully investigation by new methods is necessary:

hydrogen peroxideBrachynus crepitans L., B. explodens Duft., B. sclopeta Fabr. (COL).ammoniaPhosphuga atrata L., Silpha obscura L., Oeceoptoma thoracicum L. (COL);Formica nigricans Em., F. polycтена Först., F. pratensis Retz., F. rufa L. (HYM).nitrogen oxidesBrachynus crepitans L., Br. sp. (COL).hydrochloric acidNotodonta concinna (Abb. and Smith) (LEP).nitrous acidBrachynus crepitans L., Pheropsophus africanus Dej. (COL).nitritesPheropsophus africanus Dej. (COL).inorganic phosphatesLycosa erythrognata Luc., Phoneutria fera Perty (ARA).

Water is also present as a carrier in many defensive secretions. Some Authors mention it:

Mastigoproctus giganteus (Lucas) (URO);

Schizura leptinoides Grote (LEP);

Brachynus crepitans L., B. explodens Duft., B. sclopeta Fabr. (COL);

Eurycotis biolleyi Rehn, E. decipiens (Kirby) (BLA);

Apis mellifera L. (HYM).

Organic substances not chemically defined.

Some organic and not defined substances are indicated in the literature as parts of the defensive secretions. Other products even if not chemically defined are described in the literature with a particular name, e.g.: scorpamin, buthotoxin.

We are reporting these brief data as well, for their indicative significance.

QUINONES

quinones

Orthocricus arboreus (Sauss.), Schyzophyllum mediterraneum , Spirostreptus castaneus Attems (JUL);

Blaps gibba L., Bl. judaeorum Miller, Bl. nitens Cast., Scotobates calcaratus , Tribolium sp., Uloma impressa Melsh., (COL).

quinones with alkyl groups

Schizophyllum mediterraneum , Spirostreptus castaneus Attems (JUL);
Eleodes obsoleta (Say) (COL).

SUGARS

disaccharide

Pachydesmus crassicutis Wood (POL).

polysaccharide

Centruroides sculpturatus Ewing (SCORP).

AMINO ACIDSfree amino acids

Chrysocoris stolli Wolf (HET);

Cerura vinula L. (larvae) (LEP);

Formica rufa L., Monomorium antarcticum Wheeler, M. pharaonis (L.),

Pogonomyrmex badius (Latr.), Vespa crabro L., Vespula vulgaris L.

(HYM);

Acanthoscurria atrox Vellard, Grammostoma actaeon Pocock, Gr. molli-

coma Ausserer, Gr. pulripes Simon, Lasiodora Klugii Koch, Latrodec-

tus mactans L., Pamphobeteus roseus M.-Leitao, P. soracabae M.-Lei-

tao, P. tetracantus M.-Leitao, Scaptocosa raptoria Wik, Phoneutria

fera Perty (ARA).

PEPTIDESkinin

Apis mellifera L., Vespa crabro L., Vespula germanica Fbr., V. vul-
garis L. (HYM).

apamin

Apis mellifera L. (HYM).

mellitin

Apis mellifera L. (HYM).

ENZYMESanticoagulase

Scorpio arenicola L. (SCORP).

coagulase

Buthacus arenicola (E. Simon) (SCORP).

diastase

Ethmostygmus spinosus (SCOL).

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alkaline endopeptidasePlatymeris rhadamanthus Gaerst. (HET).enzymesLeiurus quinquestriatus H. and E. (SCORP).proteasePlatymeris rhadamanthus Gaerst. (HET).proteolytic enzymesEthmostygmus spinosus (SCOL).esterasePolistes omissa Weyrauch (HYM).phospholipase (= lecithinase)Platymeris rhadamanthus Gaerst. (HET);Apis mellifera L., Bombus pratorum L., Vespula vulgaris L. (HYM);Buthacus arenicola (E. Simon), Scorpio maurus L. (SCORP).VARIOUS SUBSTANCESindole base (probably scatole)Pheidole fallax Mayr (HYM).buthotoxinButhus martensi Karsch (SCORP).toxic saponinDiamphidia simplex Peringuey (= D. locusta Fairmaire) larvae (COL).scorpaminAndroctonus australis L., Buthus occitanus Am. (SCORP).toxalbuminDiamphidia simplex Peringuey (= D. locusta Fairmaire) larvae (COL).

PART VI - NEW SUBSTANCES FOUND FOR THE FIRST TIME IN ARTHROPODA
DEFENSIVE SECRETIONS.

Chap. 21 - Iridomyrmecin and iridoids present in Arthropoda.

Iridomyrmecin.

In 1948, with the collaboration of A. Nascimbene (223, 254) in the microbiological field, we pointed out the existence of an unknown antibacteric factor, which we called iridomyrmecin, in the Dolichoderin Ant Iridomyrmex humilis Mayr. This substance was obtained in a pure crystalline state in 1948 (258). Recognizing its insecticide property (229), we demonstrated its presence in the anal gland secretions and its employment by the ant as an offensive and defensive means against Insects. The centesimal composition $C_{10}H_{16}O_2$ was made known at the IX International Congress of Entomology at Stockholm, 1948 (published in 1952 (232)).

Iridomyrmecin is contained in a rough liquid state in a reservoir of the "anal glands" opening between the 4th and 5th urotergum. A full extraction carried out on three lots in different seasons revealed that the worker (weighing an average of 0,35 mg) contains from 3,453 gamma (about 1/100 of its body weight) (average of a lot of 20 million workers), to 2,930 gamma in the other lots examined.

Workers just formed have depigmented and delicate bodies, and their anal gland reservoir is empty; during their early life they stay confined to the underground nest; they come out and face external life when their bodies are strong and pigmented, and the iridomyrmecin venom reserve is developed.

Structure.

The structure, first partially (april 1955) and then completely (november 1955) was published by Fusco, Trave and Vercellone (128, 129).

- VI. 2 -

Iridomyrmecin is a lactone of a cycloparaffin, more exactly of (2-hydroxy-methyl-cyclopentyl) propionic acid ⁽¹⁾.

Structural research was made easier by the discovery that bicarbossilic acid obtained by iridomyrmecin oxydization is identical to one of the isomer nepetalinic acids obtained by transformation of another natural product of vegetal origin, nepetalactone.

[figure 1]

Nepetalactone is contained in the essential oil (catnip oil) of Nepeta cataria, a labiate widespread throughout Europe, Asia, America and Africa. McElvain and Eisenbraun are classic references on the products of this plant (e.g. 184 D, E; 185 A). Feline attracting substances are present in the leaves of Actinidia polygama Miq. (Actinidiaceae is known in Japan as "matatabi") ⁽²⁾; various works by Sakan and coll. starting from 1959 (286 C-N) show them to be present in iridomyrmecin, isoiridomyrmecin, dihydronepetalactone, isodihyronepetalactone and neonepetalactone. Actinidine is also found in the same plant, with a carbon atomic structure identical to that of iridomyrmecin and

(1) Isoiridomyrmecin, obtained by transformation of iridomyrmecin with alkaline alcoholates, was made known in 1948 in Stockholm at the IX International Congress of Entomology (232) and in a paper in 1951 (230); later thoroughly described by Fusco, Trave and Vercellone 1955 (128, 129). Cavill, Ford and Locksley 1956 (60) found it as a natural product in the defensive secretions of Iridomyrmex nitidus Mayr and Dolichoderus scabridus Roger Dolichoderine Ants, and they gave it the name of iridolactone; this name is used synonymously with isoiridomyrmecin as it was the earlier term for this substance. In the literature the term iridolactone was later used to refer briefly to the two isomers.

(2) Bates and Sigel 1963 (10 D). affirm that the trans-cis-isomer of nepetalactone proves extremely attractive to cats, while the cis-trans-isomer is much less attractive or inactive altogether. Sakan, Isoe, Hyeon, Katsumura, Maeda, Wolinsky, Dickerson, Slabaugh, Nelson 1965 affirm that the three iridoids dihydronepetalactone, isodihyronepetalactone, neonepetalactone are equally attractive to cats.

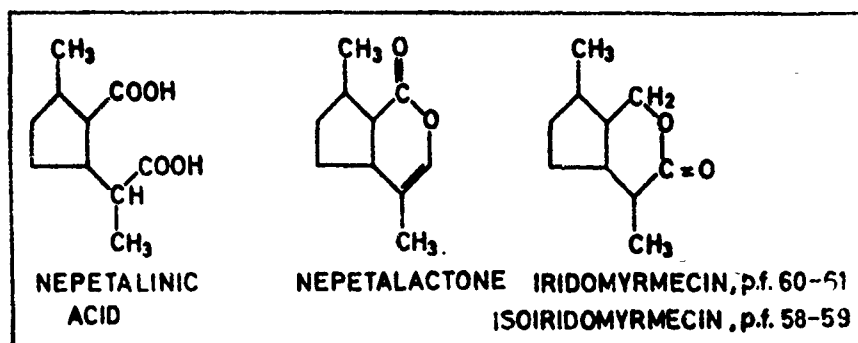


Fig. 1

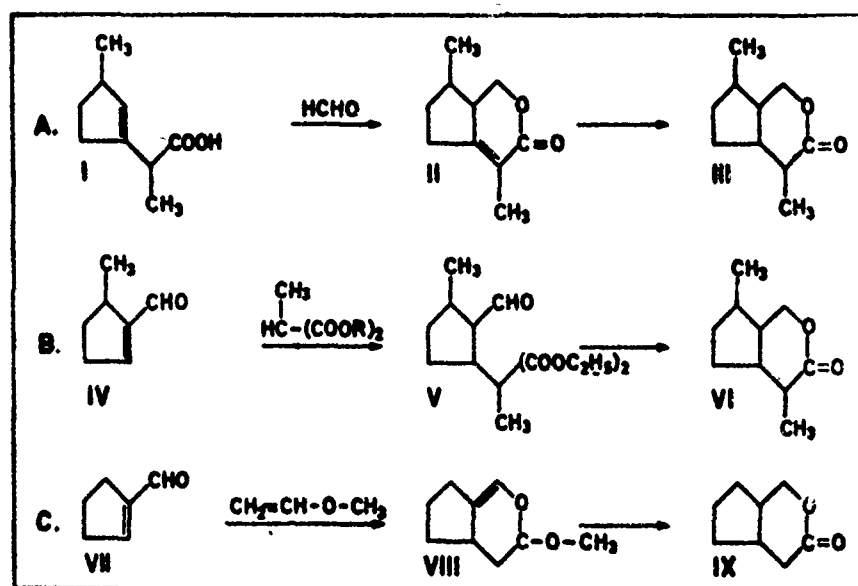


Fig. 2

- VI 3 -

and correlated. Many other products of vegetal origin have the same structural relationship as the basic substance iridomyrmecin; collectively they are referred to as iridoids. Among these we may mention skytanthine, dehydroskytanthine, hydroxyskytanthine found in the Apocinacea of South America Skytanthus acutus Meyen (Casinovi and coll. 49 A-E; Marini-Bettolo and coll. 181 A, B; Djerassi and coll.⁽¹⁾), harpagoside, harpagide, harpagide acetate, asperuloside, aucubin, catalposide, genepin, guaiol, loganin, monotropein, unedocide, verbenalin, etc.

Synthesis of iridomyrmecin and other iridoids.

Various syntheses of iridomyrmecin have been obtained in different ways. This has made it possible to obtain the synthesis of several other iridoids and to acquire information about the probable biogenetical pathways of these substances in plants and Insects. The first syntheses date back to 1958 (Korte and coll.; Clark and coll.); others followed and activity in this field is still going on.

In 1958 Korte, Falbe and Zschocke (166 B) obtain the synthesis of D,L-iridomyrmecin and of the correlate bicyclic lactones, and in 1959 (155 C) they publish further developments. In the first of these two papers the Authors give the three following schemes of synthesis.

[figure] 2

In the same year, 1958, Clark, Fray, Jaeger and Robinson (72 B) obtain the synthesis of D and L-isoiridomyrmecin starting from citronellal; in 1959 (73) starting from D-citronellal of natural origin, they synthesize D-iridodial⁽²⁾ and D-isoiridomyrmecin. The L-

(1) DJERASSI C., KUTNEY J.P., SHAMMA M., SHOOLERY J.N. and JOHNSON L., 1961. Chem.Ind.: 210.

(2) Iridodial was found simultaneously by Trave and Pavan (339) and Cavill and coll. 1956 (60). Research went on with a mutual exchange of information between the two groups, but the Italians declared they would wait for the publication of the data of Cavill and coll. before publishing their own.

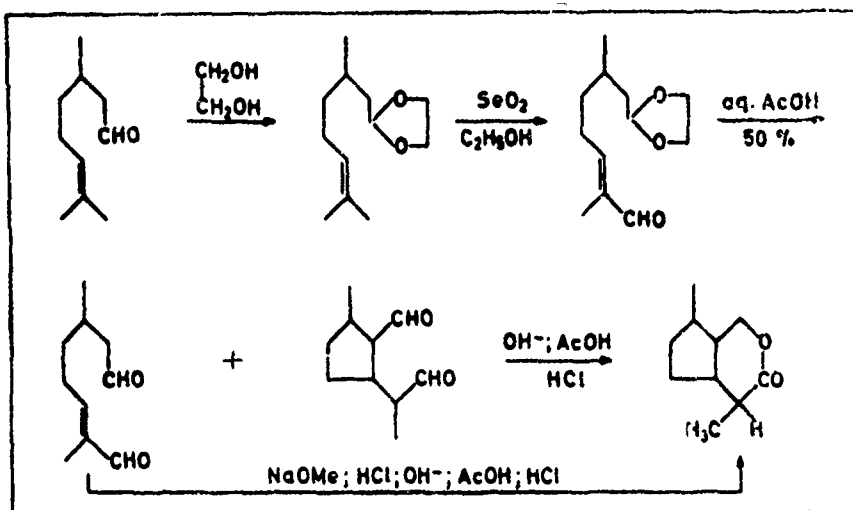


Fig. 3

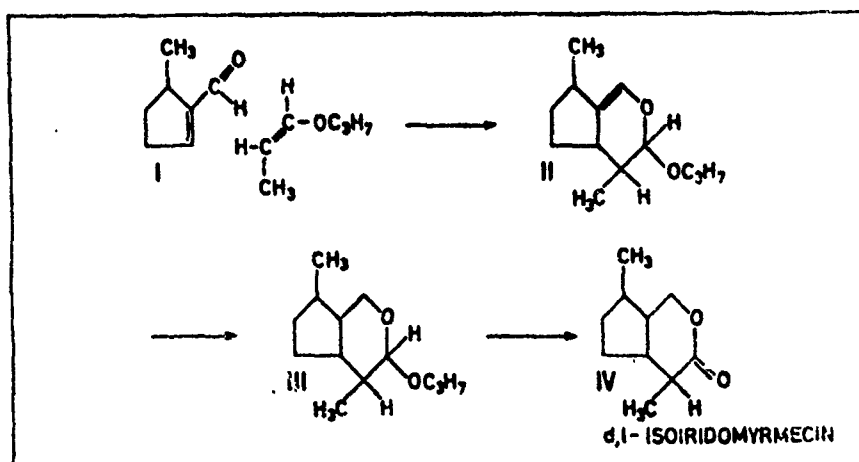


Fig. 4

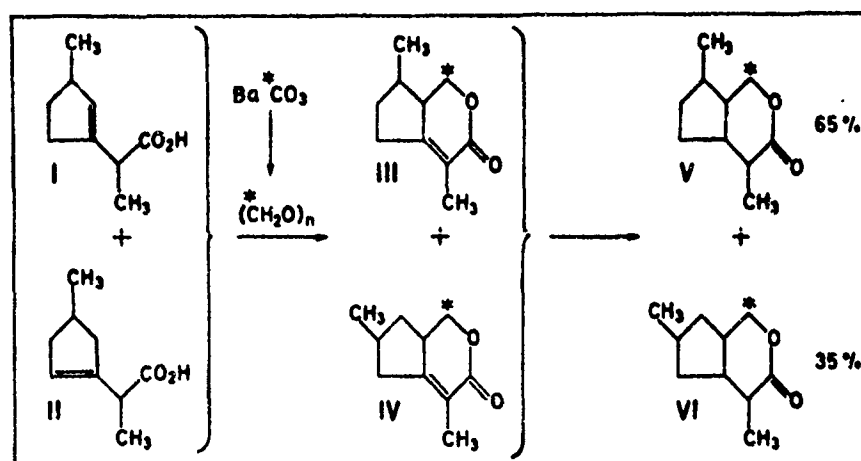


Fig. 5

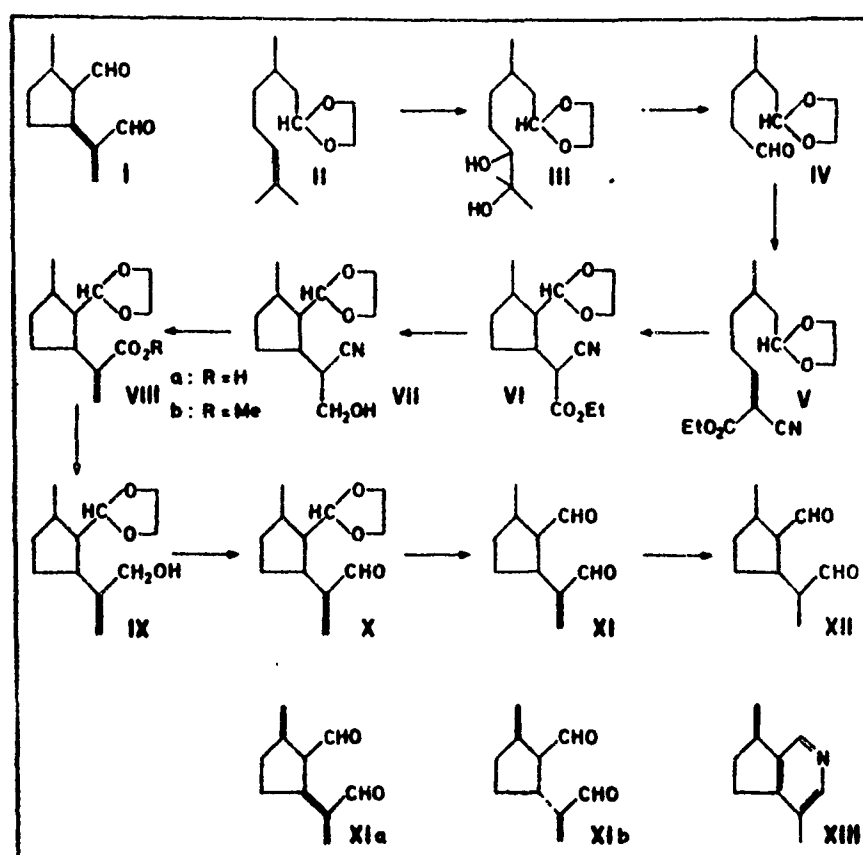


Fig. 6

citronellal, obtained from pinene through a series of chemical transformations, was also transformed into L-iridodial and L-isoiridomyrmecin.

[figure]3

Büchel and Korte 1960 (40) deal extensively with their systems of synthesis of iridomyrmecin type lactones.

Korte, Büchel and Zschocke 1961 (166 A) obtain the synthesis of D,L-isoiridomyrmecin in the pathways shown in the following diagram. Isoiridomyrmecin is epimerized into iridomyrmecin during gas chromatography at 240°C.

[figure]4

Korte and Schreiber 1962 (166 D) obtained the synthesis of marked iridomyrmecin $-(3-^{14}\text{C})$, using Barium carbonate $-^{14}\text{C}$ as in the diagram illustrated below. The marked substance was transformed with ox liver homogenate into the corresponding hydroxycarbonilic acid. Aedes aegypti larvae have a poor absorption of marked iridomyrmecin.

[figure]5

In two papers of 1962 (67 A) and 1964 (67 C) Cavill and Whitfield make known the synthesis of natural dolichodial enantiomorph (fig. 6 , I), analagous to Clark and Coll.'s synthesis of iridodial, starting from ethyl acetylene α -(2-formyl-3-methylcyclopentyl)-cyanace'ate, obtained from the transformation of D(+)citronellal. With hydrogenation of the mixture of XIa and XIb synthetic products (cis and trans dolichodial isomers) iridodial identical to that produced by Clark and coll. starting from D-citronellal was obtained. D-actinidine (XIII) is obtained from bis-2,4-dinitrophenylhydrazone of iridodial (XII) derived from hydrogenation of synthetic dolichodial.

[figure]6

The synthesis of (-)iridomyrmecin (Table⁷ III) and correlated lactones (VIII and IX) is obtained by Gibson 1964 (131 A) starting from trans-pulegenic acid (I) derived from (+)pulegone. Treatment with

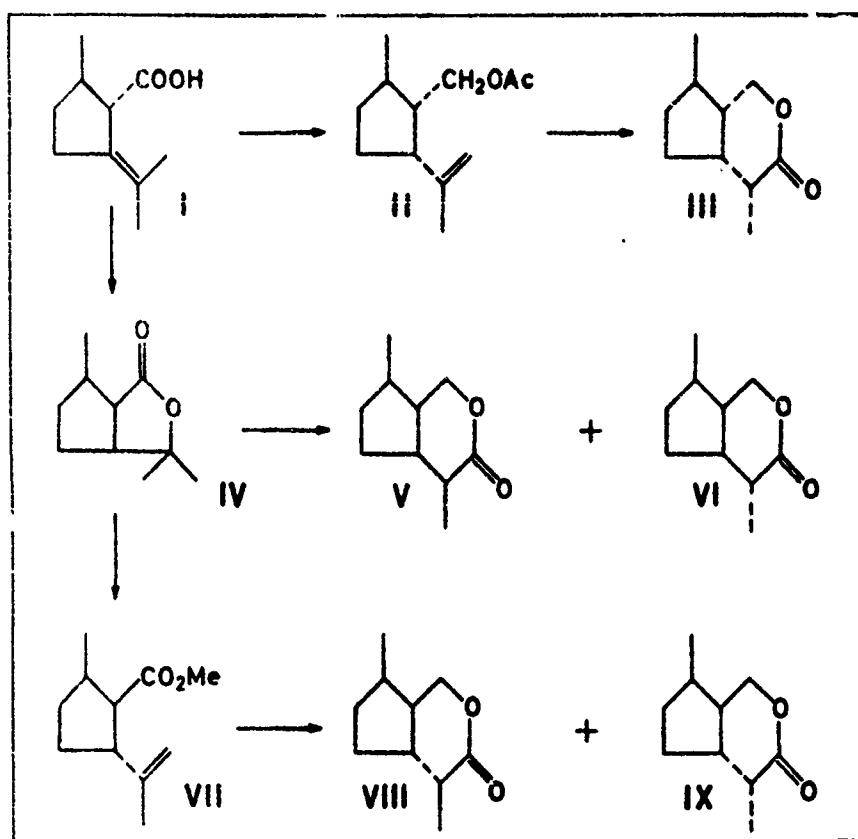


Fig. 7

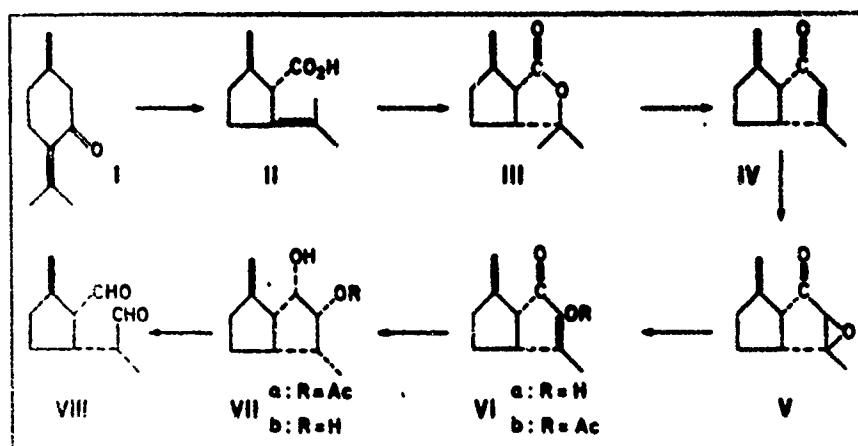


Fig. 8

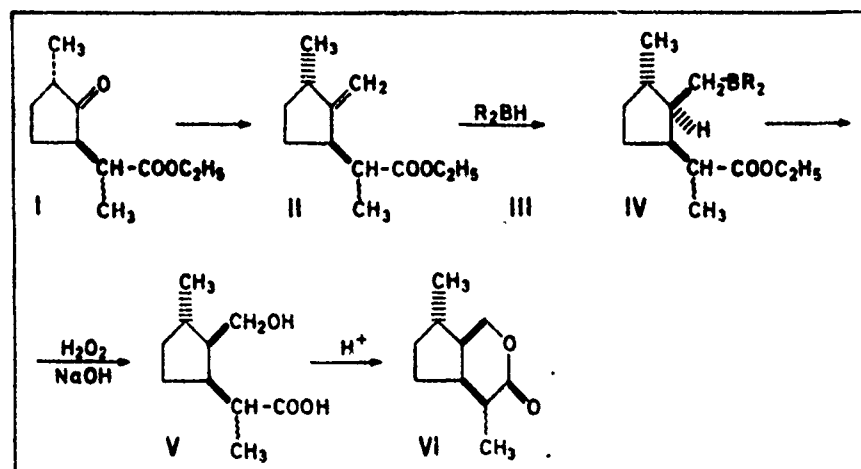


Fig. 9

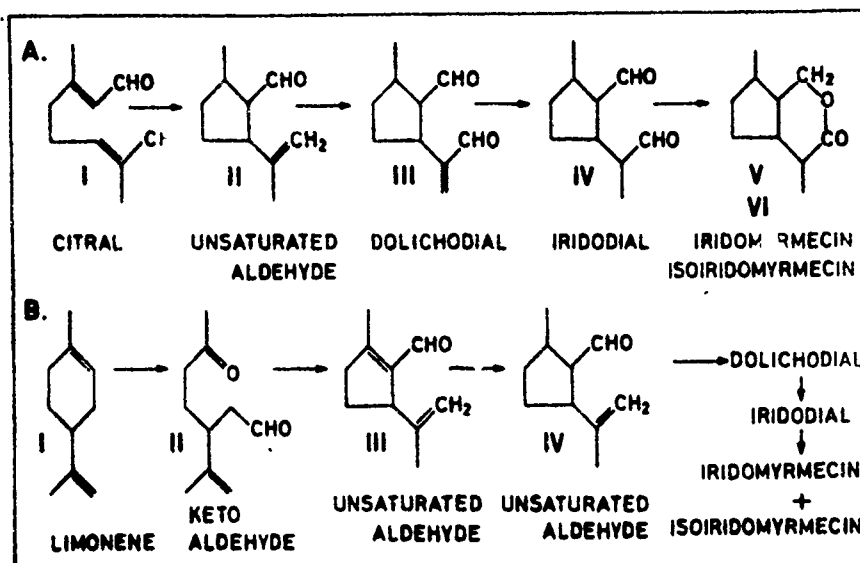


Fig. 10

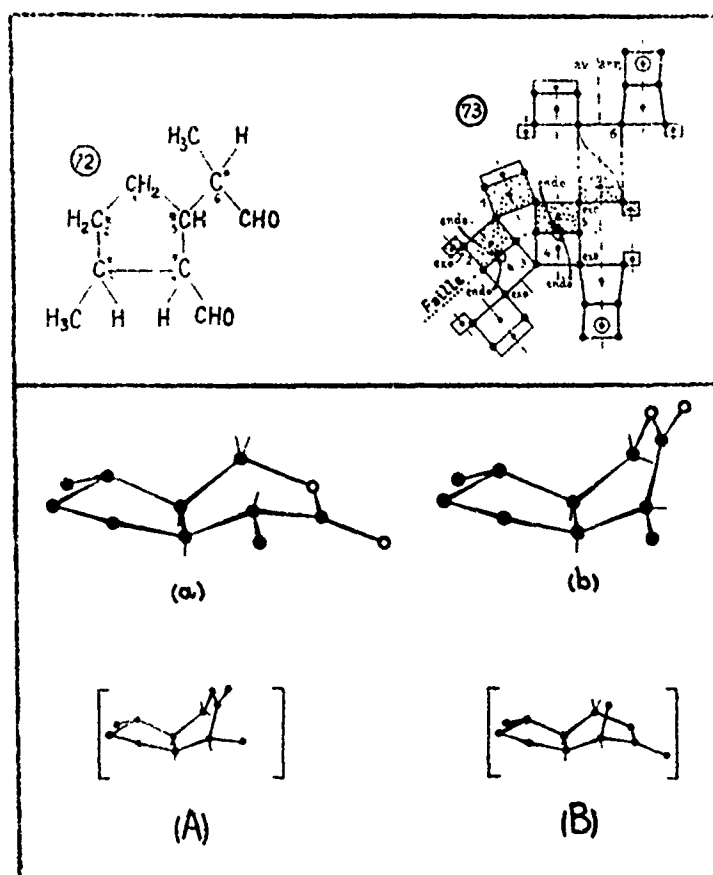


Fig. 12

a base gives (+)isoiridomyrmecin.

[figure]7

Achmad and Cavill 1963, 1961 (1, 1A), starting from trans-pulegenic acid obtained from (+)pulegone (Table 8 I) obtain the synthesis of enantiomorph VIII of natural iridodial and correlate products. By successive treatment synthetic iridodial VIII gave a product identical to natural iridodial.

[figure]8

Sisido, Utimoto and Isida 1964 (321), obtain a synthesis of iridomyrmecin starting from a derivate of cyclopentanone, ethyl 2-(3-methyl-2-oxocyclopentyl) propionate (IV) as in Table 9 .

[figure]9

Wolinsky, Gibson, Chan and Wolf 1965 (361), starting from trans-pulegenic acid, describe the stereospecific synthesis of 6 of the 8 possible iridolactones, meaning by the term iridolactone, in agreement with other authors, iridomyrmecin and isoiridomyrmecin together. They presents probable biosynthesis pathways starting from citronellal, citral and limonene (fig. 10).

Among the various syntheses of iridoids not yet found as natural substances in insects we may mention those of Cavill, Ford, Hinterberger, Solomon 1958 (59) and 1961 (59 A) regarding bisnoriridodial, bisnoriridolactone, and correlate substances, and those of Garanti 1962 (129 B), who synthesize nor-isoiridomyrmecin from trans-nor-nepetalic acid going through nor-nepetalactone, and the researches on nor-nepetalactone synthesis by Trave, Merlini, Garanti 1958 (337).

Weckering 1960 (351) presents the bicyclic skeleton stereostructure of iridomyrmecin (Table 11); from these he derives the detailed structural formula (Table 12). Iridodial is represented by Weckering with the stereoelectronic structure in Table 12 . I should

also like to mention the works of McConnel and Schcenborn 1962 (184 D), McConnel, Mathieson and Schcenborn 1962 (184 B) and 1964 (184 C) on iridomyrmecin and isoiridomyrmecin crystalline structure.

Biogenesis of iridomyrmecin and correlate products (iridoids).

It is interesting to note how both iridomyrmecin just as related products from the group of iridoids formed by plants and Insects on an identical carbon atom skeleton, follow the same isoprenic rule.

There is no definite information on the ways of biogenic derivation of iridomyrmecin. Hypotheses have been made about its biosynthesis, but experimental demonstration is still lacking. The newly formed worker, deprived of the normal regurgitated food fed to it by older workers, and nourished mainly with sucrous solutions, is able to build up its own dose of iridomyrmecin. This, however, may happen at the cost of organic substances already present in the organism since the beginning of experimentation. As already pointed out (), the structure of iridomyrmecin and correlates might go back to head-to-tail concatenation of two isoprenic residues (table). Mevalonic acid might be its precursors as is the case for other terpenic structures. Iridodial, in the opinion of various authors, may be considered as a precursor of iridomyrmecin and isoiridomyrmecin. See Chap. VII, for experiments of incorporation of products with radioactive carbon (mevalonic acid, sodium acetate, etc.) for the formation in vivo of various iridoids in plants and animals.

We have seen that citronellal is considered to be a possible natural precursor (see diagram on page fig. 10); by irradiation of citral (table 10, diagram A) aldehyde (II) was obtained which can produce dolichodial by enzyme. oxydization; this, after reduction to iridodial and disproportion, can produce iridomyrmecin and isoiridomyrmecin. Oxydization of (-) limonene to linear ketoaldehyde and successive aldolic cyclization leads to an unsaturated aldehyde as in diagram B of

table ; then enzyme reduction can produce an unsaturated aldehyde from which it is possible to go on to dolichodial, iridodial, irido and isoiridomyrmecin as in diagram A.

[figure] 10

The synthesis of iridoids from citral, a typical acyclic monoterpene, and from limonene, a typical cyclohexanoid derivative, are considered as probable also in nature. It is remarkable that hitherto iridoids appear to be present only in Insects and plants.

Biological activities of iridomyrmecin.

Antibacteric and antimitotic activity.

Iridomyrmecin show weak antibacteric properties as pointed out at the beginning of our research with A. Nascimbene (254, 257, 223, 224, 260, etc.).

According to Hamasaki 1961 (144 A), the development of fungi (Mucor mandhricus, Rhizopus javanicus, Aspergillus oryzae, A. niger, Penicillium chrysogenum Q 176) is completely inhibited with a concentration of 1×10^{-3} g/cc of D(+)-isoiridomyrmecin, but only partially in a concentration of 2×10^{-4} g/cc. It is inactive on bacteria Pseudomonas fluorescens, Escherichia coli, Staphylococcus aureus in vitro, while it completely inhibits Bacillus aureus in a concentration of 1×10^{-3} g/cc.

Insecticide activity (229, 232, 260, 245, 246, 275 A).

The insecticide activity that I found in 1959 (see 229) justifies the existence of iridomyrmecin in nature as defensive product of the ant species producing it.

Experiments on the insecticide activity carried out on 39 species of Arthropoda also by actographic recording have pointed out the toxic activity of iridomyrmecin against insects found in agricul-

tural, forestal, economic, industrial, sanitary and veterinary fields, and also against animal Acari parasites. Generally speaking, Arthropoda which are most sensitive on coming into contact with iridomyrmecin, show a precocious agitated reaction in respect to the action of DDT-pp' and HCH. According to Ronchetti 1958 (275 A) its toxicity for Arthropoda, particularly high between 50 and 100 gamma per cm², is greater than that of DDT-pp' for most of the experimentated species, and in a few cases also that of gammahexane, while its toxicity for warm-blooded animals is remarkably lower than that of the latter insecticides.

Iridomyrmecin exerts a contact toxic activity of various degrees on almost all the Arthropoda species examined: therefore, no real specificity of action or non-action on particular systematic groups is apparent. However, Formicidae in general are particularly sensitive to iridomyrmecin, as if Iridomyrmex humilis Mayr had at its disposal an offensive-defensive venom created precisely for its struggle against ants, which are the deadliest enemies of the species. This is proved by the fact that in taking possession of new ground and later expansion it provides for thorough elimination of any species of indigenous ant. Such action is so thorough as to cause changes in the balance of the fauna.

Iridomyrmex humilis Mayr is itself very sensitive to contact with its own venom.

According to Clark, Fray, Jaeger and Robinson 1959 (73) there is no difference between the insecticide activity of natural iridomyrmecin and the two epimeric lactones. Cavill and Clark 1967 (56) confirm that irido and isoiridomyrmecin are highly lethal, this being the factor that proves their efficiency in defending the species (see also .Cavill and coll. 1961 (59 A)).

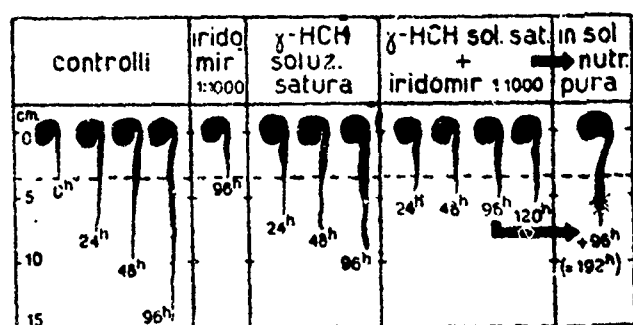
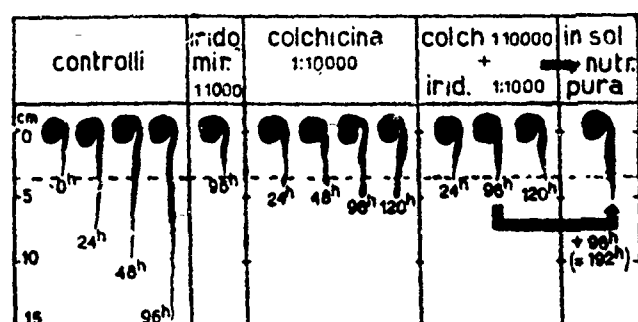
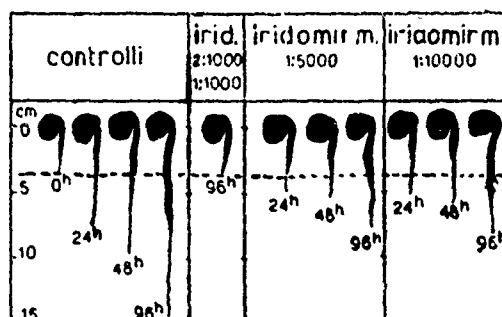


Fig. 13

Fitoinhibiting and antimitotic activity (237, 245, 246, 252, 260, 262).

Iridomyrmecin powder sprinkled on the leaves of various plants causes noticable toxic reactions. When applied in the Macht test (development of the germ of Lupinus albus Leguminosa seeds), it slows down the radical development completely or partially, depending on the concentration in the alimentary liquid, the plant may start developing again when moved to a pure alimentary environment.

When applied together with colchicine (which produces the well known c-tumour) or with HCH gamma isomer (which produces a typical swelling of the root) it eliminates the tumoral action of the two products. Later transfer into a pure nutritive solution allows a fresh start of normal growth without the typical tumoral alteration. In appropriate conditions therefore it opposes the oncogenous stimulus of colchicine and gammahexane and it eliminates the effects on Lupinus albus.

[schematic diagrams of the Lupinus 7fig. 13

Iridomyrmecin applied in a dose of 1:1000 to Allium cepa procures, after 4 hours, inhibition of the roots which later wither. The number of mitotic phases diminishes abruptly until the 4th hour of treatment and ceases at 24 hours. The reduction of the total number of stages appears due to the incapacity of the cell to enter the prophase.

[figure]

The apical meristem cells of the roots and the rare cases of mitotic phases present did not show any noticable alterations. Only after 48 hours do the cells become smaller and the nuclei no longer coloured by Feulgen reaction.

The addition of 1:1.000.000 iridomyrmecin inhibits the development causing cytoplasmatic lysis, nuclear pycnosis and remarkable cellular rarefaction on cultures of chicken embryo heart fibroblasts; a 1:2.000.000 dose produces weaker effects.

- VI 10 -

Toxicity and systemic action on warm-blooded animals (233, 245, etc.).

Iridomyrmecin has very low toxicity for warm-blooded animals. When applied in powder or oily solution to human skin over long periods, it does not provoke any cutaneous reaction.

In the white rat the average tethal dose through the stomach is 1,5 g to 1 Kg of animal (0,225 g for DDT, 0,190-0,225 g for gammahexane, 0,0125 g for parathion); a 4% oily solution with a dose of 0,5 g of iridomyrmecin per Kg, administered per endoperitoneum, has no lethal effects, while 1 g per Kg is getting close to DL 50. Toxicity is therefore very low.

When injected into the white rat in oily solution with a dose of 0,25/Kg per endoperitoneum, it enters the organs (liver, lungs kidneys, spleen, brain, blood) where it is active for a short time. It overcomes the hemato-encephalic barrier because it is also active for a short time in the brain. If in hydroalcoholic solution it persists in its active form in the organs for a longer period.

Pharmacological experiments in vivo (cardiac rhythm, pressure and breathing in an anesthetized dog) and in isolated organs (uterus of female rat in estrum) showed that iridomyrmecin, even in large doses, does not have any systemic toxic action; larger doses have shown a slightly depressive action on pressure and a limited respiratory stimulation.

The substance has therefore extremely low acute and systemic toxicity for warm-blooded animals.

Chap. 22 - Dendrolasin.

In literature the Ant Lasius (Dendrolasius) fuliginosus was remarkable for the odour it produced which has been defined in various ways. This species lives in colonies, sometimes composed of hundreds of thousands of ants, living cavities in tree-trunks. On being disturbed the workers emit a characteristic smell, similar to lemon peel or vegetal juices (for example that of the Labiata Melissa officinalis L., called citronel or lemoncine, of the Verbenacea Lippia citriodora H.B.K. or also of Andropogon citratus D.C.). This typical and very persistent smell is due to the complex mandibular gland secretion emitted from the base of the jaws.

Dendrolasin was the first component of the mandibular gland secretion of Formica Lasius (Dendrolasius) fuliginosus Latr. to be isolated (Pavan 1956, 240), and chemically defined (Quilico, Piozzi, Pavan 1956, 271; 1957, 273). It is a liquid product which is preserved ready for use in the reservoir of the glands mentioned (~~see Table~~). The crude secretion is composed of various substances, including the following: methylheptenone, perillen, cis-citral, trans-citral, farne_{sal} (Bernardi, Cardani, Ghiringhelli, Selva, Baggini, Pavan, 1967, 13A).

The emission of this mandibular gland secretion causes alarm and the secretion has a repellent and therefore defensive function, particularly regarding other ants. Insecticide activity due to contact is usually low, but it proved notably stronger than equal doses of DDT-pp' on the various species of Ants tested; L. (D.) fuliginosus itself is very resistant to its own secretion (~~Table~~).

Structure.

Dendrolasin ($C_{15}H_{22}O$), new to chemical literature, proved to be a (4:8-dimethylnon-3:7-dienyl) furan. Quilico, Grünanger, Piozzi 1957, 270A, broadened their research to include the synthesis of tetra-

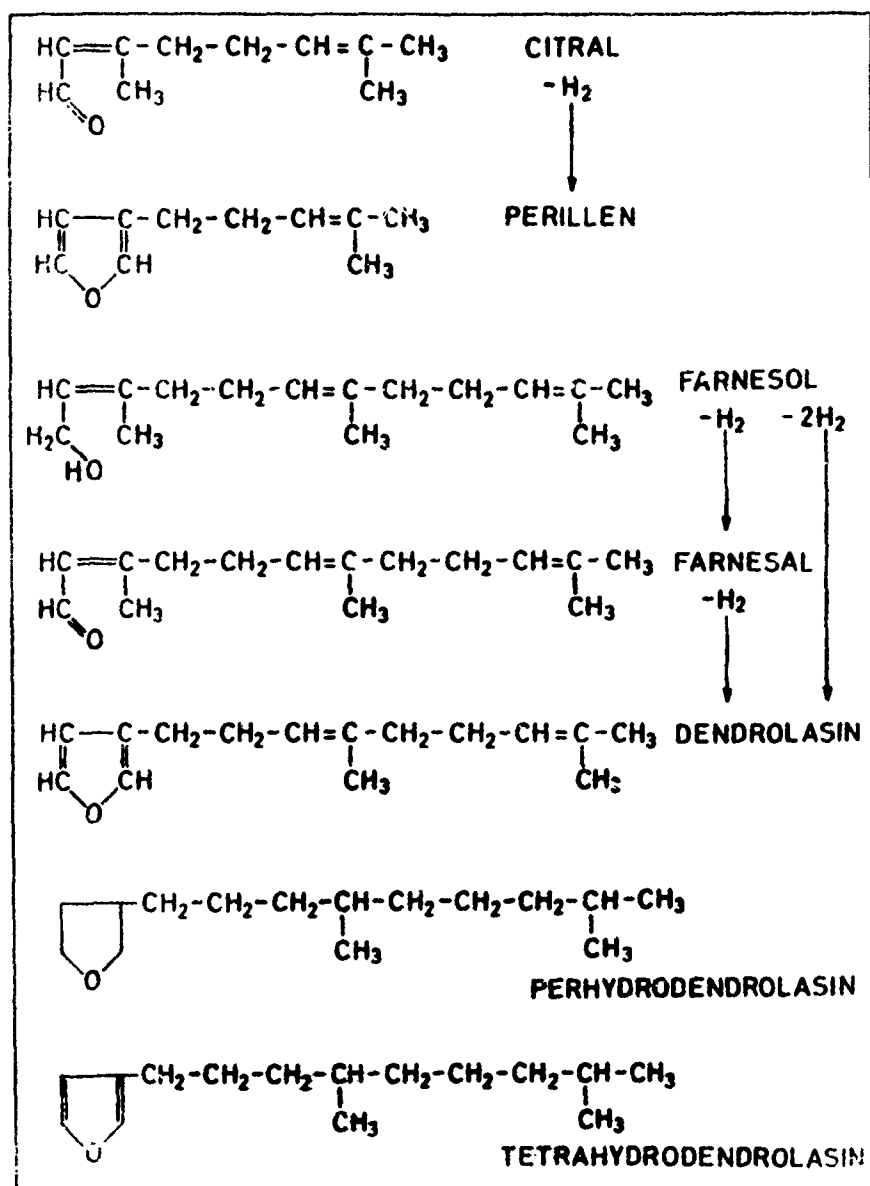


Fig. 14

hydro and perihydrodendrolasin (fig. 14 ;) confirming the structure indicated for dendrolasin. Weckering, 1960, 351, has published the stereonuclear and stereoelectronic structure of dendrolasin (fig. 15).

Dendrolasin biogenesis is still unknown. It has been pointed out (271, etc.) that the structure of the substance may correspond to the union of isoprenic residues; this is also likely for several other Arthropoda defensive secretions and for products of vegetal origin (see for example Chap. 21): in particular for citral and perillen (2 isoprenic units) and for farnesal and dendrolasin (3 isoprenic units), present in the secretion (see fig. 16). The simultaneous presence of these four products and their structural affinities pose the problem of the possible relative relationships of biogenetic derivation, which are under research at present. For the time being we may mention that radioactive dendrolasin was obtained by feeding the subjects with marked mevalonic acid: this suggested a transformation of mevalonic acid into farnesylpyrophosphate and later oxidation and furanic ring cyclization (Castellani and Pavan 1966, 54). Several products which are structurally correlated with dendrolasin (e.g. perillen) are found in plants and recently dendrolasin was found (286B) in two plants (Ipomoea batatas and Torrea nucifera Sieb. and Zucc.) together with four new sesquiterpenes nuciferal, nuciferol, torreyal, torreyol (Sakai and coll. 1963, 286B, see table 17). Comparative biogenetic study of these products present in plants and of those correlate with dendrolasin present in Insects offers an interesting line of work. The structural relationship existing between dendrolasin and farnesol and farnesal (see table 14), factors of the young hormone produced by the corpus allatum of insects, induced Wigglesworth (1963, 355A) to examine the properties of dendrolasin, which were found to be weak.

When exposed to air dendrolasin polymerizes, changing into an insoluble solid product; polymerization is activated in an acid ambient. The presence of a solid cohesive in the "cardboard" with which L. (D.) fuliginosus builds its nest, can be interpreted as polymerized dendrolasin.

Chap. 23 - Pederin, pseudopederin, pederone.

The toxic activity of several species of the Paederus genus (Coleoptera Staphylinidae) on the skin and eyes of warmblooded animals and man, met with in every continent, was pointed out in numerous publications the first of which was by Da Silva 1912 ⁽¹⁾. In literature the toxic substance responsible for dermatitis was generally identified as cantharidin, even though some authors stated that this substance was out of the question ⁽²⁾. For a more detailed knowledge of the subject, see Pavan-Bo 1952 ⁽³⁾ and Pavan 1963, 251.

Skin and eye affections due to Paederus were called "pederosi" by Maugeri and Candura 1964 ⁽⁴⁾.

The problem of the identification of the toxic substance was solved when it was obtained in its pure crystalline state from Paederus fuscipes Curt. Being a new product in chemical literature, I called this substance pederin (Pavan-Bo 1953, 253). The differential chemical, physical and biological features of cantharidin and pederin are shown in Table 18 .

Pederin is present usually with a percentage of 1% per weight of P. fuscipes that is 1 gamma per specimen, with considerable individual variations and percentages up to 10 times greater in the female.

-
- (1) DA SILVA P., 1912. Le Paederus columbinus est vésicant. Arch. de Parasit., Paris, 15: 3.
- (2) We do not believe that P. caligatus Er., closely related to P. fuscipes Curt., contains cantharidin, as was recently stated in Stepanova O.S., Alt'er E.N., Viranova L.I., 1961. (Study of P. caligatus extract). Farm.Zhur., 16: 56-57 (in russian).
- (3) PAVAN M., BO G., 1952. Ricerche sulla differenziabilità, natura e attività del principio tossico di Paederus fuscipes Curt. (Col. Staph.). Mem.Soc.Ent.It., 31: 67-82.
- (4) MAUGERI S., CANDURA F., 1964. Diffusione e prevenzione delle zoonosi. Atti II Congr.Naz.Medicina Rurale: 57-191.

from Pavan and Bo, 1953 (253)

Table 18

Possibility of differentiation between cantharidin and pederin.

Data of differentiation	Cantharidin	Pederin
I: ORIGIN:	Coleoptera Meloidae (various species of the genera <i>Lytta</i> , <i>Meloë</i> , <i>Zonabris</i> , <i>Epicauta</i> , <i>Milabris</i> , etc.)	Coleoptera Staphylinidae (<i>Paederus fuscipes</i> Curt. and probably other species belonging to the genus <i>Paederus</i>).
II: CHEMICAL TESTS		
1) Solubility		
a) Chloroform, carbon tetrachloride, acetone, ethyl ether, ethyl acetate, ethyl acetoacetate, benzene, toluene, xylene, tetralin, ethylene chlorohydrin, acetic anhydride, acetic acid, hydrochloric acid, sulfuric acid, nitric acid.	+	+
b) petroleum ether, glycerin, ammonia (33%)	0	0
c) water, physiological solution, carbon disulfide, methanol, ethanol (cold and warm), butyl alcohol, isobutyl alcohol, benzyl alcohol, amyl alcohol, ethylene glycol, triethylene glycol, propylene glycol, decalin.	0	+
d) sodium hydroxide N.	+	0
III: PHYSICAL TESTS		
Melting point ⁽¹⁾	218°C	112°C
3) May be extracted by the following methods:		
MARFORI and PIATTI 1935.	+	0
STASS-OTTO-DRAGEN-DORFF-OGIER (DOURIS 1935).	+	0
Deutsches Arzneibuch 1938.	+	0
STASS-OTTO-OGIER (DOURIS 1951).	+	0

¹⁾ Microdetermination with Kofler's apparatus.

IV: BIOLOGICAL TESTS

4) Reaction on human beings: skin

Acute: Typical vesication (bullae with serum). (1) (2).
Chronic: Unknown

Acute: (1) (2): epidermic necrotization (without bullae or serum).
Chronic: (1)(2): desquamation for many months.

5) Reaction on albino mouse:

a) skin of the head	Slight local swelling, desquamation, depilation without scarp and return of hair (2)	Huge edema of the anterior half of the body. Scalp, reconstitution of tissue with permanent loss of hair (2).
b) skin of the back	Desquamative dermatitis (2)	Dermatitis with necrosis (2)
c) pulmonary histological test	Exudates (3)	No exudates (2)
d) renal histological test	Glomerulonephritis (3)	Kidney undamaged (3)

6) Attraction for insects (4)

a) <i>Anthomyia pluvialis</i> L. (5)	+	0
b) <i>Anthicus quadriguttatus</i> Rossi (6)	+	0
c) <i>Formicomus pedestris</i> Rossi (6)	+	0
d) <i>Notoxus monoceros</i> L. (6)	+	0

- 1) Experimental and accidental tests, and literature data.
- 2) Cf. PAVAN-Bo 1952 and Bo-VALCURONE 1953.
- 3) PETRI 1930.
- 4) PAVAN, unpublished.
- 5) Diptera Anthomyidae.
- 6) Coleoptera Anthicidae.

from Pavan and Bo, 1953 (253)

During the course of chemical researches on P. fuscipes inconsistent traces of another new substances have been found; this substances was called pseudopederin (Quilico, Cardani, Ghiringhelli, Pavan 1961,269A) and a third called pederone (Cardani, Ghiringhelli, Quilico, Selva, 1967, 49), present in quantities of 25-50 mg per Kilo of insects.

Pederin was also found in the following species: P. fuscipes Curt., P. melanurus Ar., P. lithoralis Gravh., P. rubrothoracicus Goeze (all european but fuscipes is also widespread in Asia), P. rufocyaneus Bernh. (Mozambico), P. columbinus Cast. (South America).

Pseudopederin was found in P. fuscipes. Pederone was found in P. fuscipes and columbinus.

Structure.

Research on the structure of pederin and derivates required about 100 kilos of P. fuscipes (25 million individuals) which we obtained by carefully organized collection with teams of dozens of men in the countryside around the Pianura Padana and personnel for laboratory preparation (1).

The centesimal composition and structure of pederin ($C_{25}H_{45}O_9N$) and pseudopederin ($C_{24}H_{43}O_9N$) were the subject of a first publication (Quilico, Cardani, Ghiringhelli, Pavan 1961,269A) and were later completely defined in Cardani, Ghiringhelli, Mondelli, Quilico 1965, 46; 1966,47).

From the excellent studies on structure by Quilico, Cardani and coll., we learn that pederin - by hydrolysis with water - loses methanol and changes into pseudopederin; this through the action of barium

(1) This working, though careful, caused every year (since 1958 till 1965) many hospitalizations for "pederosi" and consequent complications.

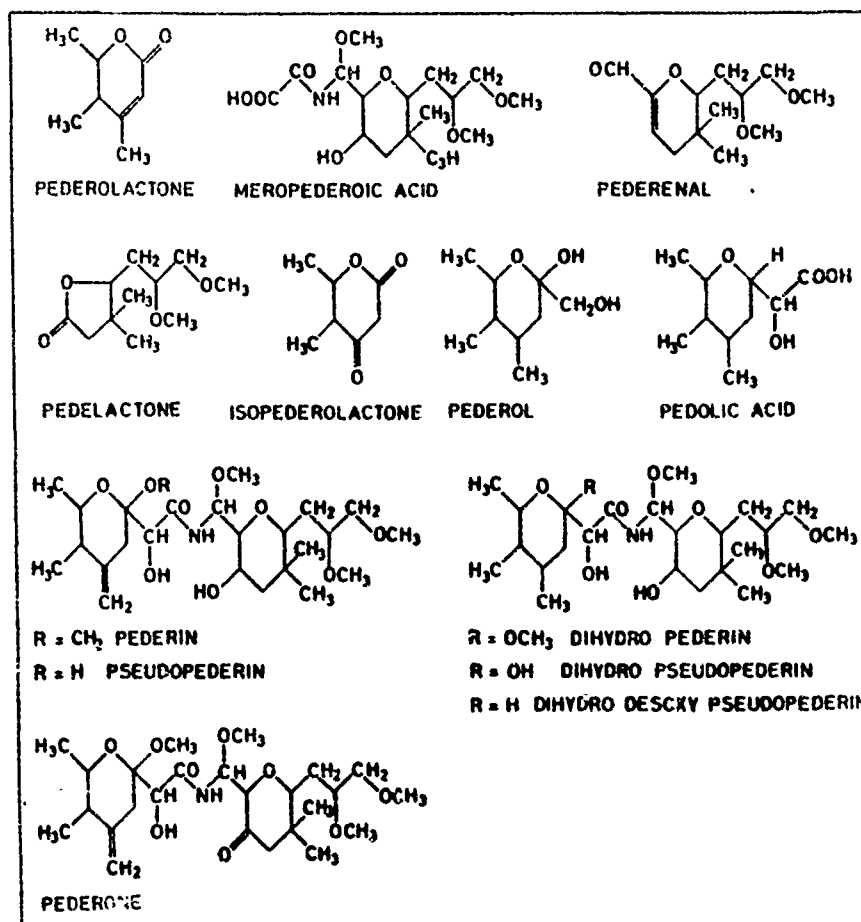


Fig. 19

metoxyde or of piperidine, gives pederolactone and meropederoic acid. The structure of the former, determined by the results of ozonization and spectrographic data, was confirmed by synthesis. The structure of meropederoic acid was determined following its acid hydrolysis which leads to pederenal, a substance that, by ozonolysis and later hydrolysis, gives pedelactone. By permanganic oxydation of pedelactone HIO_4 oxydation subject to previous bromidric hydrolysis and NMR spectrum we were able to define the structure of this compound its derivatives.

The fact that isopedrolactone was obtained by pseudopederin oxydation with lead tetracetate, together with the interpretation of the results of hydrogenation with Adams catalyzer and Pd on carbon helped to establish the position of $\text{CH}_2=$; the existence of two rings was confirmed by obtaining non-hydroxylated diacetylpederin and ritransformation in pederin by LiAlH_4 reduction; the derivation of pederol from acid hydrolysis of dihydropederin and dihydropseudopederin and of pedolic acid from acid hydrolysis of dihydrodesoxy-pseudopederin confirmed the structure given to pederin and pseudopederin and their hydroderivatives (1).

Biological properties.

Numerous publications describe the symptoms and development of skin and eye lesions caused by pederin; the biographical data are to be found in our previous publications, particularly Pavan 1963, 251, for biographical data.

Pederin is found throughout the insect's body, but the producing organ is not known. It is not employed for defensive purposes and

(1) In 1964 Matsumoto and coll. (184), dealing with partial pederin structure, published that the substance previously isolated by Ueta from P. fuscipes, to which the centesimal formula $\text{C}_{21}\text{H}_{39}\text{O}_9$ had been attributed (decidedly different from that of pederin), was to be identified with pederin, which we had isolated.

there is no organ for expelling it from the body. It acts on homeotherm skin only on direct contact with the skin, as in the case where the insect is squashed, not through mere contact with the insect, even when prolonged. Pederin does not give insecticide or repellent properties.

Applied to human skin in small doses (lower than 1 gamma) pederin provokes a slight redening and temporary pigmentation, but higher doses (for example 1 gamma, corresponding generally to the average content of one specimen of Paederus fuscipes) quickly cause a local reaction of necrotic type, with the appearance of blisters and sores: this in general develops aseptically and promptly heals without any traces of scarred tissues. This was found to be true for extensive accidental and voluntary sores, even when repeated many times on the same part of the body. This kind of cutaneous reaction, first from necrotization following from inhibition of the tissue development and later from stimulation of development, directed us towards a research on the inhibiting and stimulating properties of tissues in vitro and in vivo, in plants and animals and human tissues degenerated for other reasons. Therefore, this part was studied more thoroughly either directly or with various collaborators (Bo, Brega, De Carli, Deotto, Erspamer, Falaschi, Sirtori, Testori, Vaccari, Valcurone) or by other authors (Fioretti, Ghione, Soldati, 1966, 323) in Italy. This subject was also partially studied in Japan (Hisada, Emura 1965, 150) with P. fuscipes extracts. These researches, extensively dealt with in Pavan 1963, 251, but part of which is still under investigation and unpublished, gave the following results.

Pederin causes a fall in the number of lymphocytes in the circulating blood of rats, and of neutrophils in the circulating blood of guinea pigs. In the partially hepatectomized rat it causes a stimulation of regeneration, increasing the number of mitoses.

The treatment of tumoral fragments (sarcoma 180) before grafting between rats reduces taking faculties or inhibits them completely,

depending on the concentrations and treatment times adopted. Soldati and coll. 1966 confirmed the inhibiting activity of very small doses on both normal cells and tumoral cells cultivated in vitro (HeLa and KB strains). The substance is lethal for Protozoa of the Trichomonas genus. It also exercises a strong phytoinhibition on plants cultivated in vitro such as Lupinus albus (Leguminosae) (fig.); treatment with pederin of the same white lupin inhibits also the development of the typical tumours from colchicin and gammahexane (fig.). It acts as an antimitotic on Allium cepa, blocking the metaphase before the formation of the spindle and causing typical chromosomic alterations and general cytotoxic effects.

The application of very small doses of the substance (gamma 0,05) on large bedsores in extremely elderly chronic patients resulted in a reduction of the sore in a short time and in complete recovery in numerous cases.

On the other hand, following up our research, Hisada and Emura 1965, 150, employed metanolic extracts of P. fuscipes in the treatment of a graftable ascite rat tumour (MTK strain - sarcoma III) obtaining almost complete regression after a long period of treatment. They believe that the antimitotic action is proved, and that the DNA synthesis system is repressed but not damaged by pederin.

In several in vitro cultures of animal tissues pederin proved to have remarkable inhibiting properties on development in very small doses.

Brega, Falaschi, De Carli and Pavan ⁽¹⁾, proved that in vitro the substance inhibits the development of various strains of human and mammal tissues, with a concentration of 1,5 nanogram per ml ⁽²⁾. The analysis of macromolecular synthesis by radioacti-

(1) Studies on the mechanism of action of pederin. J. Cell Biology, 36: 485, 1968.

(2) This is the most powerful antimitotic known, much more active than puromycin.

Table

Minimum inhibitory concentrations (M.I.C.) in nanogram/milliliter (ng/ml) of pederin on different strains and cell lines.
(from Brega, Falaschi, De Carli and Pavan: Studies on the mechanism of action of pederin. J.Cell Biology, 36: 485, 1968).

Strain or line	M.I.C. ng/ml	Strain or line	M.I.C. ng/ml
EUE	1.5	MEF	1.5
E6D	1.5	CE	1.5
HeLa	1.5	BHK	1.0
KB	1.5	Z 1	3.1
Hep	1.5	M 1	3.9
Senger	1.5		

Cell strains or lines and culture procedures

The minimum inhibitory concentration was determined both on heteroploid cell lines and diploid strains. All other experiments were performed with the EUE line only.

1) Cell lines.

EUE: a human cell line isolated by Terni and Lo Monaco.

E6D: an EUE clonal subline deficient for alkaline phosphatase, isolated by De Carli et al.

HeLa: Gey et al.

Hep 2: Fjelde.

MEF: a cell line isolated in 1964 from a mouse embryo by Dr. Murthy at the Research Laboratories of the Lepetit Corporation, Milan, Italy.

KB: Eagle.

BHK 21: Stoker and MacPherson.

2) Cell strains.

Z 1: A diploid cell strain derived from human thyroid, grown in our laboratory for 5 months.

M 1: a diploid cell strain derived from human amnion, grown in our laboratory for 6 months.

- VI 18 -

ve precursors shows that pederin causes an almost immediate blocking of DNA and proteic synthesis, without however affecting RNA synthesis nor DNA polymerizing activity. It appears to act directly on the amino acid polymerization system, and that the effect on DNA is secondary.

Pseudopederin and pederone phytoinhibiting, dermatitic and toxic activity on white mice is of a roughly similar order (though the endoperitoneal toxicity in particular is lower for pederone), and is still far lower than that of pederin; pederone is different from pederin and pseudopederin inasmuch in doses applied it does not have anti-mitotic effects on Allium cepa. Pederin is, as already mentioned, very active on various animal and human cellular strains cultivated in vitro (for example etheroploid embryonal human epithelium, HeLa carcinoma of the uterus, etc.), followed by pederone and lastly by the least active pseudopederin. The very slight toxicity which accompanies pederone makes this product interesting and opens up further prospectives of study.

The pharmacological tests of pederin on warm-blooded animals have shown an acute systematic inactivity up to very heavy doses (251). Data on lethal doses for various animals are also shown in 251.

Chap. 24 - Cossins and Zeuzerin.

Cossins.

The larva of Cossus cossus L. Lepidoptera (C. ligniperda Fabr.) living in the trunk of various trees emanates a characteristic smell whose origin is in the secretion of the mandibular glands, which are supplied with a large reservoir whose excreting duct opens at the base of the jaw.

The smell and the secretion responsible for it attracted the attention of Henseval who, in 1897, published data which we found to be

mistaken (1).

Composition of the secretion.

The larva secretion, taken directly from the animal dissected under narcosis, is citrin coloured and of oily consistency. The smell is penetrating and very persistent (2).

The first chemical researches were made in 1959 and various components were isolated. The partial data which we published in 1960 (336, 338), were modified and later replaced by the latest final publication (Trave, Garanti, Marchesini, Pavan 1966, 334).

Gaschromatographic analysis proved the secretion to be composed of seven main components which, being new to chemical literature, we called cossin 1, cossin 2, cossin 3, cossin A, cossin B, cossin C, cossin B₁, cossin C₁; the respective structures are shown in table .

Therefore the seven cossins are:

cossin 1: tetradeca-5,13-dienol; cossin 2: tetradeca-3,5-13-trienol; cossin 3: tetradeca-4,6,13-trienol; cossin A: acetate of cossin 1; cossin B: acetate of cossin 2; cossin C: acetate of cossin 3; cossin B₁: acetate of cossin 2 with a different steric configuration; cossin C₁: acetate of cossin 3 with a different steric configuration.

In an attempt to find a naturalistic justification of the secretion, a preliminary research of insecticide activity through contact and breathing was made. The trials through contact were made by comparative experimentation with equal doses of DDT-pp': at 100 gamma/cm²

(1) Henseval 1897 states that the secretion is composed of a cyclic substance containing sulphur, corresponding to the centesimal composition C₂₂H₃₅S.

(2) In those places where the larva are found during springtime when they leave the trunks to bury themselves in the ground as a preparation for nymphosis, their typical smell is present in the air, and it is possible to trace where they passed and dug into the ground.

- VI 29 -

on the 13 species of Blattodea, Isoptera, Orthoptera, Emiptera, Lepidoptera and Coleoptera experimented, the secretion generally does not show any activity or, in a few cases, a very reduced activity compared with that of DDT-pp', while on 8 Imenoptera Formicidae species it has a remarkably toxic effect, generally greater than DDT-pp'. Ants are to be considered as possible enemies of the Cossus cossus larvae, because they may be competitors for the same habitat. However, the substance has a very low toxicity for Formica lugubris Zett. and Lasius (Dendrolasius) fuliginosus Latr.

Phisalix 1922 (265) also mentions the fact that the secretion has a certain toxicity for the fly, and is active on the Oospora cinna-
mea Fungus, an insect parasite; this seems to suggest a protective action. On the contrary, it does not seem to have any influence on wood, so that its employment as an auxiliary means in the attack upon wood fibres during the excavation of the tunnel seems useless.

PART VII - ASPECTS OF STUDIES ON ARTHROPODA DEFENSIVE SECRETIONS.

Distribution in the zoological orders of those chemically defined substances found in Arthropoda defensive secretions.

1. The chemically defined substances hitherto known to be present in Arthropoda defensive secretions amount to at least 194. In Table 5 they have been arranged in categories according to chemical affinity, and indicating the zoological order in which they have been found.

Table 5 - Distribution in the zoological orders of those chemically defined substances found in Arthropoda defensive secretions.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA							(*) Scolopendromorpha	Cl. I				
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida		Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
<u>HYDROCARBONS</u>													
1. <u>n</u> -undecane													
2. <u>n</u> -dodecane													
3. <u>n</u> -tridecane													
4. 1-nonene													
5. 1-undecene													
6. 1-tridecene													
<u>SULFIDES</u>													
7. dimethyldisulfide													
8. dimethyltrisulfide													
<u>ALCOHOLS</u>													
9. methanol													
10. glycerol													
11. <u>n</u> -hexanol													
12. 2-methyl-butanol									+				
13. 2-methylene butanol									+				
14. ottan-1-ol													
15. nonan-1-ol													
16. <u>cis</u> -non-3-en-1-ol													
17. <u>trans</u> -non-3-en-1-ol													
18. <u>cis</u> -dec-3-en-1-ol													
19. <u>trans</u> -dec-3-en-1-ol													
20. cossin 1													
21. cossin 2													
22. cossin 3													

A.

ch are pre-
stances
(POPODA)
(CRUSTACEA)

[illegible]

B.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA							(*) Scolopendromorpha				C
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida		Blattodea	Isoptera	Dermaptera	Phasmida
<u>AMINES AND AMINO ALCOHOLS</u>												
23. choline												
24. histamine												
25. 5-hydroxytryptamine								+				
26. 2,5-hydroxytryptamine												
<u>SATURATED ALDEHYDES</u>												
27. propanal												
28. <u>n</u> -butanal												
29. 2-methyl butanal									+			
30. <u>n</u> -hexanal												
<u>UNSATURATED ALDEHYDES</u>												
31. <u>trans</u> -prop-2-enal												
32. 2-methylene propanal									+			
33. <u>trans</u> -but-2-enal												
34. 2-methylene butanal									+			
35. 2-methylene butanal dimer									+			
36. pentenal												
37. 2-methylene pentanal									+			
38. <u>trans</u> -hex-2-enal									+			
39. <u>trans</u> -hept-2-enal												
40. <u>trans</u> -oct-2-enal												
41. <u>trans</u> -dec-2-enal												
42. <u>cis</u> -dec-2-enal												
43. <u>trans</u> -dodec-2-enal					+							

A.

ch are pre-
stances
PODA)
CRUSTACEA)

[illegible]

B.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA							(*) Scolopendromorpha	Cl. I				
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida		Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
<u>AROMATIC ALDEHYDES</u>													
44. benzaldehyde			+										
45. p-hydroxybenzaldehyde													
46. salicyl aldehyde													
47. cumin aldehyde			+										
<u>SATURATED KETONES</u>													
48. methyl-ethyl-ketone													
49. methyl-heptyl-ketone													
50. ethyl-propyl-ketone													
51. methyl-n-amyl-ketone													
52. methyl-n-undecyl-ketone													
53. 4-methyl-2-hexanone													
54. n-propyl-isobutyl-ketone													
<u>UNSATURATED KETONES</u>													
55. 2-methyl-2-hepten-6-one													
56. 4-keto-hex-2-ene													
<u>UNSATURATED KETO ALDEHYDES</u>													
57. 4-keto-trans-hex-2-enal													
58. 4-keto-trans-oct-2-enal													
<u>CARBOXYLIC ACIDS</u>													
59. formic acid													
60. acetic acid													
61. propionic acid													
62. butyric acid													
63. isobutyric acid													

A

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s CRUSTACEA)

C1. DIPLOPODA

Cl. INSECTA

C1. ARACHNIDA

[illegible]

B.

Zoological order in which are present the listed substances
 ((*) Class CHILOPODA)
 ((§) Class CRUSTACEA)

Substances which are present in the defensive secretions of Arthropoda

64. 2-methyl butyric acid

65. isovaleric acid

66. caprylic acid

67. palmitic acid

68. methacrylic acid

69. 2-methylene butyric acid

70. tiglic acid

71. 10-hydroxy-2-decenoic acid

72. D-gluconic acid

73. ascorbic acid

74. hyaluronic acid

75. benzoic acid

76. pipecolinic acid

77. oxalic acid

PHENOLS

78. phenol

79. guaiacol

80. cresol

81. m-cresol

82. p-cresol

FURANS

83. furan

84. methylfuran

85. perillen

86. dendrolasin

Cl. DIPLOPODA

Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Camalida
-----------	-------------	-------------	--------	-------------	----------------	----------

(*) Scolopendromorpha

Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
-----------	----------	------------	----------	------------

Cl. IN

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[illegible]

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA							(*)Scolopendromorpha	Cl. 1			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida		Blattodea	Isoptera	Dermaptera	Phasmida
<u>ESTERS</u>												
87. isoamyl acetate												
88. <u>n</u> -hexyl acetate												
89. <u>n</u> -octyl-acetate												
90. <u>trans</u> -hex-2-enyl-acetate												
91. <u>trans</u> - oct-2-enyl acetate												
92. <u>trans</u> -dec-2-enyl-acetate												
93. cossin A												
94. cossin B												
95. cossin C												
96. cossin B ₁												
97. cossin C ₁												
98. <u>n</u> -butyl butyrrate												
99. <u>trans</u> -hex-2-enyl butyrrate												
100. methyl- <u>p</u> -hydroxybenzoate												
101. acetylcholine												
102. <u>β</u> , <u>β</u> -dimethyl-acrylyc-choline												
<u>LACTONES</u>												
103. <u>γ</u> -gluconolactone									+			
104. <u>δ</u> -gluconolactone									+			
<u>AMIDES</u>												
105. pederin												
106. pseudopederin												
107. pederone												

A.

are pre-
nces
(ODA)
(RUSTACEA)

[illegible]

B.

Zoological orders in which are present the listed substances
 ((*) Class CHILOPODA)
 ((§) Class CRUSTACEA)

Substances which are present in the defensive secretions of Arthropoda

Cl. DIPLOPODA

Cl. 1

	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*) Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
<u>NITRILES</u>													
108. hydrocyanic acid			+										
109. D-(+)-mandelic nitrile			+										
110. glucoside of p-isopropil mandelonitrile			+										
111. mandelonitrile benzoate			+										
<u>AMINO ACIDS</u>													
112. glycine													
113. alanine													
114. serine													
115. α -aminobutyric acid													
116. β -iso-aminobutyric acid													
117. δ -aminobutyric acid													
118. threonine													
119. valine													
120. aspartic acid													
121. asparagine													
122. leucine													
123. isoleucine													
124. glutamic acid													
125. glutamine													
126. ornithine													
127. cysteine													
128. cystine													
129. methionine													
130. lysine													

A.

melonitrile

B.

Zoological orders in which are present the listed substances
 ((*) Class CHILOPODA)
 ((§) Class CRUSTACEA)

Substances which are present in the defensive secretions of Arthropoda

Cl. DIPLOPODA

Cl. INSE

Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*) Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
-----------	-------------	-------------	--------	-------------	----------------	-----------	-----------------------	-----------	----------	------------	----------	------------

131. arginine

132. proline

133. histidine

134. phenylalanine

135. tyrosine

136. tryptophane

QUINONES

137. 1,4-benzoquinone

138. 2-methyl-1,4-benzoquinone

139. 2-ethyl-1,4-benzoquinone

140. 2,3-dimethyl-1,4-benzoquinone

141. 2,5-dimethyl-1,4-benzoquinone

142. 2,3,5-trimethyl-1,4-benzoquinone

143. 2-methoxy-1,4-benzoquinone

144. 2-methyl-3-methoxy-1,4-benzoquinone

145. hydroquinone

146. 2-methyl-hydroquinone

147. 2-ethyl-hydroquinone

148. 2-methyl-3-methoxy-hydroquinone

SUGARS

149. glucose

150. fructose

TERPENIC DERIVATIVES

HYDROCARBONS

151. D,L-limonene

A.

Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class INSECTA) Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA							(*) Scolopendromorpha	Cl. II			
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida		Blattodea	Isoptera	Dermaptera	Phasmida
152. α, β -pinene									+			
<u>ALCOHOLS</u>												
153. citronellol												
<u>ALDEHYDES</u>												
154. citral												
155. citronellal												
156. farnesal												
157. iridodial												
158. dolichodial											+	
<u>LACTONES, ANHYDRIDES</u>												
159. iridomyrmecin												
160. isoiridomyrmecin												
161. isodihydronepetalactone												
162. cantharidin												
<u>STEROIDS</u>												
163. 24-methylene cholesterol									+			
164. testosterone												
165. 11-desoxycorticosterone												
166. 6-dihydrocybisterone												
167. cybisterone												
168. 6-dehydrocortexone												
169. 6-dehydroprogesterone												
170. calotropin												+
171. calactin												+

A.

h are pre-
stances
LOPODA)
INSECTA)

Cl. DIPLOPODA

C1. INSECTA

CL. ARACHNID.

stances PODA) INSECTA)	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*) Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera	Heteroptera	Lepidoptera	Diptera	Coleoptera	Hymenoptera	(§) Isopoda	Scorpiones	Uropteri	Copiliones	Aranea
										+								+					
																		+					
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Zoological orders in which are present the listed substances ((*) Class CHILOPODA) ((§) Class CRUSTACEA) Substances which are present in the defensive secretions of <u>Arthropoda</u>	Cl. DIPLOPODA							Cl. INS					
	Glomerida	Chordeumida	Polydesmida	Julida	Spirobolida	Spirostreptida	Cambalida	(*)Scolopendromorpha	Blattodea	Isoptera	Dermaptera	Phasmida	Orthoptera
<u>ALKALOIDS</u>													
172. glomerin	+												
173. omoglomerin	+												
<u>FLAVOPROTEINS</u>													
174. riboflavin													
<u>PHOSPHATIDES</u>													
175. lecithin													
<u>ENZYMES</u>													
176. adenosine triphosphatase													
177. L-amino acid dehydrogenase													
178. cholinesterase													
179. alkaline phosphatase													
180. phospholipase A													
181. phospholipase B													
182. phospholipase C													
183. β -glucosidase			+						+				
184. hyaluronidase													
185. invertase								+					
186. trypsin													

A.

ch are pre-
stances
(LOPODA)
(s CRUSTACEA)

C1. DIPLOPODA

Cl. INSECTA

Cl. ARACHNIDA

[illegible]

B.

Defensive secretions of Hymenoptera (2-6).

2. In the group of social Hymenoptera (Apidae, Vespidae, Formicidae) there are species with more simple venoms and others with the most complicated venoms hitherto known within the entire group of Arthropoda. In fact they go from the venom of many Formicidae, composed of a watery solution of formic acid, to those of the Apis mellifera (and presumably many other Apidae and Vespidae) which are extremely complex and where dozens of different substances belonging to entirely different chemical categories may be found.

3. Various types of glands producing defensive substances exist in Hymenoptera Formicidae

a) in the head the mandibular glands, present in all the Families, from which so far citral, dendrolasin, farnesal, a substance similar to this but not yet defined (Chthonolasius), various sulphides (Paltothyreus), 2-hexenal and various other odorous substances have been extracted.

b) The venomous apparatus in the abdomen, in many species with an atrophied sting. This apparatus comprises two glands (acid and alkaline) (*): it usually produces venom in small quantities, complex however, meant to be injected into the prey in those cases where the sting is active (for example in many Ponerinae, Myrmicinae, etc.). In many Formicinae with atrophied sting the glands producing formic acid in considerable quantities is extremely developed, as for example in the species of the Formica rufa group: these eject venom in visible quantities even as far as 20-30 centimeters.

In Dolichoderinae besides the poison apparatus with a sting (usually atrophied and inefficient), typically formed of an acid gland and an alkaline gland, we also find the so-called "anal

(*) The alkaline or Dufour gland in various species appears to produce a trail substance (see Gabba 1967).

glands" which are characteristic of this group; they produce the known venoms without formic acid and containing iridomyrmecin, iridodial, dolichodial, methylheptenone, etc. The first species studied was Iridomyrmex humilis Mayr from which iridomyrmecin was obtained. This gave rise to an interesting series of studies in several continents, results of which are summarized in Table 6.

Table 6

Species of <u>Formicidae</u> <u>Dolichoderinae</u>	Products of the anal glands
<u>Iridomyrmex humilis</u> Mayr	iridomyrmecin
<u>I. nitidus</u> Mayr	isoiridomyrmecin
<u>I. myrmecodiae</u> (Em.)	dolichodial
<u>I. rufoniger</u> Lowne	dolichodial; iridodial; methylheptenone
<u>I. detectus</u> (Smith)	iridodial, methylheptenone
<u>I. conifer</u> For.	" "
<u>I. nitidiceps</u> (André)	" "
<u>I. pruinus</u> (Roger)	methyl-n-amyl-ketone
<u>Conomyrma pyramica</u> (Roger)	"
<u>Tapinoma nigerrimum</u> Nyl.	iridodial; methylheptenone, propyl-isobutyl-ketone
<u>Dolichoderus</u> (<u>Acanthoclinea</u>) <u>clarcki</u> (Wheeler)	dolichodial; 4-methyl-2-hexanone
<u>D. (A.) dentata</u> (Forel)	dolichodial
<u>D. (Diceratoclinea) scabridus</u> (Roger)	iridodial; dolichodial, isoiridomyrmecin, methylheptenone
<u>Liometopum microcephalum</u> Panz.	methylheptenone

4. Hitherto studies have been particularly carried out on products of the "mandibular glands", the "anal glands" and "acid gland", with reference to the defensive secretions of the Formicidae.

Studies are only just beginning however on the species provided with an efficient sting (for example Solenopsis, Paraponera, Myrmica, etc.). These venoms are usually complex and in many cases have similar effects to those produced by the poison from Apidae and Vespidae. These poisons are of particular biological interest due to the effects they produce on animals generally (1).

5. The data collected concerning Hymenoptera Formicidae show a clear distinction between Formicinae and Dolichoderinae: Dolichoderinae always lack formic acid in the anal glands; this on the contrary, is the active factor always present in the venom produced by the acid gland of Formicinae.

The substances produced by the anal glands of Dolichoderinae are partially connected with the terpenes (iridomyrmecin, iridodial, etc.); also straight-chain substances are lacking in certain species (for example methylheptenone, propyl-isobutyl-ketone); in certain cases (for example Liometopum microcephalum Panz.) only straight-chain substances are to be found. (For example methylheptenone in Liometopum microcephalum Panz., methyl-n-amyl-ketone in Conomyrma pyramica (Roger)).

6. We now know a furanic substance in Formicinae Ants, dendrolasin, the first representative of furans found in animals, produced by the mandibular glands. A substance not yet chemically defined and presumably related to dendrolasin is present in Lasius (Chthonolasius) umbratus Nyl., a species systematically close to those which produce dendrolasin. Here again we can see the initial outline of a group of substances produced by Formicidae, with certain chemical and systematic-zoological uniformity.

(1) With regard to this we are waiting for the final results of the chemical study on solenopsine, extracted from the poison of Solenopsis geminata F. by Blum and coll. It seems to be an alcaloid but final data are still lacking.

The two dendrolasin and formic acid defensive secretions, contemporarily present in the same species, are produced by different organs.

Furans are closely related to dendrolasin and are present in plants (for exemple perillen, alfa-clausenane). Dendrolasin was later discovered also in the sweet potato and Torreya nucifera.

Heteroptera defensive secretions (7-8).

7. Defensive substances in Heteroptera adults are produced by a metathoracic odoriferous apparatus, by the Brindley glands and the thoraco-abdominal ventral glands.

In the young forme (larvae) there are dorso-abdominal glands which later generally disappear with imaginal metamorphosis, but which remain, sometimes reduced in number, in the imagines of numerous species; in certain cases they develop considerably even after the final imago, particularly in the male.

The metathoracic odoriferous apparatus, which is present in almost all Heteroptera, has its outlet on the surface of the body, often in the metasternum and by the sides of the metacoxal articulations.

The Brindley glands, paired, dorsal, present in Reduviidae s.l. and Pachynomidae, are placed at the base of the abdomen near the edge and open outwards in a region which seems to belong to the metathorax.

The thoraco-abdominal ventral glands in Reduviidae of the sub-families Phymarinae, Elasmodeminae e Holoptilinae are formed by a pair of sacculated invaginations of the thoraco-abdominal membrane.

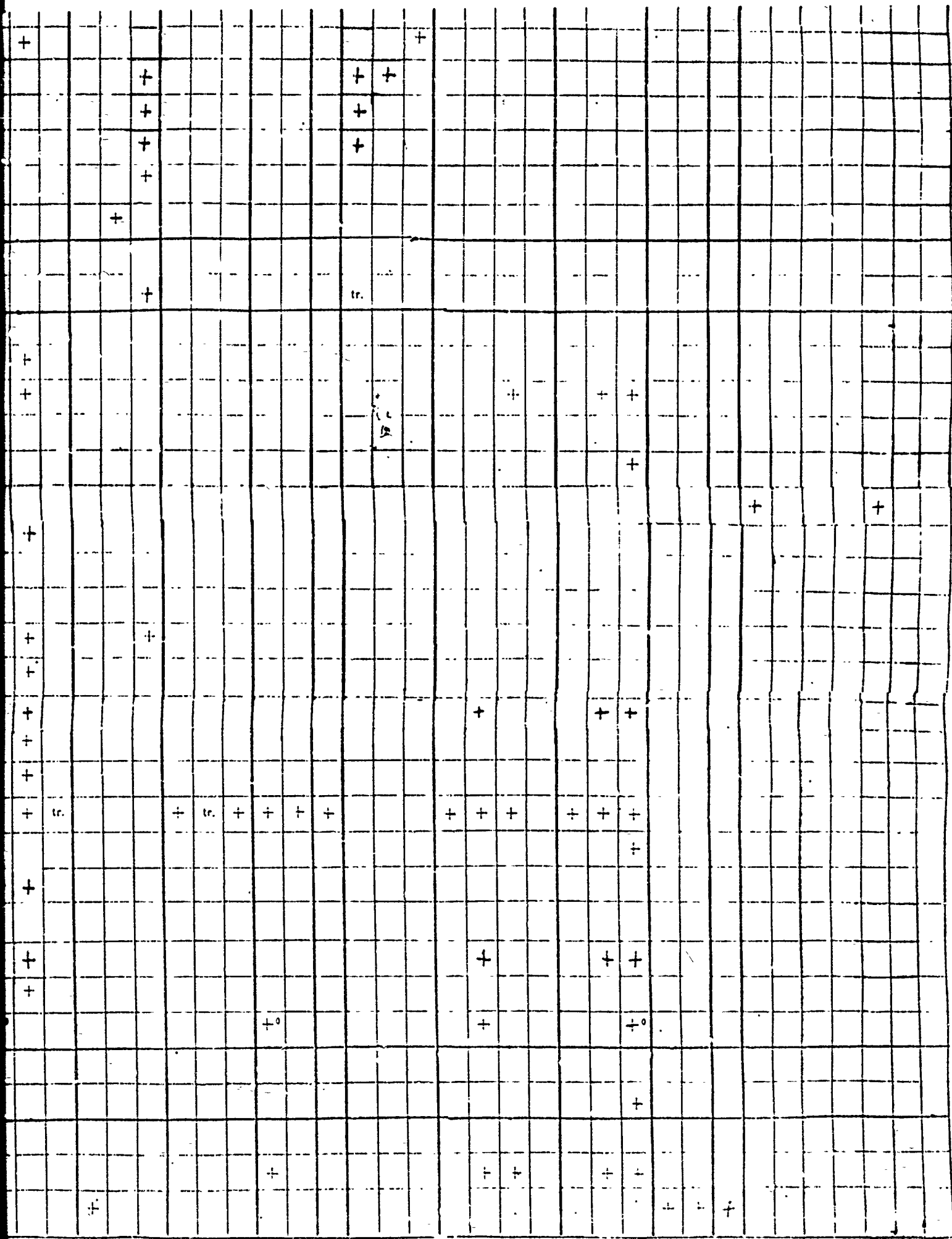
8. The defensive secretions of all the above mentioned glands are formed of very volatile substances which the insect can squirt in unilateral or bilateral jets.

The 35 substances described hitherto in about forty species are mostly straight-chain substances; only in one case (Scaptocoris divergens Fr.) are cyclic substances present together with the previous ones. In Table 7 the known data have been summarily collected.

Often we find no indication in literature of the glands from which the secretions have been collected and examined, however, they are usually taken from the metathoracic glands. Only one species studied by us (Tessaratomia aethiops Dist.) has comparatively well known metathoracic gland secretions, both from adults and larvae: the secretion of the latter did not contain two of the five components present in adult secretions.

TABELLA

[illegible]



plus pugnax (F.).

abimide dell'India che denominano Black Hemiptera Bug

D.

Examples on zoological specialization (9-10).

9. Examples of specialization in the production of defensive substances are given by Coleoptera and Myriapoda.

For example, in Coleoptera cantharidin is only present in the species belonging to Meloidae; pederin, pseudopederin and pederone only in the Staphylinidae species; tiglic acid in the Carabidae; and quinones prevalently in the Tenebrionidae.

Myriapoda Diplopoda Juliformia contain numerous quinones; in Myriapoda Diplopoda Polydesmidae however we find the production of cyanogenic substances.

10. Several quinones closely related to each other have been found in three groups of Arthropoda considered distant from a systematic point of view (Myriapoda, Insecta, Arachnida).

Considering Insecta as producers of quinones we might almost say Coleoptera Tenebrionidae specialize in the production of these substances although there are examples in Carabidae (Brachynus), Blattodea (Diploptera), and Dermaptera (Forficula), systematically very distant from the first mentioned.

Complexity of venom (11-14).

11. Regarding the complexity of composition in these poisons, they go from those with only one known substance different from water (e.g. formic acid, oxalic acid, salicylic aldehyde, iridomyrmecin, trans-hex-2-enal, cantharidin, etc.), to those which are composed of several constituents.

The most complicated cases ^{in Insecta} ~~seem to~~ be those of Apis mellifera and Vespidae who produce venoms containing many complex substances, also enzymatic. Very complex venoms are to be found in Arachnidae, particularly Araneae and Scorpiones, but although studies of these animals are numerous, a well defined composition cannot yet be attributed to

Table 8 - Components of defensive secretions of Diplopoda Juliformia.

<u>Diplopoda Juliformia</u>	1,4-benzoquinone	2-methyl-1,4-benzoquinone	2-methyl-3-methoxy-1,4-benzoquinone	2-methyl-hydroquinone	2-methyl-3-methoxy-hydroquinone	quinones	trans-dodec-2-enal
<u>Archiulus (Schizophyllum) sabulosus</u> L.	+	+	+	+	+		
<u>Aulonopygus aculeatus</u> Attems		+					
<u>Aulonopygus aculeatus barbieri</u>		+					
<u>Brachyulus unilineatus</u> Koch		+	+				
<u>Cambala hubrichti</u> Hoffman		+	+				
<u>Chicobolus spinigerus</u> Wood		+	+				
<u>Cylindroiulus teutonicus</u> Pocock		+	+				
<u>Doratogonus annulipes</u> Carl		+	+				
<u>Floridobolus penneri</u> Causey		+	+				
<u>Narceus annularis</u> Raf.		+	+				
<u>Narceus gordanus</u> Chamb.		+	+				
<u>Orthocricus arboreus</u> (Sauss.)						+	
<u>Orthoporus conifer</u> (Attems)			+				
<u>Orthoporus flavior</u> Chamb. e Mulaik		+	+				
<u>Orthoporus punctilliger</u> Chamb.		+	+				
<u>Pachybolus laminatus</u> Cook	+	+					
<u>Peridontopyge aberrans</u> Attems		+					
<u>Peridontopyge vachoni</u>		+					
<u>Rhinocricus</u> sp.		+	+	+	+		
<u>Rhinocricus insulatus</u> Chamb.		+					+
<u>Schizophyllum mediterraneum</u>	+						
<u>Spirostreptus</u> sp.		+	+				
<u>Spirostreptus castaneum</u> Attems	+						
<u>Spirostreptus multisulcatus</u> Dem.		+					
<u>Spirostreptus virgator</u> Silv.	+	+					
<u>Trigonoilulus lumbricinus</u> Gerst.		+	+				

Table 9 - Components of defensive secretions of Diplopoda Polydesmida (1) (from Barbetta-Casnati-Pavan 1966).

<u>Diplopoda</u> <u>Polydesmida</u>	Benzoic acid	Benzaldehyde	[Cuminaldehyde]	Hydrocyanic acid	[Phenol]	[Guaiacol]	[Glucoside of p-isopropyl mandelonitrile]	Mandelonitrile benzoate	D-(+)-mandelic nitrile	[Glucose]	[Disaccharid]
<u>Apheloria corrugata</u> (Wood)		+		+					+(b)		
<u>Cherokia georgiana</u> (Bollmann)				+							
<u>Gomphodesmus pavani</u> Dem.	+	+		+				+(a)	+		
<u>Nannoria</u> sp.				+							
<u>Orthomorpha coarctata</u> Sauss.	+	+		+	[+]	[+]					
<u>Orthomorpha gracilis</u> Koch (= <u>Fontaria gracilis</u> Koch, <u>Paradesmus</u> (Fontaria) <u>gracilis</u> Koch, <u>Oxydus gracilis</u> Koch)		+		+							
<u>Pachydesmus crassicutis</u> (Wood)		+		+						[+]	[+]
<u>Polydesmus collaris collaris</u> (Koch)	+	+		+				+(a)			
<u>Polydesmus</u> (Fontaria) <u>virginiensis</u> Drury (= <u>Polydesmus virginien-</u> <u>sis</u> Drury, <u>Fontaria virginiensis</u> Drury)				+							
<u>Pseudopolydesmus serratus</u> (Say)				+							
<u>Rhysodesmus vicinus</u> Sauss. (= <u>Polydesmus vicinus</u> Sauss., <u>Polydesmus</u> (Fontaria) <u>vicinus</u> Sauss.)			[+]	+			[+]				

(1) Substances between parentheses have not been isolated: they are recognized by purely indicative methods.

(a) Isolated and certainly identified product, probably evolved from mandelonitrile in the course of separative processes due to benzoic acid reaction.

(b) Product which has been roughly identified as mandelonitrile by indicative methods unsuitable for defining its steric structure.

- VII 8 -

these poisons: this is due to the fact that they mostly contain active proteinic substances which are difficult to identify.

12. There are cases of venoms consisting of a single straight-chain substance (e.g. formic acid, oxalic acid; trans-hex-2-enal) and others in which the venom is composed of several straight-chain substances, as for instance, in several species of Heteroptera.

There are cases where the venom is formed of a single cyclic substance (e.g. iridomyrmecin; cantharidin; salicylic aldehyde) and others where it is composed of several cyclic substances (e.g. in Coleoptera of Paederus genus with the presence of pederin, pseudopederin, pederone; in the cases of various quinones which are to be found together in the poison of individual species of Juliiformia; in the Glomerida species, where both glomerin and omoglomerin are present simultaneously).

There are also numerous examples of poisons composed of straight-chain and cyclic substances together, with either the former or the latter prevailing.

13. Considering straight-chain substances we note that many of these are simple in nature (formic acid, oxalic acid, trans-hex-2-enal, methylheptenone, propyl-isobutyl-ketone, etc.), compared to the relative complexity of some cyclic substances (salicylic aldehyde, dendrolasin, iridomyrmecin, cantharidin, quinones, 5-hydroxytryptamine, glomerin, pederin, etc.).

Among the more complex straight-chain substances we find for example tridecane, tridecene, the various cossins, etc. Among the more complex cyclic substances we may mention pederin, glomerin and omoglomerin, cortexone, 24-methylene cholesterol, riboflavin, etc.

14. It is perhaps worthwhile recalling that in those poisons known among saturated fatty acids the first, formic acid, the most dissociated of the series, is the most usual, although 7 other successive elements are present (acetic, propionic, butyric, isobutyric, isovaleric, caprylic, palmitic acid); therefore of saturated dicarboxylic acids

- VII 9 -

only the first and strongest is known to be present hitherto - oxalic acid.

It is a remarkable fact that the most simple substance of all the poisons chemically known, formic acid, is mostly produced and used by a clearly defined group of Ants of the Family Formicinae, and is only to be found in a few other cases besides Ants.

The natural significance of defensive secretions (16-19).

16. With regards to the meaning of Arthropoda poisonous secretions, it seems clear that most of them have an active defensive and offensive aim concerning other animals. When the venom can be used directly there is an organ to produce it, a reservoir where it is preserved and a mechanism for voluntary expulsion; in the other cases (e.g. pederin, pseudopederin, pederone) the toxic substance is diffused throughout the organism and an expulsion mechanism is missing. However, Coleoptera Meloidae which produce cantharidin, also found throughout the organism, can exude drops of haemolymph, carriers of the poison, by autohaemorrhoea.

17. Once the productive organ has been identified usually the origin of the chemically known substances of the poisons under study may be more or less exactly defined. The organs producing the poisons differ extremely as to place and significance. The productive organs of the typical Arthropoda poison pederin, are not known; the toxic substance is present in the haemolymph of the insect.

18. The reaction to these poisons regarding the same species which produce them is variable, going from extreme sensibility (e.g. in the case of Iridomyrmex humilis Mayr for iridomyrmecin), to a relative resistance (e.g. Lasius (Dendrolasius) fuliginosus Latr. for dendrolasin; Melasoma populi L. for salicylic aldehyde), to cases of complete resistance (e.g. Paederus fuscipes Curt. for pederin; Lytta vesicatoria L. for cantharidin; Julida for quinones; Polydesmida for cyanogenic poisons, etc.).

19. Where the poison is spread throughout the body we have the interesting problem of how the tissues of the organism, which are saturated with this poison, resist: a particularly interesting problem, especially for those Arthropoda which produce substances highly active on animal tissues like cantharidin and pederin. In fact pederin acts as a powerful antimetabolic in a dose of 1/000 of a gamma per cc on various types of animal tissues, and human tissues, normal and pathological, cultivated in vitro. Paederus fuscipes Curt. contains, on an average, 1 gamma of pederin to 4 mg, which corresponds to a concentration of 1 to 4000! Cantharidin, too, exercises a remarkable inhibiting action on tissues of homothermic animals. The resistance mechanism of the tissues of Insects regarding this action is of great general interest and still to be investigated.

Possible meanings of the biological properties of defensive secretions (20-22).

20. Regarding the advantages of animals producing these substances, we may divide the biological properties of poison secretions in properties for which there is a natural justification (e.g. insecticide, repellents), and properties which are difficult to justify as being to the advantage of the producing species (e.g. properties of pederin which stimulate or inhibit the growth of tissues, the phyto-inhibiting action of iridomyrmecin, etc.). On the other hand, these biological properties may be numerous and that which finds a natural justification is not necessarily the one to which a greater value can be attributed.

Some of the biological properties we have seen can be justified not only in the fight against competitors, but also as serving other needs of the species. For example, the phyto-inhibiting action of Bee poison, might also serve to block the pollen collected in the

hive. Here we might make a comparison with the paralizing property for victims, contained in the poisons of certain predatory Hymenoptera (Sphecidae, etc.), but whose chemical components are not known. The antibacterial property may be justified because it can contribute to the inhibition of the bacteria present in the honey stored in the beehive, as seems to be the case with Bees when squirting honey into the cells.

21. Considering the toxic action on animal organisms, there are poisons which over a wide zoological range (e.g. those of certain Formicidae, of Bees, Wasps, and Myriapods etc.) including both lower animals and warmblooded animals, and this is in the defensive interest of the producing species; there are poisons which act in a more limited but still fairly wide range (e.g. those of Dolichoderinae active over a wide range of Insects); poisons which have a limited specific action like dendrolasin, selective against Ants which are the chief enemies of the producing species; poisons which apparently act on warmblooded animals only, as for exemple pederin and cantharidin.

There is also a poison, cantharidin, which exercises a strong attraction over certain species of Insects (Diptera of the Anthomyia genus; Coleoptera of the Anthicidae family) which are attracted by tiny quantities of this substance. This fact also occurs in nature as individuals of the species producing cantharidin can be found with the Insects attracted clinging to them. Here we are not aware of the significance that this may ^{have} for the species producing cantharidin.

22. We can legitimately consider as toxic secretions the repellent substances of several Insecta (for example Brachynus, Paltothyrus, Dendrolasius, etc.) and of Polydesmidae protected by a cyanogenic secretion exuded freely over the surface of the body: the cyanogenic secretion produced by Gomphodesmus and Orthomorpha has been found to have a protective role in nature, for example against the Doryline Ants, the most savage African Insects which attack any living being.

Toxic substances in Arthropoda and plants (23-27).

23. Both Arthropoda and plants produce insecticides. It may be of interest to point out, in cases of known chemical substances, the essential difference between the groups of substances employed by certain Insecta in the fight against other Insecta and the groups of entirely different insecticides known in plants (e.g. pyrethrin, rotenone, nicotine, etc.).

24. Regarding the natural toxic substances we may make a comparison of a purely speculative nature between the animal and vegetable kingdom. Unfortunately we are limited in this comparison due to our lack of knowledge; on the other hand, in order to pursue this comparison, we must also include examples of poisons whose chemical structure is not known.

Regarding animals we usually find poisons which appear to be confined within those special organs in which they are produced and from which they are later secreted, and, rarer, poisons spread throughout the whole organism. In plants it is usually the case to find poisonous substances spread throughout or covering most of the organism, and rarer to find them concentrated exclusively in particular organs. For plants this would mean a greater resistance to their own poisonous substances, probably seated in a particular cellular organisation capable of accumulating, so to speak, these substances in the expectation, in certain cases, of getting rid of it as may happen in the case of shedding leaves or other parts of the plant. The loss of part of the body to get rid of harmful substances is not known among Arthropoda. The spontaneous ejection of haemolymph in Insecta capable of self-haemorrhage is not purification from poisoning but an act of defence.

It is not clear why most of the plants which produce poisonous substances should do so (e.g. the countless number of cases of

alkaloids). However, and perhaps generally amongst animals, it seems the production of poison takes place according to very precise methods in order to achieve the aims of the species. There is even the extreme case of the thrifty Melasoma populi larvae, which, after ejecting the poison, absorb the drops not used into their reservoir again so the poison can be used later.

25. Plants contain a great abundance of alkaloids and glucosides although representatives of other large chemical groups are not lacking. This category of substances form part of Arthropoda poison only in a few cases. We may mention, for example, the cyanogenic glucoside of the Myriapoda Polydesmida, the glomerin and omoglomerin alkaloids.

Analogies may be found between the urticating poisons of numerous plants (e.g. Urtica, Mucuna, etc.) and the urticating hairs of Lepidoptera larvae (for example Thaumetopoea pityocampa Sch.) or of Lepidoptera adults (for example the various species of Anaphe). The urticating secretion of these plants contains histamine and 5-hydroxytryptamine. It seems the secretion of the urticating hairs of Lepidoptera, however, contains substances capable of freeing histamine from the tissues. In any case the entire subject still has to be studied, first analitically and then comparatively.

Other comparisons are possible, for example, between the cutaneous effects (necrosis) produced by numerous plants, e.g. Rhus toxicodendron L., and those produced by certain Arthropoda, e.g. Araneae of the genus Lycosa and Insecta Coleoptera of the Paederus genus: however, the chemical structures of poisons produced by plants, Araneae and Paederus are completely different. Whereas the above mentioned Araneae use the poison in defence, in the case of plants and Paederus the defensive effect does not derive from an obvious direct action but from the experience and awareness of the being facing the toxic organisms.

26. Some curare type paralyzing substances are known in plants. Substances which paralyze other Insecta are known in the poison of certain Hymenoptera (Habrobracon, numerous species of Sphecidae, etc.) but at present it is not possible to even vaguely indicate a chemical relationship with curare. This subject too must be studied ex novo because the comparison between paralyzing venoms produced by Insecta is unknown.

Examples of a direct and analogous defence action of plants and Arthropoda against certain animals, and also partly against man, are the plant Symplocarpus foetidus (L.) Nutt., which gives off fetid gases, and the ants Megaponera foetens F. and Paltothyreus tarsatus Fabr. which emit a strong fecal smell perceivable at a distance. We have seen that in the African Ant Paltothyreus tarsatus the fetid secretion from the mandibular glands contains sulphides (dimethyldisulphide and dimethyltrisulphide) which have a defensive action. Sulphides of this type are present also in plants.

Another example is the plant Rafflesia arnoldi R. Br. which emits an offensive smell, and Erachynus (Insecta Coleoptera) which explosively produce a cloud of protective vapour, both irritating and with an unpleasant smell. In the two plants quoted, according to certain authors, the smells might serve to attract pollinating Insects; no attraction value can be attributed to the smells of the Insects just quoted, whose primary function is to repel/preying animals.

27. The fetid secretion from the mandibular glands of the Paltothyreus tarsatus Ant contains sulphides; as seen, substances of this type are also contained in plants. Dendrolasin, found for the first time in the mandibular secretion of the Ant Lasius (Dendrolasius) fuliginosus, was later found in Japan in sweet potato fusel oil (Ipomoea batatas) by Hirose et al. 1961, in the wood of Torreya nucifera together with other products of a similar structure, like torreyal

and torreyol ⁽¹⁾, by Sakan et al. 1963.

Iridomyrmecin, discovered in the "anal glands" of the Iridomyrmex humilis Ant, was also later discovered in a Japanese plant, Actinidia polygama Miq., together with isoiridomyrmecin, dihydronepetalactone, isodihydronepetalactone and neonepetalactone (Sakan et al.). An alkaloid (actinidine) is present in the same plant with the same carbon atomic structure as iridomyrmecin. A similar substance, skytanthine, is present in the plant Skytanthus acutus Meyen, from South America.

Biogenesis of Arthropoda venoms (28).

28. We still have only limited information about the biogenesis of the most characteristic products of Arthropoda venoms. Several products may be considered as resulting from a variously patterned union of isoprenic residues according to the known Ruzicka rules (see also Chap.), as shown also in the diagram below.

[Figure]

Several authors obtained the synthesis for the iridoids present in Insecta and plants from citral, citronellal and limonene (see chap. 21). It is believed that these may also be the biogenetic origins, down to iridomyrmecin and correlate molecules. It has also been suggested that mevalonic acid, precursor of terpenic structures, may be the origin of iridoid structure, and therefore also of skytanthines (Casinovi and C. 1964, 49 E), alkaloids which are provided, as we have seen, with the same carbon atomic skeleton as iridoids. Meinwald, Happ, Labows and Eisner 1966 (189), have shown by radioactive substances that in the Anisomorpha buprestoides phasmid dolichodial (= anisomorpal) is synthesized from the normal precursor

(1) Not to be confused with torreyol $C_{15}H_{26}O$ which according to Sakan et al. 1963 is identical to β -cadinol.

sors of terpenes, that is from acetate, mevalonate (mevalonic lactone) and malonate. Parallel experiments on the Nepeta cataria plant have brought to light the use of radioactive acetate and mevalonate for the formation of nepetalactone.

In the Acanthomyops claviger Ant the mandibular gland secretion includes citronellal and citral. Happ and Meinwald 1965 (145) obtained radioactive citral and citronellal by feeding workers with 1-¹⁴C-acetate sodium, 2-¹⁴C-acetate sodium, mevalonic 2-¹⁴C-lactone. This suggests that the mevalonic acid pathway may have been utilized for terpenes biosynthesis.

To study dendrolasin biogenesis in Lasius (Dendrolasius) fuliginosus Latr. ants were fed with 2-¹⁴C mevalonic acid: radioactive isolated dendrolasin was obtained. The biogenetic pathway that appears likely in this case is a transformation of mevalonic acid into farnesylpyrophosphate with successive oxydization and cyclization of the third isoprenic unity into furanic ring (Castellani and Pavan 1966) (54). The presence of other substances (methylheptenone, perillen, cis-citral, trans-citral, farnesal) in part (perillen, farnesal) correlate with dendrolasin (Bernardi, Cardani, Ghiringhelli, Selva, Baggini, Pavan 1967, 13 A) in the mandibular gland secretion of this species is a fact that makes the study of the biogenesis of these products and their interrelationships particularly interesting.

The presence of dendrolasin in Torreya nucifera Sieb and Zucc. and Ipomoea batatas plants (Sakai and coll. 1963, 286 B; Hirose and coll. 1961) poses also the comparative problem of its biogenesis in animals and plants.

Formic acid, which is widespread in Insects and plants, may derive from several biogenetic pathways, as assumed by O'Rourke 1950 (213) among others. In our preliminary experiments of feeding Formica lugubris Zett. with radioactive serine, we obtained marked formic acid (Castellani, Laterza, Pavan still underway).

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Salicyl aldehyde, present in the Melasoma populi L. larvae, for example, is thought to derive from salicyn as in the following diagram (Pavan 1953, 235; 1958, 245, 246).

[figure]

For the Arthropoda quinones we may mention the possible derivations reported in the diagrams of table (Pavan 1958, 245, 246), and 5-hydroxytryptamine, according to several Authors, probably derived from tryptophane (see Pavan 1958, 245, 246).

[figure]

In the Nezara viridula (Fabr.) Heteropter the incorporation of acetate with radioactive C takes place in the products of the complex aliphatic compound mixture of the defensive secretion (Gordon, Waterhouse, Gilby 1963, 135). On the whole, then, an interesting field of research lies ahead.

Effects of Arthropoda poison on man (29).

29. The known data may also be considered from the point of view of their relevance to man. In fact, Arthropoda have both negative and positive aspects for man, which is also true for their poisons.

Some of the poisons mentioned appear neither directly nor indirectly harmful to man. In fact, for many poisons there is no reaction on the part of a human organism, for example those produced by the anal glands of Dolichoderinae, dendrolasin. Formic acid produced by Formicinae Ants is slightly caustic and asphyxiating^h for man. The poisons injected by Apidae, Vespidae, and numerous Formicidae, cause varying reactions, also serious. The defensive secretions of many Coleoptera Carabidae cause skin irritation and burns if in contact with the cornea; the quinonic poisons of various species of Coleoptera and Myriapoda Diplopoda can produce slight burns if squirted into the

eye, but only provoke a temporary pigmentation when in contact with the skin. The salicyl aldehyde poison of Coleoptera larvae is only offensive due to its bitter smell. The vesicatory poisons with a basis of cantharidin, and lastly the most serious necrotizing poison, pederin, produce, when brought into contact with skin vesication (cantharidin), or sores due to necrotization of the tissues (pederin). Venoms injected by various Araneae (for example those in South America) provoke extensive and serious skin necrotization. The venoms of numerous species of Scorpiones and many Araneae (for example of the genus Latrodectus) can provoke serious general reactions and even death.

Useful aspects of Arthropoda defensive secretions (30).

30. Among the possible useful functions for man, to quote only a few of the most practical, worth noting is Bee poison which has recognized therapeutic applications (rheumatism) and is officially adopted in the pharmacopea of several countries. The secretion of Polydesmida (Myriapoda, Diplopoda) are used for arrow poison in Mexico due to the liberating power of hydrocyanic acid under the influence of particular enzymes present in the blood of the prey. Cantharidin has been widely used in therapy as a rubefacient and I have personally observed its use as an ingredient of the arrow poison made from plants by the Babinga pygmies of Equatorial Africa. The larvae of Coleoptera Chrysomelidae of the genera Diamphidia in Botswana are used by Bushmans, the people of Kalahari, when preparing arrow poisons. Its active principle are not chemically known. Formic acid, originally obtained from Ants three centuries ago, is applied in numerous ways in various important sectors of the chemical and pharmaceutical industries. Pederin presents aspects which might be of interesting development due to its effect on the growth of tissues: for example we were able to heal decubitus sores with quantities of the

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substance equal to hundredths of a gamma; but it is also the most active antimitotic known. As an insecticide iridomyrmecin shows us the line to take the study of poison with a certain selective action, non-toxic for warm-blooded animals. Cantharidin was useful in distinguishing and procuring interesting phytoinhibitors, a property which, as we have seen, is common to other Insecta products. Dendrolasin showed us a natural chemical structure with selective repellent action employed by animals in nature, particularly effective against other species of Ants, direct competitors of the species which produces it.

The mere fact that it indicated the way to be followed in probable researches in nature and in laboratory synthesis of insecticidal or repellent substances, endowed with a reduced range of action and very low toxicity for warmblooded animals, is enough to justify our interest in this kind of research. These aims have been recognized in high quarters by the most qualified organization also at an international level (for example O.I.L.B., International Organization for Biological Control ; U.I.C.N., International Union for Conservation of Nature and Natural Resources; Council of Europe; FAO; UNESCO, etc.) which are concerned about the effects of wide indiscriminate use of ever more toxic, long lasting insecticides with a more extensive range of action.

Also what is known about antimitotic substances, especially when they are as powerful as pederin, for example, provides a sufficient motive for a thorough naturalistic, applied biological and chemical enquiry into the sector of biologically active substances produced by Arthropoda.

General remarks (31-33).

31. In order to try and see the entire problem of the relationship between the field of studied opened and the results reached in a general and vaster framework, we might consider some statistics; examining the number of animal species known in comparison to those whose poisons have been studied, and in particular regarding the species of whose poisons we know one or more chemical constituents, we note a striking disproportion which gives us an idea of how much still remains to be studied. As we have seen, today the number of animal species scientifically described amounts about 1.200.000, most of which are Arthropoda (884.944 species) with Insecta clearly predominating (815.763 species).

Among the largest Orders we find Coleoptera, Hymenoptera and Heteroptera which also have the largest number of poison producing species, and therefore presumably a large part of the species described in these Orders are of interest to our studies. According to very cautious calculations the poisonous species included in the Insecta group might be at least 50.000. Only 342 of these have been more or less studied, among which 146 Coleoptera, 96 Hymenoptera (of which as many as 81 Formicidae), and 44 Heteroptera.

If we add to these presumably interesting species of Insecta those belonging to other Arthropoda, it is clear we may calculate as over 82.000 the number of species of Arthropoda scientifically described, and presumably producers of offensive and defensive substances. The species of Arthropoda from which chemically defined substances forming part of the poison have been extracted and recognized, are only 426. Therefore a vast field of work is left for biologically and chemically integrated researches.

Considering only the list of chemically new natural substances found in the poisons of Insecta, it must be pointed out that from the 342 species of Insecta studied 18 of these substances have been

extracted, 15 of which deriving from our researches (1-15) and 3 from the researches of Cavill and Coll. (16), and Schildknecht (17-18). These new substances are the following:

- | | |
|------------------|---------------------------|
| 1. iridomyrmecin | 10. cossin 1 |
| 2. pederin | 11. cossin 2 |
| 3. iridodial | 12. cossin 3 |
| 4. dendrolasin | 13. cossin B ₁ |
| 5. pseudopederin | 14. cossin C ₁ |
| 6. pederone | 15. zeuzerina |
| 7. cossin A | 16. dolichodial |
| 8. cossin B | 17. cybisterone |
| 9. cossin C | 18. diidrocycbisterone |

No chemically new substance has been hitherto found in the venoms of Arthropoda species other than Insecta.

The above findings may be seen in an even more interesting prospect if we think that the animal species actually existing, but not yet scientifically known and described, can be estimated to be 5-10 times as numerous as those that are known at present.

The limited knowledge we already have is indicative of the multiformity of existing conditions and the importance they may have for our biological knowledge, particularly in the field of biochemistry. They indicate the existence of fields completely unknown for vertebrates and clearly demonstrate how the Arthropoda world is, in a certain way, a world into itself.

32. I feel it might be useful to now consider methodologically the individual and complex contributions at the various stages of our research. It is clear that at the beginning of research any problem which might arise is fundamentally an entomological problem in its widest sense: in fact the entomologist will identify the species most suitable for research by following previous indications or by deliberately taking new roads. Continuing in the development of the problem

the entomologist will apply himself above all to anatomy and physiology. The phase of essential chemical research to isolate biologically active factors will require collaboration with the chemist and continuous biological control of the results deriving from chemical experiments.

When the biologically active factors are isolated, the part which the chemist must play in the study of their structural characterization is of fundamental importance and involves considerable difficulty, above all due to the small quantity of substance with which he must sometimes work. In this phase the entomologist's collaboration lies in supplying the largest possible quantities of raw material.

After this study is concluded, the structural data and the pure substances must be returned to the entomologist to verify their origin and their complex meaning in nature. In this phase the entomologist will fit these data in with the general biological and zoological knowledge, and will consequently be able to single out new lines of collaborative research to be taken with the chemist. The chemist on the other hand will have opened the truly important scientific and practical field of the synthesis of analogous products; the biologist that of comparisons between the biological activities of the new products over an ever vaster range of animal and plant tests.

33. The group of studies regarding the defensive secretions of Arthropoda, carried out especially in the last 20 years, as we have seen, has supplied chemical literature with many new substances; we must add to these synthetic products modelled on them, but which generally have not been considered here; it has also brought to light their biological properties, it has partially explained their function in nature, it has opened new fields of research with possibilities of interesting applications to various sectors of agriculture, medicine, etc.

I should particularly like to emphasize once more how only by a close collaboration of entomological research, in the narrowest sense, with biological and biochemical researches it has been possible to arrive at the wealth of new facts summarily presented in this paper.

The data I have attempted to expound, first analytically and then summarily, in this conclusion, show how wide and full of prospects our future work is, both to fill in the missing links in the sector al ready known, and to extend and deepen our knowledge of entire huge and extremely interesting fields of work whose existence we are aware of, but which still remain almost completely unexplored.

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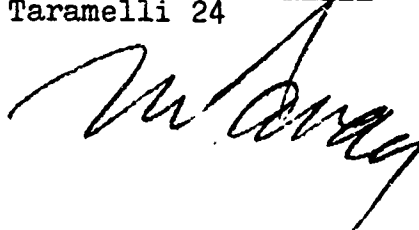
Final Technical Report
(third year) under Contract
DA-91-591-EUC-3898.

1) Subject of the research:

- 1a) Search in tropical regions will be made for Arthropods (Insects, Arachnids, Crustacea and Myriapoda) which produce toxic substances. Methods will be developed for Arthropods. The crude extracts will be tested for biological effects. Those substances showing promise will be further concentrated and purified followed by biological, chemical, and physical study of the purified products.
- 1b) The contractor will provide the service of a botanist who will travel to the Congo where he will study the process for producing poisoned arrows has practised by the native doctors (sorcerers). He will study the source of raw materials, the production of the poison from these materials, and will obtain samples of the raw materials and the poisonous product for subsequent study by the contractor and the U.S. Army.

- 2) Name of Contractor: Prof. M. PAVAN, Istituto di Entomologia Agraria dell'Università di Pavia, Via Taramelli 24, Pavia (Italy).
- 3) Contract number: DA-91-591-EUC-3898.
- 4) Type and number of report: Final Technical Report.
- 5) Period covered by report: 1.V.1967 - 30.VI.1967.
- 6) "The research reported in this document has been made possible through the support and sponsorship of the US Department of Army, through its European Research Office. This report, not necessarily in final form, is intended only for the internal management use of the Contractor and the US Department of Army".

The Contractor:
prof. Mario Pavan, director of
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11 SUPPLEMENTARY NOTES		12 SPONSORING MILITARY ACTIVITY AMC
13 ABSTRACT The report starts with the calculation that out of 885,000 known species of arthropods (of which 815,000 are insects) at least 82,500 species can synthesize poisons. The constituents of these poisons have been identified in part for only 426 species, of which 342 are insects. Arthropods of particular interest in this respect have been listed and the chemical compounds identified in the poison of each species indicated. The following are new compounds, identified for the first time in arthropod poisons: 1. iridomyrmecin; 2. pederin; 3. iridodial; 4. dendrolasin; 5. pseudopederin; 6. pederone; 7. cossin A; 8. cossin B; 9. cossin C; 10. cossin 1; 11. cossin 2; 12. cossin 3; 13. cossin B ₁ ; 14. cossin C ₁ ; 15. zeuzerina; 16. dolichodial; 17. cybisterone; 18. diidro-cybisterone. A chapter is devoted to each compound and a comprehensive concluding chapter and bibliography terminate this report.		

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