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**THIS PAGE IS UNCLASSIFIED**
Mario PAVAN

Istituto di Entomologia Agraria
dell'Università di Pavia

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
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,
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, Cos- sidae)

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 (1967) from the larva of Zeuzera pyrina L. (Lepidopt. Cos- sidae):

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 finding, 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 literature 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, propylisobutylacetone, 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 Symphila.

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 Anatonia 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, Republique 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 the 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:
- 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.
- Istituto di Farmacologia dell'Università di Bari, and then Parma, directed by prof. V. Erspamer.
- 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. Onychophora 73 species 7. Crustacea 25,000 species
2. Pauropoda 50 " 8. Merostomata 5 "
3. Diplopoda 7,000 " 9. Arachnida 33,873 "
5. Symphila 50 " 11. Pentastomida 60 "
6. Insecta 815,763 " 12. Tardigrada 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).

<table>
<thead>
<tr>
<th>Classes</th>
<th>1. Presumed no. of species described</th>
<th>2. Presumed no. of species producing defensive secretions</th>
<th>3. No. of species with known chemically defined defensive secretions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Onychophora</td>
<td>73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Pauropoda</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Diplopoda</td>
<td>7,000</td>
<td>8,000</td>
<td>43</td>
</tr>
<tr>
<td>4. Chilopoda</td>
<td>2,350</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>5. Symphila</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Insecta</td>
<td>815,763</td>
<td>50,000</td>
<td>342</td>
</tr>
<tr>
<td>7. Crustacea</td>
<td>25,000</td>
<td>1,000</td>
<td>2</td>
</tr>
<tr>
<td>8. Merostomata</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Arachnida</td>
<td>33,873</td>
<td>23,538</td>
<td>37</td>
</tr>
<tr>
<td>10. Pycnogonida</td>
<td>440</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. Pentastomida</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. Tardigrada</td>
<td>280</td>
<td></td>
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<tr>
<td>Totali</td>
<td>884,944</td>
<td>82,538</td>
<td>426</td>
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</table>
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 limnobius 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 limnobius): almost all the Crustacea (with the exception of some Isopoda) Pycnogonida, Isotomida, 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 pavari 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 (Archiulus (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 lymnobious 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
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 occasional serious cases of poisoning in man caused by the sting of Scorpiones and Araneae.
### Table 2 - Number of Arthropoda Onychophora and Myriapoda (Pauropodia, Diplopoda, Chilopoda, Symphila) species described (2), of the species presumed to produce defensive secretions (3.), and of the species producing chemically defined defensive substances (4.).

| Type ARTHROPODA | 1. presumed no. of species described | 2. presumed no. of species producing defensively secretions | 3. no. of species with known chemically defined defensive secretions |
|------------------|-------------------------------------|----------------------------------------------------------|
| **Cl. ONYCHOPHORA** | 73 |                                           |                                                       |
| **Cl. PAUROPODA** | (9,450) | (7,550) | (45) |
| **Cl. DIPLOPODA** | 50 | 0 | 43 |
| Ord. Polyxenida | 7,000 | 6,500 | |
| Glomerida | 500 | 500 | 4 |
| Glomeridesmida | | | |
| Chordeumida | | | 1 |
| Polydesmida | 2,500 | 2,500 | 12 |
| Julida | 4 | |
| Spirobolida | 9 | |
| Spirostreptida | 2,000 | 2,000 | 12 |
| Cambalida | 1 | |
| Sup.Ord. Colobognatha | | | |
| **Cl. CHILOPODA** | 2,350 | 1,000 | 2 |
| Ord. Geophilomorpha | 420 | 2 |
| Scolopendromorpha | | |
| Lithobiomorpha | | |
| Scutigeromorpha | | |
| **Cl. SYMPHILA** | 50 | 50 | |
Table 3 - Number of \textit{Insecta} species described (2.), of the species presumed to produce defensive secretions (3.), and of the species producing chemically defined defensive substances (4.).

<table>
<thead>
<tr>
<th>Class \textbf{I N S E C T A}</th>
<th>1. presumed no. of species described</th>
<th>2. presumed no. of species producing defensive secretions</th>
<th>3. presumed no. of species producing chemically defined defensive secretions</th>
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<tbody>
<tr>
<td>Ord. 1. Collembola</td>
<td>2.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Protura</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Diplura</td>
<td>380</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Thysanura</td>
<td>350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Ephemeroptera</td>
<td>1.500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Odonata</td>
<td>4.870</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Blattodea</td>
<td>2.500</td>
<td>100</td>
<td>15</td>
</tr>
<tr>
<td>8. Mantodea</td>
<td>1.800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Isoptera</td>
<td>2.000</td>
<td>150</td>
<td>4</td>
</tr>
<tr>
<td>10. Zoraptera</td>
<td>19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. Plecoptera</td>
<td>1.490</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12. Embioptera</td>
<td>149</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13. Grylloblattodea</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14. Dermaptera</td>
<td>1.100</td>
<td>150</td>
<td>1</td>
</tr>
<tr>
<td>15. Phasmina</td>
<td>2.000</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>16. Orthoptera</td>
<td>15.000</td>
<td>500</td>
<td>1</td>
</tr>
<tr>
<td>17. Psocoptera</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18. Mallophaga</td>
<td>2.675</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19. Siphunculata</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20. Thysanoptera</td>
<td>3.170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21. Heteroptera</td>
<td>31.000</td>
<td>26.000</td>
<td>44</td>
</tr>
<tr>
<td>22. Homoptera</td>
<td>26.500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23. Neuroptera</td>
<td>4.670</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24. Mecoptera</td>
<td>350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25. Trichoptera</td>
<td>4.470</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26. Lepidoptera</td>
<td>120.000</td>
<td>2.000</td>
<td>28</td>
</tr>
<tr>
<td>27. Diptera</td>
<td>85.000</td>
<td>1.000</td>
<td>6</td>
</tr>
<tr>
<td>28. Siphonaptera</td>
<td>1.100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29. Coleoptera</td>
<td>300.000</td>
<td>10.000</td>
<td>146</td>
</tr>
<tr>
<td>30. Strepsiptera</td>
<td>175</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31. Hymenoptera</td>
<td>200.000</td>
<td>10.000</td>
<td>96</td>
</tr>
<tr>
<td>Class \textbf{I N S E C T A}</td>
<td>815.763</td>
<td>50.000</td>
<td>342</td>
</tr>
</tbody>
</table>
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.).

<table>
<thead>
<tr>
<th>Type</th>
<th>1. presumed no. of species described</th>
<th>2. presumed no. of species producing defensive secretions</th>
<th>3. presumed no. of species with known chemically defined defensive secretions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crustacea (*)</td>
<td>25,000</td>
<td>1,000</td>
<td>2</td>
</tr>
<tr>
<td>(35 Orders)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isopoda</td>
<td>4,000</td>
<td>1,000</td>
<td>2</td>
</tr>
<tr>
<td>Merostomata</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arachnida</td>
<td>33,873</td>
<td>23,538</td>
<td>37</td>
</tr>
<tr>
<td>Scorpiones</td>
<td>600</td>
<td>600</td>
<td>16</td>
</tr>
<tr>
<td>Pseudoscorpiones</td>
<td>1,000</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Uropygi</td>
<td>98</td>
<td>98</td>
<td>1</td>
</tr>
<tr>
<td>Amblypygi</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palpigradi</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ricinulei</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solifugae</td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opiliones</td>
<td>2,340</td>
<td>2,340</td>
<td>1</td>
</tr>
<tr>
<td>Araneae</td>
<td>20,000</td>
<td>20,000</td>
<td>19</td>
</tr>
<tr>
<td>Acari</td>
<td>9,140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pycnogonida</td>
<td>440</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentastomida</td>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tardigrada</td>
<td>280</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(*) A list of the Crustacea Order, mostly formed by water animals (marine or lymnobius) 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.

( MYRIAPODA )
Cl. DIPLOPODA
Ord. GLOMERIDA

Fam. Glomeridae
Glomeris marginata Vill.
Glomeris conspersa Koch
  glomerin, omoglomerin: 302.
Glomeris hexasticha Brandt
  glomerin, omoglomerin: 302.
Loboglomeris rugifera Verh.
  glomerin: 302.

Ord. CHORDEUMIDA

Fam. Chordeumidae
Abacion magnum Loomis
Ord. POLYDESMIDA

Fam. Strongilosomidae

Orthomorpha 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. Eurydesmidae

Apheloria corrugata Wood

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

Rhysodesmus vicinus Sauss. (= Polydesmus vicinus Sauss., Polydesmus (Fontaria) vicinus Sauss.)
glucoside of $p$-isopropil mandelic nitrile $\rightarrow$ hydrocyanic acid, glucose, cuminaldehyde: 32, 104, 218, 363; hydrocyanic acid, glucoside of $p$-isopropil mandelic nitrile: 50; hydrocyanic acid, cuminaldehyde: 348 B.
- IV 3 -

Fam. Polydesmidae

Gomphodesmus 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: 349 B.

Pseudopolydesmus serratus (Say)

(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 3-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.
Schizophyllum mediterraneum  (= Julius terrestr-is 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, 198, 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.

Pachyboulus 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.

Pachyboulus cricrus 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.
Trigonociulus lumbricinus Gerst.
2-methyl-1,4-benzoquinone, 2-methyl-3-methoxy-1,4-benzoquinone:
50, 157, 198, 278, 348 B, 363.

Ord. SPIROSTREPTIDA

Aulononyxus coeleatus Attems
2-methyl-1,4-benzoquinone: 8.

Aulononyxus aculeatus barbieri
2-methyl-1,4-benzoquinone: 8.

Boretoconus 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 quinones and their methyl derivatives: 10, 50, 199, 245,
278, 310, 355, 363.
Fam. Odontopygidae

*Peridontopyge aberrans* Attems
2-methyl-1,4-benzoquinone: 8

*Peridontopyge vachoni*
2-methyl-1,4-benzoquinone: 8

Ord. CAMBALIDA

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

Cl. CHILOPODA

Ord. SCOLOPENDROMORPHA

*Eithmostigmus 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, Phasmina, Orthoptera and chemically defined substances of defensive secretions.

Ord. BLATTOIDEA (= DYCOTOPTERA)

Fam. Diplopteridae

*Diploptera punctata* (Eschscholtz)

Glucoside which contains benzoquinone + β-glucosidase → p. benzoquinone, 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 bollmanni* 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 (trace), 2-methylene pentanal (trace), 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 (trace), 2-methylene pentanal (trace), 2-methyl butanol, 2-methylene butyric acid: 348 A.

Platyzosteria morosa Shélford
2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (trace), 2-methylene pentanal (trace), 2-methyl butanol, 2-methylene butyric acid: 348 A.

Platyzosteria novae-zealandiae Brunner
trans-hex-2-enal, undetermined compounds in a mixture: 278; trans-hex-2-enal: 348 A, 348 B.

Platyzosteria ruficeps Shélford
2-methylene butanal, 2-methylene butanal dimer, 2-methylene butanol, 2-methylene propanal, 2-methyl butanal (trace), 2-methylene pentanal (trace), 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. Termitidae

**Nasutitermes** sp. (soldiers)

**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. Forficulidae

**Forficula 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. Pseudophasmidae

**Anisomorpha buprestoides** (Stoll)
  (anisomorph = dolichodial)

Ord. ORTHOPTERA

Fam. Acrididae

**Poekilocerus 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

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

Cimex lectularius L.

Fam. Coreidae

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

Acanthocoris sordidus (Thunberg)

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.
be-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 Brèdin
acetic acid, n-hexanal, n-hexanol, n-hexyl acetate: 4 A, 348; n-hexanal: 346 B.
Plinachtus bicoloripes Scott  
n-hexanal: 4 A, 364.

Riptortus clavatus (Thunberg)  
n-butanal: 4 A, 364.

Fam. Hycocephalidae

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

Fam. Pentatomidae

Aelia fieberi Scott  

Biprorulus bibax  

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.  

Eurygaster sp.  

Eusohistus 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)  
**Menida Scotti** (Puton)

**Musgraveia sulciventris** Stål

**Nezara alternata** Scott

**Nezara viridula** I.
4-keto-hex-2-enal: 131; trans-dec-2-enal, unidentified carbonyl compound: 4 A, 364; according to Blum and Traynharn, 1960, the gross chemistry of the secretion from scent glands is very similar to that of *Oeibalus pugnax* (F.); trans-hex-2-enal, trans-hept-2-enal, trans-dec-2-enal: 4-keto-trans-hex-2-enal, n-tridecane: 348 R.

**Nezara viridula** L. var. *smaragdula* F.

**Oeibalus pugnax** F.
Palomena viridissima P.

Poecilometis strigatus Westw.

Rhoeocoris sulciventris Stål

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

Scotinophara lurida Burmeister

Fam. Plataspidae
Ceratocoris cephalicus Mont.
n-tridecane: 4 A.

Fam. Cydnidae
Macroscyclus 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
propanal, propanal, trans-but-2-enal, trans-hex-2-enal, pentenal, trans-hept-2-enal, trans-oct-2-enal, furan, methyl-furan, 2-me
Cap. 13 - Insecta Lepidoptera and Diptera and chemically defined substances of defensive secretions.

Ord. LEPIDOPTERA

Fam. Cossidae

Cossus cossus L.


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. Pyralidae

Eurrhypara 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, methacrylic acid, tiglic acid: 134; larvae: formic acid, aminoacids: 303.
Datana ministra  
larvae: formic acid: 149.

Dicranura furcula  
larvae: formic acid: 180.

Schizura concinna (Abb. o Smith) (= Notodonte 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.

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

Fam. Arctiidae  
Arctia caja L.  
imago: choline ester, non dnyalizable heat-labile toxic substance: 16; choline ester (\(\text{CH}_2\text{CH}_2\text{CH}
\text{CH}_2\text{N} = \text{CH} \text{CH}_2\text{CH}_2\text{CH} = \text{CH})\) choline: 17, 278, 281, 283, 355 B; choline ester (\(\text{CH}_2\text{CH}_2\text{CH}
\text{CH}_2\text{N} = \text{CH} \text{CH}_2\text{CH}_2\text{CH} = \text{CH})\) histamine (traces): 124; methanol (probably): 281.

Hypocrita jacobaeae L.  
histamine: 124.

Spilosoma lubricipeda L.  

Fam. Thaumetopoeidae  
Cnestocampa sp.  

Thaumetopoea pityocampa Schiff. (Cnestocampa pityocampa)  
Fam. Saturniidae

**Automeris sp.**
- hairs, larvae: 5-hydroxytryptamine: 352.

**Automeris (illustris ?)**
- hairs: 5-hydroxytryptamine: 353.

**Dirphia sp.**

Fam. Lasiocampidae

**Dendrolimus 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. Papilionidae

**Papilio machaon** L.
- larvae: isobutyric acid, 2-methylbutyric acid: 110, 111, 348 B.

Fam. Danaidae

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

Fam. Megalopygidae

**Megalopyge sp.**

**Megalopyge urens** Berg.

Ord. DIPTERA

Fam. Fungivoridae

**Ceroplatus sp.**
- oxaic acid: 80.
Ceroplatus 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. Carabidae

*Abax 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
thyl hydroquinone $+ \text{H}_2\text{O}_2 \rightarrow 1,4$-benzoquinone, 2-methyl-1,4-
benzoquinone, $\text{H}_2\text{O} + \text{O}_2: 8, 9, 39, 80, 98, 133, 156, 245, 246,$
278, 290, 298, 335, 348 B, 355 B; nitrogen oxides, nitrous acid: 125.

**Brachynus explodens** Duft.
hydroquinone, 2-methyl-hydroquinone $+ \text{H}_2\text{O}_2 \rightarrow 1,4$-benzoquinone,
2-methyl-1,4-benzoquinone, $\text{H}_2\text{O} + \text{O}_2: 133, 278, 298, 348 B.$

**Brachynus sclopeta** Fabr.
hydroquinone, 2-methyl-hydroquinone $+ \text{H}_2\text{O}_2 \rightarrow 1,4$-benzoquinone,
2-methyl-1,4-benzoquinone, $\text{H}_2\text{O} + \text{O}_2: 133, 278, 298, 348 B.$

**Calathus sp.**
formic acid: 111, 299, 348 B.

**Calosoma prominens** Lec.
salicylaldehyde: 107, 111, 114, 134, 157, 348 B.

**Calosoma sycophanta** L.
salicylaldehyde, metacrilic acid, tiglic acid: 51, 138.

**Carabus sp.**
butyric acid: 91, 125, 217, 341.

**Carabus auratus** L.
metacrilic acid, tiglic acid: 157, 299, 311.

**Carabus auronitens** Fbr.
metacrilic acid, tiglic acid: 157, 299, 311.

**Carabus cancellatus** Illig.
metacrilic acid, tiglic acid: 299, 311.

**Carabus convexus** Fbr.
metacrilic acid, tiglic acid: 157, 299, 311.

**Carabus coriaceus** L.
metacrilic acid, tiglic acid: 157, 299, 311.

**Carabus cynneus** F.
metacrilic acid, tiglic acid: 299, 311.

**Carabus granulatus** L.
metacrilic acid, tiglic acid: 157, 299, 311.
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 Kirby
  m-cresol: 107, 111, 345 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 africenus 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 Müll.
  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. Dytiscidae

Acilius sulcatus L.
  cortisol, cybisterone, 6-dihydrocybisterone: 300 A; cortexone, 6-déhydrocortesone, cybisterone, 6-dihydrocybisterone, 6-dehydroprogesterone: 300 B.

Cybister lateralimarginalis De Geer
  p-hydroxybelzaldehyde, methyl-p-hydroxy-benzoate, stile 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.

Hydroporus palustris L.
  p-hydroxybenzaldehyde: 299, 348 B.

Ilybius fenestratus Fabr.
  testosterone: 296.
Ilybius fuliginosus Fabr.

testosterone: 296.

Fam. Silphidae

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

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

Oeoceoptoma thoracicum L. (O. thorcica L.)
ammonia (4,5% solut.): 157, 313.

Fam. Staphylinidae

Paederus 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:

156, Paederus caligatus Erichs there is cantharidin. In all the
similar species of Paederus we never found cantharidin.
Fam. Meloidae

Cissites cephalotes Oliv. (C. axillosa)
cantharidin: 94, 163.

Cyaneolytta gigas F. (Lytta gigas)
cantharidin: 94.

Cyaneolytta violacea Brandt (Lytta violacea)
cantharidin: 94.

Decapotama lunata Fall. (Mylabris lunata)
cantharidin: 94.

Eletica wahlbergia Fahr.
cantharidin: 94.

Epicauta adspersa Klug (Lytta adspersa Klug)
cantharidin: 94, 125, 137, 163.

Epicauta femoralis Br. (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.

Meloe variegatus Donov. (Mylabris variegata)
cantharidin: 94.

Meloe violaceus Marsch.
cantharidin: 94.

Mylabris bolteata 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 ...)
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 tristigmata Gerst.
cantharidin: (unpublished)

Mylabris variabilis Pell.
cantharidin: 79, 94, 163, 319.

Psal antidotea 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-benzo-
quinone: 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 boleti 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-tridecane, 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-tridecane, 1-undecene, glucose, 1-nonene (probably): 153.

Eleodes obsolsta (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.
Letheticus oryzae Wat.
unknown quinones: 245, 246, 335; 2-ethyl-1,4-benzoquinone and/or 2-methyl-1,4-benzoquinone: 177.

Moria 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-benzquinone, 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.)

(*) According to Claus (1862) there is a matter of salicylic acid.
Other authors as well reported this initial observation.
Mejasoma 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. Brachonidae
  Habrobracon hebetor Say (= Microbracon hebetor Say)

Fam. Apidae
  Apis mellifera L.
  histidine, histamine, lecithin, hyaluronidase, phospholipase A: 156, 246; histamine: 81, 176, 288, 352; apitoxin (polypeptide): 38; lecithinase A, direct hemolytic factor: 211; lecithinase, hyaluronidase: 158; protein toxin, lecithinase A, spreading factors, riboflavin, histamine, magnesium, copper: 35; formic acid, histamine, apitoxin (polypeptide - protease), riboflavin (vit.B₂), lecithinase A, 5-hydroxytryptamine (*), kinin (*), spreading hyaluronidase-like factors: 37; alanine, arginine, aspartic acid, cystine, cysteine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, tryptophane, tyrosine, valine, histamine, lecithin, hyaluronidase, phospholipase A: 163, 245, 261; tryptophane, choline, glycerol, phosphoric
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 0, 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.
- 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-decenonic acid, isocyanic acid, &-aminobutyric acid, glycine, alanine, serine, \( \alpha \)-aminobutyric acid, threonine, valine, aspartic acid, asparagine, leucine, isoleucine, glutamic acid, glutamine, ornithine, cysteine, cystine, methionine, lysine, arginine, proline, histidine, fenilalanine, tyrosine, tryptophane, apamin, mellitin, kinin, apitoxin (polypeptide-protease), histapeptide (alanine, glycine, proline, alanine, gluNH\(_2\), 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.
Polistes omissa Weyrauch
  hyaluronidase, acetylcholine: 11; hyaluronidase, esterase: 286 A.

Polistes versicolor (01.)
  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, hystamine: 287 B, acetylcholine: 321 B.

Vespula germanica Fab. (= Vespa germanica Fabr.)
  hystamine: 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.)
cholinesterase, hyaluronidase, lecithinase: 158, hyaluronidase, 5-hydroxytryptamine, kinin, histamine: 11; histamine, 5-hydroxytryptamine, kinin, phospholipase A, phospholipase B, hyaluronidase: 324; hyaluronidase: 286 A.

**Fam. Formicidae**

**Subfam. Ponerinae**

_Ectatomma tuberculatum_ (Olivier)
proteinaceous substance: 147.

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

_Nyrieacia gulosa_ (Fabr.)

_Odontomacus hematoda insularis_ Guerin
proteinaceous substance: 147.

_Pachycondila_ sp.
formic acid: 213.

_Pachycondila harpax_
formic acid: 193; proteinaceous substance: 147.

_Paltothyreus tarsatus_ (Fabr.)
dimethylsulfide, dimethyltrisulfide: 53.

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

**Subfam. Pseudomyrminae**

_Pseudomyrmex pallidus_ (Fr. Smith)
basic protein: 23, 333 A.
Subfam. Dolichoderinae

Conomyrma pyranica (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, 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. pruinosus Roger humiliis Mayr)
iridomyrmecin: 5, 30, 40, 52, 55, 60, 61, 62, 66, 80, 128, 129,
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

Subfam. Myrmicinae

Atta sexdens rubropilosa For.


Crematogaster (Atopogyne) africana Mayr

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

Crematogaster lineolata (Say) clara Mayr

formic acid (traces): 193.

Crematogaster scutellaris scutellaris Oliv.

formic acid: 137, 203, 204, 205, 224, 225, 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 Ny1.

formic acid: 66, 245, 246, 328.

Myrmicaria natalensis Fred.

D-limonene, L-limonene: 134, 248, 278, 348B; 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.
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 Tor.
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. Formicinae

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

Acanthomyops claviger Roger

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.
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.

Lasius bicornis affinis Sch.

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.
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 polyctena Först.

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,
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. CRUSTACEA
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.

c octan-1-ol: 57 (1).

(1) See pag. 42.
Chap. 17 - Ara/hnida Scorpiones, Uropygi, Araneae and chemically defined substances of defensive secretions.

Cl. ARACHNIDA

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,
iso-leucine, 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 martensi Karsch

buthotoxin: 163, 169, 212.

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

neurotoxic proteins: 196, 197, 352; scorpamin: 212; hyaluronidase

(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).

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.
- IV 44 -

Fam. Chaetidae

Euscorpius italicus (Herbst)

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

Ord. UROPYGI

Fam. Telyphonidae

Mastigoproctus giganteus (Lucas)

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

Ord. OPILIONES

Fam. Gonyjeptidae

Heteropachyloidellus 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. ARANAE

Fam. Theraphosidae

Acanthoscurria atrox Vellard

glutamic acid, \( \alpha \)-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, \( \delta \)-aminobutyric acid, four protein fractions: 169;
  four protein fractions, free amino acids: 163.

Grammostola mollicoma Ausserer
  glutamic acid, \( \delta \)-aminobutyric acid, four protein fractions: 169;
  four protein fractions, free amino acids: 163.

Grammostola pulchripes Simon
  four protein fractions, free amino acids: 163.

Lasiodora klugii Koch
  glutamic acid, \( \delta \)-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, \( \delta \)-aminobutyric acid: 169; four protein fractions,
  free amino acids: 163.

Pamphobeteus tetracanthus M.-Leitao
  glutamic acid, \( \delta \)-aminobutyric acid: 169; four protein fractions,
  free amino acids: 163.

Pterinopelma vellutinum M.-Leitao
  5-hydroxytryptamine: 353.

Fam. Lycosidae

Lycosa 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. Theridiidae

*Latrodectus 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, 184D, 206, 343; two active protein fractions: 352, lipoprotein: 163.

Fam. Argiopidae

*Araneus diadematus* Clerck

Hyaluronidase: 163.

Fam. Ctenidae

*Ctenus nigriventer* Keys (= *Phoneutria nigriventer* Keys)

Proteins, hyaluronic acid: 169; hyaluronicase 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.

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
OPF - Arachnida Opiliones
ORT - Insecta Orthoptera
PHE - Insecta Phasmida
POL - Diplopoda Polydesmida
SCOL - Chilopoda Scolopendromorpha
SCORP - Arachnida Scorpiones
URO - Arachnida Uropygi
Chap. - 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 Stãl., Nezara viridula L. var. smaragdula F., Rhoeocoris sulciventris Stãl, Macrocytus sp. (HET).

n-tridecane

Biprorulus bibax, Carpocoris purpureipennis (De Geer), Cerato-
coris cephalicus Mont., Euschistus servus Say., Macrocytus sp.,
Musgraveia sulciventris Stãl, Nezara viridula L., N. viridula L.
var. smaragdula Fabr., Oebalus pugnax Fabr., Rhoeocoris sulciven-
tris Stãl, Tessaratoma 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

dimethylsulfide

Paltothyreus tarsatus (Fabr.) (HYM).
dimethyltrisulfide

Paltothyreus tarsatus Fabr. (HYM).

ALCOHOLS

methanol

Arctia caja L. (LEP).

glycerol

Apis mellifera L. (HYM).

n-hexanol

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

2-methyl butanol

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

2-methylene butanol

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

octan-1-ol

Armadillidium sp. (CRU).

nonan-1-ol

Porcellio scaber (Latr.) (CRU).

cis-non-3-en-1-ol

Porcellio scaber (Latr.) (CRU).

trans-non-3-en-1-ol

Porcellio scaber (Latr.) (CRU).

cis-dec-3-en-1-ol

Porcellio scaber (Latr.) (CRU).
trans-dec-3-en-1-ol  
Porcellio scaber (Lutr.) (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 ALCOHOLS

choline  
Apis mellifera L. (HYM).

histamine  
Poekilocerus bufonius Klug (ORT);  
Abraxas grossulariata L., Arctia caja L. (§), Dendrolimus spectabilis Btlr. (§), D. undans Walk. (§), Dirphia sp., Euproctis flava Brem. (§), Eurrhypara hostulata L., Hypocrita jacobaeae L., Megalopyge sp., Spilosoma lubricipeda L., Thaumetopoea pityocampa Sch.(§), Zygaena loniceræ von Sch. (LEF);  
Cimex lectularius L., Platymex rhadamanthus Gaerst. (§) (HET);  
Apis mellifera L., Myrmex forficata Fabr., M. gulosa Fabr., Vespa crabro L., Vespula germanica Fabr., V. vulgaris L. (HYM);  
Lycosa erythrognata Luc. (ARA).

(§) probably.

5-hydroxytryptamine  
Scolopendra viridicornis Newport (SCOL);  
Automeris sp. (hairs, larvae), Automeris (illustris?) (hairs) (LEP);  
Apis mellifera L., Dolico vespula media De G., Polybia occidentalis scutellaris , Polistes gallicus L., P. versicolor (Ol.),
### Hydrocarbons

<table>
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<tr>
<td>CH₃-(CH₂)₉-CH₃</td>
<td>n-Undecane</td>
</tr>
<tr>
<td>CH₃-(CH₂)₁₁-CH₃</td>
<td>n-Tridecane</td>
</tr>
<tr>
<td>CH₃CH₂CH-(CH₂)₉-CH₃</td>
<td>1-Undecene</td>
</tr>
<tr>
<td>CH₃-(CH₂)₁₅-CH₃</td>
<td>1-Monene</td>
</tr>
<tr>
<td>CH₃-(CH₂)₁₇-CH₃</td>
<td>1-Tridecene</td>
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### Sulfides

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<tbody>
<tr>
<td>CH₃(S₂)CH₃</td>
<td>Dimethyl disulfide</td>
</tr>
<tr>
<td>CH₃(S)₃CH₃</td>
<td>Dimethyl trisulfide</td>
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### Alcohols

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<td>CH₂OH</td>
<td>Methanol</td>
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<tr>
<td>CH₃-(CH₂)₈-CH₂OH</td>
<td>n-Hexanol</td>
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<tr>
<td>CH₃OH-(CH₂)₆-CH₃</td>
<td>Ottan-1-ol</td>
</tr>
<tr>
<td>CH₃OH-(CH₂)₇CH₃</td>
<td>Nonan-1-ol</td>
</tr>
<tr>
<td>CH₂=CH-(CH₂)₆-CH=CH-(CH₂)₆-CH₂</td>
<td>Cossin 1</td>
</tr>
<tr>
<td>CH₂=CH-(CH₂)₈-CH=CH-(CH₂)₈-CH₂</td>
<td>Cossin 2</td>
</tr>
<tr>
<td>CH₂=CH-(CH₂)₉-CH=CH-(CH₂)₉-CH₂</td>
<td>Cossin 3</td>
</tr>
</tbody>
</table>

### Amines and Amino Alcohols

<table>
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<th>Formula</th>
<th>Name</th>
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</thead>
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<tr>
<td>CH₂OH-(CH₂)₆-CH₃</td>
<td>Choline</td>
</tr>
<tr>
<td>CH₂OH-(CH₂)₇CH₃</td>
<td>Histamine</td>
</tr>
<tr>
<td>CH₂=CH-(CH₂)₈-CH=CH-(CH₂)₈-CH₂</td>
<td>5-Hydroxytryptamine</td>
</tr>
<tr>
<td>CH₂=CH-(CH₂)₉-CH=CH-(CH₂)₉-CH₂</td>
<td>2,5-Hydroxytryptamine</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂=CH₂-CH₃</td>
<td>CH₂=CH₂-NH₂</td>
</tr>
<tr>
<td>CH₂=CH₂-CH₃</td>
<td>2,5-Hydroxytryptamine</td>
</tr>
</tbody>
</table>

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), Agriocoris froggatti Miller, A. morbus alternatus Dallas, Amorbus rhombifer West., Amorbus rubiginosus Guérin, Aulacosternum nigrorubrum Dallas, Graphosoma rubrolinatum (Westwood), Hygia opaca (Uhler), Hyocephalus n.sp., Mictis caja Stål, Mictis profana Fabr., Pachycolpura manca Breddin, Plinachtus bicoloripes Scott (HET).

UNSATURATED ALDEHYDES

trans-prop-2-enal
Nezara viridula L. var. smaragdula F., Scaptocoris divergens Froesch. (HET).
2-methylene propanal

trans-but-2-enal
Nezara viridula L. var. smaragdula F., Scaptocoris divergens Froesch. (HET).

2-methylene butanal

2-methylene butanal dimer

pentenal
Scaptocoris divergens Froesch. (HET).

2-methylene pentenal

trans-hex-2-enal
Cutilia sororor (Brunner), Eurycotic decipiens (Kirby), *E. florida* Walk., Pelmatosilpha coriacea Rehn, Platyzosteria novae seelan- diae Brunner (BLA);
Creemagogaster (Atopogyne) africana Mayr (HYM).
trans-hept-2-enal

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

trans-oct-2-enal

Aelia fieberi Scott., Cimex lectularius L., Dolichoris baccarum L.,
Eurygaster sp., Leptocoris apiclsis West., Musgraveia sulciventris
Stål, Nezara viridula L. var. smaragdula Fabr., Palomena viridissi-
ma P., Poecilotrmis strigatus Westwood, Rhoecocoris sulciventris
Stål, Scaptocoris divergens Froeschner, Scotinophara lurida Burme-
ster, Tessaratoma 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, Scotinophara lurida Burmeister
(HET).

cis-dec-2-enal

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

trans-dodec-2-enal

Rhinocricus insulatus Chamberlin (JUL).

AROMATIC ALDEHYDES

benzaldehyde

Apheloria corrugata Wood, Orthomorpha coarctata Sauss., O. gracilis
Koch, Pachydesmus crassicitus 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

Cuminaldehyde
Rhysodesmus vicinus Sauss. (POL).

SATURATED KETONES

Methyl-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-propyl-ketone
Conomyrma pyramica (Roger), Iridomyrmex pruinosus Roger (HYM).

Methyl-n-undecyl-ketone
Lasius (Chthonolasius) bicornis Forst, 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 nigerrimum Nyl. (HYM).

UNSATURATED KETONES

2-Methyl-2-hepten-6-one
Dolichoderus (Diceratolines) 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).
### ALDEHYDES

#### SATURATED

- \(\text{CH}_3-(\text{CH}_2)_n-\text{CHO}\)  
  - \(n\)-HEXANAL
- \(\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CHO}\)
- \(\text{CH}_3-\text{CH}-\text{CHO}\)
- \(\text{PROPANAL}\)  
  - \(n\)-BUTANAL
- \(2\text{-METHYL-BUTANAL}\)

#### UNSATURATED

- \(\text{CH}_2\text{=CH-CHO}\)
- \(\text{TRANS-PROP-2-ENAL}\)
- \(2\text{-METHYLENE PROPA-NAL}\)
- \(\text{TRANS-BUT-2-ENAL}\)
- \(\text{2-METHYLENE BUTANAL}\)
- \(\text{PENTENAL}\)
- \(\text{2-METHYLENE BUTANAL DIMER}\)
- \(\text{CH}_3-\text{CH}=\text{CH-CHO}\)
- \(\text{2-METHYLENE PENTENAL}\)
- \(\text{TRANS-HEPT-2-ENAL}\)
- \(\text{TRANS-OCT-2-ENAL}\)
- \(\text{CH}_3-(\text{CH}_2)_n=\text{CH-CHO}\)
- \(\text{CIS,TRANS-DEC-2-ENAL}\)
- \(\text{TRANS-DODEC-2-ENAL}\)

#### AROMATIC

- \(\text{BENZALDEHYDE}\)
- \(\text{p-HYDROXYBENZALDEHYDE}\)
- \(\text{SALICYLALDEHYDE}\)
- \(\text{CUMINALDEHYDE}\)

### KETONES

#### SATURATED

- \(\text{CH}_3\text{-CO-CH}_2\text{-CHO}\)
- \(\text{METHYL-HEPTYL-KETONE}\)
- \(\text{ETHYL-PROPYL-KETONE}\)
- \(\text{CH}_3\text{-CH}_2\text{-CO-CH}_2\text{-CHO}\)
- \(\text{METHYL-ETHYL-KETONE}\)
- \(\text{METHYL-}n\text{-AMYL-KETONE}\)
- \(\text{METHYL-}n\text{-UNDecal-KETONE}\)
- \(\text{CH}_3\text{-CO-CH}_2\text{-CHO}\)
- \(\text{CH}_3\text{-CO-CH}_2\text{-CH}_2\text{-CHO}\)
- \(\text{CH}_3\text{-CH}-\text{CHO}\)
- \(\text{4-METHYL-2-HEXANONE}\)
- \(\text{n-PROPYL-ISOBUTYL-KETONE}\)

#### UNSATURATED

- \(\text{CH}_3\text{-CH}_2\text{-CO-CH-CH}_2\text{-CHO}\)
- \(\text{4-KETO-HEX-2-ENE}\)
- \(\text{2-METHYL-2-HEPTEN-6-ONE}\)

### KETO ALDEHYDES

- \(\text{CH}_3\text{-CH}_2\text{-CO-CH-CHO}\)
- \(\text{CH}_3\text{-CH}_2\text{-CO-CH-CH}_2\text{-CHO}\)
- \(\text{4-KETO-TRANS-HEX-2-ENAL}\)
- \(\text{4-KETO-TRANS-OCT-2-ENAL}\)
4-keto-hex-2-ene
Nezara viridula L. var. smaragdula F. (HET).

UNSATURATED KETO ALDEHYDES

4-keto-trans-hex-2-enal
Corixa dentipes Thoms, Macroscytus sp., Nezara viridula L., N. v. L. var. smaragdula Fabr., Sigara falleni (Fieb.), Tessaratoma aethiops Dist. (adults and larvae) (HET).

4-keto-trans-oct-2-enal
Nezara viridula L. var. smaragdula F. (HET).

CARBOXYLIC ACIDS

formic acid
Cerura vinula L. 'larvae), Cnethocampa sp., Datana ministra (larvae), Dircranura 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 Müll (COL);

**Acetic acid**

Agriopocoris froggatti Miller, Amorbus alternatus Dallas, A. rhombifer West., A. rubiginosus Guérin, Aulacosternum nigrorubrum Dallas, Hyocephalus sp., Mic<eacute>tis 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);

2-methylene butyric acid

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

tiglic acid

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

10-hydroxy-2-decenonic acid

Apis mellifera L. (HYM).

D-gluconic acid

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

ascorbic acid

Chrysocoris stolli Wolf (HET).

hyaluronic acid

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

benzoic acid

Gomphodesmus pavana Dem., Orthomorpha coarctata Sauss., Polydesmus
**V 12**

collaris collaris Koch (POL);
Dytiscus latissimus L., D. marginalis L. (COL).

**pipecolinic acid**

Vespula germanica Fabr. (HYM).

**oxalic acid**

Ceroplatas lineatus F., Platyura discoloria Mg., Pl. fasciata Meigen,
Pl. nigricornis F., Pl. sp., Ceroplatas 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 (Dendrolasi.us) fuliginosus Latr. (HYM).

**dendrolasin**

Lasius (Dendrolasi.us) fuliginosus Latr. (HYM).
ESTERS

isoamyl 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, N. 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

trans-dec-2-enyl acetate
Biprorulus bibax, Macroscytus sp., Nezara viridula L. var. smaragdula F. (HET).

cossin A (*)
Cossus cossus L. (larvae) (LEP).

cossin B (*)
Cossus cossus L. (larvae) (LEP).

cossin C (*)
Cossus cossus L. (larvae) (LEP).

cossin E (*
Cossus cossus L. (larvae) (LEP).

(*) For cossin 1, cossin 2, cossin 3, see alcohols.
Cossus cossus L. (larvae) (LEF).

n-butyl butyrate

Amorbus rhombifer West., Mictis caja Stål. (HET).

trans-hex-2-enyl butyrate

Lethocerus indicus (Lep. and Serv.) (HET).

methyl p-hydroxy benzoate


acetylcholine

Polistes omissa Weyrauch, Vespa crabro L., Vespula germanica Fbr. (HYM);
Zygaena filipendulae L., Z. lonicerae (Von Šch.) (LEF).

β-dimethylacrylcholine

Arctia caja L. (imago) (LEF).

LACTONES

γ-gluconolactone

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

δ-gluconolactone

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

AMIDES

pederin


pseudopederin

Paederus fuscipes Curt. (COL).

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

CH₃
CH₂-CH-(CH₂)₂-OOCCH₃  CH₂-(CH₂)₂-OOCCH₃
ISOAMYL ACETATE  n-HEXYL ACETATE
CH₃-(CH₂)₂-OOCCH₃  CH₃-(CH₂)₂-CH=CH-CH₂-OOCCH₃
n-OCTYL ACETATE  TRANS-HEX-2-ENYL ACETATE
CH₃-(CH₂)₄-CH=CH-CH₂-OOCCH₃  CH₃-(CH₂)₆-CH=CH-CH₂-OOCCH₃
TRANS-OCT-2-ENYL ACETATE  TRANS-DEC-2-ENYL ACETATE
CH₂=CH-(CH₂)₆-CH=CH-(CH₂)₃-CH₂OOCCH₃  COSSIN A
CH₂=CH-(CH₂)₄-CH=CH-CH₂-CH₃-CH₂OOCCH₃  COSSIN B
CH₂=CH-(CH₂)₅-CH=CH-CH₂-CH₃-CH₂OOCCH₃  COSSIN C
CROSSIN B₁ (**)  CROSSIN C₁ (***)
CH₂-(CH₂)₃-OOC-(CH₂)₂-CH₂  CH₂-(CH₂)₆-CH=CH-CH₂-OOC-(CH₂)₄-CH₂
n-BUTYL BUTYRATE  TRANS-HEX-2-ENYL BUTYRATE

ACETYLCHOLINE

METHYL p-HYDROXY BENZOATE

LACTONES

6-GLUCONOLACTONE  y-GLUCONOLACTONE

AMIDES

PEDERIN  R = CH₃
PSEUPODERERIN  R = H

PEDERONE
peaderone

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

NITRILES

hydrocyanic acid


Zygæna 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-isopropyl mandelonitrile

Rhysodesmus vicinus Sauss. (POL).

AMINO ACIDS

glycine

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).
\(\alpha\)-aminobutyric acid

\textit{Apis mellifera} L. (HYM).

\(\beta\)-iso-aminobutyric acid

\textit{Apis mellifera} L. (HYM).

\(\gamma\)-aminobutyric acid

\textit{Acanthoscurria atrox} Vellard, \textit{Grammostoma actaeon} Pocock, \textit{Gr. mollis}-

coma Ausserer, \textit{Lasiodora klugii} Koch, \textit{Pamphobeteus soracabae} M.-Lei-
tao, \textit{P. tetracanthus} M.-Leitao (ARA).

threonine

\textit{Apis mellifera} L. (HYM);

\textit{Androctonus australis} L., \textit{Buthus occitanus} Am. (SCORP).

valine

\textit{Apis mellifera} L. (HYM);

\textit{Androctonus australis} L., \textit{Buthus occitanus} Am. (SCORP).

aspartic acid

\textit{Apis mellifera} L., \textit{Paraponera clavata} F. (HYM);

\textit{Androctonus australis} L., \textit{Buthus occitanus} Am. (SCORP);

\textit{Acanthoscurria atrox} Vellard, \textit{Lycosa erythrognata} Luc. (ARA).

asparagine

\textit{Apis mellifera} L. (HYM).

leucine

\textit{Apis mellifera} L., \textit{Paraponera clavata} F. (HYM);

\textit{Androctonus australis} L., \textit{Buthus occitanus} Am. (SCORP).

isoleucine

\textit{Apis mellifera} L., \textit{Paraponera clavata} F. (HYM);

\textit{Androctonus australis} L., \textit{Buthus occitanus} Am. (SCORP).

glutamic acid

\textit{Apis mellifera} L., \textit{Paraponera clavata} F. (HYM);

\textit{Androctonus australis} L., \textit{Buthus occitanus} Am. (SCORP).

**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);

**Proline**

- *Apis mellifera* L. (HYM);

**Histidine**

- *Apis mellifera* L. (HYM);
### Nitriles

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<thead>
<tr>
<th>Nitriles</th>
<th>Structure</th>
<th>Description</th>
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<tbody>
<tr>
<td>H-CN</td>
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<td>Hydrocyanic Acid</td>
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<tr>
<td>CH-CN</td>
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<td>Glucoside of p-Isopropyl Mandelonitrile</td>
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<td>CH-CN</td>
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<td>D- (+)-Mandelic Nitrile</td>
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<td>H-CN</td>
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<td>Mandelonitrile Benzoate</td>
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### Amino Acids

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<td>COOH</td>
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<td>Glycine</td>
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<td>Alanine</td>
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<td>CH2-CH2-COOH</td>
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<td>d-Aminobutyric Acid</td>
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phenylalanine

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

tyrosine

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

tryptophane

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

QUINONES

1,4-benzoquinone

Archiulus (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., E. explodens Duft., B. sclopeta Fabr., Bleodes hispilabris, E. longicollis Le Conte, Pheropsophus catoirei Dej, Prionychus ater Fabr.,
Scaurus dubius Sol., S. uncinus Först., Tenebrio obscurus Fabr. (COL).

2-methyl-1,4-benzoquinone

Archiulus (Schizophyllum) sabulosus L., Aulonopygus aculeatus Attems,
A. aculeatus barbieri, Brachyulus unilineatus Koch, Cambala hirbrichti Hoffman, Chicobulus spinigerus Wood, Cylindrojulus teutonicus Pocock, Doratogonus annulipes Carl, Floridobolus pennery Causey,
Narceus annularis Raf., N. gordanus Chamb., Orthoporus flavior Chamberlin e Mulaik, Or. punctilliger Chamberlin, Pachybolus laminatus Cook, Peridontopyge aberrans Attems, P. vachoni, Rhinocricus
sp., Rh. insulatus Chamberlin, Spirostreptus sp., Sp. multisulcatus
Dem., Sp. virgator Silv., Trigonoiulus lumbricinus Gerst (JUL);
Diploptera punctata (Esch.) (BLA);
Forficula auricularia L. (DER);
Scaptocoris divergens Froesch. (HET);

==ethyl-1,4-benzoquinone
Diploptera punctata (Esch.) (BLA);
Forficula auricularia L. (DER).

==dimethyl-1,4-benzoquinone
Heteropachyloidellus robustus Roewer (OPI).

==dimethyl-1,4-benzoquinone
Heteropachyloidellus robustus Roewer (OPI).

==trimethyl-1,4-benzoquinone
Heteropachyloidellus robustus Roewer (OPI).

==methoxy-1,4-benzoquinone
Tribolium castaneum Herbst (COL).
2-methyl-3-methoxy-1,4-benzoquinone

Archilus (Schizophyllum) sabulosus L., Brachyulus unilineatus Kocn.,
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., Trigonoilus lumbriciniz
Gerst. (JUL).

hydroquinone

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

2-methyl-hydroquinone

Archilus (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

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

SUGARS

glucose

Pachydesmus cras-icutis Wood, Rhysodesmus vicinus Sausa. (POL);
Eleodes longicollis Lec. (COL);
Apis mellifera L. (HYM).

fructose

Apis mellifera L. (HYM).
TERPENIC DERIVATIVES

HYDROCARBONS

D,L-limonene
Myrmicaria natalensis Fred. (HYM).

\( \Delta^2 \)-pinene
Nasutitermes sp. (soldiers), N. exitiosus (Hill.), N. graveolus Hill.,
N. walkerii Hill. (ISO).

ALCOHOLS

citronellol
Acanthomyops sp. (HYM).

ALDEHYDES

citral
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).

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

dichodial
Anisomorpha biprestoides Stoll (PHA);
Forel, D. (Diceratoclinea) scabridus Roger, Iridomyrmex sp., Ir.
myrmecodiae Em., Ir. rufoniger Lowne (HYM).
**HYDROCARBONS**

- D.L-LIMONENE
- α, β-PINENE

**ALCOHOLS**

- CITRONELLOL (MIXTURE OF a, b)

**ALDEHYDES**

- CITRAL
- CITRONELLAL (MIXTURE OF a, b)
- IRIDODIAL
- DOLICHODIAL
- FARNESAL

**LACTONES, ANHYDRIDES**

- IRIDOMYRMECIN
- ISOIRIDOMYRMECIN
- ISODIHYDRONEPETALACTONE
- CANTHARIDIN
LACTONES, ANHYDRIDES

iridomyrmecin

Iridomyrmex humilis Mayr (HYM).

isoiridomyrmecin

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

isodihydronepentalactone

Iridomyrmex nitidus Mayr (HYM).

cantharidin


STEROIDS

24-methylene cholesterol

Kasutitermes sp. (soldiers) (ISO).

testosterone

Ilybius fenestratus Fabr., Ilybius fuliginosus Fabr. (COL).
24-METHYLENE CHOLESTEROL  TESTOSTERONE  11-DEOXYCORTICOSTERONE

6-DIHYDROCYBISTERONE  6-DEHYDROCORTEXONE  6-DEHYDROPROGESTERONE

CYBISTERONE  CALOTROPIN  CALACTIN
11-desoxycorticosterone

Acilius sulcatus, Dytiscus marginalis L. (COL).

6-dihydrocybisterone

Acilius sulcatus, Dytiscus marginalis L. (COL).

6-dehydrocortexone

Acilius sulcatus (COL).

6-dehydroprogesterone

Acilius sulcatus (COL).

cybisterone

Acilius sulcatus, Cybister lateralimarginalis De Geer, Dytiscus marginalis L. (COL).

calotropin

Poekilocerus bufonius Klug (ORT).

calactin

Poekilocerus bufonius Klug (ORT).

ALKALOIDS

glomerin

Glomeris marginata Vill., Gl. conspersa Koch, Gl. hexasticha Brandt, Loboglomeris rugifera Verh. (GLO).

omoglomerin

Glomeris marginata Vill., Gl. conspersa Koch, Gl. hexasticha Brandt (GLO).

FLAVOPROTEINS

riboflavin

Apis mellifera L. (HYM).
### Alkaloids

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### Flavoproteins

- \( CH_2OH \)
- \( HOCH \)
- \( HOCH \)
- \( HOCH \)
- \( CH_2 \)
- RIBOFLAVIN

### Phosphatides

- \( CH_2-O-OCR' \)
- \( RCO-CH \)
- \( CH_2POCH_2-CH_3 \)
- LECITHIN
PHOSPHATIDES

lecithin

Apis mellifera L. (HYM).

ENZYMES

adenosine triphosphatase

Euscorpius italicus (Herbst) (SCORP).

L-amino acid dehydrogenase

Ctenus nigriventer Keys., Scaptocosa raptoria Walk (ARA).

cholinesterase

Vespula germanica Fbr., V. vulgaris L. (HYM).

alkaline phosphatase

Chrysocoris stolli Wolf (HET).

phospholipase A

Apis mellifera L., Vespa crabro L., Vespula vulgaris L. (HYM).

phospholipase B

Vespa crabro L., Vespula germanica Fbr., V. vulgaris L. (HYM).

phospholipase C

Myrmecia gulosa (F.) (HYM).

β-glucosidase

Pachydesmus crassicutis Wood (POL);

Diploptera punctata (Escholtz) (BLA).

hyaluronidase

Cimex lectularius L., Platymeris rhadamatus 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).
invertase

_Ethmostygmus spinosus_ (SCOL).

trypsin

_Ctenus 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 peroxide


ammonia

_Phosphuga atrata_ L., _Silpha obscura_ L., _Oeceoptoma thoracicum_ L. (COL);
_Formica nigricans_ Em., _F. polycetna_ Först., _F. pratensis_ Retz.,
_F. rufa_ L. (HYM).

nitrogen oxides

_Brachynus crepitans_ L., _Br. sp._ (COL).

hydrochloric acid

_Notodonta concinna_ (Abb. and Smith) (LEP).

nitrous acid

_Brachynus crepitans_ L., _Pheropsophus africanus_ Dej. (COL).

nitrites

_Pheropsophus africanus_ Dej. (COL).

inorganic phosphates

_Lycosa 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 bolleyi 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

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

SUGARS

Pachydesmus crassicutis Wood (POL).

polysaccharide

Centruroides sculpturatus Ewing (SCORP).
AMINO ACIDS

free 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);

PEPTIDES

kinin

Apis mellifera L., Vespa crabro L., Vespula germanica Fbr., V. vulgaris L. (HYM).

apamin

Apis mellifera L. (HYM).

mellitin

Apis mellifera L. (HYM).

ENZYMES

anticoagulase

Scorpio arenicola L. (SCORP).

coagulase

Buthacus arenicola (E. Simon) (SCORP).

diastase

Ethmostygmus spinosus (SCOL).
alkaline endopeptidase

**Platymeris rhadamanthus** Gaerst. (HET).

**enzymes**

**Leiurus quinquestriatus** H. and E. (SCORP).

**protease**

**Platymeris rhadamanthus** Gaerst. (HET).

**proteolytic enzymes**

**Ethmostygmus spinosus** (SCOL).

**esterase**

**Polistes 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 SUBSTANCES**

**indole base** (probably scatole)

**Pheidole fallax** Mayr (HYM).

**buthotoxin**

**Buthus martensi** Karsch (SCORP).

**toxic saponin**

**Diamphidia simplex** Peringuey (= *D. locusta* Fairmaire) larvae (COL).

**scorpamin**

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

**toxalbumin**

**Diamphidia 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 antibacterial 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 insecticidal 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).
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 nepetalic acids obtained by trasformation of another natural product of vegetal origin, nepetalactone.

\[ \text{figure 4} \]

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. (Actinidiacea 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, isodihydronepetalactone 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 alcaline 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, isodihydronepetalactone, neonepetalactone are equally attractive to cats.
Fig. 1

Fig. 2
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 Apocynaceae 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, unedoside, 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.

\[\text{Figure 2}\]

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 synthetize D-iridodial (2) and D-isoiridomyrmecin. The L-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-isoirdomyrmecin.

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-isoirdomyrmecin in the pathways shown in the following diagram. Isoirdomyrmecin is epimerized into iridomyrmecin during gas chromatography at 240°C.

Korte and Schreiber 1962 (166 D) obtained the synthesis of 14,14 marked iridomyrmecin -(3-14C), using Barium carbonate -14C 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.

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)-cyanacetate, 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.

The synthesis of (-)iridomyrmecin (Table VIIII 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
Stériostructure de la molécule d'iridomyrmécine.

Vue de face, dans la direction N.

Vue de profil, dans la direction M.

Fig. 11
Fig. 1
A base gives (+)isoiridomyrmecin.

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.

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.

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 synthetize nor-isoiridomyrmecin from trans-nor-nepetalic acid going through nor-nepetalactone, and the researches on nor-nepetalactone synthesis by Trave, Merlini, Garanti 1958 (337).

Wckering 1960 (351) presents the bicyclic skeleton stereostructure of iridomyrmecin (Table 41); from these he derives the detailed structural formula (Table 42). Iridodial is represented by Wckering with the stereoelectronic structure in Table 42. I should
also like to mention the works of McConnel and Schöenborn 1962 (184 D), McConnel, Mathieson and Schöenborn 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 ); by irradiation of citral (table , diagram A) aldehyde (II) was obtained which can produce dolichodial by enzyme oxidation; this, after reduction to iridodial and disproportion, can produce iridomyrmecin and isoiridomyrmecin. Oxidation of (-) limonene to (+) ketoaldehyde and successive aldol cyclization leads to an unsaturated aldehyde as in diagram B of
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.

The synthesis of iridoids from citral, a typical acyclic monoterpeno, 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.

Antibacterial and antimitotic activity.

Iridomyrmecin shows weak antibacterial 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 $1 \times 10^{-3}$ g/cc of D(+)-isoridomyrmecin, but only partially in a concentration of $2 \times 10^{-4}$ 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 $1 \times 10^{-3}$ 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 the 'give 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 agricultur-
natural, 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)).
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<th>iridomir 1:10000</th>
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<th>y-hch sol. sat. + iridomir 1:10000</th>
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Fig. 13
Fitoinhibiting and antimitotic activity (237, 245, 246, 252, 260, 262).

Iridomyrmecin powder sprinkled on the leaves of various plants causes noticeable 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](image)

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](image)

The apical meristem cells of the roots and the rare cases of mitotic phases present did not show any noticeable 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.
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 lethal 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 endoperitonaeum, 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 endoperitonaeum, 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, farnesal (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
Formule de structure sémantique.

Edifice stérométrique et stéréochimique.

Coupe A-B.

C18H22O

Dendrolasine. - Échelle: 1 cm = 2 Å.

Fig. 15

1. CITRAL
2. LIMONENE
3. IRIDOMYRMECIN AND VARIOUS IRIDOIDS
4. SKYTANTHINE
5. FARNESEL
6. PERILLEN
7. DENDROLASIN
8. CANTHARIDIN

Fig. 16

Fig. 17
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 farnesylpirophosphate 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 Torreya 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.
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 48.

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.


(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).


Table 18

Possibility of differentiation between cantharidin and pederin.

<table>
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<th>Data of differentiation</th>
<th>Cantharidin</th>
<th>Pederin</th>
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<tr>
<td>I: ORIGIN:</td>
<td>Coleoptera Meloidae (various species of the genera Lytta, Melo, Zonabris, Epicauta, Milabris, etc.)</td>
<td>Coleoptera Staphylini- nidae (Paederus jac- pes Curt. and probably other species belonging to the genus Paederus).</td>
</tr>
<tr>
<td>II: CHEMICAL TESTS</td>
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<tr>
<td>1) Solubility</td>
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<tr>
<td>a) Chloroform, carbon tetrachloride, acetone, ethyl ether, ethyl acetate, ethyl acetacetate, benzene, toluene, xylene, tetralin, ethylene chlorohydride, acetic acid, hydrochloric acid, sulfuric acid, nitric acid.</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>b) petroleum ether, glycerin, ammonia (33%)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>c) water, physiological solution, carbon disulfide, methanol, ethanoic (cold and warm), butyl alcohol, isobutyl alcohol, benzyl alcohol, amyyl alcohol, allyl glycol, triethylene glycol, propylene glycol, decalin.</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>d) sodium hydroxide N.</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>III: PHYSICAL TESTS</td>
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</tr>
<tr>
<td>Melting point (1)</td>
<td>218°C</td>
<td>112°C</td>
</tr>
<tr>
<td>3) May be extracted by the following methods:</td>
<td></td>
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<tr>
<td>MARFORI and PIET 1936.</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>STASS-OTTO-DRAGEN- DORFF-O GIHR (DOURIS 1892).</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Deutsches Arzneibuch 1898.</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>STASS-OTTO-O GIHR (DOURIS 1951).</td>
<td>+</td>
<td>0</td>
</tr>
</tbody>
</table>

1) Microdetermination with Kofler's apparatus.
IV: Biological tests

4) Reaction on human beings: skin

**Acute:**
- Typical vesication (bulla with serum). (1) (2)
- Epiderm necrotization (without bulla or serum). (1) (2)

**Chronic:**
- Unknown

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)

b) pulmonary histological test
- Exudates (3)
- No exudates (2)

d) renal histological test
- Glomerulonephritis (3)
- Kidney undamaged (3)

6) Attraction for insects (4)

<table>
<thead>
<tr>
<th>Insect</th>
<th>+</th>
<th>-</th>
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</thead>
<tbody>
<tr>
<td>Anthomyia plurialis L.</td>
<td>5</td>
<td>0</td>
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<tr>
<td>Anthicus quadrigatus</td>
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<td>0</td>
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<tr>
<td>Formicomus pedestris</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Notoxus monoceros L.</td>
<td>6</td>
<td>0</td>
</tr>
</tbody>
</table>

1) Experimental and accidental tests, and literature data.
2) Cic. Pavan-Do 1952 and Bo-Valcuron 1953.
3) Petr 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* Goze (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$_9$N) and pseudopederin (C$_{24}$H$_{43}$O$_9$N) 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. 10
metoxylde 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 oxidation of pedelactone $\text{HIO}_4$ oxidation subject to previous bromidric hydrolysis and NMR spectrum we were able to define the structure of this compound and its derivatives.

The fact that isopedero lactone was obtained by pseudopederin oxidation 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 $\text{CH}_2=\text{}$; the existence of two rings was confirmed by obtaining non-hydroxylated diacetylpederin and ritsartransformation in pederin by LiAlH reduction; the derivation of pederal 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 bibliographical 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), $\text{HIO}_4$ 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 gave 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 neutrophiles in the circulating blood of guinea pigs. In the partially hepatectomized rat it causes a stimulation of rigeneration, 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-


(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.

<table>
<thead>
<tr>
<th>Strain or line</th>
<th>M.I.C. ng/ml</th>
<th>Strain or line</th>
<th>M.I.C. ng/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>EUE</td>
<td>1.5</td>
<td>MEF</td>
<td>1.5</td>
</tr>
<tr>
<td>E6D</td>
<td>1.5</td>
<td>CE</td>
<td>1.5</td>
</tr>
<tr>
<td>HeLa</td>
<td>1.5</td>
<td>BHK</td>
<td>1.0</td>
</tr>
<tr>
<td>KB</td>
<td>1.5</td>
<td>Z1</td>
<td>3.1</td>
</tr>
<tr>
<td>Hep</td>
<td>1.5</td>
<td>M1</td>
<td>3.9</td>
</tr>
<tr>
<td>Senger</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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.
   - Z1: A diploid cell strain derived for human thyroid, grown in our laboratory for 5 months.
   - M1: a diploid cell strain derived from human amnion, grown in our laboratory for 6 months.
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 antimitotic 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
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.

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).

Gas chromatographic 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 CI; 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 CI: 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 C₂₂H₃₉S.

(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.
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 (Dendro- lasius) 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.
<table>
<thead>
<tr>
<th>Substances which are present in the defensive secretions of Arthropoda</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HYDROCARBONS</strong></td>
</tr>
<tr>
<td>1. n-undecane</td>
</tr>
<tr>
<td>2. n-dodecane</td>
</tr>
<tr>
<td>3. n-tridecane</td>
</tr>
<tr>
<td>4. 1-nonenene</td>
</tr>
<tr>
<td>5. 1-undecene</td>
</tr>
<tr>
<td>6. 1-tridecene</td>
</tr>
<tr>
<td><strong>SULFIDES</strong></td>
</tr>
<tr>
<td>7. dimethyldisulfide</td>
</tr>
<tr>
<td>8. dimethyltrisulfide</td>
</tr>
<tr>
<td><strong>ALCOHOLS</strong></td>
</tr>
<tr>
<td>9. methanol</td>
</tr>
<tr>
<td>10. glycerol</td>
</tr>
<tr>
<td>11. n-hexanol</td>
</tr>
<tr>
<td>12. 2-methyl-butanol</td>
</tr>
<tr>
<td>13. 2-methylene butanol</td>
</tr>
<tr>
<td>14. octan-1-ol</td>
</tr>
<tr>
<td>15. nonan-1-ol</td>
</tr>
<tr>
<td>16. cis-non-3-en-1-ol</td>
</tr>
<tr>
<td>17. trans-non-3-en-1-ol</td>
</tr>
<tr>
<td>18. cis-dec-3-en-1-ol</td>
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<tr>
<td>19. trans-dec-3-en-1-ol</td>
</tr>
<tr>
<td>20. cossin 1</td>
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<tr>
<td>21. cossin 2</td>
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<td>22. cossin 3</td>
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<tr>
<td>Cl. DIPLOPODA</td>
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<tr>
<td>---------------</td>
</tr>
<tr>
<td>Glomerida</td>
</tr>
<tr>
<td>Chordeumida</td>
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<tr>
<td>Polydesmida</td>
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<tr>
<td>Julida</td>
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<tr>
<td>Spirobolida</td>
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<td>Spirostreptida</td>
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<tr>
<td>Cambalida</td>
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</tbody>
</table>
Zoological orders in which are present the listed substances
((*) Class CHILOPODA)
((§) Class CRUSTACEA)

Substances which are present in the defensive secretions of Arthropoda

<table>
<thead>
<tr>
<th>AMINES AND AMINO ALCOHOLS</th>
<th>Glomerida</th>
<th>Chordeumida</th>
<th>Polydesmida</th>
<th>Julida</th>
<th>Spirobolida</th>
<th>Cambalida</th>
<th>(***) Scolopendromorpha</th>
<th>Blattodea</th>
<th>Isoptera</th>
<th>Dermoptera</th>
<th>Phasm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>23. choline</td>
<td></td>
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<td>24. histamine</td>
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<td>25. 5-hydroxytryptamine</td>
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<td>26. 2,5-hydroxytryptamine</td>
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</tbody>
</table>

**SATURATED ALDEHYDES**

| 27. propanal |           |             |             |       |            |           |                          |           |          |            |       |
| 28. n-butanal |           |             |             |       |            |           |                          |           |          |            |       |
| 29. 2-methyl butanal |           |             |             |       |            |           |                          |           |          |            |       |
| 30. n-hexanal |           |             |             |       |            |           |                          |           |          |            |       |

**UNSATURATED ALDEHYDES**

| 31. trans-prop-2-enal |           |             |             |       |            |           |                          |           |          |            |       |
| 32. 2-methylene propanal |           |             |             |       |            |           |                          |           |          |            |       |
| 33. trans-but-2-enal |           |             |             |       |            |           |                          |           |          |            |       |
| 34. 2-methylene butanal |           |             |             |       |            |           |                          |           |          |            |       |
| 35. 2-methylene butanal dimer |           |             |             |       |            |           |                          |           |          |            |       |
| 36. pentenal |           |             |             |       |            |           |                          |           |          |            |       |
| 37. 2-methylene pentanal |           |             |             |       |            |           |                          |           |          |            |       |
| 38. trans-hex-2-enal |           |             |             |       |            |           |                          |           |          |            |       |
| 39. trans-hept-2-enal |           |             |             |       |            |           |                          |           |          |            |       |
| 40. trans-oct-2-enal |           |             |             |       |            |           |                          |           |          |            |       |
| 41. trans-dec-2-enal |           |             |             |       |            |           |                          |           |          |            |       |
| 42. cis-dec-2-enal |           |             |             |       |            |           |                          |           |          |            |       |
| 43. trans-dodec-2-enal |           |             |             |       |            |           |                          |           |          |            |       |

A.
<table>
<thead>
<tr>
<th></th>
<th>Cl. CRUSTACEA</th>
<th>Cl. DIPLOPODA</th>
<th>Cl. INSECTA</th>
<th>Cl. ARACHNIDA</th>
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<tr>
<td></td>
<td>Glomerida</td>
<td>Chordeumida</td>
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<td>Julida</td>
<td>Spirobolida</td>
<td>Spirostreptida</td>
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<td>Cambalida</td>
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<td></td>
<td>(*) Scolopendromorpha</td>
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<tr>
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<td>Blattodea</td>
<td>Isoptera</td>
<td>Dermaptera</td>
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<td>Phasmida</td>
<td>Orthoptera</td>
<td>Heteroptera</td>
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<td>Diptera</td>
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<td>($) Isopoda</td>
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<tr>
<td>Zoological orders in which are present the listed substances</td>
<td>Cl. DIPLOPODA</td>
<td>(*) Scolopendromorpha</td>
<td>Cl. I</td>
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<tr>
<td>((*) Class CHILLOPODA)</td>
<td>Glomerida</td>
<td>Polydesmida</td>
<td>Julida</td>
<td>Spirobolida</td>
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<tr>
<td>((§) Class CRUSTACEA)</td>
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<td>(+)</td>
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</table>

Substances which are present in the defensive secretions of **Arthropoda**

**AROMATIC ALDEHYDES**

44. benzaldehyde
45. p-hydroxybenzaldehyde
46. salicyl aldehyde
47. cumin aldehyde

**SATURATED KETONES**

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

**UNSATURATED KETONES**

55. 2-methyl-2-hepten-6-one
56. 4-keto-hex-2-ene

**UNSATURATED KETO ALDEHYDES**

57. 4-keto-trans-hex-2-enal
58. 4-keto-trans-oct-2-enal

**CARBOXYLIC ACIDS**

59. formic acid
60. acetic acid
61. propionic acid
62. butyric acid
63. isobutyric acid
<table>
<thead>
<tr>
<th>Order</th>
<th>Cl.</th>
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((§) Class CRUSTACEA)

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

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Zoological orders in which are present the listed substances 
((*) Class CHILIPODA) 
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Substances which are present in the defensive secretions of Arthropoda

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Note: + indicates presence; ± indicates absence or presence in some cases.
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**Note:** The table represents a classification of arthropods, with each row indicating the presence (+) or absence (-) of certain characteristics in different orders.
Zoological orders in which are present the listed substances

((*) Class CHILIPODA)

((§) Class CRUSTACEA)

Substances which are present in the defensive secretions of Arthropoda

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<tr>
<td>132. proline</td>
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<td>133. histidine</td>
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<tr>
<td>134. phenylalanine</td>
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<tr>
<td>135. thyrosine</td>
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<td>136. tryptophane</td>
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<tr>
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</tr>
<tr>
<td>137. 1,4-benzoquinone</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>138. 2-methyl-1,4-benzoquinone</td>
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</tr>
<tr>
<td>139. 2-ethyl-1,4-benzoquinone</td>
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</tr>
<tr>
<td>140. 2,3-dimethyl-1,4-benzoquinone</td>
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<td>141. 2,5-dimethyl-1,4-benzoquinone</td>
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<td>142. 2,3,5-trimethyl-1,4-benzoquinone</td>
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<tr>
<td>143. 2-methoxy-1,4-benzoquinone</td>
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<tr>
<td>144. 2-methyl-3-methoxy-1,4-benzoquinone</td>
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<tr>
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<tr>
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<tr>
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<td>TERPENIC DERIVATIVES</td>
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</tr>
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</tr>
<tr>
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<td>Opiliones</td>
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<tr>
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<td>Chordeumida</td>
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<tr>
<td>Polydesmidia</td>
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<tr>
<td>Julida</td>
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<tr>
<td>Spirobolida</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spirostreptida</td>
<td></td>
<td></td>
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<tr>
<td>Cambalida</td>
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</table>
Zoological orders in which are present the listed substances

((*) Class CHILOPODA)

((§) Class INSECTA)

<table>
<thead>
<tr>
<th>Substances which are present in the defensive secretions of Arthropoda</th>
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<tbody>
<tr>
<td><strong>ALCOHOLS</strong></td>
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<tr>
<td>152. α,β-pinene</td>
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<tr>
<td>153. citronellol</td>
</tr>
<tr>
<td><strong>ALDEHYDES</strong></td>
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<tr>
<td>154. citral</td>
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<tr>
<td>155. citronellal</td>
</tr>
<tr>
<td>156. farnesal</td>
</tr>
<tr>
<td>157. iridodial</td>
</tr>
<tr>
<td>158. dolichodial</td>
</tr>
<tr>
<td><strong>LACTONES, ANHYDRIDES</strong></td>
</tr>
<tr>
<td>159. iridomymecin</td>
</tr>
<tr>
<td>160. isoiridomymecin</td>
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<tr>
<td>161. isodihydronepetalactone</td>
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<tr>
<td>162. cantharidin</td>
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<td><strong>STEROIDS</strong></td>
</tr>
<tr>
<td>163. 24-methylene cholesterol</td>
</tr>
<tr>
<td>164. testosterone</td>
</tr>
<tr>
<td>165. 11-desoxycorticosterone</td>
</tr>
<tr>
<td>166. 6-dihydrocybisterone</td>
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<td>167. cybisterone</td>
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<td>168. 6-dehydrocortexone</td>
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<td>170. calotropin</td>
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<td>171. calactin</td>
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<th>Glomerida</th>
<th>Chordeunida</th>
<th>Polydesmidia</th>
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<td>Phasmida</td>
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<td>Cryptoptera</td>
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<td><strong>INSECTA</strong></td>
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<td>Chordeumida</td>
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<td>Julida</td>
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<tr>
<td>Spirobolida</td>
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<tr>
<td>Spirostreptida</td>
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<tr>
<td>Cambalida</td>
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<td>(* )Scolopendromorpha</td>
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<tr>
<td>Opiliones</td>
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<td>Aranea</td>
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<tr>
<td>Substances which are present in the defensive secretions of Arthropoda</td>
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</tr>
<tr>
<td><strong>ALKALOIDS</strong></td>
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<tr>
<td>172. glomerin</td>
</tr>
<tr>
<td>173. omoglomerin</td>
</tr>
<tr>
<td><strong>FLAVOPROTEINS</strong></td>
</tr>
<tr>
<td>174. riboflavin</td>
</tr>
<tr>
<td><strong>PHOSPHATIDES</strong></td>
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<tr>
<td>175. lecithin</td>
</tr>
<tr>
<td><strong>ENZYMES</strong></td>
</tr>
<tr>
<td>176. adenosine triphosphatase</td>
</tr>
<tr>
<td>177. L-amino acid dehydrogenase</td>
</tr>
<tr>
<td>178. cholinesterase</td>
</tr>
<tr>
<td>179. alkaline phosphatase</td>
</tr>
<tr>
<td>180. phospholipase A</td>
</tr>
<tr>
<td>181. phospholipase B</td>
</tr>
<tr>
<td>182. phospholipase C</td>
</tr>
<tr>
<td>183. β-glucosidase</td>
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<tr>
<td>184. hyaluronidase</td>
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<tr>
<td>185. invertase</td>
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<tr>
<td>186. trypsin</td>
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<tr>
<td>Cl. DIPLOPODA</td>
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<tr>
<td>---------------</td>
</tr>
<tr>
<td>Glomerida</td>
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<tr>
<td>Chordeumida</td>
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<tr>
<td>Julida</td>
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<tr>
<td>Spirobolida</td>
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<tr>
<td>Cambalida</td>
</tr>
<tr>
<td>(*) Scoleopendramorphia</td>
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</table>
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 citrale, 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

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

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 example periller, alfa-clusenane). 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 forms (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 Reduvidae 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 Reduvidae of the sub-families Phymarinae, Elasmobdinae 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 (Tessaratoma 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.
<table>
<thead>
<tr>
<th>Fam. Corixidae</th>
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<tr>
<td>Corixus dentipes (Thoms.)</td>
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<td>Fam. Belostomatidae</td>
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<tr>
<td>Lettoecerus indicus Lop.</td>
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<td>Fam. Reduviidae</td>
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<tr>
<td>Acanthocoris servilis (Thunberg)</td>
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</tr>
<tr>
<td>Agria varia foggatti Miller</td>
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</tr>
<tr>
<td>Amorbus alternatus Dallas</td>
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</tr>
<tr>
<td>Amorbus rhombifer Westwood</td>
<td>+</td>
</tr>
<tr>
<td>Amorbus rubicinis Guert.</td>
<td>+</td>
</tr>
<tr>
<td>Anasactenus nigrorubrum Dallas</td>
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</tr>
<tr>
<td>Hylia opaca (Ulter)</td>
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</tr>
<tr>
<td>Leptocorpa specialis Westwood</td>
<td>+</td>
</tr>
<tr>
<td>Micca caja Sial</td>
<td>+</td>
</tr>
<tr>
<td>Micra profana (Fabricius)</td>
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</tr>
<tr>
<td>Paschylacerta manca Bredin</td>
<td>+</td>
</tr>
<tr>
<td>Plinacius bicoloripes Scott</td>
<td>+</td>
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<tr>
<td>Riptorus clarus (Thunberg)</td>
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<td>CH₃(CH₂)₄CH=CH-COCH₃</td>
<td>CH₃(CH₂)₄CH=CH-COCH₃</td>
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<td>CH₃(CH₂)₄CH=CH-COCH₃</td>
<td>CH₃(CH₂)₄CH=CH-COCH₃</td>
</tr>
</tbody>
</table>
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 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>
<thead>
<tr>
<th>Species</th>
<th>1,4-benzoquinone</th>
<th>2-methyl-1,4-benzoquinone</th>
<th>2-methyl-3-methoxy-1,4-benzoquinone</th>
<th>2-methyl-4-hydroxyquinone</th>
<th>trans-dodec-2-enal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Archiulus (Schizophyllum) sabulosus L.</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Aulonopygus aculeatus Attems</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aulonopygus aculeatus barbieri</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brachyulus unilineatus Koch</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cambala hubrichti Hoffman</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chicobolus spinigerus Wood</td>
<td></td>
<td>+</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Cylindroiulus teutonicus Pocock</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Doratogonus annulipes Carl</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Floridobolus penneri Causey</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Narceus annularis Raf.</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Narceus gordanus Chamb.</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orthocricus arboreus (Sauss.)</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>Orthoporus conifer (Attems)</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Orthoporus flavior Chamb. e Mulaik</td>
<td></td>
<td>+</td>
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</tr>
<tr>
<td>Orthoporus puntilliger Chamb.</td>
<td></td>
<td>+</td>
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<td></td>
</tr>
<tr>
<td>Pachybolus laminatus Cook</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peridontopyge aberrans Attems</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peridontopyge vachoni</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhinocricus sp.</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhinocricus insulatus Chamb.</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>Schizophyllum mediterraneum</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spirostreptus sp.</td>
<td></td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spirostreptus castaneum Attems</td>
<td>+</td>
<td>+</td>
<td></td>
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</tr>
<tr>
<td>Spirostreptus multisulcatus Dem.</td>
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<td>+</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Spirostreptus virgator Silv.</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trigonoiulus lumbricinus Gerst.</td>
<td>+</td>
<td>+</td>
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</tr>
</tbody>
</table>
**Table 9 - Components of defensive secretions of Diplopoda Polydesmida (1) (from Barbetta-Casnati-Pavan 1966).**

<table>
<thead>
<tr>
<th>Diplopoda Polydesmida</th>
<th>Benzoic acid</th>
<th>Benzaldehyde</th>
<th>Hydrocyanic acid</th>
<th>Phenol</th>
<th>Glucoside of p-isopulegol</th>
<th>Mandelonitrite benzene</th>
<th>D-(+)-mandelic nitrile</th>
<th>Diacceride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apheloria corrugata (Wood)</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(b)</td>
</tr>
<tr>
<td>Cherokia georgiana (Bollmann)</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gymnophodesmus pavani Dem.</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td>Kenoria sp.</td>
<td>+</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Orthomorpha coarctata Sauss.</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Orthomorpha gracilis Koch (= Fontaria gracilis Koch, Paradesmus (Fontaria) gracilis Koch, Oxydus gracilis Koch)</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pachydesmus crassiculus (Wood)</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[+]</td>
</tr>
<tr>
<td>Polydesmus collaris collaris (Koch)</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(a)</td>
</tr>
<tr>
<td>Polydesmus (Fontaria) virginiensis Drury (= Polydesmus virginiensis Drury, Fontaria virginiensis Drury)</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>+</td>
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</tr>
<tr>
<td>Pseudopolydesmus serratus (Say)</td>
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<td></td>
</tr>
<tr>
<td>Rhysodesmus vicinus Sauss. (= Polydesmus vicinus Sauss., Polydesmus (Fontaria) vicinus Sauss.)</td>
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<td></td>
<td></td>
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<td>[+]</td>
</tr>
</tbody>
</table>

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

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

(b) Product which has been roughly identified as mandelonitrite by indicative methods unsuitable for defining its steric structure.
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 Juliformia; 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
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 Formicinæ, 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 dandrolasin; 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 antimitotic 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
hiv. Here we might make a comparison with the paralyzing 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 warm-blooded 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 warm-blooded animals only, as for example 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 for the species producing cantharidin.

22. We can legitimately consider as toxic secretions the repellent substances of several Insecta (for example Brachynus, Paltotethyrraeus, 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 Dorylin 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. pyretrine, 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 substance 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-haemorroea 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 glycoside 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 histami-
ne from the tissues. In any case the entire subject still has to be
studied, first analytically and then comparatively.

Other comparisons are possible, for example, between the cu-
taneous effects (necrosis) produced by numerous plants, e.g. *Rhus tox-
ica*, *Uron L.*, and those produced by certain Arthropoda, e.g. Araneae
of the genus *Lycosa* and Insecta Coleoptera of the Paederus genus: ho-

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 Paede-
rus 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 paralizing substances are known in plants. Substances which paralize 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 paralizing 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 (dimethyl disulphide and dimethyl trisulphide) 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 Pachynus (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 Paltothyreys 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) fufilginosus, 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).

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.

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 (= anisomorphal) is synthesized from the normal precursors.

(1) Not to be confused with torreyol C\textsubscript{15}H\textsubscript{26}O which according to Sakan et al. 1963 is identical to \( \Delta \)-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 oxidation 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).
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).

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).

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, there, 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 for men. 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
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.) in 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 through 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 those 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
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 B₁
14. cossin C₁
15. zeuzerina
16. dolichodial
17. cybisterone
18. diidrocybisterone

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.

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 already 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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Pavia, 15.11.1968

EUROPEAN RESEARCH OFFICE
Zimmer 030 (Q-3)
IG Farben Hochhaus
6000 FRANKFURT/MAIN (GERMANY)

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).


4) Type and number of report: Final Technical Report.


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
Istituto di Entomologia Agraria
dell'Università di Pavia (Italy)
Via Taramelli 24

[Signature]
DEFENSIVE SECRETIONS OF ARTHROPODA

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 B3; 14. cossin C1; 15. zeuzerina; 16. dolichodial; 17. cybisterone; 18. diidrocystisterone. A chapter is devoted to each compound and a comprehensive concluding chapter and bibliography terminate this report.
UNCLASSIFIED
Security Classification

Defensive Secretions
Arthropod Poisons
Plant Poisons
Insect Poisons
Iridomyrmecin
Federin
Iridodial
Dendrolas
eudopederin
Jerone
Cassins
Zeuterina
Dolichodial
Gybisterone; Diidrocystobisterone

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