learned her optical proper name as well as the names of their attendants and other chimpanzees. All carried too their names in form of a plastic figure on a collar. By correctly arranging the plastic figures on a magnetic blackboard, Sarah could write, e.g.: 'Give apple Sarah'. Once – and never again – Sarah wrote the sentence 'Give apple Gursie'. Thereupon, her teacher immediately gave the apple to another chimpanzee named Gursie. Also in other captive chimpanzees, they could be brought so far that they adopted an artificial signal as a proper name and used it in the right way. They definitely identified themselves with it which belongs to the character of each true proper name. By this, they manifest a knowledge of one's own self in the above-mentioned sense.

Another way to prove the knowledge of one's own self, the identification of 'self', will also be mentioned because it – with others – shows that the animal self-consciousness, respectively its preformed nature has to remain closed by no means as many scientists think, and as AUTRUM[55] has formulated clearly: 'Consciousness and personality in animals are for us absolutely inaccessible phenomena'.

GALLUP[56] accustomed chimpanzees during a longer period to mirrors, then narcotized them for a short time and spotted them with fast drying red color at places of the body (e.g. above the eyebrows, tips of the ears) they themselves could not see. Not until the next look in the mirror could they discover the unaccustomed marks on themselves and investigate them with the fingers. Here as well, a definite identification, a recognition of one's own self, has taken place. This by no means says that strongly, optically-orientated animals always see a strange rival in the mirror that they try to combat. GALLUP could observe this recognition of one's own self in front of the mirror in chimpanzees, but not in Macaques (*Macaca fascicularis* and *Macaca irus*).

In fact, each imitation, as we find them in so many birds, namely in all birds that mock, needs a certain (primitive) consciousness as an assumption (THORPE[19], p. 78), in so far that within it a knowledge of one's own self is expressed and a knowledge of the other one being imitated. I presume that the highest level of such imitation is found in the little-investigated (scientifically) Australian lyre-bird (*Menura*) that usually imitates about 20 other bird species (SMITH[57]) as well as human voices, barking of dogs, technical noises and so on.

PORTMANN[58] concludes that there is a conscious hearing and therefore an animal self-consciousness from the extraordinary performance of imitation in Menura. – KOEHLER[59], RENSCH[32] (p. 252), DOBZHANSKY (cited in RENSCH[32]), SEIFERLE[60] and many others are of the opinion today that the animal consciousness must not remain totally closed.

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[59] O. KOEHLER, Verh. dt. zool. Ges. *1954*, 332. – O. KOEHLER, Proc. 14. Int. Congr. Zoology, Copenhagen 1953.
[60] E. SEIFERLE, *Lehrbuch der Anatomie der Haustiere* (Parey, Berlin, Hamburg 1975), Bd. 4.

# SPECIALIA

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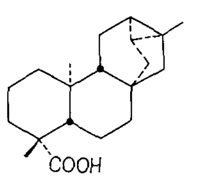
## Diterpene Acids as Larval Growth Inhibitors

C. A. ELLIGER, D. F. ZINKEL[1], B. G. CHAN and A. C. WAISS JR.[2]

*Western Regional Research Laboratory, Agricultural Research Service, U. S. Department of Agriculture, Berkeley (California 94710, USA), 20 April 1976.*

*Summary*. Kaurenoic and trachylobanoic acids from sunflower inhibited larval development in several Lepidoptera species. The tricyclic resin acids were also effective in curtailing growth of *Pectinophora gossypiella* and either reduction to carbinol or esterification of the carboxyl group lowered activity. Partial reversal of growth inhibition in the presence of relatively large amounts of cholesterol suggests an interaction with the insects' hormonal system.

A recent study[3] on the nature of resistance in sunflower (*Helianthus annuus* L.) to attack by larvae of the sunflower moth (*Homeosoma electellum* H.) showed that resistant varietes contained larger amounts of 2 larvacidal diterpenoid acids in extracts of their florets. Since first instar larvae of *Homeosoma electellum* consume florets as the major portion of their diet before burrowing into the immature seeds, the presence of the growth inhibiting chemicals was considered to be the definitive factor in this example of host plant resistance. The 2 substances, trachyloban-19-oic acid (**1**) and the biogenetically related (–)-16-kaurene-19-oic acid (**2**) whose structures had already been elucidated[4,5] (Figure 1) were isolated from the plant and incorporated into a suitable artificial diet[6] in order to determine toxicity to *Homeosoma electellum* larvae. The effect of these 2 acids upon larval growth of other Lepidoptera species, namely, *Heliothis virescens*, *Heliothis zea* and *Pectinophora gossypiella*, was also examined. Results of experiments, expressed in terms of larval weights as percent of the growth of control larvae, are summarized in Table I. While extreme toxicity (of the order of commercial insecticides) was not observed, this does not rule out effective natural antibiosis since chronic effects which even slightly reduced the development of phytophagous larvae are sufficient to provide a significant advantage to the plant[3]. It is noteworthy that considerable difference in species sensitivity was observed. The least susceptible were larvae of the sunflower moth whose lack of sensitivity may be attributed to natural selection for tolerance in this species.

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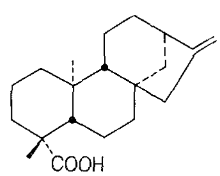


2

Inasmuch as no previous study of natural plant toxicants had uncovered compounds of this type, it was of interest to examine substances of related structure for larvacidal or inhibitory activity. The diterpene resin acids, some representative examples of which are shown in Figure 2, bear a close structural and biogenetic relationship to the sunflower acids and therefore suggested themselves as candidates for bioassay. Wood resin constituents have been implicated as factors in pest resistance[7,8]. Although the resin acids are obtainable in large amounts from natural sources, in particular from conifer oleoresin[9], extremely pure (99+%) samples were only available in rather small quantities. This made it necessary to carry out experiments on an insect whose food requirements were low. Of the insects available to us, *Pectinophora gossypiella*, the pink bollworm, was most satisfactory since its small size and low food demand meant that rearing to incipient pupation could be conveniently carried out on about 600 mg of artificial diet per individual. Screening for activity, using 10 individuals per level, up to a concentration of 1% additive in the diet, required about 100 mg of resin acid. The pink bollworm was readily propagated under laboratory conditions and was available in large numbers, whereas the sunflower moth demonstrated reduced fecundity after several generations. We selected the compounds shown in Table II as representative acids of this series, differing in place-

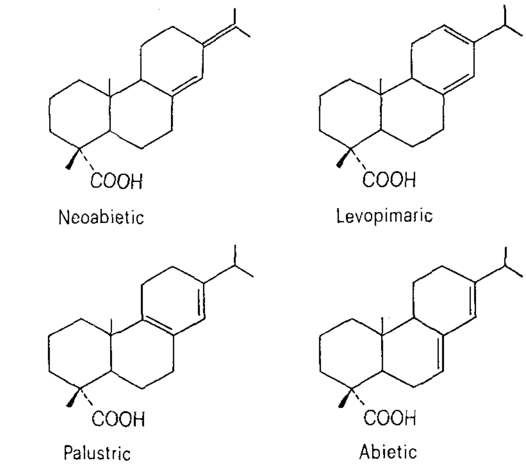


Fig. 2. Typical resin acids.

[1] U. S. Forest Service, Forest Products Laboratory, Madison, Wisconsin, USA.

[2] Acknowledgment. We wish to thank M. Rose and J. Baker for insect bioassays.

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[8] F. S. Santamour, jr., Morris Aboretum Bull. *18*, 82 (1967).

[9] L. F. Fieser and M. Fieser, *Topics in Organic Chemistry* (Reinhold, New York 1963), p. 192.

Table I. Larval growth in presence of sunflower diterpene acids

| | Larval growth[a] at dietary level (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Trachylobanoic acid | | | | Kaurenoic acid | | | |
| Larva | 0.2 | 0.5 | 1 | 2 | 0.2 | 0.5 | 1 | 2 |
| *Homeosoma electellum*[b] | 103[3] | 61 | 48 | 18 | 67[f] | 76 | 30 | 1 |
| *Heliothis virescens*[c] | 90 | 111 | 46 | 13 | 97 | 109 | 56 | 20 |
| *Heliothis zea*[d] | 22 | 1 | <1 | – | 101 | 4 | <1 | – |
| *Pectinophora gossypiella*[e] | 31 | 1 | 1 | – | 34 | 4 | 1 | – |

[a]As percent of control weights after 14 days, 10 larvae per level. [b]Av. control wts: [b] 33 mg; [c] 326 mg; [d] 202 mg; [e] 34 mg. [f] 0.25% Dietary level.

Table II. Larval growth of *Pectinophora gossypiella* on artificial diets containing resin acids

| | Growth at dietary level[a] (SD) | |
|---|---|---|
| Resin acids | 0.05% | 0.2% |
| Abietic acid | 78 (44) | 14 (7) |
| Dehydroabietic acid | 78 (41) | 34 (17) |
| Dihydropimaric acid | 48 (15) | 17 (13) |
| Isopimaric acid | 18 (9) | 1 (1) |
| Levopimaric acid | 77 (26) | 24 (11) |
| Manoyl oxide acid | 54 (20) | 14 (8) |
| Neoabietic acid | 61 (29) | 14 (9) |
| Palustric acid | 83 (22) | 14 (6) |
| Pimaric acid | 56 (36) | 14 (5) |
| Sandaracopimaric acid | 43 (43) | 5 (3) |

[a] Percent of control weight after 14 days, 10 larvae per level.

ment of unsaturation and substituent orientation but, with the exception of manoyl oxide acid (8,13-$\beta$-epoxy-14-labden-19-oic acid)[10], having the same carbocyclic skeleton.

From Table II it can be seen that growth inhibition occurs with all test compounds, and that except for the rather higher toxicity of isopimaric acid there are relatively slight differences from one to the other. This seems reasonable since examination of molecular models reveals essentially the same overall shape for these structures. Interestingly, this configuration differs appreciably from that of the sunflower acids which have the opposite stereochemical orientation at the A–B ring junction and also posses a more rigid system due to additional ring formation.

Table III. Larval growth of *Pectinophora gossypiella* on artificial diets containing isopimaric acid derivatives

| Compound | Growth at dietary level[a] | |
|---|---|---|
| | 0.05% | 0.1% |
| Isopimaric acid | 18 | 5 |
| Dihydroisopimaric acid | 23 | 10 |
| Methyl isopimarate | 71 | 68 |
| Isopimarol | 98 | 55 |

[a] Percent of control wt. after 14 days, 10 larvae per level.

Table IV. Larval growth of *Pectinophora gossypiella* on diets containing both levopimaric acid and cholesterol

| Additive | Larval weight[a] |
|---|---|
| None | 100 |
| 1% Cholesterol | 125 |
| 0.2% Levopimaric acid | 23 |
| Same + 0.05% cholesterol | 45 |
| Same + 0.1% cholesterol | 61 |
| Same + 0.2% cholesterol | 41 |
| Same + 0.4% cholesterol | 64 |
| Same + 1.0% cholesterol | 86 |

[a] Percent of control, 10 larvae per level.

Whether or not the carboxyl functionality of the resin acids is necessary for toxicity may be indicated by comparison of the respective ester or carbinol with the parent compound. Table III shows these results for the isopimaric series and includes data on the reduced side-chain form also. The latter compound, dihydroisopimaric acid, in which the vinyl group at C-13 is modified by hydrogenation, shows essentially unaltered activity which is consistent with the observations presented in Table II. Formation of the methyl ester on the other hand does reduce toxicity and loss of activity is also shown by the corresponding alcohol, isopimarol. Apparently the carboxyl group, while not absolutely essential for growth inhibition, does increase activity. Reduced effectiveness of the methyl ester might be partly counteracted by partial hydrolysis to the free acid during digestive processes. It is likely that the polar acid function facilitates transport and absorption of the compound.

Since the skeletal arrangement of the tricyclic resin acids resembles the ABC-ring system of common steroids, it seemed possible that these compounds interfere with steroid metabolism in the insect. Dietary phytosterols must be absorbed, transported and biochemically altered to produce essential hormones. Interference with any step by inhibitor action of the resin acid would certainly decrease vitality of the larva. We sought to examine this point by fortifying the test diet with increasing concentrations of cholesterol to determine whether growth inhibition could be reversed by mass action effect. The activity of levopimaric acid in the presence of added cholesterol is, in fact, reduced (Table IV). Normal growth was not completely restored, however, even at the 1% level. Larval growth in the absence of toxicant is accelerated by cholesterol resulting in average weights substantially greater than those of controls. The effect of the sterol is proportionally greater on those larvae consuming resin acid in the diet. Larvae fed the resin acid diet with 1% cholesterol showed a 270% weight increase while larvae fed the control diet augmented by 1% cholesterol showed only a 25% weight increase. It may therefore be concluded that there is antagonism between resin acid and steroid, and that the effect involves the hormonal system of the insect.

[10] Isolated from *Pinus resinosa* needles[11].

[11] D. F. ZINKEL and W. B. CLARKE, unpublished.

## Formation of Monoanion Radicals in Reactions of Vitamin $K_3$ with Sodium Sulphite

W. H. KALUS and W. G. FILBY

*Bundesforschungsanstalt für Ernährung, Institut für Strahlentechnologie, Engesserstrasse 20, D–75 Karlsruhe 1 (Federal Republic of Germany); and Institut für Radiochemie, Kernforschungszentrum, D–75 Karlsruhe (Federal Republic of Germany), 10 May 1976.*

*Summary.* It is shown that the reaction between vitamin $K_3$ and sodium sulphite under physiological conditions leads to the formation of free radical intermediates.

Much attention has been paid to sulphite and its organic addition compounds as they accumulate in foodstuffs[1–3]. Although there are many observations on biochemical alterations induced by sulphite, its role in biological systems is still subject to controversial interpretation[4]. Vitamin $K_3$ (menadione; 2-methyl-1,4-naphthoquinone) (**1**) has recently been shown to inhibit the microsomal lipid peroxidation and the iron-catalyzed lipid peroxidation of the liver cells[5,6]. It has also been shown that **1** reacts with sulphite to form a water-soluble bisulphite addition compound **2**, whose medicinal effectiveness presumably results from regeneration of the vitamin in basic intestinal fluid via elimination of sulphite[7]. So far no information is available describing these mechanisms. We have found that the attack of sulphite on **1** under physiological conditions (pH 7–8) produces free radicals which