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# Terpenoids from bark beetles, solitary bees and danaine butterflies

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Abstract: Oxygenated monoterpenes as well as tetrahydrofuranes and tetrahydropyranes showing terpenoid skeletons are identified as bark beetle pheromones. Mandibular gland secretions of female Nomada bees represent mixtures of sesqui- and norsesquiterpenoid ketones. Androconial organs of certain Danaine butterflies contain oxygenated monoterpenes and bicyclic bisnor- sesquiterpenes of the edulan type.

Besides optical, acoustical and tactile stimuli, living organisms use chemical stimuli for the transmission of informations. Chemotaxis is a widespread ancient principle and microorganisms as well as primates are capable of releasing intraspecific and interspecific chemical signals.

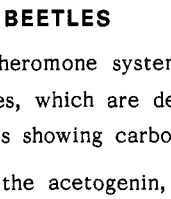
Striking similarities are found in molecular structures of compounds which are used for chemical communication. This may indicate similar biogenetic path-ways or common roots and points to more general concepts in the evolution of "chemical languages". The variability of biologically active structures does not appear to be unlimited, and communication systems seem to be established according to basic principles which follow distinct rules.

Besides unbranched acetogenins, terpenes are particularly widespread, forming a class of highly important chemical messengers. Though some of them are quite obviously derived from host compounds, others may well be synthesized "de novo" by the insects. Some new results in the identification of terpenes from insects will be given below.

## I. BARK BEETLES

The majority of pheromone systems of bark beetles attacking coniferous trees represent blends of oxygenated terpenes, which are derived from resin constituents (ref. 1,2). Some species additionally use bicyclic acetals showing carbon skeletons of terpenoids or acetogenins.

Besides traces of the acetogenin, chalcogran (**1**), a pheromone component of Pityogenes chalcographus (ref. 3), males of the related species, P. quadridens, produce 7-methyl-3-methylen-6-octen-1-ol (**2**), relatively large amounts of (E)-3,3-dimethylcyclohexylidenethanol (**3**) and grandisol (**4**). The ter-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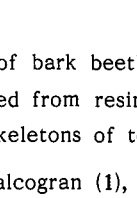

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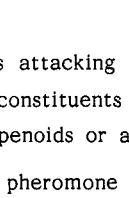

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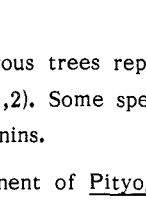
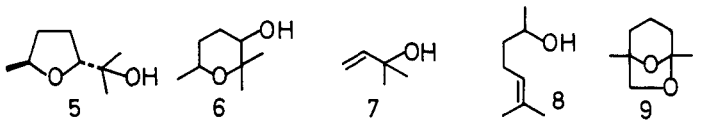


4

penes **2** and (+)-grandisol† are also present in P. calcaratus. Grandisol and (Z)-**3** are pheromone components of males of the bollweevil, Anthonomus grandis (ref. 4), while grandisol and the respective aldehyde, grandisal, have been identified as pheromones of Pissodes weevils (ref. 5). The open chain terpene **2** may well represent a link in the biosyntheses of the cyclohexane **3** and the cyclobutane **4**.

In addition to grandisol, the spruce bark beetle, Pityophthorus pityographus, uses the isoprenoid (2R, 5S)-2-(1-hydroxy-1-methylethyl)-5-methyltetrahydrofuran (**5**) as component of a male secreted aggregation pheromone (ref. 9). Along with the isoprenoid, 2-hydroxy-2-methyl-3-butene (**6**) which is known as an essential component in the pheromone systems of both Ips typographus (ref. 10) and Orthotomicus erosus (ref. 11) the elm bark beetle, Pteleobius vittatus uses (2R*, 5R*)-2-(1-hydroxy-1-methyl-ethyl)-5-methyltetrahydrofuran (**7**) and the isomeric (3R*, 6S*)-3-hydroxy-2,2,6-trimethyltetrahydropyrane (**8**) as part of the aggregation pheromone. A ternary mixture containing **6**, racemic **7** and (-)-**8** (ref. 12) proved to be highly attractive in the field (ref. 13). Structure relations between **5**, **7** and **8**, which represent desvinyl-linalooloxides, and other bark beetle pheromones such as sulcatol (**9**) (ref. 14) and frontalin (**10**) (ref. 15) are obvious. Sulcatol and the respective ketone have been also identified from ants, butterflies and plant material.

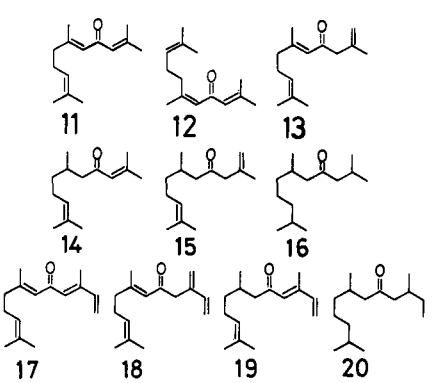



5 6 7 8 9

## II. SOLITARY BEES

Cleptoparasitic nomadine bees (Anthophoridae) are commonly named " cuckoo bee ", for their habits of ovipositing in the nest cells of their host bees. Nomadines use to parasitize host cells while the nest cell is beeing provisioned by the female host bee. Typical aspects of Nomada behaviour includes inspection on elevated points close to the host nest, wingfanning during stealthy nest entrance and orientation flights at departure (ref. 16). The presence of identical compounds both in cephalic secretions of male Nomada bees and in the Dufour gland secretions of female host bees, Melitta spp. (ref. 17) and Andrena spp. (ref. 18) gave rise to speculations on the ecological impact of such coincidences.

During intraspecific and interspecific competition females of many Nomada spp. secret a particularly pleasent smell from their cephalic glands, which can be easily perceived by the human's nose. We now identified **10** sesquiterpenoids, present in minute amounts, in 12 different Nomada spp. Dissolved in mixtures of hydrocarbons the intensely smelling ketons **11** - **20** form species specific unstable blends which are shown in the table. With the exception of 2-methylpseudodamascone (**11**)



11 12 13 14 15 16 17 18 19 20

| Nomada sp. | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|---|---|---|---|---|---|---|---|---|---|---|
| N. alboguttata | X | | | | | | | | | |
| N. bifida | | X | | X | | | | | ? | |
| N. flavoguttata | X | X | | X | X | | | | | |
| N. flavopicta | | | | X | X | | | | | |
| N. goodeniana | | | | X | | | | | | |
| N. hillana | ? | X | | X | | | | X | X | ? |
| N. lathburiana | X | X | X | X | | X | | | X | |
| N. lineola | X | X | | X | | | X | | X | |
| N. maculata | | X | | X | ? | | | | X | |
| N. marshamella | X | X | | X | ? | | | | X | |
| N. rufipes | | | | | | | X | | X | |
| N. similis | | | | | | | | | X | |

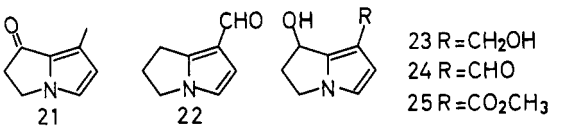
†We thank Prof. W.A. König for gaschromatographic separation of the enantiomers of grandisol (refs. 6,7) and Prof. K. Mori, Tokyo, who kindly supplied optically pure grandisol (ref. 8).

(ref. 19), to our knowledge the compounds have not been described previously. They represent derivatives of farnesenes and nor-farnesenes which could be synthesized starting from respective monoterpenes. The absolute configurations of chiral natural products remains unknown. For the most common Nomada-sesquiterpene, 3,7,11-trimethyl-1,3,10-dodecatrien-4-one (**19**) we like to suggest the trivial name "nomadone".

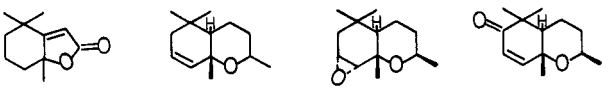
## III. DANAINE BUTTERFLIES

Danainae are tropical butterflies known for their complex pheromone biology (ref. 20). The male scent-producing organs (androconia) consist of abdominal hairbrushes ("hairpencils") and alar- or patch-like glands. Males and females are known to accumulate pyrrolizidine alkaloids from plants. The males metabolize these in parts to volatile dihydropyrrolizines (**21** - **25**), some of which may play a specific role in courtship behavior (ref. 21 - 25).

Besides alkaloids some monoterpenes like (E)-3,7-dimethyl-2-octen-1,8-diol (**26**) or the bishomoterpene (E,E)-3,7-dimethyl-2,6-decadien-1,10-diol (**27**) and corresponding higher oxidized compounds have been identified earlier from Danaus chrysippus and D. plexippus (refs. 26, 27). Since no physiological activity of these compounds could be observed, they were regarded as part of a "cosmetic formulation for the highly active alkaloids. Recently we found similar compounds showing a linalool pattern like 2,6-dimethyl-7-octen-1,6-diol (**28**) in D. genutia while in Euploea sylvester the bishomoterpene, (E)-4,8-dimethyl-4,9-decadien-1,8-diol (**29**) occurs along with the corresponding aldehyde and carboxylic acid (ref. 25). In addition, several degradation products of carotenoids such as oxoisophorone (**30**) and the hydrogenated diketone as well as the corresponding hydroxycyclohexenones could be shown to be present in Amauris echeria and E. sylvester respectively.




21 22 26 27 28 29



31 34 35 36

Derivatives of ionone seem to be common to many Danainae: Dihydroactinidiolide (**31**) could be identified from Idea iasonia, while Euploea klugii contains ß-cyclocitral (**32**), ß-ionone (**33**) and two isomers of cis-dihydroedulan (**34**). The main component in E. klugii could be identified to be (1S*, 3R*, 6S*, 9S*, 10R*)-9,10-epoxy-1,3,7,7-tetramethyl-2-oxabicyclo[4.4.0] decane (**35**) which occurs in other Euploea species, too (ref. 28) as well as in Amauris hecate. In the course of our studies on D. plexippus we came across another edulan derivative, 1,3,7,7-tetramethyl-2-oxabicyclo [ 4.4.0 ] 9-decen-8-one (**36**), the structure of which had already been deduced from spectroscopical data by Bellas et al (ref. 29). We now synthesized the compound and established the natural product to show (1R*, 3R*, 6S*)-configuration. Work is in progress to determine the absolute configurations of the new edulan derivatives as a basis for further bioassays.

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