

SEMIOCHEMICALS FROM BARK BEETLES: NEW RESULTS, REMARKS, AND REFLECTIONS

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Abstract—A brief survey is given about recent results in the identification of semiochemicals in bark beetles: Males of *Ips sexdentatus* (Boern.), stressed by the attack on resinous trees produce large amounts of (3*S*)-1-methyl-5-(1-hydroxy-1-methylethyl)-cyclohexa-1,3-diene. The compound appears to be derived from Δ^1 -carene and acts as a repellent. Males of *Ips typographus* (L.), stressed through the attack on unsuitable host material release 3-methyl-7-methylene-1,3(*E*), 8-nonatriene, which seems to act as a repellent. The odor bouquet of three species of *Pityogenes* is described. The occurrence of (+)-grandisol and other compounds related to weevil pheromones points to a close relation between Scolytidae and Curculionidae. Females of *Dendroctonus simplex* (Le Conte) use (–)-frontalin as the main pheromone. 6-Methyl-6-hepten-2-one, a minor component among the volatile compounds released by the females, is regarded as a possible precursor of frontalin. Similarly, (2*R*,5*S*)-2-(1-hydroxy-1-methylethyl)-5-methyltetrahydrofuran, pityol, a pheromone of *Pityophthorus* spp., is regarded to at least share a common biogenetic precursor with 6-methyl-5-hepten-2-ol, sulcatol. A new bicyclic acetal, 2-ethyl-1,5-dimethyl-6,8-dioxabicyclo[3.2.1]octane, is described as an aggregation pheromone of the beech bark beetle, *Taphrorychus bicolor* (Herbst). Structural relationships between bark beetle pheromones and plant volatiles are discussed.

Key Words—Bark beetle, identification, pheromone, *Dendroctonus*, *Ips*, *Pityogenes*, *Pityophthorus*, *Taphrorychus*.

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INTRODUCTION

As compared to Lepidoptera, chemical communication in bark beetles appears to be much more complex. While host odors play a major role in host selection, the beetles use so-called aggregation pheromones (Vité and Francke, 1976) to mass attack selected trees. These chemical messages are produced by the habitat-selecting sex (in most polygamous species the males) to attract both males and females. In some species, however, the signals also show certain characters of sex pheromones since the opposite sex is attracted in higher numbers. When females select the host, as in many monogamous species, the arriving males may contribute in a "dialogue" by producing signals that balance the sex ratio or which repel other individuals. Mass attack actually is the outcome of an intriguing system of intra- and intersexual communication, which in many respects appears to be more closely related to communication among social insects than to the sex pheromone systems of moths. The pheromone biology and chemical ecology of bark beetles have been extensively reviewed (D.L. Wood, 1982; Borden, 1989; Byers, 1989; Vité and Baader, 1990); syntheses of pheromones have been carefully compiled by Mori (1992).

While many chemical compounds have been identified from bark beetles, only a few proved to be truly behavior mediating. With the exception of the structures of *Scolytus* pheromones, which seem to be polyketids made up by propanoate units, bark beetle pheromones are represented by either mevalogenins (terpenoid carbon skeletons) (Francke and Vité, 1983) or acetogenins (unbranched carbon skeletons). The structures of 21 known, relevant compounds are depicted in Figure 1.

In the present paper, we present our recent results on the identification of behavior mediating compounds from bark beetles. Some new chemical structures will be presented and some (structural/biogenetic) relations will be discussed.

RESULTS AND DISCUSSION

Ips De Geer

Typical pheromones of many *Ips* species are the male-produced ipsdienol (VIII) and ipsenol (X) (Silverstein et al., 1966). While myrcenol (VII) was found to be a synergistic component of the aggregation pheromone of *Ips duplicatus* (Sahlb.) (Byers et al., 1990b), amitinol (IX), a possible rearrangement product of ipsdienol, appeared to be behavior mediating in *I. sexdentatus* (Boern.) (Kohnle et al., 1988). The structures of these compounds suggest a biogenesis from the host terpene, myrcene, as a precursor (Hughes, 1974; Hendry et al., 1980); however, recent results also show that a *de novo* synthesis by the beetles may occur, at least in some species (Ivarsson et al., 1993). While the hemiter-

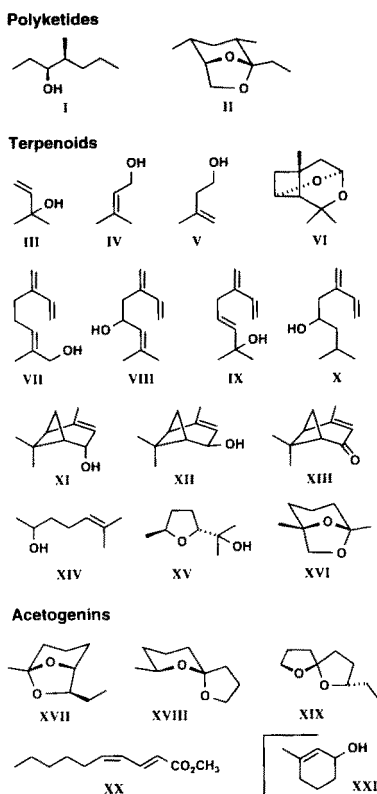


FIG. 1. Chemical structures of known bark beetle pheromones.

ene, 2-methyl-3-buten-2-ol (III), is an important pheromone of *I. typographus* (L.) (Bakke et al., 1977) and *Orthotomicus erosus* (Woll.) (Giesen et al., 1984), its isomers, 4-methyl-3-buten-1-ol (IV) and 3-methyl-3-buten-1-ol (V), are pheromones of the larch bark beetle, *I. cembrae* (Heer) (Stoakley et al., 1978) and *Polygraphus rufipennis* (Kirby), respectively (Bowers et al., 1991). The almost ubiquitous bicyclic terpenol, (*S*)-*cis*-verbenol (XI), is a particularly important compound in *I. typographus*, while its oxidation product, verbenone (XIII), acts as a repellent in many species, including *Dendroctonus*.

Ips sexdentatus (Boern.). Investigations concerning the pheromone system of *Ips sexdentatus* have been carried out earlier (Francke et al., 1986; Kohnle et al., 1988). In continuation of these studies, we analyzed the volatile compounds produced by beetles boring in highly resinous trees. Using a fused silica capillary coated with the polar stationary phase FFAP, pentane extracts of excised

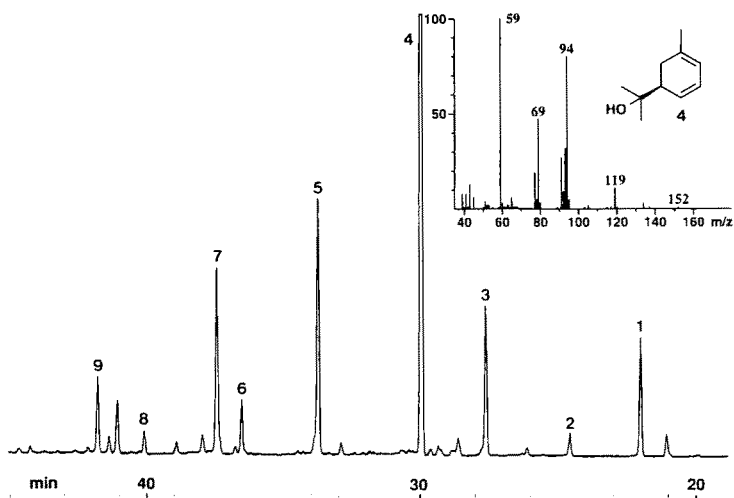


FIG. 2. Gas chromatogram of hindguts of *Ips sexdentatus* males boring in highly resinous pine trees; for conditions see text. Insert: 70-eV EI-MS of (3*S*)-(-)-1-methyl-5-(1-hydroxy-1-methylethyl)-cyclohexa-1,3-diene.

hindguts of males produced the gas chromatogram shown in Figure 2. Structure assignment of peaks was based on GC-MS investigations (a Hewlett-Packard HP 5890 was linked to a double-focusing mass spectrometer, Vacuum Generators VG 70-250SE, 70 eV) and comparison of data obtained with authentic reference samples. A list of identified compounds is shown in Table 1; peak numbers in Figure 2 and numbers in the corresponding table are congruent.

TABLE 1. *Ips sexdentatus*: HINDGUTS OF MALES BORING IN RESINOUS PINE TREE^a

1. Ipsdienone
2. Myrtenal
3. Ipsdienol (60% ee)
4. (3*S*)-(-)-1-Methyl-5-(1-hydroxy-1-methylethyl)-cyclohexa-1,3-diene
5. (+)-Myrtenol (85% ee)
6. *m*-Cymen-8-ol
7. *trans*-Myrtenol
8. β -Phenylethanol
9. 3-Caren-10-ol

^aCompound numbers refer to peak numbers in Figure 2.

The main compound (peak 4) proved to be 1-methyl-5(1-hydroxy-1-methylethyl)-cyclohexa-1,3-diene, a *m*-mentha-4,6-dien-8-ol, which had been described earlier from *Ips* (Renwick et al., 1976) and *Dendroctonus* (Pierce et al., 1987). The compound shows a mass spectrum (see insert in Figure 2), which is indistinguishable from the corresponding *p*-menthadienol, α -phellandren-8-ol, and which can be separated from the latter only by a rather selective column. Such coincidences may cause misinterpretations concerning *m*- and *p*-menthadienes—including our own report (Francke et al., 1986). Actually, the *m*-menthadienol may be much more widespread than is known today. Optically active samples of the compound were prepared according to Gollnick et al. (1966). Using a 30-m FS capillary coated with a 1:1 mixture of 2,6-di-*O*-methyl-3-*O*-pentyl- β -cyclodextrin as the stationary phase, programmed from 80 to 140°C at a rate of 2°C/min, the stereoisomers of the hydrogenated natural product could be separated and compared with synthetic samples. As a result, the *Ips*-volatile proved to show (5*S*)-configuration with an enantiomeric excess (ee) of ca. 99%.

Although the biosynthesis of the compound has not yet been investigated, it is likely that it is produced from 3-carene, since exposure of the beetles to resin with high amounts of 3-carene resulted in the production of high amounts of the (5*S*)-enantiomer of the *m*-mentha-4,6-dien-8-ol.

During field tests, enantiometrically pure samples showed strong repellent effects, which may indicate a function as a warning signal to avoid the attack of healthy (high resinous) trees with a high content of the (poisonous) monoterpene hydrocarbon, 3-carene.

Apart from the (5*S*)-(-)-*m*-mentha-4,6-dien-8-ol, the first compound of this type to show biological activity, its corresponding dehydrogenation product, the aromatic *m*-cymen-8-ol (6), was also found, which, however, did not exhibit behavior-mediating properties.

In the present samples, ipsdienone (1) and ipsdienol (3), which besides myrtenol (5) usually represent major products in the hindguts of successfully boring beetles, were found to be much less abundant. Chiral gas chromatography, using the cyclodextrin phase mentioned above, proved the myrtenol to show (1*S*)-configuration (85% ee), while the ipsdienol was represented by a 4:1 mixture of (-):(+) . The latter result is in contrast to our earlier report (Francke et al., 1986), where we found almost racemic ipsdienol, produced by successfully boring *I. sexdentatus* males.

Ips typographus (L). The chemistry of the pheromone system of *I. typographus* has been described by Bakke et al. (1977). Kohnle et al. (1991) hypothesized that 2-methyl-3-buten-2-ol and (*S*)-*cis*-verbenol play a major role as contact pheromones, while (-)-ipsdienol and (+)-ipenol, two behavior-mediating components that are produced at a later stage of the attack, are frass pheromones.

We were interested in investigating the pheromone production of male beetles under stress and forced them to bore into rather thin, rapidly drying logs of Norway spruce and collected headspace volatiles on charcoal filters by closed loop stripping (Grob and Zürcher, 1976). As a result, the beetles did not release any volatiles known as attractants. A typical gas chromatogram (50-m fused silica capillary coated with FFAP and programmed from 60 to 200°C at a rate of 3°C/min) is shown in Figure 3. The identified compounds are listed in Table 2; the numbers are congruent. Identifications are based on GC-MS and synthetic reference samples (see above). Besides an array of monoterpene hydrocarbons and a few sesquiterpenes known as host constituents, some oxygenated monoterpenes were found. Upon high-resolution GC-MS, a compound eluting between the monoterpene hydrocarbons and the region of oxygenated monoterpenes proved to be a hydrocarbon, $C_{11}H_{16}$. The compound (mass spectrum shown as an insert in Figure 2) could be hydrogenated to $C_{11}H_{24}$, which suggested an open chain. The base peak m/z 81 pointed to the methylene-homologue of m/z

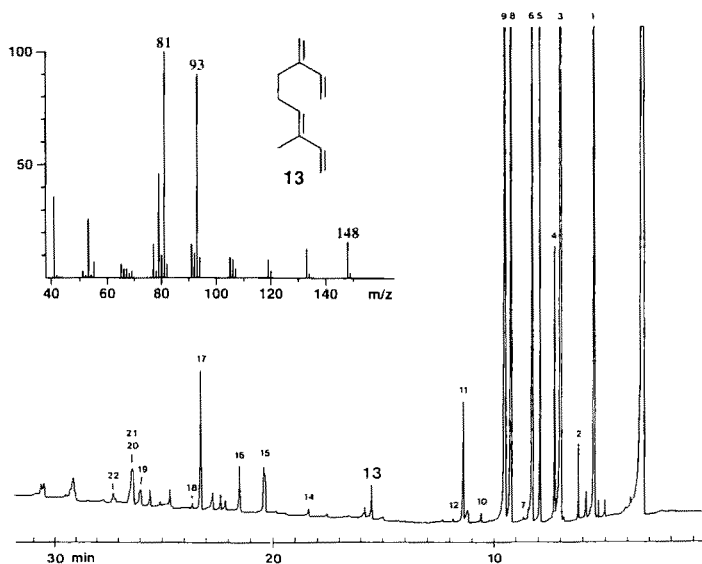


FIG. 3. Gas chromatogram of headspace volatiles collected from *Ips typographus* males boring in Norway spruce; for conditions see text. Insert: 70-eV EI-MS of 3-methyl-7-methylene-1,3(E),8-nonatriene. NMR data of this compound obtained with a Bruker AMX 400 are as follows: 1H NMR (400 MHz, $CDCl_3$) δ = 1.85 (s, 3H); 3.03 (d, J = 7 Hz, 2H); 4.90 (s, 2H); 5.03 (s, 1H); 5.08 (s, 1H); 5.10 (d, J = 10.8 Hz, 1H); 5.24 (d, J = 18 Hz, 1H); 5.72 (td, J = 16 Hz, J = 7 Hz, 1H); 6.20 (d, J = 16 Hz, 1H); 6.43 (dd, J = 18 Hz, J = 10.8 Hz, 1H).

TABLE 2. VOLATILE COMPOUNDS IDENTIFIED FROM HEADSPACE COLLECTIONS OF *Ips typographus* MALES UNDER STRESS CONDITIONS^a

-
1. α -Pinene
 2. Camphene
 3. β -Pinene
 4. Verbenene
 5. Δ^3 -carene
 6. Myrcene
 7. α -Terpinene
 8. Limonene
 9. β -Phellandrene
 10. γ -Terpinene
 11. *p*-Cymene
 12. Terpinolene
 13. 3-Methyl-7-methylen-1,3(*E*),8-nonatriene
 14. *trans*-4-Thujanol
 15. Pinocamphone
 16. Isopinocamphone
 17. Longifolene
 18. Bomyl acetate
 19. *trans*-Pinocarveol
 20. Methylchavicol
 21. Humulene
 22. α -Terpinyl acetate
-

^aCompound numbers refer to peak numbers in Figure 3.

69, which is characteristic for the typical dimethyl allyl terminus of open chain terpenes. In fact, the natural product proved to be 3-methyl-7-methylene-1,3(*E*),8-nonatriene (13), which could be easily synthesized from myrcenal (Büchi and Wuest, 1967) by Wittig reaction with triphenylmethylene phosphorane.

The carbon skeleton of the new homoterpene is the same as in the homocimene, 3,7-dimethyl-1,3,6-nonatriene, identified from army ants (Keegans et al., 1993), and resembles that of juvenile hormones. A possible biosynthesis suggests homomevalonate to be involved.

Preliminary laboratory bioassays showed a repellent effect of 3-methyl-7-methylene-1,3(*E*),8-nonatriene, indicating a possible function as a warning signal to avoid unsuitable host material.

Pityogenes Bedell/*Pityophthorus* Eichhoff

Little is known about the pheromone systems in these two genera, since only two species, *Pityogenes chalcographus* (L.) and *Pityophthorus pityographus* (Ratz.) have been investigated so far.

The acetogenin, chalcogran (XIX), has been identified as the principal pheromone component produced by male *Pityogenes chalcographus* (Francke et al., 1977) synergized by methyl (*E,Z*)-2,4-decadienoate (XX) (Byers et al., 1990a). The natural spiroacetal shows (2*S*)-configuration (Schurig and Weber, 1984), and the (2*S*,5*S*)-diastereomer proved to be nonattractive (Byers et al., 1989). The structure of chalcogran suggests a formation from five acetate units and loss of one carbon atom: it would not be too surprising if chalcogran and its synergist, the decadienoic acid ester, share a common precursor or if a long-chain unsaturated fatty acid were involved in the biosynthesis. Chalcogran as well as the isomeric spiroacetal, 7-methyl-1,6-dioxaspiro[4.5]decane (XVIII) (see below), are not made up by three propanoate units, as suggested by Vanderwel and Oehlschlager (1987), since such a biosynthesis would yield a compound showing characteristic methyl branching pattern as represented in multistriatin (II).

In a continuation of our earlier investigations, we analyzed the volatiles emitted by males of *P. quadridens* (Hartig), *P. calcaratus* (Eichh.), and *P. bidentatus* (Herbst). Gas chromatograms are shown in Figure 4 and 5A and B; a corresponding list of identified compounds is given in Table 3. Peak attribution was based on GC-MS using synthetic reference samples (see above).

P. quadridens shows an interesting bouquet (Figure 4); while expectedly it contains chalcogran and 1-hexanol, just like *P. chalcographus*, it also exhibits

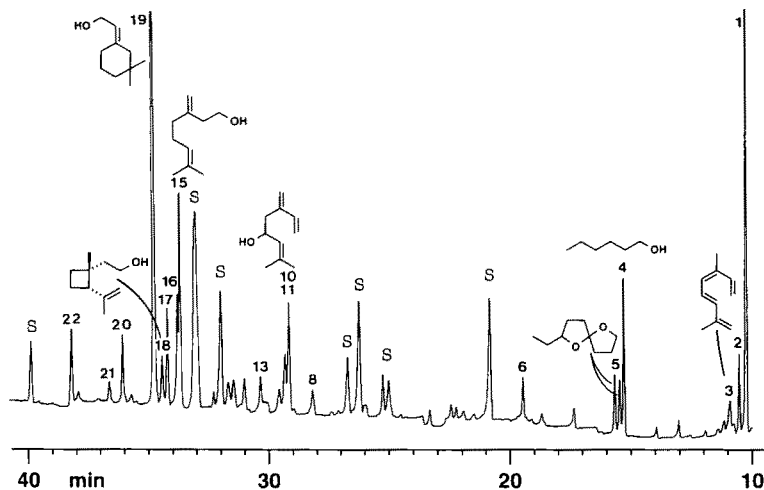


FIG. 4. Gas chromatogram of a pentane extract of *Pityogenes quadridens*; 50-m \times 0.25-m-ID glass capillary, coated with WG 11, programmed from 60 to 200°C at a rate of 3°C/min; S = sesquiterpene.

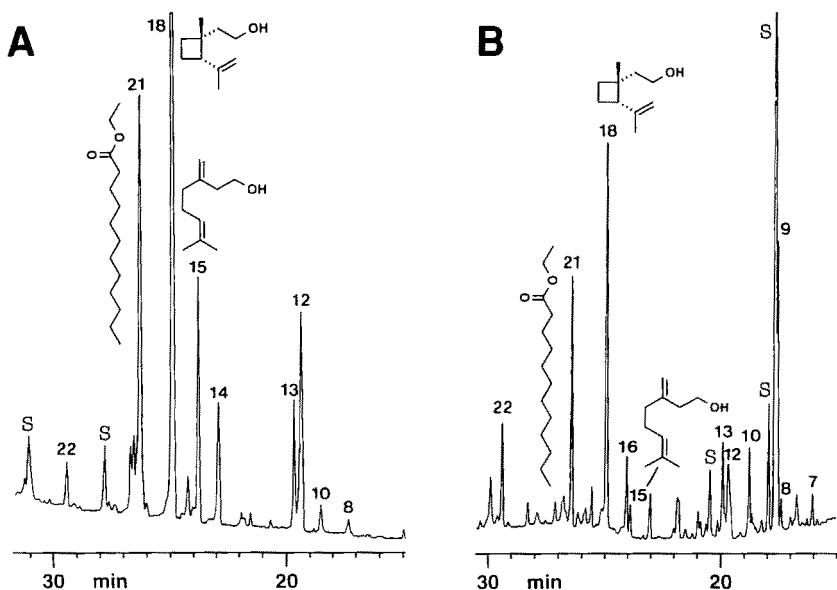


FIG. 5. (A) Gas chromatogram of a pentane extract of *Pityogenes calcaratus*; 50-m \times 0.25-mm-ID fused silica column coated with FFAP and programmed from 60 to 200°C at a rate of 3°C/min; S = sesquiterpene. (B) Gas chromatogram of a pentane extract of *Pityogenes bidentatus*; conditions as in Figure 5A; S = sesquiterpene.

typical features of *Ips* pheromones: ipsdienol—absolute configuration unknown—accompanied by traces of 2-methyl-6-methylene-1,3(*E*),7-octatriene (not listed), a possible elimination product formed from either ipsdienol or amitinol. The dehydroocimenes, 2,6-dimethyl-1,3(*E*),5(*Z*),7-octatetraene (3) and traces of its 5(*E*) isomer were also found.

A particularly surprising set of compounds points to close relationships between Scolytidae and Curculionidae: γ -isogeraniol (15), (*E*)-3,3-dimethyl- $\Delta^{1,\beta}$ -cyclohexaneethanol (19) and grandisol (18)—absolute configurations unknown—could be identified. The *cis*-isomer of 19 and grandisol are pheromone compounds of the boll weevil, *Anthonomus grandis* (Boheman) (Tumlinson et al., 1969).

During bioassays with *P. quadridens*, mixtures of chalcogran (15), (+)-grandisol (18), and 19 proved to be attractive in the field (E. Baader, unpublished). The samples obtained from *P. calcaratus* males were dominated by grandisol (Figure 5A). Enantiomeric separation of its trifluoroacetate on 2,3,6-tri-*O*-pentyl- β -cyclodextrin proved the natural product to be the (+)-enantiomer showing ca. 99% ee. It was accompanied by trace amounts of grandisal. Both

TABLE 3. VOLATILES FROM MALES OF *Pityogenes* SPECIES^a

-
1. Limonene
 2. β -Phellandrene
 3. 2,6-Dimethyl-1,3(*E*), 5(*Z*),7-octatetraene
 4. 1-Hexanol
 5. Chalcogran
 6. 1-Octen-3-ol
 7. Myrtenal
 8. *trans*-Pinocarveol
 9. *cis*-Verbenol
 10. *trans*-Verbenol
 11. Ipsdienol
 12. Borneol
 13. Verbenone
 14. Citronellol
 15. γ -Isogeraniol
 16. Myrtenol
 17. Nerol
 18. Grandisol
 19. (*E*)-3,3-Dimethyl- $\Delta^{1,\beta}$ -cyclohexaneethanol
 20. Geraniol
 21. Ethyl dodecanoate
 22. β -Phenylethanol
-

^aCompound numbers refer to peak numbers in Figure 4 and 5A and B.

grandisal and grandisol have been described as pheromones of pine weevils, *Pissodes* spp. (Booth et al., 1983). (+)-Grandisol and γ -isogeraniol were also identified in males of *P. bidentatus* (Figure 5B). All three *Pityogenes* species discussed so far contained ethyl dodecanoate (22).

With respect to chemical functionalities, structural relations between γ -isogeraniol and grandisol are similar to those between ipsdienol and lineatin (VI), the aggregation pheromone of the ambrosia beetle, *Trypodendron lineatum* (Oliv.) (Borden et al., 1979). Formation of the cyclobutane ring may follow the same biogenetic mechanism.

While γ -isogeraniol was prepared according to Brown et al. (1963), (*E*)-3,3-dimethyl- $\Delta^{1,\beta}$ -cyclohexaneethanol was obtained by reduction of the corresponding aldehyde (Bedoukian and Wolinsky, 1975). Bioassays with *Pityogenes* species using synthetic compounds are not yet finished.

It is interesting to note that (+)-grandisol was also found in *Pityophthorus pityographus* (Ratz.). In this species, the tetrahydrofuran derivative, pityol (XV), represents the most active pheromone component (Francke et al., 1987). The gas chromatogram (FFAP; standard conditions see above) depicted in Figure 6 shows the relative proportions between pityol, grandisol, and inactive com-

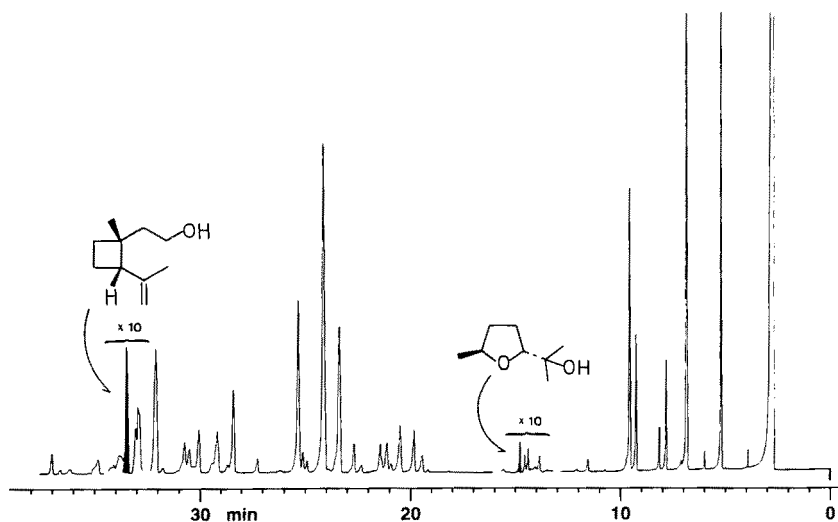


FIG. 6. Gas chromatogram of a pentane extract of *Pityophthorus pityographus*. For conditions see Figure 4.

pounds, which may form a kind of matrix for the active principle. In addition, (2*R*,5*S*)-pityol was identified from some American *Pityophthorus* species and proved to be highly attractive in the field (D. Wood, S. Seybold and W. Francke, unpublished). In pine cone borers, *Conophthorus* spp., the same compound represents a strong female specific attractant (Birgersson et al., 1995).

Although the biosynthesis of pityol is unclear, a degradation of a monoterpene precursor (geraniol or a derivative thereof) is suggested as the initial step, to yield 6-methyl-5-hepten-2-one. Reduction of this ketone would yield sulcatol (XIV), which is known as an aggregation pheromone of the ambrosia beetle, *Gnathotrichus sulcatus* (Le Conte) (Byrne et al., 1974). Enzymatic epoxidation of the double bond of sulcatol by an mfo-system and ring closure would lead to either pityol or vittatol, which had been identified from the elm bark beetle, *Pteleobius vittatus* (F.) (Klimetzek et al., 1989). The stereochemistry of the resulting 2,5-disubstituted tetrahydrofuran would be determined by the stereoselectivity of the reduction step and the stereoselectivity during epoxidation.

The spiroacetal (*E*)-7-methyl-1,6-dioxaspiro[4.5]decane (XVIII), which was first described from common wasps (Francke et al., 1979), could be identified in some *Pityophthorus* spp. (W. Francke, unpublished), in *Conophthorus* spp. (Birgersson et al., 1995), in *Cryphalus piceae* (Ratz.), and in the ash bark beetle, *Leperisinus varius* (F.). In all three species it acts as a male-produced repellent (Birgersson et al., 1995; Kohnle et al., 1992). Using chiral gas chro-

matography (40-m FS capillary coated with 2,3,6-tri-*O*-hexyl- α -cyclodextrin, programmed from 50 to 100°C at a rate of 2°C/min) in some species the natural product could be shown to exhibit (2*S*,5*S*)-configuration, just as in *Paravespula vulgaris* (W. Francke, unpublished). The synthesis of the optically active spiroacetals, used as reference samples and in field tests, followed the procedure described by Jacobsen et al. (1982).

Dendroctonus Erichson

The oxygenated monoterpenes, *trans*-verbenol and verbenone, have been frequently described as behavior-mediating volatiles from *Dendroctonus* spp. The terpenoid, frontalin (XVI) (Kinzer et al., 1969), and the acetogenin, brevicomin (XVII) (Silverstein et al., 1968), play a major role in the communication systems of many species. The compounds are secreted by different sexes and contribute to the above-mentioned dialogue. The isomers of brevicomin are obviously used both with respect to enantiomeric compositions as well as diastereomeric proportions.

In addition to the widespread monoterpenes and bicyclic acetals, 3-methyl-2-cyclohexen-1-one (Kinzer et al., 1971) and its reduction product, 3-methyl-2-cyclohexen-1-ol (XXI) (Vité et al., 1972) as well as 1-methyl-2-cyclohexen-1-ol (Libbey et al., 1983) were specifically found to be pheromones of *D. pseudotsugae* (Hopkins). Although the substituted cyclohexenone might be biosynthesized from a straight-chain precursor (e.g., 2,6-heptanedione or derivative thereof), it appears more likely that it represents a degradation product of a terpene (via a *m*-menthane derivative; see above). The tertiary alcohol may well be a product of an allylic rearrangement of 3-methyl-2-cyclohexen-1-ol, the chemical relations between these two compounds being the same as between ipsdienol and amitinol.

Dendroctonus simplex (*Le Conte*). Besides the usual array of monoterpene and sesquiterpene hydrocarbons and some oxygenated monoterpenes, four female-specific compounds could be identified in *D. simplex*. The gas chromatogram depicted in Figure 7 and Table 4 show identical numbering; identifications are based on GC-MS using synthetic reference samples (see above). The major sex specific compound was identified to be (-)-frontalin (ca. 95% ee as determined by chiral gas chromatography on the above-mentioned 2,3,6-trihexyl- α -cyclodextrin). The pure enantiomer proved to be highly attractive in the field (J.P. Vité, unpublished). In addition to frontalin, three structurally related terpenoid ketones, 6-methyl-6-hepten-2-one, 6-methyl-5-hepten-2-one, and 6-methyl-3(*E*),5-heptadien-2-one, were found. Close biogenetic relations between these ketones and known bicyclic acetals are suggested.

Bicyclic acetals showing a 6,8-dioxabicyclo[3.2.1]octane system represent

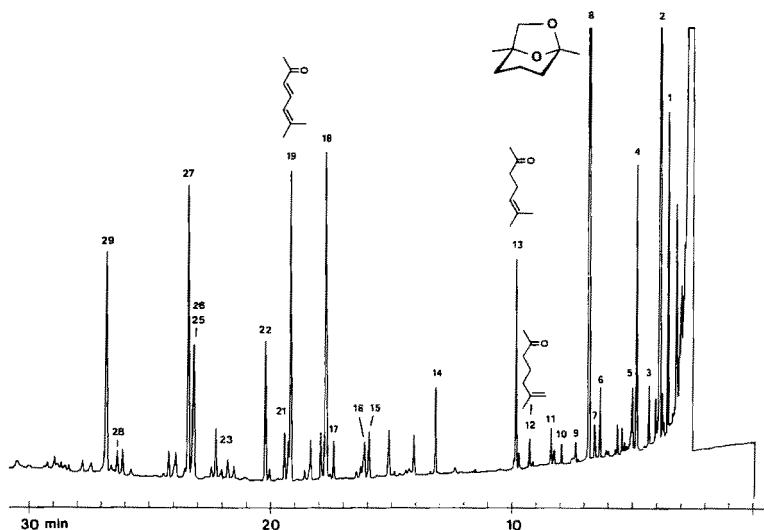


FIG. 7. Gas chromatogram of a pentane extract of *Dendroctonus simplex* males. For conditions see Figure 5.

TABLE 4. VOLATILE COMPOUNDS IDENTIFIED FROM HINDGUTS OF
Dendroctonus simplex FEMALES^a

1. Artifact	16. Pentadecane
2. α -Pinene	17. Linalool
3. Camphene	18. Longifolene
4. β -Pinene	19. 6-Methyl-3,5-heptadien-2-one
5. Sabinene	20. 3-Methyl-2-cyclohexenone ^b
6. Limonene	21. Terpinen-4-ol
7. β -Phellandrene	22. Myrtenal
8. (-)-Frontalin	23. Methylchavicol
9. γ -Terpinene	24. <i>trans</i> -Verbenol ^b
10. <i>p</i> -Cymene	25. Borneol
11. Acetoin	26. α -Terpineol
12. 6-Methyl-6-hepten-2-one	27. Verbenone
13. 6-Methyl-5-hepten-2-one	28. Perillaaldehyde
14. Artifact	29. Myrtenol
15. Camphor	

^aThe compound numbers refer to peak numbers in Figure 7.

^bNot consistently present.

cryptic ketodiols or products of intramolecular cyclizations of epoxy ketones. (*Z*)-6-Nonen-2-one, which besides *exo*-brevicommin had been identified from the ash bark beetle, *Leperisinus varius* (Francke et al., 1979), was postulated as a precursor to form *exo*-brevicommin upon epoxidation and ring closure (Francke, 1981). Recently, careful investigations by Vanderwel et al. (1992) proved this hypothesis to be true for *D. ponderosae* (Hopkins). Reactions similar to those that lead from 6-nonen-2-one to brevicommin would produce frontalin from 6-methyl-6-hepten-2-one (Figure 8). The stereoselectivity of the epoxidation would determine the stereochemistry of the final product.

It should be noted that 6-methyl-5-hepten-2-one is widespread among bees and ants and that epoxidation and ring closure of this ketone (Figure 8) may similarly be involved in the biosynthesis of 1,3,3-trimethyl-2,7-dioxabicyclo[2.2.1]heptane, which has been found in some ant species (Keegans et al., 1993).

Taphrorychus Eichhoff

Our earlier investigations on the pheromone system of the only species investigated so far revealed the presence of large amounts of acetophenone (Kohnle et al., 1987) along with other beetle-specific volatiles. We now wish to give a more complete list of volatile compounds and report on the identification of the male produced aggregation pheromone.

Taphrorychus bicolor (Herbst). The gas chromatogram depicted in Figure 9 and Table 5 show identical numbering; identifications were based on GC-MS using synthetic reference samples (see above). Pentane extracts of frass produced by boring beetles served as substrate. A most interesting mass spectrum was obtained from the male-specific peak 3, which eluted shortly after nonanal. Its EI-MS is shown as an insert in Figure 9. As determined by high-resolution GC-MS, the molecular formula was found to be $C_{10}H_{18}O_2$. The substance could not

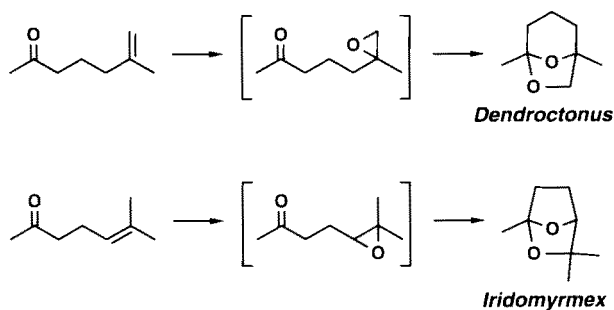


FIG. 8. Possible formation of bicyclic acetals from terpenoid precursors.

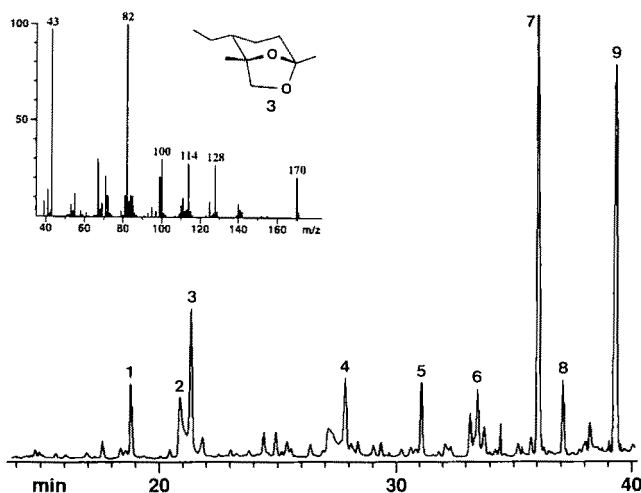


FIG. 9. Gas chromatogram of a pentane extract of frass produced by males of *Taphrotrychus bicolor*. For conditions see Figure 5. Insert: 70-eV EI-MS of 2-ethyl-1,5-dimethyl-6,8-dioxaspiro[3.2.1]octane.

be hydrogenated and did not react with silylation reagents. According to known mass spectrometric fragmentation patterns (Gore et al., 1976), the structure of a bicyclic acetal was suggested. Although initially the intense signal of m/z 82 (C_6H_{10} as determined by high-resolution MS) could not be satisfactorily interpreted, the characteristic fragments at m/z 43 and m/z 128 (M-42) pointed to a substituted 5-methyl-6,8-dioxabicyclo[3.2.1]octane. The 1H NMR spectrum of

TABLE 5. VOLATILE COMPOUNDS IDENTIFIED FROM FRASS PRODUCED BY MALES OF *Taphrotrychus bicolor*^a

1. 1-Hexanol
2. Nonanal
3. (1S, 2R, 5R)-2-Ethyl-1,5-dimethyl-6,8-dioxabicyclo[3.2.1]octane
4. Camphor
5. 1-Octanol
6. Terpinen-4-ol
7. Acetophenone
8. Nonanol
9. Verbenone

^aCompound numbers refer to peak numbers in Figure 9.

a small sample of the natural product obtained by preparative gas chromatography showed two shifted methyl singlets and a methyl triplet as well as two shifted protons in α -positions to oxygen. On the basis of this information, the fragment m/z 82 suggested an ethyl group at position 2 and a second methyl group at position 1. Thus, the compound proved to be 2-ethyl-1,5-dimethyl-6,8-dioxabicyclo[3.2.1]octane, the 2-ethyl bishomolog of frontalin. Using optically active reference samples, chiral gas chromatography (25-m FS capillary coated with 2,6-di-*O*-methyl-3-*O*-pentyl- β -cyclodextrin programmed from 60 to 150°C at a rate of 3°C/min) proved the natural product to show (1*S*,2*R*,3*R*)-configuration.

The compound that we named bicolorin was highly attractive in the field. After brevicomin, frontalin, and multistriatin, which together with (3*S*,4*S*)-4-methyl-3-heptanol (I), plays a major role in pheromone systems of *Scolytus multistriatus* (Marsh.) (Pearce et al., 1975), bicolorin is the fourth substituted 6,8-dioxabicyclo[3.2.1]octane identified as a bark beetle pheromone. Although sharing the same parent system, the four compounds seem to originate from very different precursors. Details on the synthesis of the stereoisomers of bicolorin and results of bioassays will be given in a separate paper.

REMARKS AND REFLECTIONS

Since the identification of the first bark beetle pheromone by Silverstein et al. (1966), a lot has been learned about the chemistry and function of behavior-mediating compounds among the scolytids. Although many of the known intra- and interspecific signals proved to be highly characteristic, a closer look at the chemical structures of the components that make up such chemical messages reveals many compounds that are by no means unique. Only a few of the substances depicted in Figure 1 have not yet been found in a non-bark beetle context. The hemiterpenes III, IV, and V are known from plants and Hymenoptera; and III is the alarm pheromone of European hornets, *Vespa crabro* (Veith et al., 1984). The bicyclic terpenes XI, XII, and XIII are typical constituents of many essential oils and have been known for quite some time. Furthermore, the occurrence of the myrcene derivatives is not restricted to bark beetles. "Ipsdienone," the oxidation product of ipsdienol (VIII) had already been mentioned by Naves (1948; he called it myrcenone) as a constituent of the Verbenacea, *Lippia asperifolia*. Our own analysis of the essential oil of *L. javanica* from South Africa (W. Francke and H. Meyer, unpublished) revealed high proportions of ipsdienone and ocimenone accompanied by small amounts of other monoterpenes including ipsdienol and 6,7-epoxymyrcene. Ipsdienol has also been described as a component of the fragrance of orchids that are pollinated by euglossine bees (Whitten et al., 1988). Amitinol (IX) is a constituent of the

essential oil of *Ledum palustre* (Schantz et al., 1973). Sulcatol (XIV) and the corresponding ketone are particularly widespread among the secretions of animals (including mammals); they are produced by microorganisms as well as by plants. The orchid *Aerides lawrenceae* produces a nice "bark beetle bouquet" by emitting both sulcatol and 2-methyl-3-buten-2-ol (III) (Kaiser, 1993). Although grandisol has not yet been reported from sources other than beetles, its *trans* isomer, fragranol, has been identified from *Artemisia fragrans* (Bohlmann et al., 1973). Methyl (*E,Z*)-2,4-decadienoate (XX), which along with the corresponding ethylester ("pear ester") is known to account for the typical aroma of Bartlett pears, was also found in orchids (Kaiser, 1993). Even the famous bicyclic acetals XVI, XVII, and XIX do not represent "unique beetle chemistry." We found *endo*-brevicommin in the scent of the orchid *Ophrys speculum* (W. Francke and D. Erdmann, unpublished), while 3,4-dehydrobrevicommin proved to be a pheromone of mice (Novotny et al., 1984). Chalcogran (XIX) was identified in flowers of orchids, *Liparis viridifoli*, *Eria hyacinthoides*, and *Oncidium ornithorhynchum*. Along with the isomeric spiroacetal (XVIII) it also occurs in *Dracaena fragrans* (Kaiser, 1993). The latter compound is also widespread among common wasps and was detected both in cork oak and spruce (W. Francke, unpublished). What do *Dendroctonus* and *Elephas* have in common? The "typical" bark beetle pheromone, (1*S*)-frontalin is a constituent of the temporal gland secretion exuded by male Asian elephants, during their musth cycles (Rasmussen et al., 1994). The list of parallels is long and certainly does not exclude polyketides such as the "*Scolytus* pheromones," 4-methyl-3-heptanol (I), which is known from ants, too.

Degradation and elimination of the signal with time and space is a principal feature of pheromones, and one may speculate about the environmental impact on the fate of the bark beetle pheromones once they are released. Oxygenated monoterpenes may undergo acid-catalyzed or UV-induced rearrangements, and in addition their structures may be changed by elimination of water or further oxidation. Verbenone is easily rearranged to chrysantheone and 2,4,4-trimethylbicyclo[3.3.1]hept-2-en-6-one (Hurst and Whitham, 1960). In our own investigations we found that this reaction may take place under the conditions of a sunny warm day. During our irradiation experiments (400 W, Heraeus), isopiperitone as well as (*E*)- and (*Z*)-ocimene were produced. Formation of the acyclic ketones is similar to the conversion of α -pinene to ocimenes as described by Kropp (1969). Although verbenols show a less suitable chromophore, allylic rearrangements to the corresponding bicyclic alcohols and ring-opening to *cis*-isopiperitenol and *cis*-3-methyl-6-(1-methylethenyl)-3-cyclohexen-1-ol follows the same mechanisms as in the case of verbenone. Irradiation of ipsenol and ipsdienol affects the butadiene moiety, yielding 1-substituted cyclobutenes. While 1-(2-hydroxy-4-methyl)-butylcyclobutene is formed from ipsenol, ipsdienol leads to 1-(2-hydroxy-4-methyl)-but-3-enylcyclobutene and

bicyclic alcohols. The composition of the mixture of alcohols formed from these alcohols corresponds to the mixture of hydrocarbons obtained from irradiation of myrcene (Liu and Hammond, 1967 and references cited therein). Interestingly, we identified 1-(2-hydroxy-4-methyl)-but-3-enylcyclobutene as a new natural product in some bark beetle species; however, no bioassays have yet been carried out. It would be interesting to know more about degradation products from (bark beetle) pheromones and to learn something about their (possible) bioactivities.

Some of the known systems of bark beetle pheromones look rather primitive, being made up of simple oxygenated monoterpenes that are indistinguishable from products of autoxidation processes, while other species developed elaborate biosynthetic pathways to produce and use highly sophisticated compounds. This may suggest at least a certain trend in the evolution of bark beetle pheromones. However, with respect to production and use of relevant compounds, there is no correlation between chemical structures of bark beetle pheromones and the position of the corresponding species within the phylogenetic tree, described by Steven Wood (1982). Chemical communication seems to follow higher principles, as is thought today. It makes use of a wealth of chemical compounds that seem to develop specificity through the formation of unique blends that are used in a specific biological context. With respect to bark beetles, we are just starting to learn how chemical ecology works.

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