heated, and an analytical sample was not prepared. The assigned structure was confirmed by comparison of the nmr spectrum (δ (Me_2SO-d_6) 5.20, CH_2) to that of **22**.

4-Cyclohexylsemicarbazide (12). A solution of cyclohexyl isocyanate (11.5 g) in ether (100 ml) was added dropwise to a rapidly stirred solution of 97% hydrazine (5 g) in ether (150 ml) at 0°. After the addition was complete, the mixture was stirred briefly at room temperature, then the white solid **12** was collected by filtration and recrystallized from a 3:1 mixture of benzene and hexane. The yield was 12.2 g (85%), mp 126.5–127.5°. *Anal.* Calcd for $C_7H_{15}N_3O$: C, 53.48; H, 9.62; N, 26.73. Found: C, 53.44; H, 9.56; N, 26.69.

RESULTS AND DISCUSSION

All the compounds in Table I caused complete sterility with at least one concentration, though high mortality accompanied the sterility in several cases. The occurrence of mortality is indicated by footnotes. In all other cases NO refers to no oviposition by live flies. Some compounds were tested at lower concentrations than those shown in Table I but were ineffective at those levels. Of the 33 compounds effective against mixed sexes, only three, **27** (96% sterility at 1% in fly food), **17** (98% sterility at 0.05% in fly food), and **12** (100% sterility at 1% in fly food) were effective male sterilants. Several of the same compounds (**12, 18, 22–24, 27**) have also shown sterilant activity against the screwworm, *Cochliomyia hominivorax* (Coquerel) (Oliver and Crystal, 1972), and **10** was active against the boll weevil, *Anthonomus grandis* Boheman (Oliver *et al.*, 1974a).

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Isolation and Identification of Host Compounds Eliciting Attraction and Bite Stimuli in the Fruit Tree Bark Beetle, *Scolytus mediterraneus*

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The host extracts and their chemical components eliciting attraction and bite stimuli in *Scolytus mediterraneus* were investigated. The ether extract exhibited the highest activity as expressed by the number of holes on a Styropor disk impregnated with the extract. Taxifolin (V), pinocembrin (I), and dihydrokaempferol (III) showed high activity, whereas naringenin (II), quercetin (VI), kaempferol (IV), 5,7-dihydroxy-2-methylchromone (VIII), and scopoletin (VII) exhibited low activity. These compounds may function as primary attractants of the beetle in the field.

Scolytus mediterraneus (Egger) is a bark beetle that attacks and inflicts much damage to deciduous fruit trees in various parts of Israel. The heavy economic loss and the lack of a general applicable means of regulating the beetle population in the field induced us to study host factors affecting the behavioral response of these beetles. The initial attack of the beetle, usually occurring on physiologically damaged trees, is followed by a secondary mass attack which causes severe damage to the tree.

Advanced studies of the behavioral response of bark beetles attacking forest trees have been reported and reviewed by various authors (Pesson and Chararas, 1969; McNew, 1970; Renwick, 1970; Silverstein, 1970; Coster, 1970). Sex pheromones have been extracted and identified from various bark beetles (Pitman *et al.*, 1968; Silverstein *et al.*, 1968; Renwick and Vité, 1968; Kinzer *et al.*, 1969). However, field bioassays indicated that, in general, these pheromones had little or no activity on their own, but their combination with host resins usually induced attraction (Vité and Pitman, 1969a,b). The behavioral patterns of bark beetles and the compounds involved in their attraction vary considerably in different bark beetle species. α-Pinene was found to be the most effective host terpene for *Dendroctonus frontalis* and *D. penderosae* while 3-carene, β-pinene, myrcene, or their mixtures were effective for *D. brevicomis* (Renwick and Vité, 1970).

In contrast, very little is known about the behavioral response of bark beetles attacking deciduous trees. Preliminary studies with *Scolytus mediterraneus* (Gurevitz and Ishaaya, 1972; Ascher and Gurevitz, 1972) showed that host extracts in general elicited attraction and bite stimuli in this species, whereas those from an infested host were the most effective. This study was conducted in order to isolate and identify the active host compounds eliciting attraction and bite stimuli in *Scolytus mediterraneus*.

MATERIALS AND METHODS

Rearing Method and Bioassay. The beetles were reared on plum or apricot twigs as previously described (Gurevitz and Ishaaya, 1972). The bioassay tests were carried out by employing the Styropor method; the number of holes made by the beetles was used as a record for attraction and bite stimuli (Gurevitz and Ishaaya, 1972; Ascher and Gurevitz, 1972).

Isolation and Identification of Compounds. Melting points were made on a Fisher-Johns apparatus and are uncorrected. All uv spectra were taken in methanol solution on a Cary 14 spectrophotometer. Nmr spectra were taken in deuterated Me_2SO solution with TMS as an in-

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ternal standard on the 90-MHz HFX10 Brücker spectrometer.

Infested ground apricot bark (1 kg) was extracted in succession with petroleum ether, ether, and methanol at room temperature. The petroleum ether extract yielded 3.4 g and had no biological activity. The ether extract was concentrated to a syrup, 100 ml of 80% aqueous methanol was added, and the solution was extracted with petroleum ether yielding 0.8 g of a nonactive fraction. An equivolume of water was added to the methanolic solution and exhaustively extracted with ether (5 × 11). The ether layer was collected and dried over anhydrous magnesium sulfate, and on removal of the solvent *in vacuo* a crude residue (10 g) was left which contained all the initial activity.

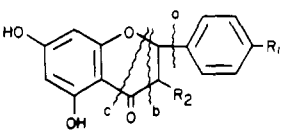
Analysis of the active fraction indicated the presence of phenolic compounds (positive $FeCl_3$ test) which were separated on a polyamide column (Woelm, 250 g) eluting with water and continuing with successive 5% increases of methanol. The initial fractions composed of high R_f nonphenolic compounds were not active. Elution with 30% aqueous methanol gave a compound (80 mg) homogeneous on a tlc polyamide layer irrigated with 95% aqueous methanol (R_f 0.53), fluorescing blue under uv, and recrystallized from methanol as long needles: mp 210–211°; uv λ_{max} 342, 296, 256, and 228 nm indicative of a coumarin system. The structure of scopoletin (VII) was confirmed by analysis of its nmr spectrum: OCH_3 at δ 3.77 (s, 3 H), 4-H at 7.86 (d, J = 10 Hz), 3-H at 6.27 (d, J = 10 Hz), 8-H at 7.18 (s), 5-H at 6.75 (s), and OH at 10.33 (s), disappearing upon exchange with D_2O. The molecular ion peak M^- 192 (100%) in the mass spectrum of compound VII corresponds to the empirical formula $C_{10}H_8O_9$. Fragments at m/e 177 arose from the loss of CH_3 and m/e 164 for loss of CO, and those with m/e 149, 121, and 92 correspond to the consecutive loss of CO, typical of the substituted coumarins (Vulfson *et al.*, 1963).

Aqueous methanol (50%) eluted a solid (52 mg) which was crystallized from methanol, mp 280–281°, and identified as 5,7-dihydroxy-2-methylchromone from the following physical data: uv λ_{max} 334, 304, 262 nm. Addition of $AlCl_3$ showed a bathochromic shift from 334 to 358 nm, indicating the presence of a 5-OH group. The nmr spectrum showed a C-2 vinylic methyl group at δ 2.3 (s, 3 H), 3-H at 6.06 (br s), 6-H at 6.13 (d, J = 2 Hz), 8-H at 6.24 (d, J = 2 Hz). The signals at δ 10.80 and 11.30 disappeared upon exchange with D_2O, indicating the presence of two hydroxyl groups. Mass spectral data showed a molecular ion peak at M^- 192 corresponding to the empirical formula $C_{10}H_8O_4$. The fragment with a m/e 152 arising from the loss of the $CH_3C{\equiv}CH$ (m/e 40) moiety from the molecular ion was the base peak. Also evident were peaks at m/e 124 and 96 corresponding to the successive loss of CO (m/e 28) from the base peak (Vulfson *et al.*, 1963).

Elution with 60% aqueous methanol yielded a mixture of four flavonoids (500 mg): R_f 0.66, 0.50, 0.40, and 0.23 on a tlc polyamide layer irrigated with benzene–butanone–methanol (3:1:1). This mixture was rechromatographed on a polyamide column (Woelm, 13 g) and elution with benzene containing successive 1% increases of methanol yielded pinocembrin (I) (65 mg) recrystallized from 80% aqueous MeOH: mp 195–196°; uv λ_{max} 289, 328 nm (+NaOAc, 258 and 326 nm; +$AlCl_3$, 312 and 378 nm) indicating the presence of a 5-OH group; nmr 2′3′4′5′6′ protons at δ 7.45 (m, 5 H), 6- and 8-H at 5.93 (br s, 2 H), 2-H at 5.5 (d of d, J = 14, 3 Hz) due to coupling with the C-3 methylenic protons centered at δ 3.0.

The mass spectrum of pinocembrin (I), M^- 256 ($C_5H_{12}O_4$), shows fragments with m/e 179, 167, and 152 arising from fragmentation pathways a, b, and c, respectively.

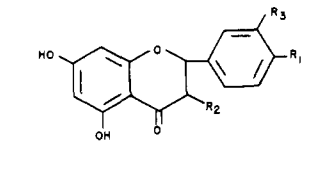
The second compound, naringenin (II) (146 mg), was crystallized from aqueous methanol: mp 242–246°; uv



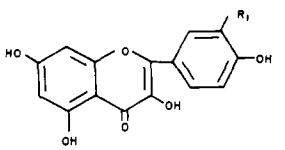
I, R_1=H; R_2=H
II, R_1=OH; R_2=H
III, R_1=R_2=OH

λ_{max} 290, 334 nm (+NaOAc, 287 and 332 nm; +$AlCl_3$, 313 and 381 nm). The nmr spectrum showed signals for the 2′,6′-H at δ 7.4 (d, 2 H, J = 8 Hz), 3′- and 5′-H at 6.8 (d, 2 H, J = 8 Hz), and 6- and 8-H at 5.86 (s, 2 H). The signal at δ 5.39 (d of d, J = 14, 3 Hz) was assigned to the 2-H split by the methylenic protons at C-3. Of the two 3-H protons the equatorial is at δ 2.77 (d, J = 3 Hz), whereas the axial is at δ 3.2 (d, J = 14 Hz). The 5- and 7-OH signals are at δ 12.13 and 10.66, respectively, both disappearing upon exchange with D_2O.

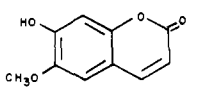
The mass spectrum of compound II showed fragments with m/e 179, 166, and 153 arising from fragmentation pathways a, b, and c. All these data are in good agreement with those reported for substituted γ-pyrones (Budzikiewicz *et al.*, 1964).



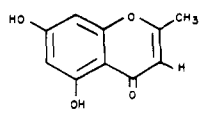
Pinocembrin I, R_1=R_2=R_3=H
Naringenin II, R_1=OH; R_2=R_3=H
Dihydrokaempferol III, R_1=R_2=OH; R_3=H
Taxifolin V, R_1=R_2=R_3=OH



Kaempferol IV, R_1=H
Quercetin VI, R_1=OH



Scopoletin VII



5,7-dihydroxy-2-methylchromone VIII

Dihydrokaempferol (III) was crystallized from aqueous methanol (95 mg): mp 232–234°; uv λ_{max} 292 and 338 nm (+NaOAc 249, 294, and 326 nm; +$AlCl_3$, 272, 317, and 386 nm) indicating the presence of a 5-OH group. The nmr spectrum showed a 2′- and 6′-H at δ 7.33 (d, 2 H, J = 8 Hz), 3′- and 5′-H at 6.8 (d, 2 H, J = 8 Hz), 6- and 8-H at 5.85 (br s, 2 H). The signal centered at δ 5.04 (d, J = 12 Hz) was assigned to the 2-H, while that at δ 4.56 (d of d, J = 12, 6 Hz) was assigned to the 3-H with splitting (J = 6 Hz) arising from its interaction, through space, with the hydroxyl group at C-3. Upon addition of D_2O, the 3-H signal collapsed to a doublet (J = 12 Hz). The three hydroxyl proton signals at δ 9.6, 10.69, and 11.98 disappeared upon exchange with D_2O. The mass spectrum showed the molecular ion M^+ 288 corresponding to the empirical formula ($C_{15}H_{12}O_6$) as well as fragments with m/e 153 (100%) arising through pathway b and m/e 259 (M^+ − CHO) from pathway d.

The fourth compound, taxifolin (V) (50 mg), was crystallized from water, mp 227–229°, and verified with an authenic sample, mmp 226–228°: nmr 2′-H at δ 6.9 (s), 5′- and 6′-H at 6.85 (br s, 2 H), and 6- and 8-H at 5.84 (s, 2 H). The signal at δ 4.9 (d, J = 8 Hz) was assigned to the 2-H while that at 4.4 (d, J = 8 Hz) was assigned to the 3-H.

Further elution from the polyamide column (95% aqueous methanol) yielded kaempferol (IV) (100 mg), mp and mmp 275–276°, identical in all respects with an authentic

Table I. Response of Adult Beetles to Various Concentrations of EE, DBEE, or PEE Extracts[a]

Test no.	Extract	Mean no. of holes per disk: mg per disk 10	2	0.2	0.02	0.002	Mean no. per test ± SE
1	EE	15.5	15.5	14.3			45.3 ± 3.2
2	DBEE	14.4	11.6	15.6			41.6 ± 3.2
3	PEE	5.9	2.7	5.1			13.7 ± 1.5
4	EE			15.9	6.9	2.7	25.5 ± 1.9
5	DBEE			13.6	7.5	4.9	26.0 ± 1.7
6	PEE			4.1	3.8	3.2	11.1 ± 1.2

[a] Forty-five insects were used for each test and ten replicates were made of each treatment; EE, ether extract; DBEE, defatted bark ether extract; PEE, petroleum ether extract.

Table II. Choice Response of Adult Beetles to DBEE and PEE Extracts at Different Concentrations[a]

Test no.	mg of extract per disk	Mean no. of holes per disk: DBEE	PEE
1	0.2	18.6	4.6
2	0.02	12.2	4.8
3	0.002	5.6	2.0

[a] Thirty insects were used for each test and five replicates were made of each treatment; DBEE, defatted bark ether extract; PEE, petroleum ether extract.

sample (Gupta *et al.*, 1957). With 100% methanol small quantities of quercetin (VI) were obtained, mp 312°, and identified by comparison with an authentic sample (Gupta *et al.*, 1957).

RESULTS AND DISCUSSION

Choice Response of *Scolytus mediterraneus* to Ether Extract from Host Bark. In a previous publication (Gurevitz and Ishaaya, 1972) it was shown that *Scolytus mediterraneus* responds positively to various host extracts. Ether extract was the most effective in eliciting attraction and bite stimuli. The relationship between the beetles' response to different concentrations of the total ether (EE), petroleum ether (PEE), and defatted bark ether (DBEE) extracts is summarized in Table I. Each test was carried out in a petri dish containing three disks of Styropor impregnated with the corresponding extract. The DBEE fraction elicited a response similar to the EE extract at both high and low concentrations. On the other hand, the PEE fraction elicited only a weak response. Statistical analysis of the results indicated that the response of the beetles to the DBEE and PEE fractions differed significantly ($P < 0.0001$), at both high and low concentrations. In contrast, no significant difference was found between the EE and the DBEE. The difference between DBEE and PEE extract was further manifested in a choice response test summarized in Table II. In the three concentrations examined (ranging from 0.2 to 0.002 mg of extract per disk), the response to DBEE fraction was far greater than that to the PEE fraction. The difference was most pronounced, reaching fourfold, at a concentration of 0.2 mg of extract per disk. It was therefore concluded that the DBEE fraction contained most of the activity.

Choice Response of the Beetles to the Individual Compounds Isolated from the Defatted Bark Ether Fraction. In the light of this finding the defatted bark ether extract was chromatographed. Eight compounds were isolated, namely, pinocembrin (I), naringenin (II), dihydrokaempferol (III), kaempferol (IV), taxifolin (V), quercetin (VI) (all flavonoids), scopoletin (VII) (a coumarin), and 5,7-dihydroxy-2-methylchromone (VIII) (a chromone). The beetles' response to the purified compounds was determined and the results are summarized in Table III. Flavonoids such as taxifolin (V), pinocembrin (I), and dihydrokaempferol (III) were the most effective compounds, eliciting the highest activity as expressed by the number of holes, ranging between 14 and 17 holes per test. Naringenin (II), quercetin (VI), and kaempferol (IV) were much less effective, eliciting a weak response of 8.3, 7.6, and 5.6 holes per test, respectively. Similar activities were observed for 5,7-dihydroxy-2-methylchromone (VIII) and scopoletin (VII) (see Table III).

Table III. Response of Adult Beetles to Compounds Isolated from the Defatted Bark Ether Extract[a]

Test no.	Compounds	Mean no. of holes per disk: mg per disk 0.2	0.02	0.002	Mean no. per test ± SE
1	Taxifolin (V)	6.9	4.8	3.9	15.6 ± 0.8
2	Pinocembrin (I)	5.3	5.5	6.1	16.9 ± 0.8
3	Dihydrokaempferol (III)	4.5	4.8	4.9	14.2 ± 0.8
4	Naringenin (II)	1.9	4.0	3.4	9.3 ± 0.9
5	Quercetin (VI)	1.0	2.7	3.9	7.6 ± 1.2
6	Kaempferol (IV)	2.1	2.3	1.2	5.6 ± 0.9
7	5,7-Dihydroxy-2-methylchromone (VIII)	2.6	4.2	3.8	10.6 ± 1.1
8	Scopoletin (VII)	2.0	2.1	2.3	6.4 ± 1.1

[a] Forty-five beetles were used for each test and ten replicates were made of each treatment.

Statistical analysis indicates that the response of the beetles to taxifolin (V), pinocembrin (I), and dihydrokaempferol (III) differs significantly from that to all the other compounds ($P < 0.001$); on the other hand, no significant difference was found between the other three flavonoids. These results indicate that at least three host compounds are involved in eliciting attraction and bite stimuli in *Scolytus mediterraneus*.

A recent study (Gurevitz and Ishaaya, 1972) indicated that infested bark gave a stronger response than uninfested bark; this may be due to a joint effect of beetle secretion and host compounds as in the case of the forest bark beetle (Vité and Renwick, 1968). In the light of this fact a further study is needed to determine the contribution of the beetle secretion separately or in combination with the host compounds in producing attraction and bite stimuli in *Scolytus mediterraneus*.

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Synthesis and Morphogenetic Activity of Derivatives and Analogs of Aryl Geranyl Ether Juvenoids

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1-(4′-Ethylphenoxy)-3,7-dimethyl-6,7-epoxy-*trans*-2-octene (the ethyl epoxide juvenoid) and its nonepoxidized intermediate (the ethyldiene) were used to prepare compounds involving 34 modifications of the geranyl moiety including 13 mono- and bicyclic derivatives. Mechanisms are proposed for tetrahydrofurandiol formation on oxidative cyclization of the ethyldiene, ethyl epoxide, and their 6,7-diol derivative. Additional syntheses yielded analogs involving 17 modifications in the aryl moiety. The ethyl epoxide is more active in the *Tenebrio molitor* juvenoid assay than any of its chemical degradation products. Some 7-alkoxide derivatives are more potent than the ethyl epoxide in *Tenebrio* assays but they are less active in the ecdysone-stimulated *Drosophila* imaginal disk evagination assay. High potency in the *Tenebrio* test may depend, in part, on structural features appropriate to enter a pool or combine with a site in the insect where the juvenoid is refractory to degradation.

Several substituted-phenyl epoxy geranyl ether juvenoids are potent morphogenetic agents on a variety of pest insects. One of the most effective compounds of this type in *Tenebrio molitor* pupal assays and *Culex pipiens quinquefasciatus* larval assays is 1-(4′-ethylphenoxy)-3,7-dimethyl-6,7-epoxy-*trans*-2-octene (R 20458 of Stauffer Chemical Co.; the ethyl epoxide) (Jacobson *et al.*, 1972; Pallos and Menn, 1972; Pallos *et al.*, 1971; Walker and Bowers, 1973). Any potential use of this compound or related ones in insect control requires an understanding of their metabolism and environmental degradation. Accordingly, a series of unlabeled degradation products and derivatives was made for use in comparing with radioactive metabolites and photoproducts (Gill *et al.*, 1974; Hammock, 1973; Hammock *et al.*, 1974; Singh, 1973). Several additional reactions were carried out on the degradation products in order to characterize them and to obtain additional compounds for bioassay. Other aryl geranyl ethers are included to examine structure–activity relationships in light of recent findings on the metabolism of juvenoids.

MATERIALS AND METHODS

Chemicals. The ethers examined include 18 variations in the aryl group (**A**–**R**) and 39 modifications in the aliphatic moiety (**1**–**39**). Figure 1 gives the structures for these compounds and their code designations. Some of the compounds are given trivial names which refer to the 4 substituent of the phenyl group and the nature of the geranyl-derived moiety; thus, **1A** is the ethyldiene, **2A** is the ethyl epoxide, **3A** is the ethyl diepoxide, and **17A** is the ethyldiol. The synthesis of each compound is stated briefly in this report and given in detail by Hammock (1973) or Singh (1973).

Chromatography. The conditions for thin-layer chromatography (tlc) and gas–liquid chromatography (glc) are given elsewhere (Gill *et al.*, 1974; Hammock, 1973; Hammock *et al.*, 1974). Column chromatography was used to purify 1–10-g amounts of the ethyldiene, ethyl epoxide, ethyl diepoxide, and ethyldiol used as starting materials in many reactions. For example, dry column chromatography with alumina (activity grade III, Woelm, Eschwege, Germany) gives R_f values of 0.88 for the ethyldiene, 0.40 for the ethyl epoxide, and 0.08 for the ethyl diepoxide on development with carbon tetrachloride. A dry packed column of Florisil (60–100 mesh, Floridin Co., Berkeley Springs, W. Va.) separates the ethyldiene, ethyl epoxide, ethyl diepoxide, and ethyldiol, the first three being eluted in sequence with a hexane–ether gradient and the last compound with an ether–methanol gradient. These compounds are also separated on columns prepared from slurries of Florisil or silicic acid in hexane with development using the solvent gradients indicated above.

Chromogenic Agents, Functional Group Tests, and Spectroscopy. The compounds were detected on silica gel F_{254} tlc plates (EM Laboratories, Inc., Elmsford, N. Y.) by their quenching of gel fluorescence when viewed under short-wavelength uv light (254 mμ) or with one of the following reagents: iodine vapor, molybdophosphoric acid, anisaldehyde, vanillin, and isatin as relatively nonspecific reagents (Stahl, 1969); diazotized benzidine for phenols and lead tetraacetate for vicinal diols (Stahl, 1969); diphenylamine (7% w/v in acetone) followed by exposure to uv for aliphatic chlorides and bromides; 2,6-dibromo-*N*-chloro-*p*-benzoquinone imine for sulfur-containing compounds (Menn *et al.*, 1957); and 4-(*p*-nitrobenzyl)pyridine (2% w/v in acetone) and heat and then tetraethylenepentamine (10% v/v in acetone) for epoxides. This latter reagent which detects 1–10 μg of unhindered epoxides (Hammock, 1973) proved very useful in these studies and in related investigations on pyrethroids (Ueda *et al.*, 1974).

The following functional group tests assisted in charac-

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