by a single, appropriate factor which makes the largest number of those ratios equal to or approximately 1. The results of such a treatment of the European and North American shales and the Russian Platform average are shown in Table 2. The European and North American shale distributions are identical to within \pm 10 percent standard deviation, since more than two-thirds of the normalized ratios are between 0.90 and 1.10. (Only our results were used in this comparison, to eliminate any systematic discrepancies between analysts.)

The Russian Platform average agrees with the European and American shale distributions to within \pm 15 percent standard deviation. The magnitudes of the differences are about what is expected from analytical and sampling errors. We conclude, therefore, that the relative elemental abundances of the rare earths are the same (at least to within 15 percent) for separate, large areas of the continental crust. The absolute rareearth contents of shales are somewhat less well known, since the American. European, and Russian samples vary from 190 to 280 parts per million.

Comparison of the data for the American and European shales with rareearth abundances in 20 chondritic meteorites (12) gives no indication that Eu was selectively retained by any residual material out of which the crust might have been derived.

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Sex Attractants in Frass Produced by Male Ips confusus in Ponderosa Pine

Abstract. The attractant response of Ips confusus to frass produced by male beetles boring in ponderosa pine can be reproduced, in a laboratory bioassay, by a combination of compound I with either compound II or compound III, all isolated from frass. The same response by both sexes was elicited by mixtures of synthesized compounds. Compound I is (-)-2-methyl-6-methylene-7-octen-4-ol; compound II, (+)-cis-verbenol; and compound III, (+)-2-methyl-6-methylene-2,7-octadien-4-ol.

We have isolated and identified three terpene alcohols from the frass produced by male Ips confusus (LeC.) boring in ponderosa pine, which we believe are the principal components of the sex attractant that is responsible for the mass attack following initial boring activity. The compounds, each of which has been synthesized, are shown in Fig. 1.

In the laboratory bioassay, a typical attractant response (1) was elicited by each of two mixtures: 1 µg of compound I with 0.01 μ g of compound II, and 1 μ g of compound I with 1 μ g of compound III. Neither optimum combinations nor minimum levels have been determined. The compounds were inactive singly at these levels: compound I at 100 μ g, compound II at 20 μ g, and compound III at 100 μ g; they were not tested at higher levels.

We have not accounted for all the activity of the total frass extract. Apparently there are a number of other components whose total activity is greater than the sum of their individual activities, but the compounds described in this report appear to be the principal active components. In the laboratory bioassay, insects responded to combinations of these components in the same way that they did to the frass or frass extract. Also, the response to mixtures of synthesized compounds mimicked that obtained from the corresponding mixtures of compounds isolated from frass.

These synergistic effects are striking, and they emphasize the difficulties involved in monitoring fractions and obtaining quantitative estimates of potency by bioassay. An apparently inactive fraction cannot be discarded until it has been tested in combination with other fractions. No masking effects have as yet been encountered in this study.

The compounds were isolated from 4.5 kg of frass produced by male beetles (1). Isolation of compound I and procedural details through the second gas-liquid chromatography fractionation (carbowax column) for the isolation of compounds II and III have been reported (2). The material that was eluted from the carbowax column from 29 to 35 minutes (100 mg) contained compounds II and III; this was chromatographed again under the following conditions: 15 percent TCEP on Chromosorb W; aluminum tubing, 10 feet by 1/4 inch (3 m by 0.6 cm); column temperature, 105°C; detector temperature, 120°C; 54 cm³ of He per minute; on-column injection; retention time 37 to 52 minutes; 19 mg collected.

This fraction contained compound II together with a larger component that was eluted immediately afterward. Compound III was collected from 58 to 73 minutes (56 mg). The 19-mg fraction containing compound II was chromatographed again under these conditions: 10 percent TCEP on Chromosorb W; aluminum tubing, 6 m by 0.6 cm; column temperature, 100°C; detector temperature, 120°C; 40 cm³ of He per minute; retention time 75 to 80 minutes; 11 mg was collected. This step was repeated and 3.5 mg was collected. None of the other columns available separated compound II from the larger component. A final gas-liquid chromatography fractionation was carried out to remove TCEP contamination (column bleed): 8 percent carbowax 20 M on Chromosorb G; glass tubing, 0.9 m by 4 mm (inside diameter); column temperature, 120°C; detector temperature, 135°C; 40 cm³ of He per minute;



Fig. 1. Compounds I, (-)-2-methyl-6-methylene-7-octen-4-ol; II, (+)-cis-verbenol; and III, (+)-2-methyl-6-methylene-2,7-octadien-4-ol.



Fig. 2. Synthesis of compound I.

retention time 13.5 to 16 minutes; 1.5 mg of pure compound II was collected. A small portion (25 μ g) of compound III was chromatographed again for bioassay under the following conditions: 4 percent Ucon polar on Chromosorb G; aluminum tubing, 3 m by 0.3 cm; column temperature, 110°C; detector temperature, 130°C; 7 cm³ of He per minute; retention time 54 to 58 minutes.

Evidence for the identity of compound I has been presented (2).

The mass spectrum of compound II showed the following diagnostic peaks (mass/charge, m/e): 152 (P), 137 $(P-CH_3)$, 134 $(P-H_2O)$, 119 (P-33). The base peak was 43. The infrared spectrum (CCl₄ solvent) showed the following diagnostic peaks (μ) : 2.98 (OH), 6.04 (C=C), 9.65 and 9.90 (C-OH), 7.27 [notched, $C(CH_3)_{2}$]. The nuclear magnetic resonance (NMR) spectrum (CCl₄, τ) was: 4.73 (broadened, =CH), 5.71 (broadened, CHOH), 7.5 to 8.2 (multiplet, four protons), 8.30 (singlet, $=C-CH_3$), 8.68 (singlet, CH_3), 8.77 (singlet, OH), 8.97 (singlet, CH₃). The ultraviolet spectrum (hexane) was: λ 215 m_µ, ϵ 4000; optical rotation (0.1 percent in acetone): $[\alpha]_D^{21} = +4 \pm 3^\circ$, and the melting point was 69°C.

The mass spectrum of compound III showed the following diagnostic peaks: 152 (P), 134 (P-H₂O), 119 (P-CH₃-H₂O), 85 (adjacent to OH, allylic to two double bonds, base peak). The infrared spectrum (film, μ) showed: 3.02 (OH), 6.26 (conjugated C=C), 9.80(C-OH), 10.08 and 11.10 (CH=CH₂). The NMR spectrum (CDCl₃, τ) was 3.63 (=C-CH=CH₂, two pairs), 4.6 to 5.1 (multiplet, five olefinic protons), 5.52 (multiplet, CHOH), 7.61 (apparent doublet, CH₉), 8.30 and 8.34 (each split by small allylic coupling, two CH₃ groups), 8.40 (OH). In acetone (K_2CO_3) added), the OH peak was found as a sharp doublet (J, 5 cy/sec) at 6.75, and the apparent doublet of the CH₂ group became a multiplet. Decoupling (in $CDCl_3$) the proton at 5.52 collapsed the doublet at 7.61 to a singlet and altered the five-proton olefinic pattern. The ultraviolet spectrum (hexane)

was: λ 226 m μ , ϵ 15,000, and the optical rotation (1.0 percent in methanol): $[\alpha]_D^{20} = +10 \pm 0.9^\circ$.

Compound I was synthesized by the sequence shown in Fig. 2. Compound II was synthesized by NaBH₄ reduction of (-)-verbenone, and compound III through the sequence depicted for compound I, with the use of blocked β , β -dimethylacrolein.

The mass, infrared, NMR, and ultraviolet spectra of the synthesized samples were congruent with those of the respective isolated compounds.

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- 3. Infrared spectra were run on a Perkin-Elmer 221 and 137, NMR spectra on a Varian HR 100, ultraviolet spectra on a Cary 14 M, mass spectrum of compound II on a CEC 21-103C at 70 ev, and optical rotation on a Perkin-Elmer 141. The mass spectrum of compound III was run under nonstandard conditions at a microgram level on a modified CEC 21-103C instrument. Gas chromatography was carried out on an Aerograph A90P3. Analytical runs and separation on the 0.3 cm column were done on an Aerograph 204 (stream splitter and flame ionization detector).
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Schizophyllum commune: New Mutations in the B Incompatibility Factor

Abstract. Two new mutations in the B factor of Schizophyllum commune provide additional indications regarding control by the incompatibility factors of mating and sexual morphogenesis in this and other tetrapolar fungi.

Events leading to sexual fertility in the higher Basidiomycetes include reciprocal nuclear exchange and nuclear migration, nuclear pairing, conjugate division, and hook-cell formation and fusion (1). In tetrapolar forms, typified by Schizophyllum commune, this sequence of events is regulated by an incompatibility system composed of two series of factors, A and B, each of which is constituted of two linked loci, A_{α} - A_{β} and B_{α} -B β , with multiple alleles (2). In either series of factors, A or B, each unique combination of specific alleles at the α and β loci determines a distinct factor that is compatible with all others of the series. A homokaryotic strain carries an A factor and a B factor; mating to initiate the entire sequence in a fertile heterokaryon, the dikaryon, occurs only between strains having neither factor in common $(A \neq B \neq)$. Matings between strains having one factor $(A \neq B = \text{ and } A = B \neq)$ or both factors in common (A=B=) lead to the establishment of three distinct infertile heterokaryons. The major characteristics of the four types of heterokaryons, as related to the incompatibility factors, are listed in Table 1.

Mutations in the incompatibility loci were first reported in 1960 in S. commune (3, 4, 5) and Coprinus lagopus (6); 20 such mutations have now been characterized. All are located in the $A\beta$ and $B\beta$ loci, and each results in loss of the factor's normal discriminatory functions of selfrecognition and self-sterility. This loss simulates the presence of two different normal factors of the same series and makes the homokaryon a mimic of the corresponding common-factor heterokaryon. In 1965 another mutation was detected (5), a secondary mutation, $B\beta 2(1-1)$, derived from a primary mutation, $B\beta 2(1)$, found earlier in the $B\beta 2$ allele of S. commune (4). (The first number in parentheses is the code number of a primary mutation; a second number, when present, is the code number for a mutation generated from a primary mutant allele.) This secondary mutation was morphologically normal, was capable of self-recognition, and had a new allelic specificity; it differed, however, from wild-type factors in that

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