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The Action of Boron Trifluoride Etherate on Geraniol — Formation of Di-monoterpene Ether

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The reaction of *d*-limonene with an alcohol, such as methyl, ethyl, butyl or octyl alcohol, in the presence of boron trifluoride etherate, to yield alkyl ether of α-terpineol has already been reported.[2]

In this work, the reaction of geraniol with boron trifluoride etherate at room temperature for 7 days was carried out, and the reaction product was fractionally distilled to obtain four fractions of (1) bp 80—100° (10 mmHg) (*ca.* 1%), (2) 100—110° (*ca.* 16%), (3) 110—160° (*ca.* 59%) and (4) above 160° (*ca.* 24%).

Di-monoterpene ether. Fraction 3, bp 110—160° (10 mmHg), which was obtained in a larger quantity, was found to consist of two components by thin-layer chromatography (TLC) on silica gel and gas chromatographic analysis. These components were isolated as colorless and a little viscous liquid, by passing through a silica gel column using benzene.

Digeranyl ether. In the mass spectrum (Fig. 1), besides the fragment ion peaks at *m/e* 69 (base peak), 123, 137 and 153, the molecular ion peak at *m/e* 290 corresponding to the formula $C_{20}H_{34}O$ are observed. IR ν_{max}^{liq} cm^{-1}: 1662 and 825 ($>C=CH-$), 1100 and 1059 (C–O–C). This spectrum is similar to that of digeranyl ether which was synthesized by Naylor.[3] The nuclear magnetic resonance (NMR) spectrum in deuteriochloroform (Fig. 2) was similar to that of geraniol. This spectrum shows the signals due to methyl groups attached to double bonds ($(CH_3)_2C=C<$, $>C=\overset{|}{C}-CH_3$; at about δ 1.65 ppm), methylene group adjacent to a double bond

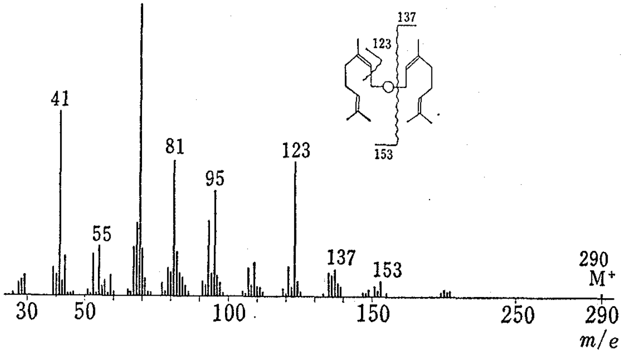

Fig. 1. Mass Spectrum of Digeranyl Ether

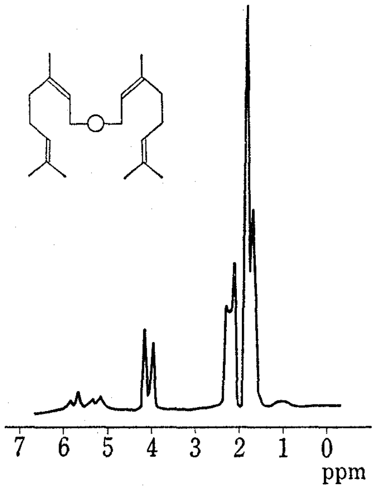

Fig. 2. NMR Spectrum of Digeranyl Ether ($CDCl_3$)

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[1] Location: *No. 1750, Honjo-cho, Fukuyama.*

[2] K. Suga and S. Watanabe, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **81**, **1139** (1960).

[3] R.F. Naylor, *J. Chem. Soc.*, **1947**, 2724.

($>\overset{|}{C}=C-CH_2-$; at δ 2.10 ppm) and to protons on ether oxygen-bearing carbon (doublet, $J=7$ Hz, 4H, $-CH_2-O-CH_2-$; at δ 4.00 ppm). Thus this ether was shown to be digeranyl ether.

Linalyl geranyl ether. The mass spectrum indicates the molecular ion peak at *m/e* 290 corresponding to $C_{20}H_{34}O$. The peaks of *m/e* 69 (base peak), 123, 137 and 153 are also observed in the mass spectrum (Fig. 3). IR $\nu_{\max}^{\text{liq}}$ cm^{-1}: 1670 and 830 ($>C=CH-$), 1000 and 917 ($CH_2=CH-$), 1108 and 1050 (C–O–C). The NMR spectrum in deuteriochloroform (Fig. 4) shows the signals due to a methyl group (singlet, $CH_3-\overset{|}{\underset{|}{C}}-O-$; at δ 1.28 ppm), methyl groups attached to double bonds ($(CH_3)_2C=C<$, $CH_3-C=C<$; at about δ 1.65 ppm), methylene group adjacent to a double bond ($>C=\overset{|}{C}-CH_2$; at δ 2.10 ppm) and to protons on ether oxygen-bearing carbon (doublet, $J=7$ Hz, 2H, $-CH_2-O-C$; at δ 3.82 ppm). Thus this ether was confirmed to be linalyl geranyl ether.

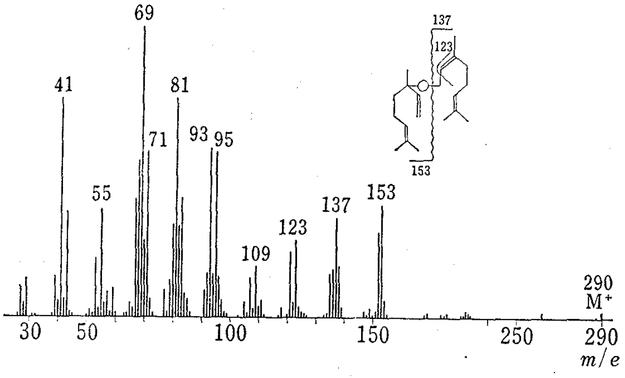


Fig. 3. Mass Spectrum of Linalyl Geranyl Ether

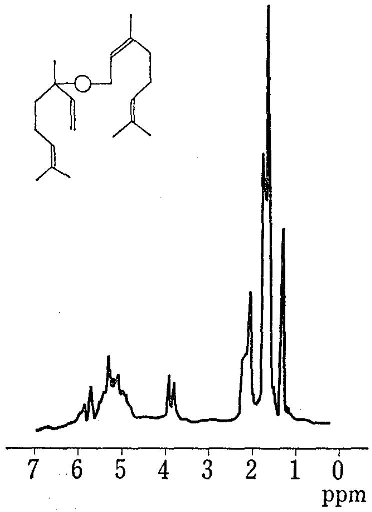
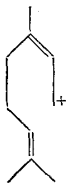
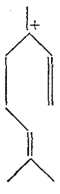


Fig. 4. NMR Spectrum of Linalyl Geranyl Ether ($CDCl_3$)



[I]



[II]

Monoterpene hydrocarbon and alcohol. In the fraction 1, the presence of β-pinene, myrcene, α-terpinene, dipentene, γ-terpinene, β-phellandrene, *p*-cymene and of terpinolene were detected by gas chromatography. Gas chromatography of the fraction 2 shows three peaks which correspond to linalool, α-terpineol and geraniol respectively.

It is presumed that in this reaction geraniol forms the carbonium ions [I] and [II] which react with geraniol to form digeranyl ether (*ca.* 30%) and linalyl geranyl ether (*ca.* 28%). The formation of a large quantity of di-monoterpene ether is noteworthy.

Experimental

Sample——Geraniol was purified by repeated distillation, and exhibited only one peak on gas chromatography with thermol-1 and carbowax 6000. bp 114.8° (4 mmHg), phenylurethane, mp 123.5—124.0°. The infrared (IR) spectrum was identical with an authentic geraniol.[4]

Boron trifluoride etherate used was of commercially available first order (BF_3 47%).

To 10 g of geraniol was added dropwise 0.4 ml of boron trifluoride etherate and the reaction mixture was allowed to stand for 7 days at room temperature (*ca.* 13°). After the addition of 10 ml of ethyl ether, the reaction mixture was washed with a saturated aqueous sodium carbonate solution and water successively, and distilled under nitrogen to give four fractions 1, 2, 3 and 4. Fraction 3, bp 110—160° (10 mmHg), was found to consist of two components by TLC on silica gel using benzene, *Rf* 0.42 and 0.70, and by gas

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4) D. Barnard, L. Bestman, A.J. Harding, H.P. Koch, N. Sheppard and G.B.B.M. Sutherland, *J. Chem. Soc.*, **1950**, 915.

chromatography using SE-30 (T_R 10.3 and 6.2). The two components were isolated from this mixture by column chromatography on silica gel with benzene.

Digeranyl Ether——The component from the first eluate (Rf 0.42 and T_R 10.3) showed n_D^{25} 1.4829, d_4^{25} 0.8728, mol. wt., 290 (mass spectrum), 289 (Rast method). This compound in acetic acid absorbed 4 mole equivalents of hydrogen in the presence of platinum oxide.

Linalyl Geranyl Ether——The component from the second eluate, Rf 0.70 and T_R 6.2, showed n_D^{25} 1.4815, d_4^{25} 0.8805, mol. wt., 290 (mass spectrum), 288 (Rast method). This compound in acetic acid absorbed 4 mole equivalents of hydrogen in the presence of platinum oxide.

Monoterpene Hydrocarbon——The components of the fraction 1, bp 80—100° (10 mmHg), were detected by gas chromatography using carbowax 6000 at 80° and confirmed by addition of authentic specimens. Maleic anhydride was reacted with the fraction 1 for 20 days at room temperature. After the separated crystals were removed by filtration, the remaining oil was gas chromatographed. The peaks assigned to α-terpinene and myrcene disappeared, and the peak assigned to γ-terpinene and β-phellandrene (these showed the same retention value) was reduced.

Linalool——The compound which showed T_R 2.9 on gas chromatography with thermol-1 was isolated by distillation from the fraction 2, bp 100—110° (10 mmHg). The IR spectrum is identical with that of linalool.[4] Phenylurethane, mp 62.5—63.0°, $[\alpha]_D^{25}$ ±0.

α-Terpineol and Geraniol——After elution by n-hexane to separate hydrocarbons, two components (T_R 4.5 and 7.0 on gas chromatography using thermol-1) were isolated by column chromatography on silica gel using ethyl acetate. The IR spectrum of the first eluate (T_R 4.5) is identical with that of α-terpineol.[5] Phenylurethane, mp 112.5—113.0°. The IR spectrum and phenylurethane, mp 123.5—124.0°, of the second eluate (T_R 7.0) are identical with those of geraniol.

Gas Chromatography——A Shimadzu GC-2 apparatus equipped with a thermal conductivity detector was used. For monoterpene hydrocarbon analysis, celite 545 (60—80 mesh) coated with carbowax 6000 (30%) was used at 80°, and for monoterpene alcohol, quartz powder (150—200 mesh) coated with thermol-1 (5%) was used at 100°. Carrier gas, helium; flow rate, 60 ml/min. For di-monoterpene ether, a Hitachi GCF-2 apparatus equipped with a flame ionization detector, and diasolid (60—80 mesh) coated silicon SE-30 (2%) was used at 200°.

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[5] M. Indo, *The Koryo*, 36, 1 (1955).

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Symmetric Neutral Sulfates of Carbohydrates

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Symmetric neutral sulfates of diisopropylidene hexoses were synthesized from structural interest and their behavior to sodium methoxide was tentatively investigated.

Preparation of bis (1,2;5,6-di-O-isopropylidene-D-glucofuranose) 3,3′-sulfate (III) and bis-(1,2;3,4-di-O-isopropylidene-D-galactopyranose) 6,6′-sulfate (VII) was achieved by permanganate oxidation of their sulfite esters, (II) and (VI), respectively, which were obtained from the corresponding diisopropylidene hexoses, (I) and (V), respectively, by reaction of equivalent amount of thionyl chloride in the presence of pyridine. The reaction of thionyl chloride with 2,3:5,6-di-O-isopropylidene-D-mannofuranose (VIII), however, gave low yield of 2,3;5,6-di-

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