The Formation of Ethers from Nerol and *l*-Linalool in the Presence of Boron Trifluoride Etherate

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Upon treatment with boron trifluoride etherate at room temperature, *dl*-linaloyl neryl, *dl*-geranyl linaloyl, *dl*-neryl α-terpenyl, and dineryl ethers were obtained from nerol and linaloyl neryl, *l*-geranyl linaloyl, *dl*-neryl α-terpenyl, and *l*-linaloyl piperityl ethers, from *l*-linalool. Of these ethers, linaloyl piperityl ether was thought to be formed by the cyclization of linaloyl neryl and geranyl linaloyl ethers.

In connection with previous papers on the formation of ethers from geraniol,[1] *d*-borneol, *dl*-isoborneol,[2] and *l*-isopulegol,[3] the action of boron trifluoride etherate ($BF_3 \cdot Et_2O$) on nerol (I) and *l*-linalool (II) was examined in the present work; five ethers were obtained, and their structures were determined to be *dl*-linaloyl neryl (III), *l*-geranyl linaloyl (IV), *dl*-neryl α-terpenyl (V), dineryl (VI), and *l*-linaloyl piperityl (VII) ethers.

To date, several works have been reported on the reaction of I and II with an acidic catalyst, but they have dealt with the characterization of monomeric products; there are no descriptions of higher-boiling products.[4,5]

Results and Discussion

Nerol and *l*-linalool were treated with boron trifluoride etherate under the various conditions listed in Table 1. Each reacted mixture was fractionated into monomeric (bp 60—90 °C/4 mmHg) and dimeric (bp 90—120 °C/4 mmHg) fractions, and the monomeric fraction was further separated by elution chromatography into the two portions of hydrocarbons and the oxygen-containing compounds.

Characterization of Monomeric Products. The monomeric hydrocarbon portions thus separated from reacted mixtures of I and II commonly showed eight peaks in glc, although their relative intensities were different. The components, after being isolated through preparative glc, were identified as myrcene, α-terpinene, dipentene, β-ocimene X,[6] β-ocimene Y,[6] γ-terpinene, *p*-cymene, and terpinolene by mass and IR spectroscopy and by glc admixing authentic samples.

The monomeric oxygen-containing portions from reacted mixtures of I and II were examined by glc and IR, NMR, and mass spectroscopy; linalool, α-terpineol, and geraniol were identified in the case of I other than unreacted alcohol, and *d*-α-terpineol, nerol, and geraniol, in the case of II.

Characterization of Dimeric Products. The dimeric fractions from the reacted mixtures of I and II were eluted over a silica gel column with benzene to separate the individual components. Thus, III, IV, V, and VI were characterized in the case of I, and III, IV, V, and VII, in the case of II, as will be shown below.

dl-*Linaloyl Neryl Ether (III)*: A colorless, oily compound was isolated from dimeric fractions of both I and II as a less polar substance than geranyl linaloyl ether.[1] The molecular formula of this compound was determined to be $C_{20}H_{34}O$, which corresponds to that of terpene ether based on the molecular ion in the mass spectra; the IR spectrum showed characteristic ether bands at 1118, 1098, 1048, and 1039 cm^{-1}, and the NMR spectrum revealed proton signals of five vinylic methyl groups at δ 1.60 (6H), 1.67 (6H), and 1.72 (3H), whose chemical shifts are in good correspondence with those of the isopropyridene of II (δ 1.60, 1.67, each 3H, br. s)[8] and of isopropyridene (δ 1.60, 3H, br. s, δ 1.68, 3H, d, J=1 Hz) and the vinylic methyl signals (δ 1.72, 3H, d, J=1 Hz) of I.[8] The correspondence of the proton signals was also observed between vinylic methyls of geranyl linaloyl ether[1] and its mother alcohols. This evidence suggests that the compound is linaloyl neryl ether.

The ether was subjected to catalytic hydrogenation over an Adams catalyst in acetic acid to give an octahydro derivative, $C_{20}H_{40}O$, which was identified as tetrahydrolinaloyl tetrahydroneryl ether based on the coincidence of the IR and NMR spectra with those of an authentic ether synthesized from *dl*-tetrahydrolinalool and tetrahydronerol (tetrahydrogeraniol) according to Williamson's procedure.[7] Thus, it is certain that the compound was *dl*-linaloyl neryl ether (III).

l-*Geranyl Linaloyl Ether (IV)*: This ether, $C_{20}H_{34}O$, $[\alpha]_D^{18}$ −16.7°, was isolated as a secondary, eluted, colorless, oily compound from dimeric fractions of II. The IR, NMR, and mass spectra were superimposable on those of the geranyl linaloyl ether which had been obtained in the reaction of geraniol with boron trifluoride etherate and whose structure has been proposed.[1] The compound took up four molar equivalents of hydrogen in catalytic hydrogenation over platinum oxide in acetic acid to give an octahydro derivative which was identical with tetrahydrogeranyl tetrahydrolinaloyl ether in glc and spectroscopy. This ether, IV, was also detected as a trace in glc of the reacted mixture from I.

dl-*Neryl α-Terpenyl Ether (V)*: A third colorless, oily ether was isolated from dimeric fractions of I and II as a more polar substance than geranyl linaloyl ether.

The $C_{20}H_{34}O$ ether absorbed three molar equivalents of hydrogen in catalytic hydrogenation over platinum oxide in acetic acid to give a hexahydro derivative, $C_{20}H_{40}O$, which was identified as tetrahydroneryl dihydro-α-terpenyl ether by a comparison of the IR, NMR, and mass spectra with those of an authentic synthesized ether.

The IR and NMR spectra of the ether exhibited the presence of an ether linkage (1162, 1141, 1056, and 1040 cm^{-1}; δ 3.87, 2H, d, J=7 Hz) connecting an allylic methylene and a tertiary carbon, gem-dimethyls

Table 1. Reaction of nerol and *l*-linalool with boron trifluoride etherate

No. of experiment	Nerol[a]			Linalool[a]			
	1	2	3	4	5	6	7
$BF_3 \cdot Et_2O$ (ml)	0.7	0.7	0.7	0.5	0.6	0.7	0.7
Reaction temp. (°C)	20	20	10	30	30	30	20
Reaction period (hr)	24	72	24	30	30	30	24
Conversion (%)[b]	68.0	96.0	31.0	75.0	83.0	87.0	65.0
C_{10}-Hydrocarbons acyclic (%)	0.3	2.0	0.8	0.5	0.9	1.6	1.0
C_{10}-Hydrocarbons cyclic (%)	0.7	5.0		1.5	2.5	4.0	5.0
Geraniol (%)	1.0	2.0	trace	2.0	2.5	1.5	3.0
Nerol (%)	—	—	—	1.0	0.8	0.5	1.0
α-Terpineol (%)	17.0	30.0	1.6	13.0	14.0	14.0	11.0
Linalool (%)	4.0	6.0	0.8	—	—	—	—
Linaloyl neryl ether (%)	6.0	7.0	2.4	3.0	2.2	2.7	3.0
Neryl α-terpenyl ether (%)	8.0	9.0	2.4	4.0	2.4	4.3	1.0
Dineryl ether (%)	6.0	7.0	3.0	—	—	—	—
Geranyl linaloyl ether (%)	trace	trace	trace	16.0	15.9	15.9	10.0
Linaloyl piperityl ether (%)	—	—	—	11.0	11.8	10.5	2.0
Residue (%)	25.0	28.0	20.0	23.0	30.0	32.0	28.0
Total cyclization (%)	25.7	44.0	4.0	29.5	30.7	32.8	19.0

a) Ten grams of the alcohol were used in each experiment. b) Composition of reacted mixtures was determined with the aid of gas chromatography.

on an oxygen-bearing carbon atom (1381 and 1369 cm^{-1}; δ 1.13, 6H, s), four vinylic methyls (1675 and 830 cm^{-1}; δ 1.60, 3H, br. s, δ 1.67, 6H, br. s. and δ 1.72, 3H, d, J=1 Hz), three vinylic protons (δ 5.30, 3H, m), and four allylic methylenes (δ 2.10, 8H, br. s). Moreover, the proton signals of the four vinylic methyls showed a good correspondence with those of a vinylic methyl and an isopropyridene group of nerol and of a vinylic methyl of α-terpineol. Thus, the ether could be characterized as *dl*-neryl α-terpenyl ether (V).

Dineryl Ether (VI): The $C_{20}H_{34}O$ ether, which was isolated as the most polar substance in the elution chromatography of the dimeric fractions from I, took up four molar equivalents of hydrogen in catalytic hydrogenation over platinum oxide in acetic acid to give an octahydroether, $C_{20}H_{42}O$, whose IR, NMR, and mass spectra were superimposable upon those of ditetrahydroneryl ether synthesized from tetrahydronerol.

The IR and NMR spectra of the ether showed the presence of an ether linkage connecting two allylic methylenes (1100, 1068 cm^{-1}; δ 4.03, 4H, d, J=7 Hz), each of which was coupled with a vinylic proton (1672 and 835 cm^{-1}; δ 5.30, 4H, m), and both of isopropyridene and vinylic methyl (δ 1.60, 6H, br. s and δ 1.67, 1.72, each 6H, d, J=1 Hz).[8] The methyl signals of the isopropyridene and vinylic methyl also corresponded to those of nerol. Thus, it is certain that this compound was dineryl ether (VI).

l-*Linaloyl Piperityl Ether (VII)*: The most polar compound, $C_{20}H_{34}O$, $[\alpha]_D^{18}$ −38.3°, which was isolated from the dimeric fraction of II showed absorption bands attributable to an ether linkage at 1148, 1118, 1108, and 1085 cm^{-1} and an *m/e* 137 (14%) ion, $C_{10}H_{17}$, characteristic of the mass spectra of the terpene ethers mentioned above. The compound gave a dihydro derivative, $C_{20}H_{36}O$, in catalytic hydrogenation over platinum oxide in methanol and a saturated hexahydro derivative, $C_{20}H_{40}O$, in catalytic hydrogenation over the same catalyst in acetic acid. The evidence revealed the compound to be a mixed ether of acyclic and monocyclic terpene alcohols.

The NMR spectrum of the compound showed a typical ABX signal attributable to a terminal vinyl group (δ 5.95, q, J_{AX}=18 Hz, J_{BX}=10 Hz; δ 5.15, q, J_{AB}=2 Hz, J_{AX}=18 Hz; δ 4.95, q, J_{AB}=2 Hz, J_{AX}=10 Hz, each 1H), overlapped with signals of other olefinic protons. This signal disappeared in the spectrum of the dihydro derivative, which contained the proton signals attributable to two secondary methyls (δ 1.11 and 1.16, each 3H, d, J=6 Hz), three vinylic methyls (δ 1.60 and 1.68, 6H and 3H, each br. s), two vinylic protons (δ 5.08, 2H, m), two allylic methylenes (δ 2.00, 4H, br. s), an oxygen-bearing methine (δ 3.95, 1H, d, J=7 Hz), and a methyl attached to an oxygen-bearing tertiary carbon (δ 1.10, 3H, s); the signal of the last methyl showed an upper-field shift by 0.18 ppm compared with that of the corresponding methyl group in the original ether (δ 1.28, 3H, s), as well as those of the methyls attached to an oxygen-bearing tertiary carbon in both linalool (δ 1.28, 3H, s) and dihydrolinalool (δ 1.10, 3H, s). On the other hand, the hexahydro derivative of VII was heated with hydroiodic acid and also treated with acetic anhydride and boron trifluoride etherate to give menthyl iodide and menthyl acetate respectively. The evidence certainly indicates that the ether is linaloyl l-*p*-menthenyl ether.

As the position to which the linalooxy residue is attached, three carbons, $C_{(3)}$, $C_{(5)}$, and $C_{(6)}$, of the l-*p*-menthenyl moiety are possible.

As has been mentioned above, both oxygen-bearing

Table 2. Conversion of *dl*-linaloyl neryl ether and *dl*-geranyl linaloyl ether by boron trifluoride etherate

	Linaloyl neryl ether (%)	Geranyl linaloyl ether (%)
Unreacted ether	2.0	6.2
Monoterpene hydrocarbons	33.0	6.8
Linalool	—	8.2
α-Terpineol	20.1	4.7
Nerol	—	trace
Geraniol	—	2.3
Linaloyl piperityl ether	25.0	57.0
Polymer	13.5	10.1
Other compounds	6.4	4.7

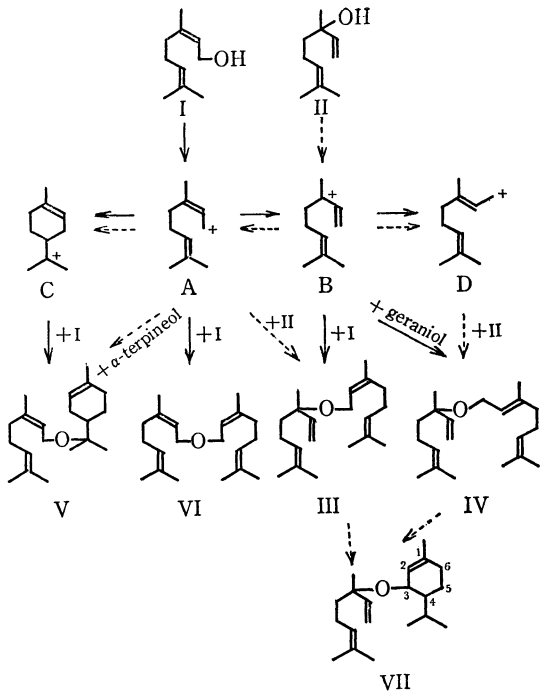
methines of VII and its dihydro derivative commonly showed the doublet at δ 3.95 (J=7 Hz), while the methine group of the hexahydro derivative of VII showed the triplet at δ 3.40. Such an upward shift and change in the signal pattern depending upon the saturation of the 1-*p*-menthene residue picked up the $C_{(3)}$ from the above possible position as the ether-linked position. Thus, the structure of the ether is probably *l*-linaloyl piperityl ether.

The Dreiding model examination of VII, furthermore, showed the following facts: when the isopropyl group holds the pseudoequatorial conformation, the dihedral angle between $C_{(2)}$–H and $C_{(3)}$–H is approximately 80°, and that between $C_{(3)}$–H and $C_{(4)}$–H, 170°; when the isopropyl group holds the axial conformation, they are, respectively, 45° and 75°. On the other hand, the NMR spectra of VII and its dihydro derivative showed a doublet with 7 Hz as the proton signals due to the C_3-methine groups. According to Karplus' equation[9] these results indicate that both $C_{(3)}$–H and $C_{(4)}$–H in the molecule of VII are in the axial conformation. This ether was also obtained by treating III and IV with boron trifluoride etherate, as is shown in Table 2.

The Course of Formation. Under the same conditions (Experiments 1 and 7), although I and II showed a nearly equal conversion, an appreciable difference was observed in the relative yields of the hydrocarbons, alcohols, ethers, and residues (polymers): the yields of the monoterpene alcohols and the ethers were higher in the case of I, whereas the monoterpene hydrocarbons and the residue (polymer) were obtained in higher yields from II (*cf.* Table 1).

All the monoterpene hydrocarbons identified in the present investigation can be explained as being formed by the deprotonation of the carbonium ions listed in Scheme 1, A, B, C, and D, which may be produced from I and II in the presence of boron trifluoride etherate, and the formation of all the monoterpene alcohols is attributable to the coupling of these cations and the hydroxyl anions.

Of the ethers, the III, V, and VI characterized in the reaction of I and the III and IV characterized in the reaction of II may be formed by a combination between these carbonium ions and the mother alcohol, I or II; besides, VII, as has been mentioned above, is



Scheme 1.

attributable to the cyclization of III and IV. Regarding the formation of IV in the reaction of I and that of V in the reaction of II, the contribution of geraniol and α-terpineol, which are produced in large amounts in these reactions, may be supposed.

Experimental

Apparatus. The IR spectra were taken either in liquid film or a CCl_4 solution, and the NMR spectra, on a 60 MHz spectrometer in a $CDCl_3$ solution, using TMS as the internal reference. The mass spectra were measured by means of a Hitachi RMS-4 spectrometer under these operating conditions: 80 eV, ionization-chamber voltage; 80 μA, total emission; 1800 eV, ion-accelerating voltage, and 200 °C, ionization-chamber temperature. The combined glc-mass analyses were carried out on a Shimadzu-LKB 9000 gas chromatograph, and the mass spectrometer, in connection with a 3 mm×3 m glass tube packed with Carbowax 20 M (10%) on Diasolid (60—80 mesh) under a 5 °C/min temperature program from 50 °C to 120 °C; 70 eV, ionization voltage; 3500 eV, ion-accelerating voltage and 200 °C, ionization temperature. The glc was carried out on a FID-type apparatus in connection with stainless-steel column (3 mm×3 m) packed with Carbowax 6000 (10%) on Diasolid (60—80 mesh), DEGS (10%), on Shimalite W (60—80 mesh) and Silicone SE-30 (10%) on Uniport B (60—80 mesh) under the 20 ml/min flow rate of a N_2 carrier.

Materials. Commercial nerol and *l*-linalool were used after repeated fractional distillation. They each showed one peak in glc with DEGS- and Carbowax 6000-packed columns, and the IR spectra of these materials coincided with authentic ones.[10] Nerol: bp 109 °C/10 mmHg, n_D^{20} 1.4630, $[\alpha]_D^{20}\pm0°$ ($CHCl_3$); linalool: bp 70 °C/4 mmHg, n_D^{25} 1.4650, $[\alpha]_D^{16}-19.7°$ ($CHCl_3$), phenylurethane, mp 63—64 °C.

A chemical-grade reagent of $BF_3\cdot Et_2O$ (BF_3 47%) was used without any purification.

Reaction of Nerol (I) and l-Linalool (II) with $BF_3\cdot Et_2O$.

To each 10 g portion of I and II, the amount of $BF_3 \cdot Et_2O$ listed in Table 1 was added, drop by drop. The mixture was then allowed to react under several temperatures for periods from 24 hr to 72 hr. The reacted mixtures were shaken with a saturated aqueous solution of sodium carbonate to decompose the remaining $BF_3 \cdot Et_2O$, washed with water, dried over anhydrous sodium sulfate, and fractionated under reduced pressure to separate two fractions (bp 60—90 °C/4 mmHg and 90—120 °C/4 mmHg).

Characterization of Monoterpene Compounds. Each low-boiling fraction (bp 60—90 °C/4 mmHg) separated from the reacted mixtures of I and II was eluted over a silica gel column with *n*-hexane and then ethyl acetate to separate it further into two hydrocarbon and alcohol portions. The hydrocarbon portions from I and II, both showing eight peaks in glc with a Carbowax 6000-packed column, was gas-chromatographed by admixing them with authentic samples and subjected to combined glc-mass analysis; they were thus identified as myrcene, β-ocimene X, β-ocimene Y, α-terpinene, γ-terpinene, dipentene, *p*-cymene, and terpinolene.[11] The IR spectra of these compounds which were taken after the isolation by preparative glc showed good agreement with those of authentic samples.

The alcohol portions from I and II each showed three peaks other than the peak of unreacted alcohol in glc with DEGS. By comparison with authentic samples through glc, and by taking the IR spectra of isolated individual components, the components were identified as linalool, α-terpineol, and geraniol in the case of I and as α-terpineol, $[\alpha]_D^{20}+31.0°$, nerol, and geraniol in the case of II. α-Terpineol phenylurethane (mp 112—113 °C) and geraniol phenylurethane (mp 123.5—124.0 °C) were also prepared.

Characterization of Dimeric Products from Nerol (I). The high-boiling fractions (bp 90—120 °C/4 mmHg) from reaction mixtures of I showed the existence of four compounds in tlc carried out with silica gel and benzene and in glc with Silicone SE-30- and Carbowax 20M-packed columns at 200 °C. By elution over a silica gel column with benzene, the compounds were isolated.

dl-*Linaloyl Neryl Ether (III).* The compound showing a peak of t_R 8.7 on the SE-30 was isolated as the most quickly-moving colorless, viscous oil in the elution chromatography with benzene. n_D^{17} 1.4714. $[\alpha]_D^{17}\pm0°$ ($CHCl_3$), $C_{20}H_{34}O$ (M^+ 290). $\nu_{max}^{CCl_4}$ cm^{-1}: 3080, 930, 1645 (CH_2=CH–), 1673, 840 (–CH=C–), 1118, 1098, 1048, 1039 (C–O–C). $\delta_{ppm}^{CDCl_3}$: 1.27 (3H, s, $C\underline{H}_3$–C–O), 1.60 (6H, br. s, $C\underline{H}_3$–C=C–), 1.67 (6H, br. s, $C\underline{H}_3$–C=C–), 1.72 (3H, d, J=1 Hz, $C\underline{H}_3$–C=C–), 3.80 (2H, d, J=7 Hz, –C=CH–$C\underline{H}_2$–O–), 4.90—5.97 (5H, m, $C\underline{H}_2$=C$\underline{H}$– and –C$\underline{H}$=C–). Mass: *m/e* 41(80%), 69(base), 71(21), 81(67), 93(36), 95(36), 101(34), 121(11), 123(9), 136(18), 137(21), 153(6), 154(7), 247(2, $M^+-C_3H_7$), 290 (1, M^+, $C_{20}H_{34}O$).

Catalytic Hydrogenation of III: Compound III (200 mg) was hydrogenated over platinum oxide (20 mg) in acetic acid (6 ml) to give an octahydro derivative as a colorless oil in a good yield. $\nu_{max4}^{CCl_4}$ cm^{-1}: 1381, 1366 (CH_3–C$\underline{H}$–CH_3), 1149, 1072 (C–O–C). $\delta_{ppm}^{CDCl_3}$: 0.90 (15H, d, J=6 Hz, $C\underline{H}_3$–CH–), 1.10 (3H, s, $C\underline{H}_3$–C–O–), 3.30 (2H, t, J=6 Hz, –C–O–$C\underline{H}_2$–CH_2–). The spectra were superimposable on those of the tetrahydrolinaloyl tetrahydroneryl ether synthesized in the following section.

Synthesis of Tetrahydrolinaloyl Tetrahydroneryl Ether. Tetrahydronerol (3 g) was dissolved in a mixture of hydrobromic (48%, 10 g) and concentrated sulfuric acids (3 g), and the solution was refluxed for 6 hr. The reacted mixture, after being cooled to room temperature, was successively washed with water, a 10% aqueous solution of sodium bicarbonate, and water, dried over sodium sulfate, and fractionated under ordinary pressure. The tetrahydroneryl (tetrahydrogeranyl) bromide was thus obtained as a colorless oil (bp 222—223 °C) in a yield of 60%. $\nu_{max}^{CCl_4}$ 4 cm^{-1}: 1391, 1374 (CH_3–C$\underline{H}$–CH_3). $\delta_{ppm}^{CDCl_3}$: 0.85 (9H, d, J=6 Hz, $C\underline{H}_3$–CH–), 1.21 (8H, br.s, –$C\underline{H}_2$–), 3.42 (2H, t, J=7 Hz, –CH_2–$C\underline{H}_2$–Br).

dl-Tetrahydrolinalool (1 g) was refluxed with metallic sodium (0.3 g) in dried ether (10 ml) for 18 hr. After the unreacted sodium had been filtered off, the tetrahydroneryl bromide (0.5 g) prepared above was added to the filtrate; the mixture was then refluxed again for 18 hr. The mixture thus reacted was washed with water, dried over anhydrous sodium sulfate, and fractionated under reduced pressure to give tetrahydrolinaloyl tetrahydroneryl ether as a colorless oil in a 10% yield. n_D^{18} 1.4850, $[\alpha]_D^{20}\pm0°$ ($CHCl_3$). ν_{max}^{liq} cm^{-1}: 1381, 1366 (CH_3–C$\underline{H}$–CH_3), 1149, 1072 (C–O–C). $\delta_{ppm}^{CDCl_3}$: 0.89 (15H, d, J=6 Hz, $C\underline{H}_3$–CH–), 1.10 (3H, s, $C\underline{H}_3$–C–O–), 3.30 (2H, t, J=6 Hz, –C–O–$C\underline{H}_2$–CH_2–).

dl-*Neryl α-Terpenyl Ether (V).* The compound, t_R 10.5 on the SE-30, was isolated as a colorless oil by elution chromatography with benzene. n_D^{17} 1.4809, $[\alpha]_D^{20}\pm0°$ ($CHCl_3$), $C_{20}H_{34}O$ (M^+ 290). $\nu_{max}^{CCl_4}$ cm^{-1}: 1381, 1369 (CH_3–C$\underline{H}$–CH_3), 1162, 1141, 1056, 1040 (C–O–C), 1675, 830 (–C=CH–). $\delta_{ppm}^{CDCl_3}$: 1.13 (6H, s, $(C\underline{H}_3)_2$–C–O–), 1.60 (3H, br. s, $C\underline{H}_3$–C=CH–), 1.67 (6H, br. s, $C\underline{H}_3$–C=CH–), 1.72 (3H, d, J=1 Hz, $C\underline{H}_3$–C=CH–), 3.87 (2H, d, J=7 Hz, –C=CH–$C\underline{H}_2$–O–), 5.30 (3H, m, –C$\underline{H}$=C–). Mass: *m/e* 41(53%), 69(68), 81(base), 83(20), 93(27), 95(53), 107(7), 109(4), 117(38), 119(34), 121(14), 136(36), 137(51), 154(9), 272(2, M^+-H_2O), 290 (1, M^+, $C_{20}H_{34}O$).

Catalytic Hydrogenation of V: Compound V (250 mg) was subjected to catalytic hydrogenation over platinum oxide (30 mg) in acetic acid (7 ml) to give a hexahydro derivative as a colorless oil in a good yield. $\nu_{max}^{CCl_4}$ cm^{-1}: 1383, 1368 (CH_3–C$\underline{H}$–CH_3 and CH_3–C–CH_3), 1173, 1150, 1121, 1070 (C–O–C). $\delta_{ppm}^{CDCl_3}$: 0.86 (12H, d, J=6 Hz, $C\underline{H}_3$–CH–), 1.08 (6H, s, $(C\underline{H}_3)_2$–C–O–), 3.31 (2H, t, J=6 Hz, –C–O–$C\underline{H}_2$–CH_2–). Mass: *m/e* 39(5%), 41(22), 43(48), 55(34), 57(80), 59(40), 69(22), 71(78), 81(10), 85(65), 99(17), 123(7), 139(9), 140(7), 141(38), 142(6), 199(base), 211(4), 281(4, M^+-CH_3), 296(2, M^+, $C_{20}H_{40}O$). The spectra were in good agreement with those of the tetrahydroneryl dihydro-α-terpenyl ether to be synthesized in the following section.

Synthesis of Tetrahydroneryl Dihydro-α-terpenyl Ether. Dihydro-α-terpineol (1 g) was refluxed with metallic sodium (0.3 g) in dried ether (10 ml) for 18 hr. After the unreacted sodium had then been filtered off, the tetrahydroneryl bromide (0.5 g) prepared in the above section was added to the filtrate, the mixture being refluxed for 18 hr. The reacted mixture was afterwards treated by a usual procedure to give tetrahydroneryl dihydro-α-terpenyl ether as a colorless oil in a yield of 15%. $\nu_{max}^{CCl_4}$ cm^{-1}: 1382, 1368 (CH_3–C$\underline{H}$–CH_3), 1173, 1150, 1121, 1070 (C–O–C). $\delta_{ppm}^{CDCl_3}$: 0.86 (12H, d, J=6 Hz, $C\underline{H}_3$–CH–$C\underline{H}_3$), 1.08 (6H, s, $(C\underline{H}_3)_2$–C–O–), 3.31 (2H, t, J=6 Hz, –C–O–$C\underline{H}_2$–CH_2–). Mass:

m/e 41(22%). 43(48), 55(34), 57(80), 59(40), 69(22), 71(78), 81(20), 85(65), 123(7), 139(9), 141(38), 199(base), 281(4), 296(2, M^+, $C_{20}H_{40}O$).

Dineryl Ether (VI). The compound, t_R 11.8 on the SE-30, was isolated as the last colorless oil in the elution chromatography of the dimeric fraction of I. n_D^{17} 1.4771; $C_{20}H_{34}O$ (M^+ 290). $\nu_{max}^{CCl_4}$ cm^{-1}: 1672, 835 (-C=CH-), 1100, 1068 (C-O-C). $\delta_{ppm}^{CDCl_3}$: 1.60 (6H, br. s, CH_3-C=CH-), 1.67 and 1.72 (each 6H, d, J=1 Hz, CH_3-C=CH-), 4.03 (4H, d, J=7 Hz, -C=CH-CH_2-O-), 5.30 (4H, m, -CH=C-). Mass: *m/e* 41(96%), 69(base), 81(72), 83(27), 93(49), 95(36), 107(12), 117(45), 119(45), 121(14), 123(13), 135(13), 136(28), 137(21), 154(12), 290(1, M^+, $C_{20}H_{34}O$).

Catalytic Hydrogenation of VI: Compound VI (200 mg) was hydrogenated over a platinum oxide catalyst (20 mg) in acetic acid (6 ml) to give an octahydroether in a good yield. ν_{max}^{liq} cm^{-1}: 1390, 1383, 1371 (CH_3-CH-CH_3), 1119 (C-O-C). $\delta_{max}^{CDCl_3}$: 0.85 (18H, d, J=6 Hz, CH_3-CH-), 3.40 (4H, t, J=6 Hz, -CH_2-CH_2-O-). Mass: *m/e* 39 (19%), 41(62), 43(base), 55(50), 57(52), 69(37), 70(31), 71(30), 83(24), 85(18), 97(15), 140(10), 141(6), 163(6), 298(1, M^+, $C_{20}H_{42}O$). The spectra were superimposable upon those of the ditetrahydroneryl ether to be synthesized in the following section.

Synthesis of Ditetrahydroneryl Ether. Tetrahydroneryl bromide (1 g) was added to a dried ether solution of sodium tetrahydronerolate which had been prepared from tetrahydronerol and metallic sodium, the mixture being refluxed for 18 hr. The ditetrahydroneryl ether was thus obtained as a colorless oil in a 12% yield. ν_{max}^{liq} cm^{-1}: 1390, 1383, 1371 (CH_3-CH-CH_3), 1119 (C-O-C). $\delta_{ppm}^{CDCl_3}$: 0.85 (18H, d, J=6 Hz, CH_3-CH-), 3.40 (4H, t, J=6 Hz, -CH_2-CH_2-O-). Mass: *m/e* 39(19%), 41(62), 43(base), 55(50), 57(52), 69(37), 70(31), 71(30), 83(24), 85(18), 97(15), 140(10), 141(6), 298(1, M^+, $C_{20}H_{42}O$).

Characterization of Dimeric Products from l-Linalool (II). The high-boiling fraction (bp 90—120 °C/4 mmHg) from each reaction product of II showed the existence of four compounds in the tlc carried out with silica gel and benzene and in the glc carried out with the Silicone SE-30- and Carbowax 20 M-packed columns at 200 °C. These compounds were isolated by being eluted over a silica gel column with benzene and were characterized as is shown below.

l-Geranyl Linaloyl Ether (IV). The colorless oil, t_R 9.5, was isolated as the secondary eluted compound from the dimeric fraction of II by silica gel column chromatography with benzene. n_D^{15} 1.4834, $[\alpha]_D^{18}$ −16.7° ($CHCl_3$); $C_{20}H_{34}O$ (M^+ 290, Rast's mol. wt. 293). ν_{max}^{liq} cm^{-1}: 1670, 830 (-C=CH-), 1000, 917 (CH_2=CH-), 1108, 1050 (C-O-C). $\delta_{max}^{CDCl_3}$: 1.28 (3H, s, CH_3-C-O-), 1.60, 1.68 (15H, br. s, CH_3-C=CH-), 3.82 (2H, d, J=6 Hz, -CH_2-O-C-), 4.95—5.95 (6H, m, CH_2=CH- and -CH=C-). Mass: *m/e* 41 (62%), 55(21), 69(base), 81(50), 93(32), 95(29), 109(10), 121(14), 123(17), 137(22), 153(26), 290(2, M^+, $C_{20}H_{34}O$). These spectra were coincident with those of geranyl linaloyl ether.[1)]

Catalytic Hydrogenation of IV: Compound IV (100 mg) was hydrogenated over a platinum oxide catalyst (10 mg) to give an octahydro derivative as a colorless oil in a good yield. ν_{max}^{liq} cm^{-1}: 1381, 1366 (CH_3-CH-CH_3), 1149, 1072 (C-O-C). $\delta_{max}^{CDCl_3}$: 0.90 (15H, d, J=6 Hz, CH_3-CH-), 1.10 (3H, s, CH_3-C-O-), 3.30 (2H, t, J=6 Hz, -C-O-CH_2-CH_2-). These spectra were coincident with those of tetrahydrogeranyl tetrahydrolinaloyl ether synthesized as will be shown below.

Synthesis of dl-*Tetrahydrogeranyl Tetrahydrolinaloyl Ether.* Tetrahydrogeranyl bromide (1.0 g) and sodium *dl*-tetrahydrolinaloolate (1 g) were treated according to the abovementioned procedure to give tetrahydrogeranyl tetrahydrolinaloyl ether in a 10% yield. n_D^{18} 1.4850; $[\alpha]_D^{20}$ ±0° ($CHCl_3$). ν_{max}^{liq} cm^{-1}: 1381, 1366 (CH_3-CH-CH_3), 1149, 1072 (C-O-C). $\delta_{max}^{CDCl_3}$: 0.89 (15H, d, J=6 Hz, CH_3-CH-), 1.10 (3H, s, CH_3-C-O-), 3.30 (2H, t, J=6 Hz, -C-O-CH_2-CH_2-).

l-Linaloyl Piperityl Ether (VII). The compound, t_R 11.2, was isolated as the most slowly-moving component by the elution chromatography of the dimeric fractions of II. n_D^{15} 1.4871; $[\alpha]_D^{18}$ −38.3° ($CHCl_3$), $C_{20}H_{34}O$ (M^+ 290, Rast's mol. wt. 286). ν_{max}^{liq} cm^{-1}: 3080, 1650, 991, 918 (CH_2=CH-), 1680, 835 (-C=CH-), 1388, 1371 (CH_3-CH-CH_3), 1148, 1118, 1108, 1085 (C-O-C). $\delta_{ppm}^{CDCl_3}$: 1.11, 1.16 (each 3H, d, J=6 Hz, CH_3-CH-), 1.28 (3H, s, CH_3-C-O-), 1.60, 1.68 (6H and 3H, each br. s, CH_3-C=CH-), 2.00 (4H, br. s, -CH_2-C=C-), 3.95 (1H, d, J=7 Hz, -O-CH-CH=C-), 4.95 (1H, q, J_{AB}=2 Hz, J_{BX}=10 Hz), 5.15 (1H, q, J_{AB}=2 Hz, J_{AX}=18 Hz), 5.95 (1H, q, J_{AX}=18 Hz, J_{BX}=10 Hz), 5.08 (2H, m, -CH=C-). Mass: *m/e* 41(56%), 43(23), 55(17), 69(base), 71(6), 80(7), 81(34), 93(20), 95(26), 107(12), 109(8), 121(11), 123(31), 137(14, $C_{10}H_{17}$), 275(2, M^+-CH_3), 290(2, M^+, $C_{20}H_{34}O$).

Dihydro Derivative of VII: When VII (150 mg) was submitted to catalytic hydrogenation over platinum oxide (20 mg) in methanol (6 ml), one molar equivalent of hydrogen was taken up. The reacted mixture was treated according to a usual procedure to obtain a dihydro derivative as an oil. ν_{max}^{liq} cm^{-1}: 1660, 835 (-C=CH-), 1385, 1376 (CH_3-CH-CH_3), 1140, 1024 (C-O-C). $\delta_{ppm}^{CDCl_3}$: 0.90 (3H, t, J=6 Hz, CH_3-CH_2-), 1.10 (3H, s, CH_3-C-O-), 1.11, 1.16 (each 3H, d, J=6 Hz, CH_3-CH-), 1.60, 1.68 (6H and 3H, br. s, CH_3-C=CH-), 2.00 (4H, br. s, -CH_2-CH=C-), 3.95 (1H, d, J=7 Hz, -C-O-CH-CH=C-), 5.08 (2H, m, -CH=C-).

Hexahydro Derivative of VII: The dihydro derivative of VII (120 mg) was again submitted to catalytic hydrogenation over platinum oxide (10 mg) in the same methanol solvent (7 ml) at room temperature; the hexahydro derivative was thus obtained. On the other hand, VII (300 mg) was also hydrogenated over platinum oxide (30 mg) by using acetic acid instead of methanol as a solvent at room temperature to give the same hexahydro derivative. ν_{max}^{liq} cm^{-1}: 1384, 1375 (CH_3-CH-CH_3), 1131, 1020 (C-O-C). $\delta_{ppm}^{CDCl_3}$: 0.85 (9H, d, J=6 Hz, CH_3-CH-), 1.11, 1.61 (each 3H, d, J=6 Hz, CH_3-CH-CH_3), 3.40 (1H, t, J=6 Hz, -O-CH-CH_2-), 1.10 (3H, s, CH_3-C-O-). Mass: *m/e* 41(33%), 43(40), 55(48), 69(40), 70(base), 71(43), 81(15), 83(43), 95(18), 97(22), 109(20), 111(19), 123(27), 126(19), 137(14), 139(6),

153(10), 238(28), 267(55, $C_{18}H_{35}O$), 281(16, M^+-CH_3, $C_{19}H_{37}O$), no molecular ion.

Ether Cleavage of the Hexahydro Derivative of VII with Hydroiodic Acid: Hexahydro derivative (200 mg) was refluxed with hydroiodic acid ($d=1.7$, 1 ml) for 10 min. The reaction product extracted from the reacted mixture was eluted over a silica gel column with *n*-hexane to separate a nonhydrocarbon portion as a colorless oil showing a peak at t_R 10.3 in glc with Silicone SE-30; 5% yield. n_D^{20} 1.5088. $\nu_{max}^{CCl_4}$ cm^{-1}: 1389, 1380, 1360, 1171. $\delta_{ppm}^{CDCl_3}$: 0.82, 0.92 (9H, d, $J=6$ Hz, $C\underline{H}_3$-CH-), 4.09 (1H, dt, $J=3$, 10 Hz, $-CH_2-C\underline{H}-I$). Mass: *m/e* 41(50%), 43(45), 55(70), 69(65), 83(base), 95(10), 97(12), 127(3, I^+), 139 (40, $C_{10}H_{19}$), 266 (1, M^+, $C_{10}H_{19}I$). These IR, NMR, and mass spectra were all superimposable on those of menthyl iodide which had been prepared by heating a mixture of menthol (2.0 g), red phosphorus (0.1 g), and resublimed iodide (1.0 g) at 150 °C for 2 hr.

Ether Cleavage of the Hexahydro Derivative of VII with Acetic Anhydride and $BF_3.Et_2O$: Hexahydro derivative (100 mg) was treated with acetic anhydride (0.2 ml) and $BF_3\cdot Et_2O$ (0.02 ml) in dried ether (1 ml) at room temperature for 48 hr. The reaction product separated according to a usual manner was chromatographed over silica gel with *n*-hexane and then a mixture of *n*-hexane and ethyl acetate (95 : 5) to separate an oxygen-containing compound as a colorless oil showing a peak at t_R 5.5 in glc with Silicone SE-30 in a yield of 5%. $\nu_{max}^{CCl_4}$ cm^{-1}: 1735, 1245, 1125 (-CO-OCH_3), 1389, 1371 ($CH_3-CH-CH_3$). $\delta_{ppm}^{CDCl_3}$: 0.80, 0.89 (9H, d, $J=6$ Hz, $C\underline{H}_3$-CH-$C\underline{H}_3$, $C\underline{H}_3$-CH-), 4.70 (1H, dt, $J=4$, 10 Hz, $-C\underline{H}-OCOCH_3$), 2.00 (3H, s, $-OCOC\underline{H}_3$). Mass: *m/e* 41(42%), 43(base), 55(22), 67(18), 81(27), 95(31), 109(5), 123(11), 138(19, M^+-CH_3COOH), 198 (trace, M^+). The IR, NMR, and mass spectra were respectively superimposable on those of a synthetic sample of *l*-menthyl acetate.

Conversion of III and IV by $BF_3\cdot Et_2O$. The III ether (200 mg) was dissolved in dried ether (1 ml) and mixed with 0.02 ml of $BF_3\cdot Et_2O$. On the other hand, IV (300 mg) was dissolved in dried ether (1.5 ml) and mixed with 0.03 ml of $BF_3\cdot Et_2O$. After the two mixtures had been allowed to stand at room temperature for 18 hr, a small amount of water was added to each of the reacted mixture to decompose the excess reagent. The reacted mixtures thus treated were then gaschromatographed on the DEGS separation column to determine their compositions; *cf.* Table 2. In these cases, the characteristics of the monoterpene hydrocarbons were assumed based on the retention times, while the monoterpene alcohols, linalool, α-terpineol, nerol, and geraniol, were tentatively identified by comparing the retention times with those of authentic samples. Linaloyl piperityl ether, after being isolated by preparative glc, was identified through a determination of the IR, NMR, and mass spectra.

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