cis- and trans-β-Sesquiphellandrol. Two New Sesquiterpene Alcohols from Oil of Ginger (*Zingiber officinale*, Roscoe)

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Two new sesquiterpene alcohols (*cis*- and *trans*-β-sesquiphellandrol) have been isolated from ginger oil. The structures were elucidated by analysis of ir, uv, ms, and nmr spectra and were shown to be stereoisomers of 5-(1,5-dimethyl-4-hexenyl)-2-methylene-3-cyclohexenol.

The composition of ginger oil has been the subject of numerous papers dating back to the early 1900's. Guenther (1952) compiled much of the then known data. Jain *et al.* (1962) and others cited therein have made significant contributions to what is known of the composition of ginger oil. More recent research by Varma *et al.* (1962), Nigam *et al.* (1964), and Connell (1970) has served to greatly expand the knowledge of the total composition of the essential oil of ginger. In the present work, we report the identification of two new sesquiterpene alcohols found in ginger which have previously been shown to have possible significance to ginger flavor (Bednarczyk and Kramer, 1971; Bednarczyk, 1973).

EXPERIMENTAL SECTION

The two sesquiterpene alcohols being reported (peaks 28 and 29 in Figure 1) were purified by gas chromatography (gc) from a ginger oil that was steam distilled from a ginger oleoresin prepared in our laboratory. The compounds were collected in glass capillary tubes as described by Jennings *et al.* (1964). Initial collections were made on a Hewlett-Packard 5750-A thermal conductivity gas chromatograph using an 8 ft × 0.156 in. i.d. glass column packed with 20% Carbowax 20M on 80–100 mesh Chromosorb WAW. The column oven temperature was programmed from 100 to 240° at 8°/min with a helium flow rate of 35–40 cm^3/min. The compounds were further purified on a Varian 90-P thermal conductivity gas chromatograph using a 10 ft × 0.156 in. i.d. glass column packed with 5% SF-96 on 80–100 mesh Chromosorb WAW. The column temperature was 175° isothermal with a helium flow rate of 40 cm^3/min.

Infrared (ir) spectra were recorded by scanning from 4000 to 625 cm^{-1} using a 4× beam condenser on a Perkin-Elmer 257 ir spectrophotometer. The spectra were scanned as thin liquid films deposited on a 1 mm^2 area etched in a KBr plate on which a second KBr plate was placed to sandwich the liquid sample.

Mass spectra were obtained *via* gas chromatography–mass spectrometry (gc–ms) techniques using a Varian series 1400 flame ionization gc coupled to a DuPont 21-490 ms operated at an ionizing voltage of 70 eV.

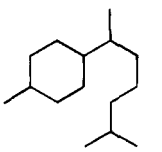
The nuclear magnetic resonance (nmr) spectrum of peak 28 was obtained using a Varian HA-100, 100-MHz nmr spectrometer and a micro cell. The decoupling experiment for peak 28 was run using a Jeol MH-100, 100-MHz nmr spectrometer with a low volume cell.

The nmr spectrum of peak 29 was obtained using a Varian HA-100, 100-MHz nmr spectrometer interfaced to a Digilab NMR-FTS-3 Fourier transform nmr system. The spectrum required pulsing an 800-Hz bandwidth 400 times. In all cases, $CDCl_3$ was used as the solvent and tetramethylsilane (TMS) was used as an internal standard.

Ultraviolet (uv) spectra were obtained with a Beckman DBGT grating spectrophotometer. Absorption maxima (λ_{max}) were determined in methanol using a 1-cm path length silica cell with methanol as a reference.

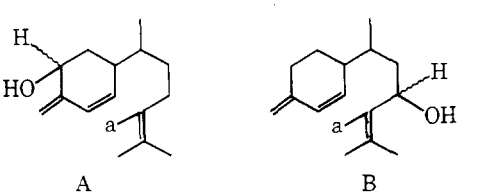
RESULTS AND DISCUSSION

On-column hydrogenation of peak 28 (per Kepner and Maarse, 1972), using neutral platinum, yielded a mixture of bisabolanes and dihydro-*ar*-curcumene (identified by gc–ms) which indicated that peak 28 has the bisabolane carbon skeleton:



The mass spectrum of peak 28 (Figure 2) showed a molecular ion at *m/e* 220. The ir spectrum (included as supplementary material in the microfilm edition) showed absorption bands (with per cent transmittance) at: 3400 (51), 3010 (58), 2960 (31), 2920 (28), 2870 (38), 1452 (50), 1378 (47), 1264 (64), 1059 (50), 1027 (53), 982 (69), 891 (46), and 803 cm^{-1} (69). The nmr (included as supplementary material in the microfilm edition) showed a 3 H doublet at δ 0.88 (J = 7 Hz), a 6 H doublet at 1.61 (J = 7 Hz), an 8 H multiplet from 1.2 to 2.2, a 1 H broadened singlet at 2.45, a 1 H multiplet at 4.39 (J = 3–4 Hz), a 1 H multiplet at 5.09 (J = 8 Hz) partially obscured by a 2 H doublet centered at 4.93 (J = 10 Hz), a 1 H doublet (J = 10 Hz) with fine splitting centered at 5.74, and a 1 H doublet (J = 10 Hz) with multiple fine splitting centered at 6.12. (The nmr closely resembled that described by Connell and Sutherland (1966) for β-sesquiphellandrene.) Peak 28 exhibited a uv absorption (λ_{max}) at 231 nm.

A mass peak at *m/e* 202 (P − 18) and an ir absorption at 3400 cm^{-1} indicated an alcohol moiety. The empirical formula for *m/e* 220 ($C_{15}H_{24}O$) showed peak 28, being monocyclic, to contain three unsaturated sites. The uv absorption (λ_{max} 231 nm) showed that two of the double bonds were in conjugation. An ir absorption band at 890 cm^{-1} confirmed the presence of a terminal methylene group. The nmr spectrum showed five vinylic protons and two vinyl methyl groups which could not be part of the conjugated system since this would have meant a farther downfield position. The nmr multiplet at δ 4.39 showed the alcohol function to be allylic. The only two possible structures that could fit all these criteria are:



A B

McCormick & Co., Inc., Hunt Valley, Maryland 21031 (A.A.B., W.G.G.), and the University of Maryland, Department of Horticulture, College Park, Maryland 20742 (A.K.).

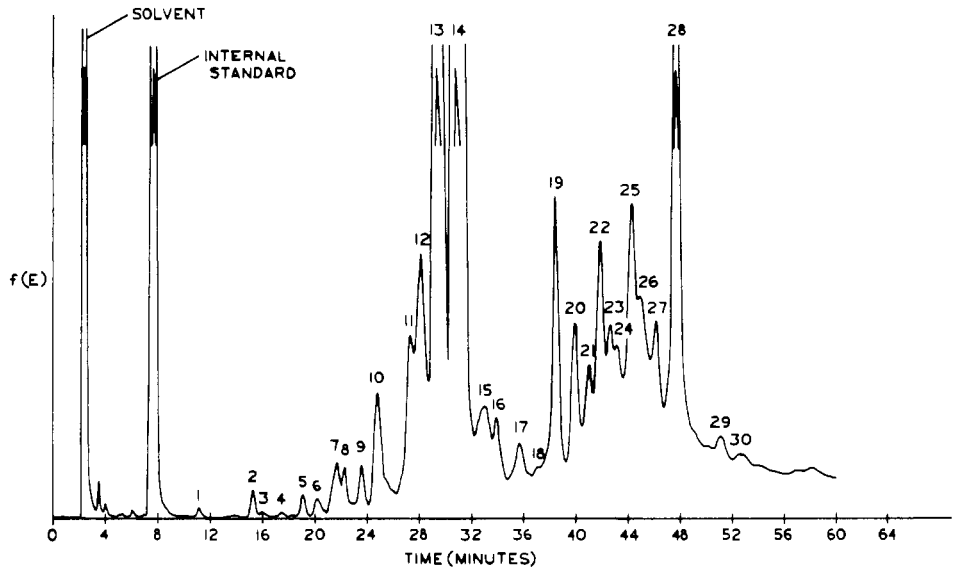


Figure 1. Typical gas–liquid chromatogram for steam distilled ginger essential oil. Conditions were: 8 ft × 0.156 in. i.d. stainless steel column packed with 5% Carbowax 20M on 80–100 mesh Chromosorb WAW; column temperature, 90–230° programmed at 4°/min; carrier gas flow rate, 60 cm^3/min; injection port and detector temperatures, 240°.

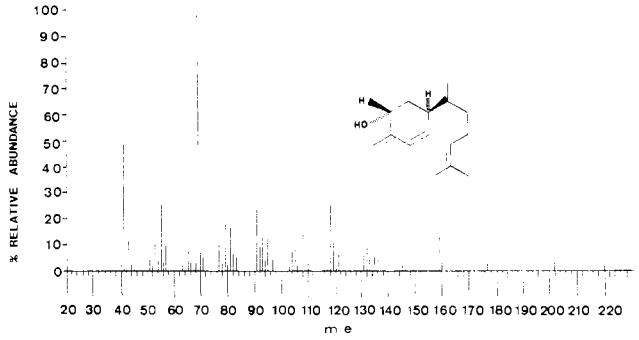


Figure 2. Mass spectrum of peak 28, *trans*-β-sesquiphellandrol. The absolute stereochemistry has not been established. The structure is drawn relative to the parent hydrocarbon β-sesquiphellandrene, the absolute stereochemistry of which is known, and is intended only to better illustrate the cis–trans relationship of the hydroxyl group and the side chain.

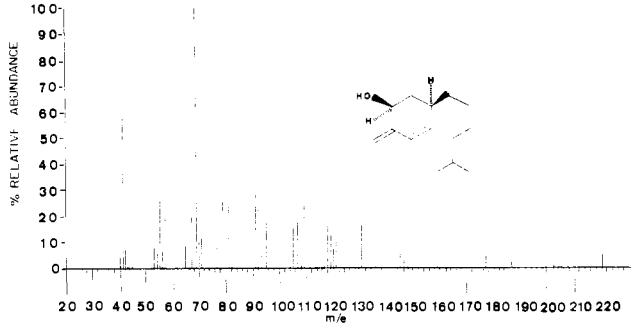
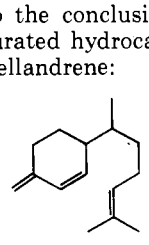


Figure 3. Mass spectrum of peak 29, *cis*-β-sesquiphellandrol. The absolute stereochemistry has not been established. The structure is drawn relative to the parent hydrocarbon β-sesquiphellandrene, the absolute stereochemistry of which is known, and is intended only to better illustrate the cis–trans relationship of the hydroxyl group and the side chain.

Since the multiplet at δ 5.09 (corresponding to proton a in the above structures) was partially obscured by the doublet centered at 4.93, it was unclear as to whether the multiplet was a skewed doublet (corresponding to structure B) or a triplet (corresponding to structure A). The question was resolved by a spin decoupling experiment. When the proton on the hydroxyl containing carbon (δ 4.39) was irradiated, no change in the multiplet at 5.09 was observed. These data allowed us to conclude that peak 28 must be as shown in structure A. Had peak 28 been structure B the multiplet would have collapsed to a singlet upon irradiation at δ 4.39. Structure A is an alcoholic derivative of β-sesquiphellandrene, a major component of ginger oil.

Peak 29 was also shown to have the bisabolane carbon skeleton by using the on-column hydrogenation technique. The mass spectrum of peak 29 (Figure 3) matched closely that of peak 28, suggesting a high degree of similarity between the two compounds. The ir spectrum (included as supplementary material in the microfilm edition) of peak 29 showed absorptions (with per cent transmittance) at 3400 (61), 3010 (68), 2960 (48), 2930 (44), 2860 (53), 1450 (65), 1376 (65), 1257 (79), 1080 (60), 1035 (73), 990 (79), 940 (85), 888 (63), 800 (86), and 778 cm^{-1} (86). The nmr spectrum showed a 3 H doublet centered at δ 0.82 (J = 9 Hz), a 6 H doublet centered at 1.58 (J = 5 Hz), an 8 H multiplet from 1.1 to 2.2, a 2 H doublet centered at 5.05 (J = 26 Hz), a 1 H multiplet centered at 5.10, a 1 H doublet with multiple fine splitting at 5.60 (J = 10 Hz), and a 1 H doublet with superimposed 2–3 Hz splitting centered at 6.15 (J = 10 Hz). (Impurities in the sample obscured the position of the hydrogen on the hydroxyl-containing carbon, and the hydroxyl hydrogen was not evident after the Fourier transformation.) Peak 29 exhibited a uv absorption (λ_{max}) at 233 nm.

The ms of peak 29 suggested an empirical formula of $C_{15}H_{24}O$. This necessitated the presence of three unsaturated sites, two of which are in conjugation (as confirmed by uv). The nmr chemical shift of the two vinyl methyls (δ 1.58) excludes that double bond from being part of a conjugated system. The presence of a terminal methylene group (ir absorption at 888 cm^{-1}) and the chemical shift and splitting pattern similarity of the vinyl protons at δ 5.60 and 6.15 lead to the conclusion that peak 29 must have the same unsaturated hydrocarbon skeleton as peak 28, namely β-sesquiphellandrene:



As with peak 28, the presence of a P − 18 peak in the ms and an ir absorption band at 3400 cm^{-1} confirmed peak 29 as an alcohol.

The absence of an nmr absorption in the region δ 3.5–4.0, which would correspond to the hydrogen on the hydroxyl-containing carbon, excludes the possibility of peak 29 being a nonallylic secondary alcohol. The splitting of the side-chain alkyl methyl group and the secondary splitting of the vinyl proton at δ 6.15, caused by the methine proton at the ring-side chain juncture, excludes the possibility of peak 29 being a tertiary alcohol. As in the case of peak 28, we are left with only two possible structures for peak 29, A and B, as shown previously. Structure B can be eliminated since we do not have an nmr absorption near δ 4.1–4.4, corresponding to an allylic proton on the hydroxyl-containing carbon. Structure B would also preclude the similarity in the mass spectra of peaks 28 and 29.

Obviously, the only difference between peaks 28 and 29 is the cis and trans relationship between the hydroxyl group and the side chain. This difference is responsible for the shifting of the hydrogen on the hydroxyl-containing carbon from its expected absorption at δ ~4.4 to a position farther downfield which was obscured by impurities. Cis and trans assignments have been made on the corresponding monoterpene alcohols (*cis*- and *trans*-yabunikeol) by Fujita *et al.* (1970) based on gc retention data and selected ir information. Accordingly, we would expect the trans isomer (peak 28) to elute before the cis isomer (peak 29) under our gc conditions. We feel this assignment is substantiated by the nmr since, in the case of peak 29, there is a downfield shift of δ 0.2 for one of the exocyclic methylene protons. This shift in δ can be explained by the deshielding effect of the hydroxyl oxygen when it is brought into closer proximity to one of the methylene protons as is the case in the cis *vs.* trans isomers. To the best of our knowledge, peaks 29 and 28 are two novel compounds which we are giving the names *cis*- and *trans*-β-sesquiphellandrol [5-(1,5-dimethyl-4-hexenyl)-2-methylene-3-cyclohexenol] from the parent hydrocarbon β-sesquiphellandrene.

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Supplementary Material Available. Figures showing ir and nmr spectra of peak 28, *trans*-β-sesquiphellandrol, and the ir spectrum of peak 29, *cis*-β-sesquiphellandrol, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JAFC-75-499.

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Components Contributing to Beef Flavor. Volatile Compounds Produced by the Reaction of 4-Hydroxy-5-methyl-3(2*H*)-furanone and Its Thio Analog with Hydrogen Sulfide

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Reaction of 4-hydroxy-5-methyl-3(2*H*)-furanone or its thio analog with H_2S produces a complex mixture of compounds with an overall odor resembling that of roasted meat. The major components of the product mixtures have been isolated by gas chromatography, and many of the components have been identified by infrared and mass spectrometry. The compounds identified included mercapto-substituted furan and thiophene derivatives.

The flavor of cooked meat is considered to be partly produced by sugar–amino acid reactions. Morton et al. (1960) patented reactions of cysteine and other amino acids with sugars producing a flavor with a basic meat character. Since then much research effort has been spent on studying the volatile compounds that contribute to beef flavor; Herz and Chang (1970) reviewed the literature covering this topic. Reactions between amino acids and reducing sugars can account for many of the compounds reported.

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