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Sesquiterpenoids of *Parabenzoin praecox*

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The essential oil of *Parabenzoin praecox* (Sieb. et Zucc.) Nakai, distributed in the southern part of Japan, has been reported to be composed mainly of several monoterpenoids, with *cis*-ocimene the major one, together with a few sesquiterpenoids, such as caryophyllene.[1] In this paper, we wish to report the analysis of the sesquiterpenoid fraction of this oil and the structural determination of two new sesquiterpenoids, α-copaene-11-ol (I) and 8-acetoxy-elemol (III), isolated from this source. In our experiments, unlike as in the previous results,[1] camphor was isolated as the main component of the oil and the following known sesquiterpenoids were isolated, α-copaene, β-elemene, β-caryophyllene, elemophyllene, α-muurolene, β-selinene, δ-cadinene, γ-cadinene, nerolidol, elemol, ledol, epicubenol, spathulenol, γ-eudesmol, T-cadinol, T-muurolol, δ-cadinol, α-eudesmol, β-eudesmol, and α-cadinol.

α-Copaene-11-ol, Compound (I) ($C_{15}H_{24}O$ (M^+ *m/e* 220), needle crystals, mp 99.5—100.5°C, $[\alpha]_D$ +9.2° in $CHCl_3$) was shown to have the following groupings, $-C(CH_3)_2OH$ (ν_{max} 3350 cm^{-1} (hydroxyl group), $\delta^{CCl_4}_{ppm}$

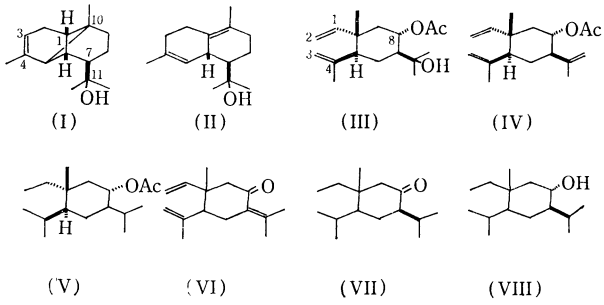
1) H. Shinozaki, *Kogyo Kagaku Zasshi*, **24**, 444 (1921); H. Komae, N. Hayashi, S. Kosela, and T. Aratani, *Flavour Industry*, **2**, 427 (1971).

1.04 (6H s.), *m/e* 59 ($C_3H_7O^+$, 100%)), $>CCH_3$ (δ 0.77 (3H s.)), and $-HC=C(CH_3)-$ (δ 1.62 (3H br.s.), 5.13 (1H br.s.)). The dihydro-derivative of I obtained by catalytic reduction (PtO_2/EtOH) was further hydrogenolyzed with PtO_2 in acetic acid to yield two hydrocarbons (both M^+ *m/e* 206) in a ratio of 3: 1, they were identical with copane and ylangane respectively. The dehydration of I with thionyl chloride in pyridine and the subsequent selective hydrogenation of the resulting terminal double bond with tris(triphenylphosphine) chlororhodium in benzene afforded α-copaene as the main product. From these results, Compound (I) was concluded to have α-copaene skeleton and a hydroxy group at C-11, as is shown by Formula (I). Although the absolute configuration of this compound was not determined, it is presumed that I has the same stereostructure as (−)-α-copaene on the basis of the coexistence of this and α-copaene($[\alpha]_D$ −4.9°) in the same oil. The isomerization of this alcohol, catalyzed by 0.1N hydrochloric acid in 80% aqueous dioxane, yielded a new bicyclic compound (II) ($C_{15}H_{24}O$ (M^+ *m/e* 220) $[\alpha]_D$ +52°). The spectral data of this compound showed the presence of $-C(CH_3)_2OH$ (ν_{max} 3400 cm^{-1}, δ 1.14 and 1.19 (each 3H s.) and *m/e* 59 (100%)), tri- and tetrasubstituted double bonds (δ 1.58 (6H s.) and 5.63 (1H br.s.)). This compound was presumed to be δ-cadinene-11-ol, since the mother hydrocarbon, α-copaene, yields δ-cadinene and α-murolene on acid treatment.[2)]

In another experiment, α-copaene-11-ol was isolated from the wood oil of *Litseae japonica* (Thumb.) Juss. as the major component of the sesquiterpene alcohol fraction.

8-Acetoxyelemol, Compound III ($C_{17}H_{28}O_3$ (M^+ *m/e* 280)), a minor component of the oil, showed the following spectral data, ν_{max} 3350, 1730, 1240, 910, and 890 cm^{-1}, δ 1.08 (3H s.), 1.15 (6H br.s.), 1.69 (3H br.s.), 2.00 (3H s.), 4.60—5.00 (5H m.), and 5.75 (1H d.d.). These spectra are identical with those of elemol except for the additional signals due to an acetoxy group (ν_{max} 1730 and 1240 cm^{-1}, and δ 2.00 (3H s.)). On heating in a sealed tube or on glc separation at 200°C, this compound afforded a dehydrated derivative (IV) ($C_{17}H_{26}O_2$). The NMR spectrum of IV showed the presence of an isopropenyl group instead of a $-C(CH_3)_2OH$ group in III. The NMR spectrum of the hexahydro-derivative (V), obtained by the hydrogenation of IV, exhibited the presence of a proton at δ 4.75, this confirmed the secondary nature of the acetoxy group. The position of this acetoxy group was decided to be at C-8 on the basis of the following experiments. β-Elemenone (VI) was hydrogenated with PtO_2 in acetic acid to yield a saturated ketone (VII). The subsequent lithium aluminium hydride reduction of VII afforded two secondary alcohols, VIII and IX, the minor product (VIII), carrying an equatorial hydroxyl group (H-8 at δ 3.40, $W_1/_2$ 24 Hz), was acetylated with Ac_2O in pyridine to yield an acetate which was identical with V in all respects. From these results, the structure of Compound III can be represented by Formura (III). The coexistence of III and elemol ($[\alpha]_D$ −3.5°) in the same oil also suggests the stereochemistry.

At present, there have been found only a few cadalene-type compounds carrying a hydroxyl group at C-11 as our alcohol (I) does, and since, in the genesis of cadalene-type alcohols a S_N1-like attack of a water molecule on the C-10 carbonium ion from the mediate germacrenoid cation is generally accepted, the hydroxylation at C-11 probably occurs after the cadalene skeleton has been formed. Such *de novo* hydroxylation is quite rare in sesquiterpenoids, and further study of the biogenesis of the compounds of this type should be undertaken.



Experimental

Stems (16.5 kg) and leaves (15.0 kg) of *Parabenzoin praecox* were collected in Osaka Prefecture. Each was extracted with acetone, and the extract, after the evaporation of the solvent, was steam-distilled. After the removal of acidic components from the distillate, neutral oils were obtained in the amounts of 12.9 g and 20.8 g from the stems and the leaves respectively. No significant difference in their constituents could be detected by analytical gas chromatography using a capillary column (HB-2000, 45 m×0.25 mm), therefore, the two oils were combined for analysis. The combined oil was separated into a hydrocarbon fraction (18.8 g) and a fraction of oxygenated compounds (14.1 g) by column chromatography on neutral alumina. Each component of the hydrocarbon fraction was purified by column chromatography on silica gel, followed by preparative glc (Varian, model 90-P, 20 ft. ×3/8 in. aluminium column packed with 10%-Carbowax 20M on Diasolid L at 180—200°C, using helium as the carrier gas). The oxygenated compound fraction was distilled under reduced pressure (3 mmHg) to separate sesquiterpenoids from monoterpenoids roughly. Each sesquiterpenoid, as well as α-copaene-11-ol (I) and 8-acetoxyelemol (III), was purified by column chromatography on silica gel, this was followed by preparative glc under the same condition as those for used for hydrocarbons except in the case of III. 8-Acetoxyelemol (III) was isolated using a 5ft.×3/8 in. column of Carbowax 20 M at 175°C. The compounds thus isolated were identified with authentic samples by comparing their RT on glc, and thier IR, NMR, and MS spectra.

α-Copaene-11-ol (I); *m/e* 220 (rel. int. 2%, M^+), 202 (7.5%, M^+-H_2O), 187 (11%, $M^+-H_2O-CH_3^+$), 162 (52%, $M^+-C_3H_6O^+$), 159 (41%), 147 (30%), 132 (38%), 119 (47%), 105 (55%), 91 (43%), 59 (100%, $C_3H_7O^+$).

8-Acetoxyelemol (III); *m/e* 280 (0.05%, M^+), 220 (0.3%, $M^+-CH_3CO_2H$), 202 (0.9%, $M^+-CH_3CO_2H-H_2O$), 162 (22%), 147 (23%), 119 (69%), 117 (71%), 108 (47%), 59 (42%, $C_3H_7O^+$), 43% (100%, $C_3H_7^+$).

2) Y. Ohta, K. Ohara, and Y. Hirose, *Tetrahedron Lett.*, **1968**, 4181.