

COMMUNICATIONS

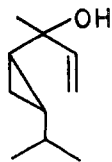
Occurrence of *Cis* and *Trans* Sabinene Hydrate in Oil of Black Pepper

Synthesis by Oxymercuration–Demercuration Procedure

Both the *cis* and *trans* isomers of sabinene hydrate have been isolated from oil of black pepper and the

mass, infrared, and nm spectra were shown to agree with those of synthesized compounds.

Earlier work (Russell and Jennings, 1969) reported the isolation of a compound of unknown structure from the oxygenated fraction of oil of black pepper. The compound, a white solid melting at 60.5° C, had a mass spectrum with a molecular ion at m/e 154, and a major peak at m/e 136, to which accurate mass determination assigned the molecular formula $C_{10}H_{16}$. The infrared spectrum exhibited absorptions at 3400 cm^{-1} (hydroxyl), and 3080, 990, and 910 cm^{-1} (terminal vinyl). Diluted in CCl_4 , the infrared spectrum showed the hydroxyl absorption was centered at 3615 cm^{-1} , characteristic of a tertiary alcohol. Infrared absorptions at 1360 and 1380 cm^{-1} on both sides of a methyl absorption band at 1370 cm^{-1} , combined with an M-43 peak in the mass spectrum, indicated the presence of an isopropyl group. The structure most consistent with these data was



Other unrelated work offered an opportunity to collect larger quantities of this substance, which permitted obtaining a nuclear magnetic resonance spectrum. This was characterized by a lack of absorption above 2.0 δ ruling out any olefinic protons and hence establishing that the postulated structure above could not be correct.

To maintain the C—H ratio while excluding the terminal vinyl group, we are forced to close the ring, which would produce sabinene hydrate. Daly *et al.* (1958) reported the isolation of *trans*-sabinene hydrate from American peppermint oil. Our melting point data appeared to agree with theirs, and the structure of sabinene hydrate can be correlated with all observed spectral data except the infrared absorptions at 3080, 990, and 910 cm^{-1} , which are normally observed only in compounds possessing a terminal vinyl group. Accordingly, both the *cis* and *trans* isomers were synthesized for comparison with the isolated compound.

MATERIALS AND METHODS

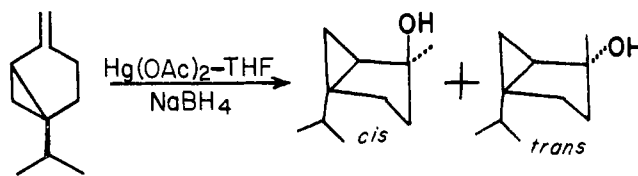
Reagents. Sabinene was freshly distilled (Nester-Faust Teflon annular spinning band column) from oil of savin (Magnus, Mabee, and Reynard, New York, N.Y.) at 25 mm Hg.

Instruments. Gas chromatographic separations utilized a Varian-Aerograph Model 202 gas chromatograph with thermal conductivity detection, containing dual 25 ft \times 0.23 in. i.d. stainless steel columns packed with (1) 3% Triton X-305 on 70 to 80 mesh HMDS treated Chromosorb G, and (2) 3% SF96 (50) admixed with 5% w/w Igepal CO 880 on

70 to 80 mesh HMDS treated Chromosorb G. Injectors were maintained at 225° C, detectors at 250° C, and the columns programmed from 70 to 220° C at a rate of 2°/min. Helium carrier gas was supplied at a rate of 50 ml/min. Infrared spectra were taken between sodium chloride plates in a Perkin-Elmer Model 257 infrared spectrophotometer. Nuclear magnetic resonance spectra were determined in a Varian A-60 nuclear magnetic resonance spectrometer. Samples were run in CCl_4 at room temperature utilizing tetramethylsilane as a reference.

PROCEDURE

Cis and *trans* sabinene hydrate were synthesized following the procedure reported by Brown and Geoghegan (1967). The products of Markownikoff hydration of the freshly distilled sabinene were isolated from each other and from the tetrahydrofuran by gas chromatographic separation.



RESULTS AND DISCUSSION

Kovats Indices [1035 and 1352 on SF96(50) and Triton X-305, respectively], infrared, and nmr data were identical for the synthetic *trans* sabinene hydrate and the compound from black pepper oil. In addition, the *cis* isomer was also isolated from black pepper oil, and retention and spectral data found to agree with those of the synthetic *cis* isomer. Kovats indices for the latter were 1050 and 1441 on SF 96(50) and Triton X-305, respectively. These data establish that the compound in question is sabinene hydrate, and not the structure previously postulated.

LITERATURE CITED

- Brown, H. C., Geoghegan, P. Jr., *J. Amer. Chem. Soc.* **89**, 1522 (1967).
Daly, J. W., Green, F. C., Eastman, R. H., *J. Amer. Chem. Soc.* **80**, 6330 (1958).
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