

The Structure of Sarisan, an Isomer of Myristicin, Isolated from the Leaf Oil of *Beilschmiedia miersii*

The structure of the principal component in the leaf oil from *Beilschmiedia miersii*, an avocado relative from Chile, has been deduced to be 1-allyl-2-meth-

oxy-4,5-methylenedioxy benzene, II, and named sarisan.

Small samples of the principal component in the oil that is steam distilled from the leaves of *Beilschmiedia miersii* (Gay) Kosterm. can be isolated by gas chromatography. The mass spectrum indicated a molecular weight of 192 and the material was first believed to be a previously reported natural product, myristicin. However, comparison with an authentic sample, isolated from oil of myristica, proved that the two were not identical. Because of the current interest in the chemistry of natural phenols and their toxicity to animals and related physiological activity (Singleton and Kratzer, 1969; Truitt *et al.*, 1961), the question of the structure of this oil, which we called sarisan, was pursued further.

EXPERIMENTAL

Infrared absorption spectra were obtained with a Beckman IR-12 using a 0.05 mm path micro cell with a neutral density in the reference beam.

Nmr spectra were obtained with a Varian Model-T spectrometer.

Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6D in the Chemistry Department.

Washed leaves were ground in a Waring Blendor and steam distilled under reflux using a Clevenger collection trap for oils lighter than water.

A Loenco gas chromatograph Model 15-B using a $\frac{1}{4}$ -in. \times 5-ft polydiethylene glycol succinate column, isothermally at 175° C, elutes sarisan in 26 min, and myristicin in 32 min with 40 cc/min helium as the carrier gas.

A sample of oil from a 20 μ l injection was collected in a 1.8 \times 100 mm melting point capillary tube at the exhaust port using dry ice. The infrared, nmr, and mass spectra, and elemental analysis were determined: ir (CCl₄) cm^{-1} 3088, 1645, 1012, 919 (—CH=CH₂), 2784 (O—CH₂—O), 863 (1, 2, 4, 5 substituted phenyl); nmr (CCl₄) δ 6.53 (s, 1, aromatic H), 6.36 (s, 1, aromatic H), 5.80 (s, 2, O—CH₂—O), *ca.* 5.80 (m, 1, C—CH=C), 4.90 (d, 2, $J = 14$ Hz, C = CH₂), 3.70

(s, 3, O—CH₃), 3.20 (d, 2, $J = 6$ Hz, C—CH₂—C); mass spectrum 80 ev m/e 192 parent ion.

Anal. calcd. for C₁₁H₁₂O₃: C, 68.73; H, 6.30.

Found: C, 69.01; H, 6.20.

Oil of myristica was purchased from Dodge and Olcott Inc., New York, N.Y. The highest boiling oil was recognized as myristicin from its infrared, nmr, and mass spectra and refractive index; ir (CCl₄) cm^{-1} 3090, 1636, 998, 922 (—CH=CH₂), 2784 (O—CH₂—O); nmr (CCl₄) δ 6.22 (s, 2, aromatic-H), 5.80 (s, 2, O—CH₂—O), *ca.* 5.80 (m, 1, C—CH=C), 4.96 (d, 2, $J = 12$ Hz, C = CH₂), 3.80 (s, 3, O—CH₃), 3.18 (d, 2, $J = 6$ Hz C—CH₂—C); mass spectrum 80 ev m/e 192 parent ion; n_D^{25} 1.5400; bp 94–95° (.45 mm); [lit. (Heilbron *et al.*, 1965) n_D^{20} 1.5403; bp 95–97° C (.2 mm)].

DISCUSSION

Only small differences exist in the data comparing sarisan with myristicin. The parent ion is the same and the fragmentation pattern of the two compounds in their mass spectra are very similar.

The nmr spectra of sarisan and myristicin bear a strong resemblance to that of safrole (Bhacca *et al.*, 1962) and the identification for the methylenedioxy and allyl group was straightforward. Both sarisan and myristicin have an additional methoxyl group resonance in the appropriate region. The aromatic hydrogens in myristicin coincide in a singlet absorption as is the case for safrole. However, the two aromatic hydrogens in sarisan appear as separated singlets and this establishes that its structure must differ from myristicin.

Three of the six possible isomers, IV, V, and VI, which come into consideration (Figure 1) can be eliminated because they have adjacent aromatic hydrogens which should show a pair of doublets in their nmr spectra. Myristicin, I, is ruled out by direct comparison and this leaves only two possibilities. The two differ in that one is a 1,2,4,5-substituted benzene,

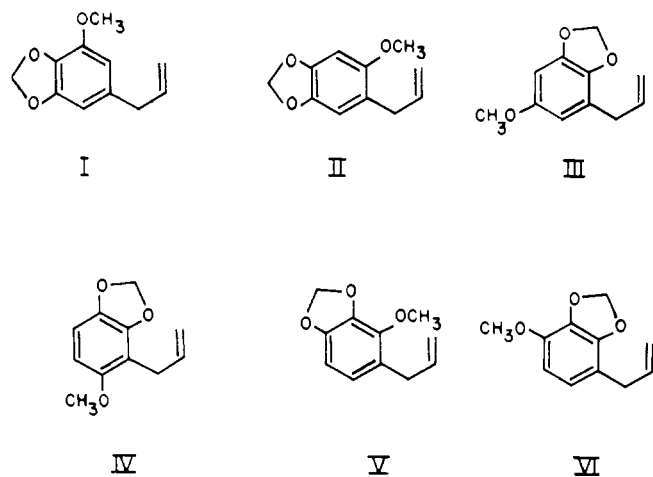


Figure 1. Isomers of myristicin

and the other is a 1,2,3,5-substituted derivative. Sarisan has a strong infrared absorption at 863 cm^{-1} , which is in the characteristic region for a 1,2,4,5-substituted benzene ring (Nakanishi, 1964).

We concluded that the structure of sarisan is 1-allyl-2-methoxy-4,5-methylenedioxy benzene, II. The trimethoxy derivative corresponding to myristicin is known as elemicin and a trimethoxy derivative corresponding to sarisan with the double bond isomerized into conjugation is known as asarone (Baxter *et al.*, 1962).

The original plant material was grown at the Southcoast Field Station, University of California, field 5-2-20, CH-12 from seed collected in Chile by G. A. Zentmeyer. A voucher specimen (Scora 3068) is on file in the herbarium of the Citrus Research Center at Riverside.

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