

*trans*-2-METHOXY-4,5-METHYLENEDIOXYPROPENYL BENZENE  
(CARPACIN) FROM A *CINNAMOMUM* SP. FROM BOUGAINVILLE

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From the Carpano tree, an unidentified *Cinnamomum* sp. of the family Lauraceae which is native to Bougainville and used in folk medicine, a simple oxygenated C<sub>9</sub>-C<sub>9</sub> compound, carpacin, has been isolated. Carpacin is neutral in character, stable to hot aqueous alkali, and the infrared spectrum shows the absence of both carbonyl and hydroxyl groups. The ultraviolet spectrum suggests an aromatic ring in conjugation with an olefinic group.<sup>1</sup>

Carpacin was oxidized to a substituted benzaldehyde whose structure was shown to be 2-methoxy-4,5-methylenedioxybenzaldehyde from its n.m.r. spectrum consisting of five singlets. The following assignments are unequivocal:<sup>2</sup>  $\delta$  (p.p.m.) 10.3 (aldehyde proton), 6.00 (methylenedioxy), 3.87 (methoxy). The two remaining protons at 7.2 and 6.53 are the aromatic protons and their appearance as singlets indicates that they are *para* to one another, the proton at the lower field being between the methylenedioxy group and the aldehyde.

The structure of carpacin follows from the structure of its oxidation product and its n.m.r. spectrum. The aldehyde proton signal in the oxidation product is replaced by the signals due to the different protons in a CH<sub>3</sub>-CH=CH- grouping typical of an A<sub>3</sub>XY system.

The fine splitting ( $J_{AY}$  1.5 c/s) of the methyl doublet at 1.84 is due to the coupling with the olefinic proton at 6.63 (H<sub>Y</sub>). The magnitude of the major splitting ( $J_{XY}$  16 c/s) of this proton indicates that it is coupled to another proton and that the two coupled protons are *trans* about a double bond. The olefinic proton quartet (1:3:3:1) at 6.10 (H<sub>X</sub>) is coupled to the methyl group ( $J_{AX}$  6.5 c/s). The splitting ( $J_{XY}$  16 c/s) of the quartet is due to the coupling with the other olefinic proton at 6.63 across the double bond. The remainder of the spectrum shows singlets at 6.85 (H 6), 6.44 (H 3), 5.83 (methylenedioxy), and 3.72 (methoxy).

Carpacin is, therefore, *trans*-2-methoxy-4,5-methylenedioxypropenylbenzene (I) and is a structural isomer of myristicin,<sup>3</sup> isomyristicin,<sup>4</sup> and croweacin.<sup>5</sup> Though it

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<sup>1</sup> Scott, A. I., "Interpretation of the Ultraviolet Spectra of Natural Products." (Pergamon: London 1964.)

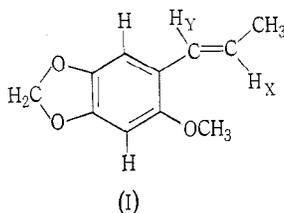
<sup>2</sup> Mathieson, D. W., "Interpretation of Organic Spectra." (Academic Press: New York 1965.)

<sup>3</sup> Power, F. B., and Salway, A. H., *J. chem. Soc.*, 1907, 91, 2037.

<sup>4</sup> Rao, B. S., and Subramanian, K. S., *J. chem. Soc.*, 1937, 1338.

<sup>5</sup> Baker, W., Penfold, A. R., and Simonsen, J. L., *J. chem. Soc.*, 1939, 439.

is the first time that this compound has been isolated from a plant, it has been synthesized<sup>6</sup> as a possible insecticide.



### Experimental

All melting points are uncorrected. Microanalysis was carried out by the Australian Microanalytical Service, Melbourne. Ultraviolet spectra were measured in methanol; infrared spectra were run in KBr disks, n.m.r. spectra in  $\text{CDCl}_3$  at 60 Mc/s with tetramethylsilane as internal standard. Light petroleum refers to the fraction b.p. 60–80°. Neutral alumina (B.D.H. chromatographic grade) was used for column chromatography.

### Isolation of Carpacin

The bark (10 kg) was dried in an air-oven (120°), milled to a fine powder, and extracted exhaustively with light petroleum. The combined extracts, on removal of the solvent under reduced pressure, gave a brown oil (150 g). Column chromatography of this oil over alumina using light petroleum, benzene, ether, chloroform, and methanol, was followed by rechromatography of the combined light petroleum, benzene, and ether fractions, developed firstly with light petroleum and then with a mixture of light petroleum and benzene (1:1). A yellow oil was obtained from the latter fraction. This was dissolved in light petroleum and kept at -15°; colourless crystals of carpacin (8.5 g) separated out, m.p. 47° (lit.<sup>6</sup> 48–49°);  $\lambda_{\text{max}}$  259.5  $\mu$  ( $\epsilon$  13550) and 322  $\mu$  ( $\epsilon$  8940);  $\nu_{\text{max}}$  1505, 1485, 1042, and 942  $\text{cm}^{-1}$  (aromatic methylenedioxy), 970  $\text{cm}^{-1}$  (*trans* olefinic hydrogens), and 1615, 1505, 870, 860, and 765  $\text{cm}^{-1}$  (1,2,4,5-tetrasubstituted benzene moiety) (Found: C, 69.0; H, 6.3. Calc. for  $\text{C}_{11}\text{H}_{12}\text{O}_3$ : C, 68.8; H, 6.3%).

### Permanganate Oxidation of Carpacin

Carpacin (200 mg) in acetone was oxidized with potassium permanganate (2 g) in acetone for 24 hr at room temperature. The manganese dioxide was filtered off and the solvent removed. The residue was dissolved in ether and washed exhaustively with 2% sodium bicarbonate solution.

From the ether solution were obtained crystals of 2-methoxy-4,5-methylenedioxybenzaldehyde, m.p. 113° (lit.<sup>7</sup> 111.5–112°).

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<sup>6</sup> Alexander, B. H., Gertler, S. I., Brown, R. T., Oda, T. A., and Beroza, M., *J. org. Chem.*, 1959, **24**, 1504.

<sup>7</sup> Fukui, K., and Nakayama, M., *Nippon kagaku zasshi*, 1963, **84**, 606 (*Chem. Abstr.*, 1964, **60**, 5385g).