Alkaloids of a New Type from *Elaeocarpus polydactylus* Schl. (Family Elaeocarpaceae)

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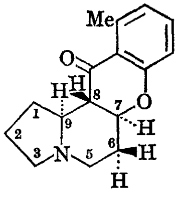
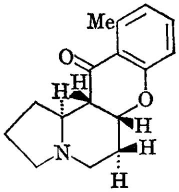
No structural information regarding alkaloids of the family Elaeocarpaceae has previously been reported. We now report that two new alkaloids, elaeocarpine, $C_{16}H_{19}NO_2$, m.p. 81—82°, $[\alpha]_D$ *ca.* +0·1° in $CHCl_3$, and an isomer, isoelaeocarpine, m.p. 51—52°, $[\alpha]_D$ *ca.* +0·4° in $CHCl_3$, isolated from the leaves of a New Guinea species *Elaeocarpus polydactylus* Schl., are the first members of a new class of indolizidine alkaloids. The complete stereochemistry of elaeocarpine (I) has been established by an *X*-ray crystal structure analysis of elaeocarpine hydrobromide which crystallizes in the triclinic system with two formula units in a unit cell of dimensions $a = 12·46$, $b = 7·38$, and $c = 8·05$ Å, $\alpha = 96·1°$, $\beta = 92·8°$ and $\gamma = 94·0°$. The $N(z)$ versus z test[1] clearly shows the space group to be $P\bar{1}$, indicating that the crystals are essentially racemic. The electron-density map, based on the bromine atom co-ordinates derived from the Patterson function, shows the position of all C, N, and O atoms, and the complete structure is shown in perspective in the Figure.

The isomeric alkaloid, isoelaeocarpine (II), has been shown to be closely related to elaeocarpine by interconversion of the two alkaloids in methanolic potassium hydroxide solution at room temperature. Both alkaloids show carbonyl absorption bands (I), $\nu(CCl_4)$ 1694 cm.$^{-1}$; (II) $\nu(CCl_4)$ 1680 cm.$^{-1}$, and their mass spectra are closely similar (M^+, m/e 257), differing only in the relative intensities of some peaks. The 100 Mc./sec. n.m.r. spectra of both (I) and (II) show a sharp three-proton singlet assigned to the aryl *C*-methyl group [δ 2·60 in (I) and δ 2·63



(I)



(II)

in (II)], and similar ABX systems between 670 and 740 c./sec. for the three aromatic protons.

Consideration of the n.m.r. spectra of the two alkaloids shows that isoelaeocarpine is the C-7 epimer of elaeocarpine. The signal from the C-7 proton of elaeocarpine appears as a broad multiplet at δ 4·15, and approximate values have been determined for the coupling constants by the double irradiation technique which shows $J_{7,8}$ 11·8 c./sec. and $\frac{1}{2}(J_{7,6\beta} + J_{7,6\alpha})$ 7·8 c./sec., consistent with the two large *trans*-diaxial couplings and smaller *cis*-axial, equatorial coupling expected from the dihedral angles measured from molecular models of (I). By contrast, the C-7 proton multiplet at δ 4·64 in the spectrum of isoelaeocarpine is narrow, and the relatively small coupling constants [$J_{7,8}$ 2·1 c./sec.; $\frac{1}{2}(J_{7,6\beta} + J_{7,6\alpha})$ 2·8 c./sec.] are consistent with the assigned C-7, C-8 *cis*-stereochemistry as depicted in (II). The signal from the C-8 proton appears as a quartet at δ 2·51 ($J_{7,8}$ 11·8 c./sec.; $J_{8,9}$ 10 c./sec.) and at δ 2·42 ($J_{7,8}$ 2·1 c./sec.; $J_{8,9}$ 10 c./sec.) in the spectra of (I) and (II) respectively, and confirms the same C-8, C-9 stereochemistry in both (I) and (II). Proton assignments in the n.m.r. spectra were confirmed and the spectra simplified for spin–spin decoupling experiments by examining solutions of C-8 deuterio-substituted (I) and (II) in CD$_3$OD containing a trace of NaOD. At 30° the rate of substitution at C-8 by deuterium under these conditions can be followed by observing the change in the n.m.r. spectrum at intervals, while the slower interconversion of (I) and (II) can also be observed.

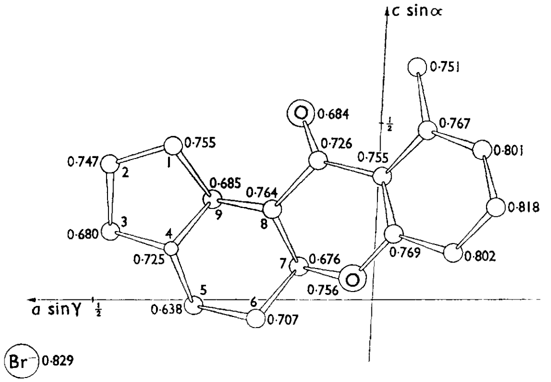


FIGURE. *Perspective view of the molecule viewed down the* b-*axis. Values of the* y *co-ordinates are given beside each atom.*

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[1] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.