Three New Indolizidine Alkaloids Related to Elaeocarpine and Isoelaeocarpine

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Two new alkaloids isolated from the leaves of *Elaeocarpus dolichostylis* Schl. bear a close relationship to the alkaloids (±)-elaeocarpine (I) and (±)-isoelaeocarpine (II) previously obtained from *Elaeocarpus polydactylus* Schl.[1] The isomeric alkaloids (+)-elaeocarpiline and (—)-isoelaeocarpiline which have the molecular formula $C_{16}H_{21}NO_2$ are shown to be (+)-15,16-dihydroelaeocarpine (III) and (—)-15,16-dihydroisoelaeocarpine (IV), in which the relative stereochemistry at C-16 and the absolute configuration remain unassigned.

(+)-Elaeocarpiline (III), m.p. 165—166°, $[\alpha]_D$ + 395° ($CHCl_3$), M^+ at m/e 259, has λ_{max} (EtOH) 221, 241 infl, and 323 mμ (ϵ 5000, 4600, and 7200), and ν_{max} (CCl_4) 1657 cm.$^{-1}$ typical of a conjugated dienone system. The n.m.r. spectrum* has signals at δ 0·95 (3H, d, J 6·7 c./sec., assigned to the methyl group at C-16), 6·27 (m, 14-H), and δ 5·85 (q, 13-H, showing a large vicinal and a small allylic coupling J_{vic} 10·0 c./sec., J_{all} 2·9 c./sec.). A broad multiplet at δ 4·06 (7-H) is similar to the signal observed for the 7-H in the spectrum of (±)-elaeocarpine (I), which was shown to be consistent with a *trans*-diaxial configuration for the C-7 and C-8 protons.[1] Chemical proof of the relationship of (+)-elaeocarpiline (III) to (±)-elaeocarpine (I) was obtained by heating (III) with palladium–charcoal (10%) in benzene, as this reaction affords as a major product (+)-elaeocarpine, m.p. 104—106°, $[\alpha]_D$ + 206° ($CHCl_3$),

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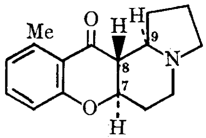
* All n.m.r. spectra were measured at 100 Mc./sec. in $CDCl_3$ solutions, and chemical shifts are relative to tetramethylsilane.

identical in its i.r., n.m.r., and mass spectra with (±)-elaeocarpine.

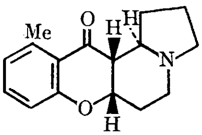
(−)-Isoelaeocarpiline (IV), m.p. 146—147°, $[\alpha]_D$ − 400° ($CHCl_3$), M^+ 259, λ_{max} (EtOH) 224, 240 infl, and 323 mμ, (ε 3700, 3500, and 7700), ν_{max} (CCl_4) 1657 cm.$^{-1}$, is isolated from *E. dolichostylis* in larger amounts than (III). The n.m.r. spectrum of (IV) shows δ 0·85 (d, 16-Me, J 6·7 c./sec.), 6·26 (m, 14-H), 5·88 (q,13-H, J_{vic} 10·0, J_{all} 2·8 c./sec.). A narrow multiplet at δ 4·54 (7-H) closely resembles the signal for the 7-H in the spectrum of (±)-isoelaeocarpine (II)[1] and indicates a similar *cis*-7,8 ring junction. Heating (IV) with palladium–charcoal in benzene, gives a mixture of (−)-isoelaeocarpine, a colourless gum, $[\alpha]_D$ − 120° ($CHCl_3$), picrate m.p. 260—263° (decomp.), identical in its i.r., n.m.r., and mass spectra with (±)-isoelaeocarpine, and a product characterized as (−)-13,14,15,16-tetrahydroisoelaeocarpine, m.p. 121—122°, $[\alpha]_D$ − 219° ($CHCl_3$), M^+ 261, λ_{max} (EtOH) 275 mμ, (ε 8900), ν_{max} (CCl_4) 1667 cm.$^{-1}$.

With sodium borohydride in ethanol at room temperature the 13,14-double bond of (−)-isoelaeocarpiline (IV) is reduced quantitatively to give (−)-13,14,15,16-tetrahydroisoelaeocarpine, but the carbonyl group is unaffected. (+)-Elaeocarpiline (III), on the other hand, reacts with sodium borohydride under the same conditions to give a tetrahydro-derivative, m.p. 197—198°, $[\alpha]_D$ + 135° ($CHCl_3$), M^+ 263, which can be shown to be the alcohol (V). Hydrogenation of (III) over platinum oxide in ethyl acetate gives (+)-13,14,15,16-tetrahydroelaeocarpine, m.p. 92—94°, $[\alpha]_D$ + 317° ($CHCl_3$), λ_{max} (EtOH) 273 mμ, (ε 8900), ν_{max} (CCl_4) 1666 cm.$^{-1}$.

A new phenolic alkaloid, isoelaeocarpicine, $C_{16}H_{21}NO_3$, m.p. 164—166°, $[\alpha]_D$ + 29° ($CHCl_3$), M^+ 275, ν_{max} ($CHCl_3$) 1665 cm.$^{-1}$, λ_{max} (EtOH) 248 and 294 mμ (ε 3150 and 2100), is isolated from *E. polydactylus* leaves, together with (I) and (II), from which it differs in molecular composition by H_2O. Isoelaeocarpicine can be shown to be (VI), for on warming with potassium hydroxide in methanol solution it is converted into a mixture of (I) of low optical rotation ($[\alpha]_D$ + 20° in $CHCl_3$) and (II) which is essentially racemic. The n.m.r. spectrum of (VI) has a signal at δ 4·30 (7-H), which shows couplings of a similar magnitude to those observed for the 7-H in isoelaeocarpine,[1] and at δ 3·82 (q,$J_{7,8}$ 2·5, $J_{8,9}$ 11·0 c./sec.), which is assigned to 8-H. The coupling constants of the C-7 and C-8 protons indicate a *cis* axial–equatorial configuration of these two protons in (VI) and an equatorial conformation for the bulky substituent attached to the indolizidine ring at C-8.



(I)



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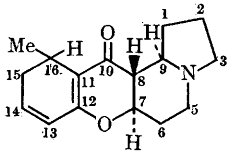
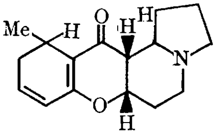
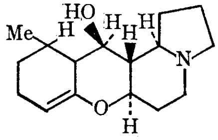


(III)



(IV)



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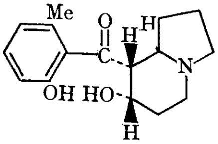

(VI)

E. dolichostylis, like the other species previously examined[1,2] occurs in New Guinea, and its leaves contain in addition to (III) and (IV), the indole alkaloid elaeocarpidine[2] and traces of (I) and (II).

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[1] S. R. Johns, J. A. Lamberton, A. A. Sioumis, and J. A. Wunderlich, *Chem. Comm.*, 1968, 290.

[2] S. R. Johns, J. A. Lamberton, and A. A. Sioumis, *Chem. Comm.*, 1968, 410.