New Alkaloids from *Elaeocarpus kaniensis* Schltr.: Nuclear Magnetic Resonance Study

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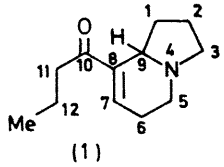
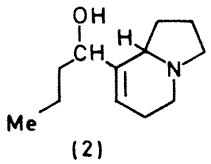
Summary Of the alkaloids from *Elaeocarpus kaniensis* Schltr., the structures of elaeokanines A (**1**), B (**2**), C (**3**), D(**4**), E (**5**), and elaeokanidine A (**6**) have been determined, while elaeokanidines B and C have been shown to be stereoisomers of elaeokanidine A.

LEAVES of *Elaeocarpus kaniensis* Schltr., a rain-forest species found in New Guinea, have yielded a complex mixture of alkaloids from which eight have been isolated. On the basis of detailed spectroscopic studies, of biosynthetic considerations, and of previous work on alkaloids from related species,[1] structures can be assigned to six alkaloids, elaeokanines A, B, C, D, E, and elaeokanidine A.



(1)



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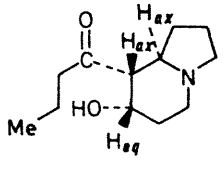

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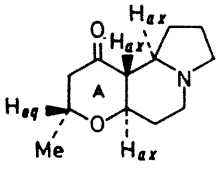
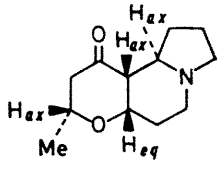


(4)



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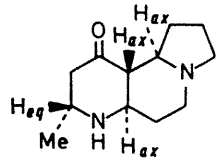

(6)

Elaeokanidines B and C are stereoisomers of elaeokanidine A, but their structures cannot be assigned unequivocally. The alkaloids have been isolated by preparative t.l.c. and g.l.c., and insufficient material has been available for chemical interconversion or degradation of the alkaloids. The absolute configurations of all the alkaloids are unknown and structural formulae depict only relative stereochemistry.

Elaeokanine A, $C_{12}H_{19}NO$, a colourless oil, $[\alpha]_D$ +13° ($CHCl_3$), ν_{max} (CCl_4) 1667 ($\alpha\beta$-unsaturated carbonyl), 2600—2900 cm^{-1} (Bohlmann bands), M^+ 193, crystalline picrate, m.p. 163—165°, can be assigned structure (**1**). The n.m.r. spectrum† shows the presence of an n-butyryl system [δ 0·88 (t, 12-Me), 1·67 (sextet, 12-CH_2), 2·55 (t, 11-CH_2)] and the u.v. absorption, λ_{max} 229 nm (ϵ 9820), indicates that the double bond is in conjugation with the carbonyl group as shown in (**1**). Signals at δ 6·84 [($J_{7,6ax}$ + $J_{7,6eq}$) 4·0, $J_{7,8}$ 2·0 Hz] and at 3·42 ($J_{9,1}$ 9·0, $J_{9,1}$ 7·0 Hz), assigned, respectively, to 7-H and 9-H, indicate that both 7-H and 9-H are adjacent to methylene groups (at C-1 and C-6). The molecular formula requires a two-ring system with nitrogen at a ring junction (absence of NH groups), and the presence of an indolizidine system is confirmed by Bohlmann bands in the i.r. spectrum and by the similarity of the mass spectral fragmentation pattern to those of related indolizidines.[1]

Elaeokanine B, $C_{12}H_{21}NO$, a colourless gum $[\alpha]_D$ −72° ($CHCl_3$), M^+ 195, no crystalline derivatives, ν_{max} (CCl_4) 3210 cm^{-1} (OH), is considered to be (**2**). The n.m.r. spectrum shows a *C*-methyl triplet at δ 0·92 (J 7·0 Hz), which unlike that of (**1**), shows typical "end-of-chain" broadening from virtual coupling to the β-methylene protons. One proton multiplets at δ 5·67 (7-H) and at 4·08 (10-H) and a one proton broad singlet at 3·18 (OH, exchangeable with D_2O), support this structure.

Elaeokanine C,‡ a colourless gum, $[\alpha]_D$ −14° ($CHCl_3$), ν_{max} (CCl_4) 3550 (OH), 1690 cm^{-1} (H-bonded carbonyl) M^+ 211, is considered to be (**3**). The n.m.r. spectrum [δ 0·86 (t, J 7·0 Hz, 12-Me), 1·63 (sextet, J 7·0 Hz, 12-CH_2), 2·46 (t, J 7·0 Hz, 11-CH_2)] indicates an n-butyryl system as in (**1**), and the narrow doublet of triplets (δ 4·16, all couplings *ca.* 2·5 Hz) assigned to 7-H suggests an equatorial conformation for 7-H. Analysis of the signal assigned to 8-H [δ 2·46 (q, $J_{7,8}$ 2·5, $J_{8,9}$ 9·5 Hz] shows that 8-H, 9-H are *trans* diaxial and that the bulky n-butyryl group is equatorial. When elaeokanine C is heated with ethanolic potassium hydroxide an $\alpha\beta$-unsaturated ketone (λ_{max} 227 nm) is obtained with retention time on g.l.c. identical with that of elaeokanine A.

Elaeokanine D, $C_{12}H_{19}NO_2$, m.p. 76—78° $[\alpha]_D$ +51° ($CHCl_3$), ν_{max} (CCl_4) 1705 cm^{-1} (carbonyl), M^+ 209, can be assigned the structure (**4**). The n.m.r. spectrum shows δ 1·26 (d, J 7·0 Hz, 12-Me), 4·62 (qt of d, $J_{12,11ax}$ 7·0, $J_{12,11eq}$ 2·0, $J_{12,Me}$ 7·0 Hz, 12-H), 3·65 (d of t, $J_{7,8}$ 10·0, $\frac{1}{2}[J_{7,6ax} + J_{7,6eq}]$ 8·0 Hz, 7-H) and 2·34 (t, $J_{7,8}$ 10·0, $J_{8,9}$ 10·0 Hz, 8-H). On the assumption that ring A has a chair conformation, these coupling constants indicate that 7-H, 8-H and 8-H, 9-H are both *trans* diaxial and 12-H is equatorial.

Elaeokanine E, $C_{12}H_{19}NO_2$, m.p. 57—58·5°, $[\alpha]_D$ +35° ($CHCl_3$), ν_{max} (CCl_4) 1705 cm^{-1} (carbonyl), M^+ 209 has been assigned the structure (**5**). The close resemblance between the i.r. and mass spectra of elaeokanine D and elaeokanine E indicates that the alkaloids are stereoisomers. The n.m.r. spectrum shows two overlapping multiplets at δ 3·76 ($J_{12,Me}$ 7·0, $J_{12,11ax}$ 14·0, $J_{12,11eq}$ *ca.* 1·0 Hz, 12-H) and a narrow multiplet at 3·85 (7-H). The large coupling between 12-H and the axial 11-H indicates a *trans* diaxial conformation for these protons while the narrow 7-H multiplet shows that 7-H is equatorial and that the C-7, C-8 ring junction is *cis*.

† All n.m.r. spectra were measured at 100 MHz in $CDCl_3$ solutions and chemical shifts are relative to $SiMe_4$.
‡ Not analysed for C, H, N.

Elaeokanidine A, $C_{12}H_{20}N_2O$, m.p. 38—38·5°, $[\alpha]_D$ +9° ($CHCl_3$), ν_{max} (CCl_4) 3440 (NH), 1705 cm^{-1} (carbonyl), M^+ 208, dipicrate, m.p. 153—155°, is considered to be (**6**). The n.m.r. spectrum, which indicates a close similarity to elaeokanine D, shows a quintet of doublets at δ 3·73 ($J_{12,Me}$ 7·0, $J_{12,11ax}$ 7·0, $J_{12,11eq}$ 2·0 Hz, 12-H), a doublet at 1·16 (J 7·0 Hz, 12-Me), a quintet at 2·67 ($J_{12,11ax}$ 7·0, $J_{11ax,11eq}$ 13·0 Hz, 11*ax*-H) and a quartet at 2·18 ($J_{12,11eq}$ 2·0, $J_{11ax,11eq}$ 13·0 Hz, 11*eq*-H). Double irradiation confirms these assignments and indicates a triplet at δ 2·15 ($J_{8,9}$ 11·0, $J_{8,7}$ 11·0 Hz, 8-H) and overlapping multiplets at 2·90 (7-H) and 3·12 (9-H). The large 7-H, 8-H and 8-H, 9-H couplings together with the 12-H couplings confirm the suggested stereochemistry of (**6**).

Elaeokanidine B, m.p. 93—94°, $[\alpha]_D$ ±0° ($CHCl_3$) and elaeokanidine C, m.p. 56—58°, $[\alpha]_D$ +1° ($CHCl_3$) both have the molecular formula, $C_{12}H_{20}N_2O$. Their i.r. spectra [ν_{max} (CCl_4) 1705 (carbonyl) and 3440 cm^{-1} (NH)] and mass spectra (M^+ 208) indicate that they are stereoisomers of elaeokanidine A. Overlap of significant n.m.r. signals prevents analysis of the multiplets, but the chemical shift of 12-H (between 280—320 Hz) indicates that 12-H is axial in both compounds. One isomer may have a C-7, C-8 *cis* junction with 12-H axial (analogous to elaeokanine E) while the other may be the C-12 epimer of elaeokanidine A.

It was previously suggested[1] that the *Elaeocarpus* alkaloids with the elaeocarpine–isoelaeocarpine ring skeleton, were biosynthetically derived from ornithine and a C_{12} polyketide chain. By analogy, it is suggested that the new *Elaeocarpus kaniensis* alkaloids (**1**—**6**) can be formally derived from condensation of ornithine with a C_8 polyketide chain.

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[1] S. R. Johns, J. A. Lamberton, A. A. Sioumis, and R. I. Willing, *Austral. J. Chem.*, **1969**, **22**, 775; S. R. Johns, J. A. Lamberton, and A. A. Sioumis, *ibid.*, p. 793.