Co-occurrence of Diterpene Acids of the Eperuane and Labdane Series in *Oxystigma oxyphyllum*

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CHROMATOGRAPHY on silica gel (Merck) of the light petroleum extract of the wood of *Oxystigma oxyphyllum* gave two acidic fractions A and B which were further separated by chromatography of their methyl esters on silver nitrate–silica gel to give the compounds A-1 and A-2, B-1 and B-2 respectively. The methyl ester of A_1, $\eta_D^{20} = 1{\cdot}5130$, $[\alpha]_D^{22} + 25°$ ($c = 1{\cdot}0$) was analysed for $C_{21}H_{34}O_2$, M, 318 (mass spectrum). It shows absorption in the infrared at ν_{max} 1725 (CO_2Me), 1645 (C=C), 890 (exocyclic double bond) and 865 (trisubstituted double bond) cm^{-1}, and ultraviolet absorption at λ_{max} 223 mμ (ϵ 12,500). Its n.m.r. spectrum and its positive optical rotation suggested that A-1 was labda-8(20),13-dien-15-oic acid (Ia) (lit.[1] $[\alpha]_D + 26°$). This was confirmed by lithium aluminium hydride reduction to give the allyl alcohol (Ib) η_D^{20} 1·5211, $[\alpha]_D^{22} + 28°$ ($c = 1{\cdot}0$), *p*-nitrobenzoate, m.p. 102—104° {lit.[1]: η_D^{20} 1·5220, $[\alpha]_D + 33{\cdot}2°$, *p*-nitrobenzoate, m.p. 107—108·5°}. The i.r. spectrum of the allyl alcohol (Ib) is identical with that published[1] for labda-8(20),13-dien-15-ol.

The methyl ester of A-2, $\eta_D^{22} = 1{\cdot}5135$, $[\alpha]_D^{22} -26{\cdot}4°$ ($c = 1{\cdot}2$) was analysed for $C_{21}H_{34}O_2$. Its spectral properties are similar to those of the A-1 methyl ester except that in place of the exocyclic double bond is a trisubstituted double bond (ν_{max} 820, 796 $cm.^{-1}$ and n.m.r. signal at τ 4·60 (br)]. This suggested that A-2 may be the $\Delta^{7,13}$-isomer of A-1. However hydrogenation of its methyl ester gave a lævorotatory tetrahydro-derivative, $[\alpha]_D^{22} - 22°$, indicating an opposite stereochemical series to that of A-1 (*cf.*, hydrogenation of methyl eperuate to methyl dihydroeperuate,[2]

$[\alpha]_D$ − 26°, and hydrogenation of methyl cativate[3] to methyl dihydrocativate $[\alpha]_D$ + 23°). A-2 is thus eperu-7,13-dien-15-oic acid {*p*-phenylphenacyl ester, m.p. 109—111°, $[\alpha]_D$ − 29·8° (*c* = 0·155)}.

Notwithstanding the agreement in the properties of A-1 with those of the labda-8(20),13-dien-15-oic acid synthesised[1] from sclareol, it will be observed that the magnitude of the optical rotation of its methyl ester (+25°) is different from that reported for methyl (−)-copalate (−45°) to which the enantiomeric structure has been assigned.[5] This suggests that A-2 contains a small amount of the enantiomeric acid, arising probably from the isomerisation of A-2. This was shown to be the case. Ozonolysis of A-1 methyl ester gave a diketone, treatment of which with dilute alkali, followed by fractional crystallisation of the αβ-unsaturated ketones obtained gave (II), m.p. 62—65°, $[\alpha]_D$ + 41° (G. Ourisson *et al.*,[5] report m.p. 64—66°, $[\alpha]_D$ − 37° for the enantiomer) as well as its racemate, m.p. 89–90° (lit.,[6] m.p. 89°).

The spectral properties of its methyl ester show that B-1 is eperuic acid (III): methyl ester η_D^{23} 1·4960, $[\alpha]_D$ − 26° [lit.,[2,4] η_D^{18} 1·4982, $[\alpha]_D$ − 28°, −36°. On ozonolysis it gave a keto-acid, $C_{19}H_{32}O_3$ (IIIb) as a gum: $[\alpha]_D^{20}$ + 13 (lit.,[4] + 20); oxime, m.p. 223—226°, $[\alpha]_D^{22}$ − 83° (*c* = 1·3 in dioxan) (lit.,[4] m.p. 224—226° $[\alpha]_D$ − 86°). B-2 was also shown to be the Δ^7 isomer of B-1 (methyl ester $[\alpha]_D^{23}$ − 8°, η_D^{22} 1·4962). Its methyl ester was hydrogenated to give methyl dihydroeperuate, η_D 1·4900, $[\alpha]_D^{22}$ − 30° (*c* = 1·4) {lit.,[2] η_D^{18} 1·4902, $[\alpha]_D^{25}$ − 26° (*c* = 3·2)}.

Thus five diterpene acids have been identified in the wood of *Oxystigma oxyphyllum*, four of which belong to the eperuane series while the fifth is of the antipodal labdane series. To our knowledge this is the first example of the co-occurrence of the two series.

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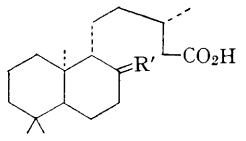
(a: R = CO_2H)
(b: R = CH_2·OH)



(III)
(a: R′ = CH_2)
(b: R′ = O)

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[1] G. Ohloff, *Annalen*, 1958, 617, 134.
[2] F. E. King and G. Jones, *J. Chem. Soc.*, 1955, 658.
[3] F. W. Grant and H. H. Zeiss, *J. Amer. Chem. Soc.*, 1954, **76**, 5001.
[4] C. A. Henrick and P. R. Jefferies, *Tetrahedron*, 1965, **21**, 1175.
[5] G. Hugel, A. C. Oehlschlager, and G. Ourisson, personal communication. We thank these authors for a copy of their manuscript before publication.
[6] J. A. Barltop and N. A. J. Rogers, *J. Chem. Soc.*, 1958, 2566.