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EBENACEAE

STEROLS AND TRITERPENES OF *DIOSPYROS MONTANA*

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Plant. Diospyros montana. Uses. Medicinal.[1–3] *Previous work.* On stem bark.[4]

The dried leaves of the plant were extracted with light petroleum and the extract was chromatographed on neutral alumina. Light petroleum–benzene (4:1) fraction afforded lupeol, $C_{30}H_{50}O$ (m.p., m.m.p., $[\alpha]_D$, IR, TLC; m.p., m.m.p. and $[\alpha]_D$ of acetate). Light petroleum–benzene (1:2) fraction afforded sitosterol, $C_{29}H_{50}O$ (m.p., m.m.p. and $[\alpha]_D$; m.p., m.m.p. and $[\alpha]_D$ of acetate) and stigmasterol, $C_{29}H_{48}O$ (m.p., m.m.p. and $[\alpha]_D$; m.p., m.m.p. and $[\alpha]_D$ of acetate).

Benzene–ether (4:1) fraction afforded epi-uvaol, a new triterpene (I), $C_{30}H_{50}O_2$ (M^+ 442), m.p. 212–214°, $[\alpha]_D$ +49·7°, ν_{max}^{Nujol} 3300 cm^{-1} (—OH) and betulin, $C_{30}H_{50}O_2$ (m.p., m.m.p., $[\alpha]_D$, IR; m.p., m.m.p. and $[\alpha]_D$ of acetate). They are separated by chromatography of their acetates on $AgNO_3$ impregnated silica gel.[5]

The triterpene (I) forms an amorphous diacetate, $C_{34}H_{54}O_4$ (M^+ 526), m.p. 116°, ν_{max}^{Nujol} 1725 cm^{-1}, 1260 cm^{-1} (C=O). The NMR spectrum shows methyl signals at δ 0·91 (S, 9H), 1·02 (S, 3H), 1·04 (S, 6H) and 1·15 (S, 3H) ppm. The spectrum also shows the characteristic signals at δ 2·11 (S, 6H, 2X-$OCOCH_3$), 3·98 (q, 2H, —$C\underline{H}_2OAC$), 4·65 (dd, 1H, $\rangle$ $C\underline{H}OAC$) and at 5·31 (t, 1H, —$C\underline{H}$=C⟨⟩) ppm. The mass fragmentation pattern of the triterpene is typical of Δ^{12}-ursene or Δ^{12}-oleanene skeleton.[6] The mass spectrum shows prominent ions at *m/e* 442, 76% (M^+); 427, 20% (M^+-CH_3); 424, 21·5% (M^+-H_2O); 411, 66% (M^+-CH_2OH); 393, 8% (M^+-CH_2OH-H_2O); 234, 68% (Fragment a); 216, 51% (a-H_2O); 203, 100% (a-CH_2OH); 207, 78% (Fragment b); 189, 70% (a-CH_2OH-C-2H and b-H_2O).

The triterpene (I) on oxidn. with Jones reagent[7] followed by esterification with CH_2N_2 and subsequent purification by chromatography on silica gel furnished a compd.; m.p. 192°, $[\alpha]_D$ +78°, ν_{max}^{Nujol} 1700 cm^{-1} (⟩C=O), 1730 cm^{-1} (—$COOCH_3$), identical with methyl ursonate (m.p., m.m.p., $[\alpha]_D$, IR, TLC). This indicated the triterpene to be an epimer of uvaol, urs-12-ene-3α, 28-diol (I) isolated for the first time from nature. This was further confirmed by comparison of the triterpene with an authentic sample of uvaol (urs-12-ene-3β, 28-diol) prepared by the reduction of methyl ursonate with $LiAlH_4$ and the

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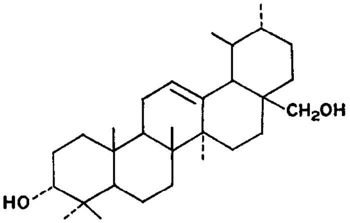
naturally occurring epimer was found to be different (TLC of the corresponding acetate on $AgNO_3$ impregnated silica gel).



(I)

Benzene–ether (1:1) eluate afforded oleanolic acid, $C_{30}H_{48}O_3$ (m.p., m.m.p., $[\alpha]_D$, IR; m.p., m. m.p., $[\alpha]_D$ and IR of its methyl ester).

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Key Word Index—*Diospyros montana*; Ebenaceae; sterols; epi-uvaol; oleanolic acid.

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LAURACEAE

TERPENES FROM *ACTINODAPHNE*, *MACHILUS* AND *NEOLITSEA* SPECIES

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Plant. *Actinodaphne lancifolia* (Sieb. et Zucc.) Meisn. *Date*. Collected in July 1971. *Source*. Kochi Prefecture, Japan. *Uses*. None known. *Previous work*. None.

Leaves. The essential oil (458 mg, n_D^{25} 1·4877, 0·0015% yield) was obtained by steam distillation from fresh leaves (3·0 kg). The individual constituents were isolated by preparative GLC (Carbowax 20 M at 160°) and identified by IR and NMR spectra: *cis*-ocimene (8·2%), *trans*-ocimene (2·5%), caryophyllene (10·0%, α,β-selinene (28·9%), unidentified (50·4%).

Plant. *Actinodaphne longifolia* (Blume). *Date*. Collected in August 1971. *Source*. Kagoshima Prefecture, Japan. *Uses*. None known. *Previous work*. None.

Leaves. The essential oil (6·52 g, n_D^{25} 1·5032, 0·065% yield) was obtained from fresh leaves (5·5 kg) by steam distillation. The individual constituents were isolated by preparative GLC (Carbowax 20 M–20% at 170°) and identified by IR and NMR spectra: *cis*-ocimene (0·73%), *trans*-ocimene (3·4%), caryophyllene (8·3%), β-elemene (7·5%), unidentified (80·1%).