Phytochemistry, 1973, Vol. 12, pp. 217 to 218. Pergamon Press. Printed in England.

ASCLEPIDACEAE

TRITERPENOIDS FROM THE ROOTS OF *HEMIDESMUS INDICUS*

S. N. PADHY, S. B. MAHATO and N. L. DUTTA

Indian Institute of Experimental Medicine, Calcutta-32, India

(*Received* 14 *August* 1972. *Accepted* 7 *September* 1972)

Key Word Index—*Hemidesmus indicus*; Asclepidaceae; lupeol octacosanate; β-amyrin acetate.

Plant. Hemidesmus indicus R. Br. *Uses.* Medicinal.[1] *Previous work.* On roots,[2–4] on leaves.[5]

Present work. The petrol extract of *H. indicus* roots on repeated chromatographic separation yielded, according to increasing order of polarity, hexatriacontane,[6] lupeol octacosanoate (a new ester), β-amyrin acetate, lupeol acetate, α-amyrin, lupeol, β-amyrin and sitosterol. The new ester was found to have m.p. 81–82°, $[\alpha]_D$ +17·7° ($CHCl_3$) and analyse for $C_{58}H_{104}O_2$. Strong IR absorptions at 1740 and 1175 cm^{-1} was suggestive that it is an aliphatic ester, while absorptions at 1640 and 880 cm^{-1} indicated a terminal double bond. On saponification with 6% ethanolic KOH it furnished a triterpene alcohol, $C_{30}H_{50}O$, m.p. 212–213°; $[\alpha]_D$ +30·4° ($CHCl_3$) identical with lupeol (m.p., m.m.p., $[\alpha]_D$, IR; m.p., m.m.p., $[\alpha]_D$ and IR of acetate) and an acid, $C_{28}H_{56}O_2$, m.p. 82–84°. On esterification with CH_2N_2 the acid yielded a methyl ester, $C_{29}H_{58}O_2$, m.p. 60–62°. MS gave the molecular ion peak at *m/e* 438 and other prominent peaks at *m/e* 410, 396, 382, 354, etc. characteristic of a straight chain fatty acid methyl ester identical with methyl octacosanoate.[7] Consequently, the new ester was characterized as lupeol octacosanoate.

EXPERIMENTAL

M.ps are uncorrected. IR spectra were recorded as Nujol mulls, the NMR spectrum was taken at 60 MHz in $CDCl_3$ and TMS as internal standard and the MS was at 70 eV.

Extraction and chromatography. Dried roots of *H. indicus* (900 g) were exhaustively extracted with petrol. (60–80°) for 60 hr and the dark brown residue (40·2 g) obtained after removal of the solvent was separated into six distinct fractions, 1 (10·1 g), 2 (4·6 g), 3 (2·7 g), 4 (4·2 g), 5 (2·6 g), 6 (2 g) by chromatography over alumina (1 kg) and successive elution with petrol., petrol.–benzene (4:1), benzene and benzene–Et_2O mixture (1:1).

Fraction 1 on rechromatography over alumina (300 g) was separated into two fractions, Ia and Ib. Ia on crystallization from $CHCl_3$ yielded needles (200 mg), m.p. 74–75° identical with hexatriacontane[6] (m.p., m.m.p., IR and co-TLC). Ib on crystallization from *n*-hexane yielded lupeol octacosanoate (3·3 g) m.p. 81–82°; $[\alpha]_D^{27}$ +17·7° ($CHCl_3$); IR 1740, 1175 (ester carbonyl), 880, 1640 (terminal double bond), 715 cm^{-1} (methylene chain): NMR δ 0·82 (*s*, 3H), 0·85 (*s*, 9H), 0·96 (*s*, 3H), 1·06 (*s*, 3H), 1·31 (broad *s*, 50H) 1·71 (broad *s*, 3H), 1·92–2·5 (*m*, 4H), 4·33–4·85 (*m*, 3H) (Found: C, 83·72; H, 12·82. $C_{58}H_{104}O_2$ requires: C, 83·65; H, 12·50%). Lupeol octacosanoate on saponification furnished lupeol, m.p. 212–213°; $[\alpha]_D$ +30·4° ($CHCl_3$); IR 3250 (hydroxyl), 880 cm^{-1} (=CH_2) and octacosanoic acid, m.p. 82–84°; IR 1705 (acid carbonyl),

[1] *The Wealth of India*, Vol. V, p. 33, C.S.I.R., New Delhi (1959).
[2] R. C. CHATTERJEE and B. K. BHATTACHARYYA, *J. Indian Chem. Soc.* **32**, 485 (1955).
[3] A. T. DUTTA, S. GHOSH and R. N. CHOPRA, *Arch. Pharm.* **276**, 333 (1938).
[4] P. B. RAMAMURTI and T. R. SESHADRI, *Proc. Indian Acad. Sci.* **13A**, 399 (1941).
[5] S. S. SUBRAMANIAN and A. G. R. NAIR, *Phytochem.* **7**, 1703 (1968).
[6] I. HEILBRON, *Dictionary of Organic Compounds*, Vol. II, p. 677, Oxford University Press, Oxford (1953).
[7] C. F. KREWSON, *J. Am. Chem. Soc.* **73**, 1365 (1951).

3300 (H-bonded hydroxyl), 718, 728 cm^{-1} (methylene chain) (Found C, 79·28; H, 13·26. Calc. for $C_{28}H_{56}O_2$: C, 79·24; H, 13·20%). The acid on esterification with CH_2N_2 yielded its methyl ester; IR 1740 (ester carbonyl), 719, 729 cm^{-1} (methylene chain) (Found: C, 79·48; H, 13·26. Calc. for $C_{29}H_{58}O_2$: C, 79·45; H, 13·24%).

Fraction 2 (4·6 g) was separated into fractions 2a and 2b by rechromatography over $AgNO_3$ impregnated silica gel. Fraction 2a on crystallization from $CHCl_3$–MeOH yielded β-amyrin acetate in needles (700 mg), m.p. and m.m.p 234–236°; $[\alpha]_D^{27}$ +79° ($CHCl_3$). Fraction 2b on crystallization from $CHCl_3$–MeOH afforded lupeol acetate (2·8 g), m.p. and m.m.p. 216–218°; $[\alpha]_D^{27}$ +42° ($CHCl_3$).

Fraction 3 (2·7 g) on rechromatography on $AgNO_3$ impregnated silica gel yielded α-amyrin and lupeol (characterized by m.p., m.m.p., co-TLC, IR). *Fraction* 4 on rechromatography over alumina yielded β-amyrin and sitosterol (characterized by m.p., m.m.p., co-TLC, IR). *Fraction* 5 on further purification by chromatography over alumina afforded more sitosterol (characterized by m.p., m.m.p., co-TLC, IR).

Acknowledgements—Our thanks are due to Dr. M. M. Dhar, CDRI, Lucknow for the MS and NMR spectra and Dr. B. Bhattacharjee, Jadavpur University for microanalysis.

Phytochemistry, 1973, Vol. 12, pp. 218 to 220. Pergamon Press. Printed in England.

BERBERIDACEAE

ANTHOCYANINS IN FRUITS OF *BERBERIS BUXIFOLIA*

A. B. POMILIO

Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, Buenos Aires, Argentina

(*Received* 30 *August* 1972. *Accepted* 1 *October* 1972)

Key Word Index—*Berberis buxifolia*; Berberidaceae; petunidin; peonidin; malvidin and delphinidin plycosides.

The genus *Berberis* (Berberidaceae) has not been fully investigated although nearly 150 species are distributed all over the world. Recently Mamaev and Semkina[1,2] identified the anthocyanins of *Berberis thunbergii* and *B. vulgaris* (common barberry) and observed a maximum pigment concentration in spring. The leaves of the purple-leaf and green-leaf forms of barberry contained five anthocyanin pigments, the main ones being 3-monoglycosides of peonidin, cyanidin and delphinidin. No reports on isolation of anthocyanins from *Berberis* fruits are known.

The present work describes the identification of ten anthocyanins isolated from *Berberis buxifolia* Lam. fruits, which is indigenous to Argentina and south of Chile. Chromatography of the crude extract yielded six coloured bands, in amounts decreasing in the order IV > III ⩾ II > I > V > VI, the latter band being feint. Each band was rechromatographed in 15% HOAc to give complete purification. R_fs are shown in Table 1. Only pigments IIIa, IIIb, IVb, IVc, Va and Vb changed to blue with 1% ethanolic $Pb(OAc)_2$.[3]

The visible and UV spectra of pigments IVa and Va were characteristic of 3,5-diglycosides and only differed by substitution in the B-ring.[4] The other spectra corresponded to 3-glyco-

[1] S. A. MAMAEV and L. A. SEMKINA, *Rast. Resvr.* 7, 280 (1971); *Chem. Abs.* 75, 95377p (1971).
[2] L. A. SEMKINA, *Ekologika* 45 (1971); *Chem. Abs.* 75, 85143v (1971).
[3] T. FULEKI and F. J. FRANCIS, *Phytochem.* 6, 1161 (1967).
[4] J. B. HARBORNE, *Biochem. J.* 70, 22 (1958).