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TRITERPENOIDS OF *CENTAURIUM ERYTHRAEA*

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Key Word Index—*Centaurium erythraea*, Gentianaceae, β-amyrin, erythrodiol, oleanolic acid, oleanolic lactone, maslinic acid

Plant Centaurium erythraea Rafn (Voucher A Batelli 5070 specimen is deposited in the Herbarium of this University) *Uses* In folk medicine and as an ingredient in bitters *Previous work* Mainly concerned with the identification of the bitter glucoside, erythaurin,[1,2] whereas work on the steroid-triterpenoic fraction has been limited to the identification of sitosterol[3] and oleanolic acid[4]

Besides the identification of sitosterol and oleanolic acid, the present report describes the isolation of β-amyrin, erythrodiol, oleanolic lactone and maslinic acid The oleanolic lactone is reported for the first time as a natural product

EXPERIMENTAL

The materials for column chromatography were alumina (Fluka 507-C neutral) silica gel 922 and silica-alumina 113 (GRACE Co) IR spectra were recorded with a Perkin-Elmer IR 427 and NMR spectra on a Varian Associates HA-100 TLC was performed on silica gel-H (Fluka) Developing systems C_6H_6–EtOAc (9 1 or 7 3). Spots were detected by spraying the plates with H_2SO_4 and heating them at 100° for several minutes

The dried aerial parts of *C erythraea* (800 g) were percolated with Et_2O 27 g of sticky residue were obtained and then suspended in hexane and filtered The soluble fraction was chromatographed on alumina, sitosterol, β-amyrin (free and esterified) and some erythrodiol were isolated

The insoluble fraction was acetylated and chromatographed on silica gel with C_6H_6 and increasing gradients of EtOAc, erythrodiol diacetate, oleanolic lactone acetate, oleanolic acid acetate and maslinic diacetate were separated

Sitosterol m p 136–137°, $[\alpha]_D^{20}$ −37°, identified by mixed m p IR and co-TLC of the sterol and its acetate

β-Amyrin The mixed natural esters were hydrolysed either by alcoholic-KOH or $LiAlH_4$ The free triterpenoid (some free β-amyrin and its acetate were also found in the plant) was then purified by chromatography and crystallized from MeOH (300 mg) m p 194–195°, $[\alpha]_D^{20}$ +87° ($CHCl_3$), acetate m p 237–238°, $[\alpha]_D^{20}$ +80° ($CHCl_3$), IR and NMR spectra were identical to those of an authentic sample of β-amyrin acetate

Erythrodiol Identified as its acetate The oily product obtained from the silica gel column was again purified on a small alumina column Crystallization from MeOH afforded needles (200 mg), m p 182–183°, $[\alpha]_D^{22}$ + 60° ($CHCl_3$) The IR and NMR spectra were identical to those of a sample of erythrodiol diacetate obtained by acetylation of the $LiAlH_4$ reduction product of methyl oleate acetate

Oleanolic acid The insoluble acetylated fraction was chromatographed on a silica gel column (TLC grade, no binder) which had been prepared in C_6H_6 and eluted with C_6H_6–EtOAc (93 7) The first fractions eluted traces of β-amyrin acetate and some erythrodiol diacetate oleanolic acid acetate followed The oleanolic acid acetate

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[1] NAKAOKI, T and HIDA, Y (1943) *J Pharm Soc Japan* **53,** 554

[2] KUBOTA, T and TOMITA, Y (1961) *Tetrahedron Letters* 176

[3] POETKE, W , WILHELM, A and ARNOLD, W (1951) *Arch Pharm* **284,** 385

[4] POETKE, W , WILHELM, A and ARNOLD, W (1950) *Arch Pharm* **283,** 269

(2 3 g) was crystallized 1 × from C_6H_6 and 2 × EtOAc m p 258–260°, $[\alpha]_D^{20}$ +73° ($CHCl_3$) The IR and NMR spectra were identical to those of a pure sample of oleanolic acid acetate

Oleanolic acid lactone The mother liquors from the crystallization of oleanolic acid acetate were adsorbed on a column of silica-alumina prepared in hexane Elution with hexane–EtOAc (24 1) afforded the lactone immediately, whereas the acid was retained much more strongly by the active adsorbent The lactone (22 mg) crystallized from MeOH m p 293–294°, $[\alpha]_D^{20}$ +12° ($CHCl_3$) The IR spectrum was identical to that of a sample of oleanolic acid lactone acetate obtained from the oleanolic acid acetate reaction with HCl in CCl_4 as described by Barton[5]

Maslinic acid[6] Identified as its diacetate or diacetate methyl ester Maslinic acid acetate closely followed oleanolic acid acetate in the chromatographic elution described above Repeated crystallization from MeOH yielded silky needles (1 2 g) m p 235–236°, $[\alpha]_D^{20}$ +30° ($CHCl_3$) IR Snatze's[7] ‘A’ and ‘B’ zones showed the characteristic bands of a triterpenoid of the oleanolic series [AUI 1391 cm^{-1}, AUII 1381 cm^{-1} AUIII 1362 cm^{-1} BUI 1308 cm^{-1}, BUII 1270 cm^{-1} BUIII 1244 cm^{-1} (sh)] The compound after methanolic KOH hydrolysis of the two acetic groups gave an acetonyl derivative The IR spectra of the diacetate or diacetate methyl ester derivatives of the natural compound were identical to those of authentic samples of equivalent maslinic acid derivatives

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[5] BARTON, D H R and HOLNESS N J (1952) *J Chem Soc* 78

[6] CAGLIOTI L and CAINELLI, G (1961) *Gazz Chim Ital* **91**, 1387

[7] SNATZKE, G, LAMPERT, F and TSCHESCHE R (1962) *Tetrahedron* **18**, 1417

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PHENYLPHENALENONES FROM *WACHENDORFIA* SPECIES

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Key Word Index—*Wachendorfia paniculata, W thyrsiflora* Haemorodaceae 9-phenylphenalenones

Plants Wachendorfia paniculata[1] and *W thyrsiflora*[2] Berm *Uses* Ornamental *Previous Work* None *Part examined* Roots TLC analysis (polyamide MeOH, acid washed SiO_2 EtOAc–C_6H_6, 1 1) of the $CHCl_3$ soluble compounds present in the root systems of *W paniculata* and *W thyrsiflora* showed the presence of several 2-hydroxyphenalenone pigments (colors purple to orange, turning blue to green on exposure to NH_3)

Chromatography of the extracts (cellulose–C_6H_6) resulted in the isolation of the following phenalenones, previously isolated from other species of the family all identical (NMR,

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[1] We are grateful to Professor G W Perold, University of the Witwatersrand South Africa for obtaining this plant material

[2] Grown from seed at Storrs Connecticut