

TRITERPENOIDS AND STEROIDS FROM *RHODOMYRTUS TOMENTOSA*

WAI-HAAN HUI, MAN-MOON LI and KONG LUK

Department of Chemistry, University of Hong Kong, Hong Kong

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Key Word Index—*Rhodomyrtus tomentosa*; Myrtaceae; rose myrtle; pentacyclic triterpenoids; phytosterols.

Plant. *Rhodomyrtus tomentosa* (Ait.) Hassk. Commonly known as rose myrtle. An abundant flowering shrub in Hong Kong and China, with rose-pink flowers and dark-purple edible bell-shaped fruits.

Previous work. None. On sister species: *R. macrocarpa* -rhodomyrt toxin [1] and ψ -rhodomyrt toxin [2].

Present work. The light petrol. extract of the leaves of *R. tomentosa* has been shown to contain the triterpenes, lupeol, β -amyrin, β -amyrenol (3β -hydroxy-olean-12-en-11-one), betulin, and an unidentified diol, R_1 , $C_{30}H_{50}O_2$ (M^+ , *m/e* 442), mp 237-239°, ν_{\max} 3330 (OH), 1655, 990, 915 cm^{-1} ($-\text{HC}=\text{CH}_2$), and that of the stems friedelin, lupeol, α -amyrin, taraxerol, betulin-3-acetate, betulin, and two probably new compounds: R_2 , $C_{32}H_{48}O_5$ (M^+ , *m/e* 512), mp 329-331°, containing an acetyl group (ν_{\max} 1735, 1245) and a γ -lactone ring (ν_{\max} 1770 cm^{-1}), and R_3 (in minute quantity) $C_{32}H_{50}O_5$ (M^+ , *m/e* 514), mp 281-283°, containing a hydroxyl group (ν_{\max} 3550), an acetyl group (ν_{\max} 1740, 1250) and a γ -lactone ring (ν_{\max} 1775 cm^{-1}). A mixture of sitosterol, stigmasterol and campesterol has also been found in the extracts of both the leaves and the stems.

β -Amyrenol was first prepared in the pure state in 1939 [3] through allylic oxidation of β -amyrenyl benzoate followed by mild hydrolysis of the product, but has never been isolated from natural sources. The occurrence of betulin-3-acetate has been reported from *Lyonia ovalifolia* [4] and *Mallotus philippinensis* [5]; this is its third isolation.

EXPERIMENTAL

IR spectra were recorded for KBr discs, UV spectrum in 95% EtOH, and optical rotations in CHCl_3 solns. Light petrol. had bp 60-80°. Known compounds were identified by TLC, mmp and IR spectral comparisons with authentic samples.

Leaves. Milled air-dried leaves (22.5 kg) were twice extracted with light petrol., and the combined extracts were concentrated and chromatographed on alumina (3 kg). Elution with light petrol. gave lupeol (1.0 g), mp 208-210°, ν_{\max} 3340 (OH), 3080, 1645, 880 cm^{-1} ($>\text{C}=\text{CH}_2$); light petrol.- C_6H_6 (1:1), β -amyrin (0.02 g), mp 205-207°, ν_{\max} 3300 (OH), 3050, 1675, 818 cm^{-1} ($>\text{C}=\text{CH}_2$), then a sterol mixture (0.1 g), mp 140-141°, ν_{\max} 3360, 970, 959 cm^{-1} separated by GLC into campesterol (2%), stigmasterol (4%) and sitosterol (94%), and finally β -amyrenol (11 mg), mp 229-230° (from light petrol.), $[\alpha]_D + 106^\circ$ ($C_{30}H_{48}O_2$, M^+ 440), ν_{\max} 3300 (OH), 1690, 1620 cm^{-1} ($>\text{C}=\text{C}-\text{C}=\text{O}$), λ_{\max} 242 nm (ϵ 12 000) (benzoate mp 263-265°, identical with an authentic sample prepared from β -amyrin [3]); C_6H_6 , betulin (0.5 g), mp 259-261°, ν_{\max} 3380 (OH), 3070, 1650, 882 cm^{-1} ($>\text{C}=\text{CH}_2$), (diacetate, mp 222-224°); C_6H_6 - CHCl_3 (1:1), fine needles of R_1 (10 mg), mp 237-239° (from CHCl_3), (found: M^+ 442, $C_{30}H_{50}O_2$ requires M^+ 442), ν_{\max} 3330 (OH), 1655, 990, 915 cm^{-1} ($-\text{HC}=\text{CH}_2$).

Stems. Milled dried stems (52 kg) were extracted with light petrol. and chromatographed on alumina (3 kg) as for the leaves. Elution with light petrol. yielded first friedelin (10 mg), mp 259-261°, then lupeol (3.0 g); light petrol.- C_6H_6 (1:1), α -amyrin (0.02 g), mp 185-187°, $[\alpha]_D + 79.0^\circ$, ν_{\max} 3320 (OH), 3050, 1650, 830 cm^{-1} ($>\text{C}=\text{CH}_2$), then taraxerol (0.5 g), mp 284-285°, ν_{\max} 3500 (OH), 3060, 1650, 820 cm^{-1} ($>\text{C}=\text{CH}_2$), followed by a sterol mixture (1.0 g) as for the leaves, and finally betulin-3-acetate (0.05 g), mp 262-263° $[\alpha]_D + 40.0^\circ$ $C_{32}H_{50}O_3$, M^+ , *m/e* 484, strong fragmentation ions, *m/e* 453 ($M-\text{CH}_3\text{OH}$), 393 ($M-\text{CH}_2\text{OH}-\text{MeCOOH}$, bp) ν_{\max} 3400, 1029 (CH_2OH), 1740, 1250 (OAc), 3080, 1650, 890 cm^{-1} ($>\text{C}=\text{CH}_2$), acetylation of which gave betulin diacetate, mp 222-224°, $[\alpha]_D + 26.0^\circ$, ν_{\max} 1750, 1740, 1240 (OAc), 3080, 1650, 890 cm^{-1} ($>\text{C}=\text{CH}_2$), identical with an authentic sample; C_6H_6 , prisms of R_2 (50 mg), mp 329-331° (from chloroform) (found: M^+ 512, C, 75.1; H, 9.55. $C_{32}H_{48}O_5$ requires M^+ 512, C, 75.0; H, 9.45%). ν_{\max} 1735, 1245 (OAc), 1770 cm^{-1} (γ -lactone), then betulin (0.5 g), mp 253-255°; C_6H_6 : CHCl_3 (1:1) fine needles of R_3 (5 mg), mp 281-283° (from CHCl_3), (found: M^+ 514. $C_{32}H_{50}O_5$ requires M^+ 514) ν_{\max} 3550 (OH), 1775 (γ -lactone), 1740, 1250 cm^{-1} (OAc).

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DIHYDROSANGUILUTINE, A NEW ALKALOID FROM *SANGUINARIA CANADENSIS*

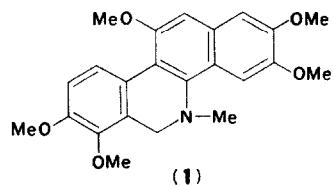
DON K. KIM and FRANK R. STERMITZ*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80521, U.S.A.

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Key Word Index—*Sanguinaria canadensis*; Papaveraceae; dihydrosanguilutine.

Plant. *Sanguinaria canadensis* L. roots. **Source.** Purchased as ground powder from S. B. Penick, New York and authenticated by them (reports 71B-2880 and 71B-3612). **Previous work.** See, for example, J. Slavik and L. Slavikova (1960). *Coll. Czech. Chem. Comm.* **25**, 1667.



Present work. Florisil chromatography of mother liquor residues from which chelerythrine, protopine and sanguinarine had been removed yielded crystals of a colorless base (1), mp 154–155°, R_f 0.72 (Si gel; EtOAc); NMR ($CDCl_3$): s,

2.61 δ (3H); s, 3.85 (3H); s, 3.92 (3H); s, 3.96 (3H); s, 4.03 (3H); s, 4.11 (3H); s, 4.26 (2H); m, 7.0–7.7 (5H); UV (MeOH): 238 nm (log ϵ 4.21), 262 (4.38), 275 (4.42), 325 (4.22); MS: m/e 395 (30%), 394 (100), 379 (20). **Anal.** Calcd for $C_{23}H_{25}NO_3$: C, 69.86; H, 6.37; N, 3.54. Found: C, 69.29; H, 6.16; N, 3.15%.

A hot soln of 10 mg (1) in 6 ml aq. HOAc was treated with 100 mg mercuric acetate and heated for 2 hr. The cooled mixture was filtered and evaporated to dryness to leave a residue of sanguilutine identical with an authentic sample isolated from the same plant. These data show the unknown to be dihydrosanguilutine (1), a previously unreported alkaloid.

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