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PHYTOSTEROLS IN EUPHORBIACEAE AND RUTACEAE*

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Key Word Index—*Fluggea microcarpa*; Euphorbiaceae; hexacosane; friedelin; friedelanol; sitosterol; *Sapium baccatum*; Euphorbiaceae; acetoxy aleuritic acid; *Skimmia wallichii*; Rutaceae; taraxerone; 3-epitaraxerol; taraxerol; sitosterol.

Plant. *Fluggea microcarpa* Blume [2,3]. (Syn *Flueggea microcarpa* Blume); Euphorbiaceae. **Occurrence.** Throughout India; from Kashmir ascending the Himalaya to 5000 ft, to Bhutan, and Assam and southwards to Malacca and Travancore. **Uses.** Medicinal [4]. **Previous work** [5]. Bergenin and isocoumarin in leaves.

Isolation and identification. The powdered trunk bark was extracted with C_6H_6 and the neutral fraction on chromatography over deactivated alumina afforded several crystalline solids: *hexacosane*, mp 58–59°; *friedelin*, mp 259–261°, $[\alpha]_D - 32^\circ$, ν_{max} 1708 cm^{-1} (six-membered ring ketone), *oxime*, mp 293–295°, $[\alpha]_D + 54.6^\circ$; *friedelanol*, mp 296–298°, $[\alpha]_D + 15.5^\circ$, acetate, mp 314–316°, and *sitosterol*, mp 136–137°, $[\alpha]_D - 34^\circ$, acetate, mp 127–129°, $[\alpha]_D - 39^\circ$. The identity of the above compounds was confirmed by mmp IR and co-TLC with authentic samples.

Plant. *Sapium-baccatum* Roxb; [6]. Euphorbiaceae. **Occurrence.** Assam, Sylhet and Khasia Mountains, India. **Previous work.** [7–10] Isolation

and characterization of taraxerone, taraxerol, sitosterol 1-hexacosanol, 3-3'-di-O-methyl ellagic acid [11].

Isolation and identification. The acidic fraction from the C_6H_6 extract of the stem and trunk bark of the plant on esterification with CH_2N_2 followed by chromatography furnished a crystalline solid, mp 241–243°. $[\alpha]_D + 21.8^\circ$, no UV absorption above 220 nm, $\nu_{max}^{CHCl_3}$ 1738 cm^{-1} (broad, $-OCOMe$ and $COOMe$, 1245 cm^{-1} ($-OCOMe$), NMR signals at δ 5.45 (1H, vinyl proton, trisubstituted double bond), δ 4.42 (1H, H-C-O-COMe), δ 2.05 (3H, $-OCOMe$), δ 3.54 (3H, $-COOMe$) and several sharp signals between δ 0.8 to 1.55 (21H, seven methyl groups). Hydrolysis of the ester with 5% methanolic KOH yielded an alcohol, mp 208–210°, $[\alpha]_D + 15.6^\circ$, $\nu_{max}^{CHCl_3}$ 3490 cm^{-1} ($-OH$), 1738 cm^{-1} ($-COOMe$). Oxidation of alcohol by $CrO_3-C_6H_5N$ complex-furnished a ketone, mp 174–176°, $[\alpha]_D + 14.2^\circ$, ν_{max}^{KBr} 1708 cm^{-1} (C=O), 1738 cm^{-1} ($-COOMe$). The acid obtained from the plant is therefore *acetoxy aleuritic acid*, the physical data on the ester, alcohol and ketone being strikingly similar to those obtained for the known compound [12].

* Part 2 of a series on Plant Phytosterols; for Part 1 see Ref. [1].

Plant. *Skimmia wallichii* Hk [13]; Rutaceae.
Occurrence. A small procumbent shrub about 4 ft. high, fairly common in Singalila Range, from 9000–11000 ft. **Previous work.** None. **Isolation and identification.** The powdered bark of the plant was extracted with C_6H_6 and the neutral fraction on chromatography over deactivated alumina first gave four crystalline compounds; the first mp $238-239^\circ$, $[\alpha]_D + 11^\circ$, ν_{max} 1710 cm^{-1} (six membered ring ketone) was identical with *taraxerone* (mmp and IR); 3-*epitaraxerol* [14] mp $261-263^\circ$, $[\alpha]_D - 25.6^\circ$, ν_{max} 3420 cm^{-1} (—OH) and 825 cm^{-1} (trisubstituted double bond), acetate, mp $160-162^\circ$, $[\alpha]_D - 43$. Oxidation of the alcohol by $CrO_3-C_6H_5N$ complex-furnished taraxerone. The alcohol, 3-*epitaraxerol* and its oxidised product, taraxerone were identified by mmp, IR and co-TLC; *taraxerol*, mp $272-274^\circ$, $[\alpha]_D + 5.5^\circ$, acetate, mp $295-297^\circ$, $[\alpha]_D + 10^\circ$ confirmed by mmp, IR and co-TLC with an authentic sample; and *sitosterol* (mmp and IR).

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BREVIFOLIN, CORILAGIN AND OTHER PHENOLS FROM GERANIUM THUNBERGII

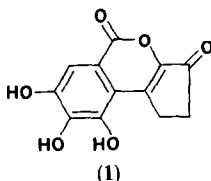
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Key Word Index—*Geranium thunbergii*; Geraniaceae; polyphenols; brevifolin; corilagin; ellagic acid.

Plant. *Geranium thunbergii* Sieb. et Zucc.
Source. Collected at Okayama University, August 1973. **Uses.** Official antidiarrhoics in Japan. **Previous work.** Isolation of gallic acid, succinic acid, quercetin [1], kaempferol-7-rhamnoside and kaempferitrin [2].



Present work. The aqueous extract of the aerial parts of the plant was concentrated and the ppt which formed was recrystallized from C_6H_5N to yield ellagic acid (IR). The mother liquor was concentrated to a syrup which was extracted with MeOH. The MeOH soln, on concentration gave solid KCl, and the filtrate (A) was then continuously extracted with Et_2O . The Et_2O extract gave a solid, recrystallized from MeOH, to give brevifolin **1**, $C_{12}H_{18}O_6$, (M^+ 248), m.p. $>360^\circ$, trimethyl ether **2** (CH_2N_2), $C_{15}H_{24}O_6$, (M^+ 290), mp $209-210^\circ$. These data together with UV, IR,