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A NEW DIPHYLLIN GLYCOSIDE FROM *GLEISTANTHUS COLLINUS*

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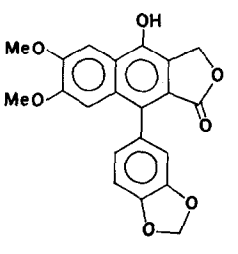
Key Word Index—*Cleistanthus collinus*; Euphorbiaceae; diphyllin-4-*O*-[β-2,3,di-*O*-methylxylopyranosyl (1 → 4)] β-D-glucopyranoside.

Cleistanthus collinus Roxb., is an extremely poisonous tree [1] which yields hard and durable heartwood useful for agricultural implements [2]. Recently, diphyllin (**1**) was isolated free and also as 3,4-di-*O*-methylxylopyranoside from its leaves [3,4] and as its β-D-glucopyranoside from its bark [5]. The fruits were shown to contain sitosterol and lupeol [6].



(**1**)

A new diphyllin diglycoside is now reported from its heartwood. From the methanolic extract, the $CHCl_3$ soluble fraction was treated with benzene and the benzene-insoluble residue crystallized ($CHCl_3$–MeOH) as colourless plates, $C_{34}H_{38}O_{16}$, M^+ 702, mp 220–21°, $[\alpha]_D$ −33° (c, 1% dioxan) R_f 0·22 $CHCl_3$–MeOH (9:1) TLC Si gel G. IR ν_{max} (nujol) 3350, 1770, 1620, and 930 cm^{-1}; λ_{max}^{EtOH} 350, 297, 265 nm (log ε 4·31, 4·32 and 4·79). Since the Molisch test was positive, the glycoside was hydrolysed and the aglycone identified as diphyllin (**1**) through mmp, IR and via its acetate and dimethyl ether. PC of the hydrolysate revealed β-D-glucopyranose and another spot not identical with xylose or its 3,4-dimethyl ether. This second sugar was extracted with $CHCl_3$ from the acid hydrolysate as colourless plates, mp 81–82°, $[\alpha]_D$ + 22° (*c* 1% H_2O) R_G 0·74. These constants agree with those of 2,3-di-*O*-methyl xylose [7,8]. It was further confirmed by oxidation with Br_2 water to di-*O*-methylxylono-lactone as a gum. Its IR spectrum showed two peaks at 1730 and 1770 cm^{-1} corresponding with δ and γ lactones. The isomeric 3,4-di-*O*-methylxylose can give rise to only to a δ-lactone.

Six moles of $NaIO_4$ were consumed by the glycoside hydrolysate, consistent with 1 mol of D-glucopyranose and one of 2,3-di-*O*-methylxylose in the sugar moiety. Permethylation followed by hydrolysis furnished an equimolecular mixture of 2,3,6-tri-*O*-methyl-D-glucopyranose and 2,3,4-tri-*O*-methylxylose. Since the glycoside was not hydrolysed with β-glucosidase, the glycoside is regarded as 4-*O*-[β-2,3-di-*O*-methyl-D-xylopyranosyl (1 → 4)]-β-D-glucopyranoside.

The ^1H NMR of the glycoside tetra-acetate confirmed this structure; colourless needles mp 152–54°, $[\alpha]_D$ +12·5° (*c* 1% $CHCl_3$). IR, ν_{max} (nujol) 1760, 1620, 930 cm^{-1}; λ_{max}^{EtOH} 355, 295, 265 nm (log ε 4·12, 4·18 and 4·69); ^1H NMR (60 MHz in $CDCl_3$ TMS), δ 1·82, 2·02, 2·03, 2·12 (S, 3H each, 4 acetoxyls) 2·87–3·38 (*m*, 6H sugar protons), 3·47, 3·63 (S 3H each, 2 aliphatic methoxyls), 3·81, 4·13 (S 3H each, 2 aromatic methoxyls), 4·05 (*d*), *J* 6 Hz and 3·98 (*d*) *J* 6 Hz (2H, sugar anomeric protons), 4·92–5·2 (*m*, 5H on acetoxyl carbons), 5·48 (2H, methylene of the lactone), 6·07 (*q*, 2H methylenedioxy) and 6·85–7·83 (*m* 5H aromatic).

Cleistanthus collinus Roxb. is unique in elaborating two glycosides of diphyllin containing 2,3- and 3,4-di-*O*-methylxyloses. Xylose, but not its methyl ethers, is known to occur as part of the sugar moiety of several natural glycosides. The methyl ethers are however, known to be common constituents of xylans and mucilages.

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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 aleuritolic 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°, $[\alpha]$, −32°, ν_{max} 1708 cm^{-1} (six-membered ring ketone), oxime, mp 293–295°, $[\alpha]_D$ + 54·6°; *friedelanol*, mp 296–298°, $[\alpha]_D$ + 15·5°, acetate, mp 314–316°, and *sitosterol*, mp 136–137°, $[\alpha]_D$ − 34°, acetate, mp 127–129°, $[\alpha]_D$ − 39°. 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°, 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°, $\nu_{max}^{CHCl_3}$ 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°, ν_{max}^{KBr} 1708 cm^{1} (C=O), 1738 cm^{-1} (–COOMe). The acid obtained from the plant is therefore *acetoxy aleuritolic 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].