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DALPANICULIN, A *C*-GLYCOSYLISOFLAVONE FROM *DALBERGIA PANICULATA* SEEDS

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Key Word Index—*Dalbergia paniculata*; Leguminosae; seeds; (+)-pinitol; caviunin 7-*O*-rhamnoglucoside; isocaviunin 7-*O*-glucoside; dalpaniculin; dehydrodalpanol *O*-glucoside.

Abstract—Further examination of seeds of *Dalbergia paniculata* has yielded (+)-pinitol, caviunin 7-*O*-rhamnoglucoside, isocaviunin 7-*O*-glucoside and two new compounds: a *C*-glycosylisoflavone, dalpaniculin which is 8-*C*-*β*-D-glucopyranosyl-5,7-dihydroxy-2′,4′,5′,6-tetramethoxyisoflavone (8-*C*-glucosylcaviunin) and an *O*-glycosyldehydrorotenoid, dehydrodalpanol *O*-glucoside.

INTRODUCTION

In continuation of our earlier studies [1–4] on the seeds of *Dalbergia paniculata* Roxb, we report the isolation of (+)-pinitol, caviunin 7-*O*-rhamnoglucoside, isocaviunin 7-*O*-glucoside, a new *C*-glycosylisoflavone named dalpaniculin (**1**) and dehydrodalpanol *O*-glucoside (**2**), from the acetone extract. The structure of the latter two compounds is presented in this paper.

RESULTS AND DISCUSSION

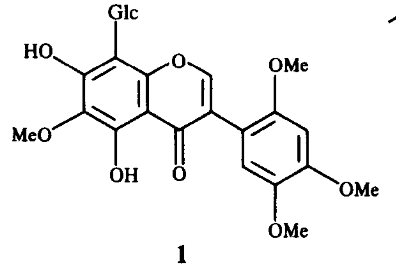
All the *C*-glycosylisoflavones [5] reported so far are from Leguminosae and the present report of dalpaniculin represents the first example of a *C*-glycosylisoflavone where the isoflavone moiety possesses hexaoxygenation. The aglycone corresponding to dalpaniculin is caviunin [6] and shown to be present in almost every organ of *D. paniculata* [7, 8].

Dalpaniculin (**1**) is the fourth *C*-glycosylisoflavone to be isolated from *D. paniculata*, the other three being paniculatin [9], dalpanitin [2] and 8-*C*-glucosylprunetin [10, 11]. It is interesting to note that in *D. paniculata* there is the co-occurrence of flavones [12], isoflavones [3, 4, 7, 12], *C*- and-*O*-glycosylisoflavones [2, 8–11], a *C*-glycosylisoflavanone [2, 13], a rotenoid [1], an *O*-glycosylrotenoid [14], a dehydrorotenoid [3] and an *O*-glycosyldehydrorotenoid (**2**).

EXPERIMENTAL

Shade-dried seeds (2.3 kg) of *D. paniculata* were powdered and Soxhleted successively with C_6H_{14} (60–80°), $CHCl_3$ and Me_2CO. $CHCl_3$ extn gave [4] caviunin, isocaviunin, 3′-*O*-methylorobol, dalpalatin, sitosterol-*O*-glucoside and dalpanol-*O*-glucoside. Me_2CO extract on concn deposited (+)-pinitol. The mother liquor, polyamide CC employing $MeOH–H_2O$ mixts as eluting solvents, yielded caviunin 7-*O*-rhamnoglucoside [8], isocaviunin 7-*O*-glucoside [15] (mp, mmp, co-chromatography and identical UV and IR spectra corroborated the identifications) and two new compounds, dalpaniculin (230 mg) and dehydrodalpanol-*O*-glucoside (28 mg).

Dalpaniculin (**1**) was obtained as crystals ($MeOH–C_6H_{14}$), mp 198–200° (dec); $[\alpha]_D^{28} -41°$ (MeOH; *c* 0.52); (Found: C, 53.9; H, 5.6; OMe, 22.6; $C_{21}H_{16}O_9(OMe)_4 . H_2O$ requires: C, 54.15; H, 5.45; OMe, 22.39%). λ_{max}^{MeOH} nm (log ε): 268 (4.35) and 295 (4.16); λ_{max}^{NaOAc} nm; 276, 297 and 336; $\lambda_{max}^{AlCl_3}$ nm: 280 and 300; $\lambda_{max}^{(AlCl_3-HCl)}$ nm: 280 and 300; ν_{max}^{KBr} cm^{-1}: 3440 br, 3300 (OH), 1665 (conj. C=O), 1623 (chromene C=C), 1585, 1525, 1465 (arom. C=C), 1040, 1010 (*C*-glycosyl) [16]; ^{1}H NMR spectrum (90 MHz, DMSO-d_6) δ 12.55 (1H, *s*, OH-5, exch.) 10.85 (1H, *br s*, OH-7, exch.), 8.37 (1H, *s*, H-2) [17], 6.96 (1H, *s*, H-6′), 6.84 (1H, *s*, H-3′), 5.38–3.30 (10H, *m*, sugar protons), 4.70 (1H, *d*, $J = 10$ Hz, H-1″) [18], 3.85 (6H, *s*, OMe-5′ and OMe-6), 3.75 (3H, *s*, OMe-4′) and 3.72 (3H, *s*, OMe-2′) [19]; EIMS 70 eV, *m*/*z* (rel. int.): 518 $[M-H_2O]$ (100), 500 $[M-2H_2O]$ (49.4), 482 $[M-3H_2O]$ (63.5), 387 $[M-149]$ (70.4), 374 $[M-162]$ (54.3) [20]; 360 (22.8), 359



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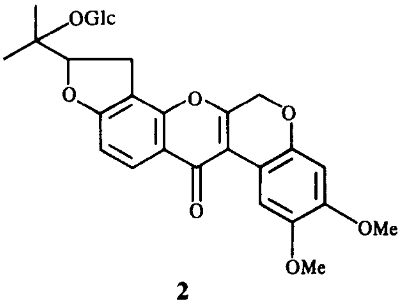

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(26.2), 343 (11.0), 331 (17.3), 195 (5.4), 192 (3.7), 191 (5.7), 187 (2.8), 183 (2.6), 182 (3.1), 179 (4.3).

Dalpaniculin gave a green ferric reaction, and positive Molisch and Wolfrom [21] tests. It gave no colour in the Shinoda test [22]. The compound (10 mg) failed to yield any sugar or aglycone, even on prolonged acid hydrolysis (7% aq. alc H_2SO_4, 10 ml, at 100° for 6 hr). Wessely–Moser rearrangement [23, 24] of dalpaniculin (3 mg) with HCl in EtOH (3 M, 5 ml) gave its isomer (isocaviunin-6-*C*-glucoside) which showed by PC a higher R_f value [25] than that of the original compound in 15% aq. EtOH or BAW(U). The isomeric compound also gave negative Gibbs reaction [26]. Viscontini degradation [27] of dalpaniculin gave glycerol. Glucose (plus a small amount of arabinose) was formed from $FeCl_3$ oxidation [28] of dalpaniculin.

Acetylation of dalpaniculin (50 mg) with $Ac_2O + NaOAc$, at 100° for 1.5 hr gave the hexaactate (50 mg) as crystals from C_6H_6–C_6H_{14}, mp 116–118°. (Found: C, 56.2; H, 5.2; $C_{37}H_{40}O_{19}$ requires: C, 56.34; H, 5.11%) λ_{max}^{MeOH} nm: 253 and 300sh; ν_{max}^{KBr} cm^{-1}: 1770 (br) (acetate C=O), 1660 (conj. C=O), 1620 (chromene C=C), 1595, 1520, 1485, 1465, 1450 (aromatic C=C), 1380, 1215 (br), 1130, 1060 (br), 1040, 1010, 910; ^{1}H NMR spectrum: (90 MHz, $CDCl_3$) δ7.95 (1H, *s*, H-2), 6.95 (1H, *s*, H-6′), 6.78 (1H, *s*, H-3′), 5.72 (1H, *d*, *J* = 10 Hz, H-1″), 5.46–5.12 (4H, *m*, H-2″, H-3″, H-4″ and H-5″), 4.20 (2H, *d*, *J* = 18 Hz, H_2-6″), 3.93 (3H, *s*, OMe-6), 3.88 (3H, *s*, OMe-5′), 3.85 (3H, *s*, OMe-4′), 3.76 (3H, *s*, OMe-2′), 2.42 (3H, *s*, OAc-5), 2.35 (3H, *s*, OAc-7), 2.10 (6H, *s*, OAc-3″ and OAc-4″), 2.05 (3H, *s*, OAc-6″), 1.75 (3H, *s*, OAc-2″) [25, 29]. The compound gave no colour with alc $FeCl_3$.

Oxidation of dalpaniculin hexaacetate (15 mg) by refluxing in Me_2CO (40 ml) with solid $KMnO_4$ for 5 hr gave 2,4,5-trimethoxybenzoic acid (4 mg), mp 142–144° (confirmed by mmp, co-chromatography and superimposable IR spectra with authentic specimen).

Dehydrodalpanol *O*-glucoside (**2**) was crystallized from aq. EtOH as yellow crystals, mp 248–250° (dec.); (Found: C, 60.6; H, 5.8; $C_{29}H_{32}O_{12}$ requires: C, 60.83; H, 5.63%); $[\alpha]_D^{28}$ − 140° MeOH; *c* 0.62); λ_{max}^{MeOH} nm: 240, 280 and 310; ν_{max}^{KBr} cm^{-1}: 3400 br (OH), 1650 (conj. C=O), 1620, 1605, 1580, 1520, 1458 (arom. C=C), 1375, 1370, 1280, 1255, 1240, 1210, 1190, 1155, 1140, 1105, 1080, 1065, 1033, 1003, 958, 925, 895, 880, 860, 840, 815, 750, 725, 630 cm^{-1}. The compound was not soluble in C_6H_6, Et_2O, $CHCl_3$ or Me_2CO but readily soluble in alcohol. It gave positive Molisch and Wolfrom tests but no colouration in the Shinoda test. Acetylation of **2** (10 mg) with $Ac_2O + NaOAc$, at 100° for 1.5 hr, afforded the tetraacetate (10 mg) as yellow crystals from $CHCl_3$–C_6H_{14}, mp 168–170° (Found: C, 59.7; H, 5.6; $C_{37}H_{40}O_{16}$ requires: C, 59.99; H, 5.44%); λ_{max}^{MeOH} nm: 238, 279 and 310. Acid hydrolysis (6% aq. alc HCl, at 100° for 3 hr) of **2** (10 mg) gave the aglycone crystallized from $CHCl_3$–MeOH as yellow crystals (5 mg), mp 237–239° (identified as dehydrodalpanol [3] by mmp, co-chromatography, UV and IR spectra) and the sugar identified as glucose by PC.

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