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COROMANDELIN, A NEW ISOFLAVONE APIOGLUCOSIDE FROM THE LEAVES OF *DALBERGIA COROMANDELIANA*

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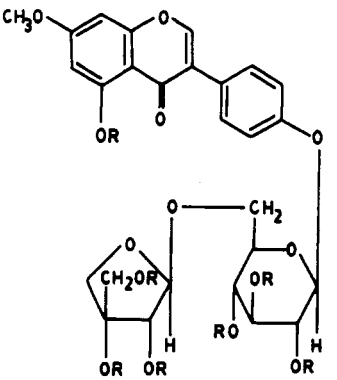
ABSTRACT.—A new isoflavone glycoside, isolated from the leaves of *Dalbergia coromandeliana* has been characterized as prunetin-4′-*O*-apiosyl-(1→6)-glucoside [**1**] and has been named coromandelin.

Dalbergia coromandeliana Prain (Fabaceae) is a stiff shrub with white flowers arranged in a disticous manner (1). As there is no record of any phytochemical work on *D. coromandeliana*, we have systematically examined its leaves and report herein a new isoflavone glycoside, prunetin-4′-*O*-apiosyl-(1→6)-glucoside [**1**], which has been accorded the trival name coromandelin. This is the first report of the occurrence of an apioglucoside of prunetin in Nature and the second report of the occurrence of apioglucose in the genus *Dalbergia*.



1 R=H
2 R=Ac

From an EtOH extract of shade-dried leaves of *D. coromandeliana*, prunetin and a new isoflavonoid [**1**] were isolated. The identity of prunetin was established by direct comparison (mmp, co-tlc, co-ir, and ^{1}H nmr) with an authentic sample from *D. spinosa* (2) available in our laboratory.

The new isoflavonoid [**1**] mp 192–193°, exhibited a green color with Fe^{3+} and a positive Molisch test and had uv absorptions at 262 and 343 (sh) nm indicative of its isoflavone nature (3). On acetylation (Ac_2O/pyridine), it gave an acetate [**2**]. On acidic (2 N methanolic HCl, 1 h) and almond emulsin hydrolysis, **1** yielded 5,4′-dihydroxy-7-methoxyisoflavone (prunetin), D-glucose, and a pentose that was identified as D-apiose by direct comparison with an authentic sample of D-apiose obtained by the acid hydrolysis of adicardin (7-apioglucoside of umbelliferone) (4), kindly supplied by Prof. P.S. Rao. A comparison of the color reactions and spectral data (uv and ^{1}H-nmr) of **1** with those of the aglycone (prunetin), indicated the involvement of the 4′-hydroxyl in glycosylation, and the isolate was identified as prunetin-4′-apioglucoside.

The ^{13}C-nmr chemical shifts of the sugar carbons (Table 1) were consistent with the corresponding data in lanceolarin (5). Of particular interest are the signals due to C-2 and C-6 of the glucose moiety. The glucose C-2 signal appeared at δ 73.22 ppm, while that of C-6 appeared at δ 67.59 ppm, suggesting that the interglycosidic linkage is apiosyl-(1→6)-glucose (6). If the linkage were to be apiosyl-(1→2)-glucose, the values for the C-2 and C-6 signals should have been δ 77.2 and 60.9 ppm, respectively (6). Permethylation (Hakomori method) (7) of **1** followed by hydrolysis afforded 2,3,4-tri-*O*-methylglucose, 2,3,4-tri-*O*-methylapiose, and 5,7-dimethoxy-4′-hydroxyisoflavone (8). The β-configuration of the glycosidic linkages was evident from the observed ^{13}C-nmr chemical shifts

TABLE 1. ^{13}C-Nmr Chemical Shifts of Compounds **1** and **2**.

Carbon	Compound	
	1[a]	**2**[b]
C-2	153.64 (d)	153.14 (d)
C-3	122.86 (s)	123.31 (s)
C-4	180.45 (s)	180.61 (s)
C-5	157.73 (s)	157.94 (s)
C-6	98.09 (d)	98.24 (d)
C-7	165.35 (s)	165.57 (s)
C-8	92.17 (d)	92.47 (d)
C-9	157.47 (s)	156.99 (s)
C-10	105.83 (s)	106.20 (s)
C-1′	124.35 (s)	125.63 (s)
C-2′	129.99 (d)	130.31 (d)
C-3′	116.45 (d)	116.86 (d)
C-4′	162.19 (s)	162.69 (s)
C-5′	116.45 (d)	116.68 (d)
C-6′	129.99 (d)	130.31 (d)
C-1″	100.68 (d)	98.89 (d)
C-2″	73.22	71.17
C-3″	76.93	72.75
C-4″	70.14	71.17
C-5″	75.79	68.83
C-6″	67.59	66.60
C-1‴	109.58 (d)	106.04 (d)
C-2‴	76.41	73.36
C-3‴	79.04	76.12
C-4‴	73.80	72.43
C-5‴	64.51	62.90
Methoxyl	55.78 (q)	55.80 (q)
Carbonyl (acetoxyl)		169–170
Methyl (acetoxyl)		20–21

[a]In DMSO-d_6.
[b]In $CDCl_3$.

for the anomeric carbons of glucose (δ 100.68) and apiose (δ 109.58) (9). Based on these data, **1** has been characterized as prunetin-4′-*O*-apiosyl-(1→6)-glucoside.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps are uncorrected. Ir spectra were recorded in KBr. ^{1}H- (400 MHz and 90 MHz) and ^{13}C-nmr (100 MHz) spectra were recorded on a JEOL GSX 400 spectrometer, using TMS as internal standard.

PLANT MATERIAL.—Leaves of *D. coromandeliana* were collected from the Alagar Hills in September 1992 and the plant was identified by Prof. T. Sriganesan, Department of Botany, Madura College, Madurai, India. A voucher specimen has been deposited at Madura College Herbarium, Madurai, India.

EXTRACTION AND ISOLATION.—The shade-dried leaves (2 kg) were extracted with EtOH (2×5 liters) and the residue (10 g) from an EtOH extract using a cc (Si gel, 400 g) separation afforded prunetin (C_6H_6-$CHCl_3$, 2:8) (80 mg) and [**1**] (EtOAc-MeOH, 9:1) (320 mg).

Coromandelin [**1**].—Mp 192–193° (MeOH); green color with Fe^{3+}; uv (MeOH) λ max (log ε) 262 (3.53), 343 (sh), (+NaOAc) 262, (+$AlCl_3$) 275 nm; ir (KBr) ν max 3380, 1647, 1490, 1330, 1165, 1100, 1040, 860, 820 cm^{-1}; ^{1}H nmr (DMSO-d_6, 400 MHz) δ 3.73 (3H, s, OMe), 3.80–4.82 (11H, m, sugar protons), 4.85 (1H, br s, H-1‴), 5.02 (1H, br s, H-1″), 6.10 (1H, d, J=2.5 Hz, H-6), 6.30 (1H, d, J=2.5 Hz, H-8), 6.75 (2H, d, J=8 Hz, H-3′, H-5′), 7.23 (2H, d, J=8 Hz, H-2′, H-6′), 8.00 (1H, s, H-2), 12.30 (1H, s, OH-5); ^{13}C-nmr data, see Table 1.

Heptaacetate [**2**].—When **1** (60 mg) was acetylated with Ac_2O/pyridine in the normal manner, 40 mg of **2** were produced: mp 129–130°; ^{1}H nmr ($CDCl_3$, 90 MHz) δ 1.90–2.00 (21H, m, OAc), 3.70 (3H, s, OMe), 4.00–5.00 (12H, m, sugar protons), 5.08 (1H, d, J=9 Hz, H-1″), 6.15 (2H, s, H-6, H-8), 6.70 (2H, d, J=7 Hz, H-3′, H-5′), 7.20 (2H, d, J=7 Hz, H-2′, H-6′), 7.65 (1H, s, H-2); ^{13}C-nmr data, see Table 1.

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