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TWO PRENYLATED FLAVANONES FROM *MUNDULEA SUBEROSA*

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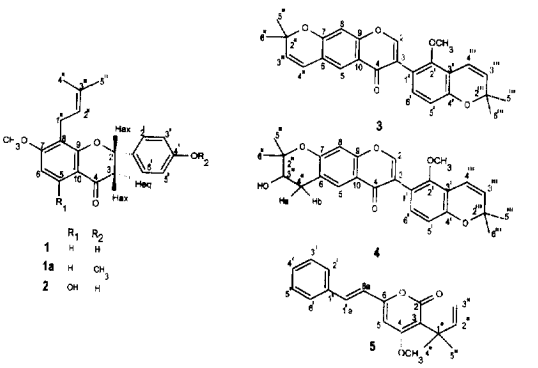
Abstract—Two new prenylated flavanones, mundulea flavanones A and B, were isolated from the chloroform extract of stembark of *Mundulea suberosa* along with the previously reported compounds munetone, mundulone and mundulea lactone. Their structures were established by spectral data as 4′-hydroxyisoderricin and 7-methyl-4′-hydroxyglabranin. © 1997 Elsevier Science Ltd

INTRODUCTION

Mundulea suberosa Benth (Syn. *M. sericea* (Willd.) (Greenway) is a stout shrub widely distributed in western and southern India and South Africa. Various rotenoids, isoflavones, flavanones, chalcones, and an imidazole derivative have been reported [1–14]. In a continuation of our studies on leguminous plant flavonoids [15], we have re-examined the chemical constituents of this plant. This has led to the isolation of two new prenylated flavanones, mundulea flavanones A and B, in addition to the compounds munetone (**3**), mundulone (**4**) and mundulea lactone (**5**) which were reported earlier [5, 8–10]. Mundulea flavanone A (**1**) was characterised as 4′-hydroxyisoderricin. It was reported to have been synthesised [16] but not isolated earlier from any natural source. Mundulea flavanone B (**2**) was characterised as 7-methyl-4′-hydroxyglabranin.

RESULTS AND DISCUSSION

Compound **1** was obtained as crystals, mp 136–138°. It showed a $[M]^+$ at *m/z* 338 consistent with the formula $C_{21}H_{22}O_4$. Its UV (λ_{max}^{MeOH} nm 280, 329), ^1H NMR [δ 2.85 (1H, *dd*, J = 17, 3 Hz), δ 3.05 (1H, *dd*, J = 17, 13 Hz) and δ 5.4 (1H, *dd*, J = 13, 3 Hz) and ^{13}C NMR [δ 79.2 (C-2), δ 44.1 (C-3)] spectral data indicated it to be a flavanone. The presence of 3-methylbut-2-enyl group (prenyl) and a methoxyl group were indicated by a set of peaks in ^1H NMR at δ 1.63, 1.65 (3H each, *s*), δ 3.35 (2H, *d*, J = 7 Hz), δ 5.15 (1H, *t*, J = 7 Hz) and δ 3.9 (3H, *s*, OMe). It formed a monomethyl ether (**1a**) with diazomethane,



suggesting the presence of one phenolic hydroxyl group. The substitution pattern of ring B was analysed by ^1H NMR [δ 7.35 (2H, *d*, J = 9 Hz) and δ 6.9 (2H, *d*, J = 9 Hz)] and mass spectrum (*m/z* 120) which revealed a hydroxyl group at the 4′-position. Based on the presence of two *ortho* coupled doublets in ^1H NMR [δ 7.85 (1H, *d*, J = 9 Hz, H-5), and δ 6.65 (1H, *d*, J = 9 Hz, H-6)] and biogenetic considerations, the methoxyl group and prenyl group were assigned to the positions 7 and 8, respectively. The high value of the coupling constant ($J_{2,3}$ = 13 Hz) between protons in the 2 and 3 positions, which was indicative of axial–axial coupling, revealed the C-2 hydrogen was axial and ring B equatorial [19]. The chiral centre C-2 was assigned the *S*-configuration on the basis of its negative optical rotation $[\alpha]_D$ −44.57° and equatorial B-ring [20]. Thus **1**, for which the trivial name mundulea flavanone A is proposed, is 2(*S*)-7-methoxy-8-prenyl-4′-hydroxylflavanone (4′-hydroxyisoderricin).

Compound **2** was also obtained as crystals, mp 167–169°. It showed a $[M]^+$ at *m/z* 354 consistent with the formula $C_{21}H_{22}O_5$. From its UV (λ_{max}^{MeOH} nm 292, 328) ^1H NMR [δ 2.82 (1H, *dd*, J = 17, 3 Hz), δ 3.02 (1H,

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Table 1. ^{1}H NMR spectra data of **1**, **1a** and **2** [400 MHz, $CDCl_3$, Coupling constants J (Hz)]

H	1	1a	2
2	5.4 *dd* (3, 13)	5.4 *dd* (3, 13)	5.35 *dd* (3, 13)
3 eq	2.85 *dd* (3, 17)	2.85 *dd* (3, 17)	2.82 *dd* (3, 17)
3 ax	3.02 *dd* (13, 17)	3.02 *dd* (13, 17)	3.05 *dd* (13, 17)
5	7.85 *d* (9)	7.85 *d* (9)	
5-OH			12.15 *s*
6	6.65 *d* (9)	6.65 *d* (9)	6.1 *s*
7-OMe	3.9 *s*	3.9 *s*	3.85 *s*
2′,6′	7.35 *d* (9)	7.4 *d* (9)	7.35 *d* (9)
3′,5′	6.9 *d* (9)	6.95 *d* (9)	6.9 *d* (9)
4′-OMe		3.85 *s*	
1″	3.35 *d* (7)	3.35 *d* (7)	3.2 *d* (7)
2″	5.15 *t* (7)	5.15 *t* (7)	5.15 *t* (7)
4″	1.63 *s*	1.63 *s*	1.6 *s*
5″	1.65 *s*	1.65 *s*	1.65 *s*

dd, J = 17, 13 Hz), δ 5.4 (1H, *dd*, J = 13, 3Hz) and δ 12.15 (1H, *s*, D_2O exchangeable)] and ^{13}C NMR [δ 78.4 (C-2) and δ 43.3 (C-3)] spectra it was evident that it is a 5-hydroxyflavanone. The ^{1}H NMR spectrum also indicated the presence of a 3-methylbut-2-enyl moiety [δ 1.6, 1.65 (3H each, *s*), δ 3.2 (2H, *d*, J = 7 Hz), 5.15 (1H, *t*, J = 7 Hz)] and a methoxyl group [δ 3.85 (3H, *s*)]. From biogenetic considerations the methoxyl group was assigned to C-7. The presence of a bathochromic shift in the UV spectrum, after the addition of aluminium chloride, indicated the *ortho* position (C-6) to the chelated hydroxyl group is free [21]. Hence the prenyl group must be at C-8. The singlet at δ 6.1 in ^{1}H NMR was assigned to C-6. The presence of two doublets at δ 7.35 (2H, *d*, J = 9 Hz) and δ 6.9 (2H, *d*, J = 9 Hz) in the ^{1}H NMR spectrum and a fragment ion at m/z 120 in the mass spectrum showed the presence of 4′-OH in the B-ring. Based on the axial-axial coupling constant ($J_{2,3}$ = 13 Hz) between 2 and 3 protons and its negative optical rotation $[\alpha]_D$ −28.5° the chiral centre C-2 was assigned *S*-configuration [20]. Thus **2**, for which the trivial name mundulea flavanone B is proposed, is 2(*S*)-5-hydroxy-7-methoxy-8-prenyl-4′-hydroxylflavanone (7-methyl-4′-hydroxyglabranin).

Compound **3** was obtained as crystals, mp 198–200°. Its UV, IR, mass and ^{1}H NMR spectra data were consistent with munetone, isolated earlier from this plant [5, 9]. In the literature [9] the assignments for the low field absorptions in ^{1}H NMR were only given. The ^{1}H (400 MHz) and ^{13}C NMR (22.5 MHz) data are now reported in Tables 3 and 4. Compound **4** was obtained as crystals, mp 194–196°. Its IR, UV, mass and ^{1}H NMR spectra data were consistent with mundulone, isolated earlier from this plant [8, 9]. The ^{1}H (400 MHz) and ^{13}C NMR (22.5 MHz) data are now reported in Tables 3 and 4 for which the assignments for the low field absorptions in ^{1}H NMR were only given in the literature [9]. Compound **5** was obtained as yellow crystals, mp 103–105°. From its IR, UV, mass and ^{1}H NMR spectral data, it was identified as mundulea lactone isolated earlier from this plant [10]. The high resolution ^{1}H NMR and ^{13}C NMR data are now given in Tables 3 and 4.

Table 2. ^{13}C NMR spectra data of **1** and **2** (22.5 MHz, $CDCl_3$)

C	1*	2†
2	79.2	78.4
3	44.1	43.3
4	192.5	196.5
5	131.8‡	163.0
6	105.0	92.5
7	163.6	166.0
8	115.3	107.0
9	160.5	161.0
10	117.7	103.0
1′	126.4	127.0
2′,6′	127.7	127.8
3′,5′	115.6	115.6
4′	156.2	156.2
1″	22.2	21.7
2″	121.9	122.5
3″	131.1‡	131.3
4″	17.8	17.7
5″	25.8	25.8
OMe	55.9	55.9

* Data assigned by comparison with ref. [17].
† Data assigned by comparison with ref. [18].
‡ Values interchangeable.

EXPERIMENTAL

General. Mps. Uncorr. ^{1}H NMR: 400 MHz on Bruker VM-400 FT NMR spectrometer, 200 MHz on

Table 3. ^{1}H NMR spectra data of **3**, **4** and **5** [$CDCl_3$, Coupling constants J (Hz)]

H	3*	4*	H	5†
2	7.89 *s*	7.95 *s*	5	6.04 *s*
5	7.93 *s*	8.00 *s*	2′,6′	
8	6.8 *s*	6.85 *d* (9.2)	3′,5′	7.3 *m*
5′	6.61 *d* (9.2)	6.61 *d* (9.2)	4′	
6′	7.14 *d* (9.2)	7.15 *d* (9.2)	2″	6.15 *dd* (18, 10)‡
3″-H	5.75 *d* (9.2)	3.89 *dt* (8,5)§	3″-a	4.85 *dd* (10,1)‡
3″-OH		2.15 *d* (5)§	3″-b	4.9 *dd* (18,1)‡
4″-Ha	6.45 *d* (9.2)	2.91 *dd* (16, 8)§	4″,5″	1.49 *s*
4″-Hb		3.19 *dd* (16, 5)§	1′a	6.55 *d* (16)
5″,6″	1.5 *s*	1.38 *s* and 1.42 *s*	6a	7.5 *d* (16)
3‴	5.65 *d* (9.2)	5.65 *d* (9.2)		
4″	6.65 *d* (9.2)	6.65 *d* (9.2)		
5‴,6‴	1.46 *s*	1.45 *s*		
OMe	3.59 *s*	3.6 *s*		

* 400 MHz.
† 200 MHz.
‡ Data assigned by comparison with ref. [23].
§ Data assigned by comparison with ref. [22].

Gemini-200 NMR spectrometer and ^{13}C NMR: 22.5 MHz on Jeol Ex-90 FT NMR spectrometer using $CDCl_3$ as the solvent and TMS as standard reference.

Plant material. Stem bark of *M. suberosa* was collected in February 1993, near Coimbatore, Tamil Nadu, India.

Table 4. ^{13}C NMR spectral data of **3**, **4** and **5** (22.5 MHz, $CDCl_3$)

C	3	4	C	5*
2	153.8	154.1	2	166.6 *s*
3	121.7	121.4	3	112.2 *s*
4	175.9	176.1	4	157.6 *s*
5	123.6	127.9	5	96.8 *d*
6	119.8†	118.6†	6	162.6 *s*
7	158.0‡	158.0‡	1′	135.4 *s*
8	104.0†	104.0†	2′,6′	127.4 *d*
9	157.6‡	156.4‡	3′,5′	128.9 *d*
10	119.8	118.6	4′	129.3 *d*
1′	118.8	118.4	1″	40.1 *s*
2′	154.6§	154.5§	2″	148.5 *d*
3′	114.9	115.0	3″	108.0 *t*
4′	154.2§	154.2§	OMe	55.9 *q*
5′	112.4	112.4	1′a	135.3 *d*
6′	131.8	131.9	6a	118.7 *d*
2″	77.8	78.4†	4″,5″	27.7 *q*
3″	131.7	69.2†		
4″	121.4	31.1†		
5″,6″	28.5	22.0 and 25.3†		
2‴	76.0	76.0		
3‴	130.2	130.3		
4‴	117.2	117.2		
5‴,6‴	28.0	28.0		
OMe	61.8	61.8		

* Multiplicities by DEPT.
† Data assigned by comparison with ref. [22].
‡,§ Values interchangeable.
Data assigned by comparison with ref. [14].

Extraction and isolation. The powdered stem bark (450 g) was extracted repeatedly with $CHCl_3$. After removal of solvent, the residue (13 g) was fractionated into hexane solubles (7 g) and hexane insolubles (6 g). These two residues were subjected to CC on silica gel (ACME, 100–200 #) and eluted with hexane, EtOAc and MeOH and their mixts in increasing order of polarity. The frs were analysed by silica gel TLC in the solvent system hexane–EtOAc detecting the compounds by UV and heating the plates to 100° after spraying with 5% methanolic H_2SO_4.

Mundulea flavanone A (**1**). Mp 136–138° $[\alpha]_D^{25}$ −44.57° (MeOH: *c* 0.2); IR ν^{CHCl_3} cm^{-1}: 3148 (OH) 2922 (>C=CH), 1656 (>C=O), 1596, 1520; UV λ_{max}^{MeOH} nm 280, 329; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2; EIMS: *m/z* (rel. int.): 338 $[M]^+$ (100), 337 $[M-H]^+$ (4.7), 283 $[M-C_4H_7]^+$ (29.8), 218 $[M-120]^+$ (23.4), 190 $[M-(B\ ring+C_4H_7)]^+$ (31.6), 120 $[M-218]^+$ (23.4).

Mundulea flavanone B (**2**). Mp 167–169°; $[\alpha]_D^{25}$ −28.5° (MeOH; *c* 0.14); IR ν^{CHCl_3} cm^{-1}: 3520 (OH), 3122 (OH), 2922 (>C=CH), 1622 (>C=O), 1518, 1444 (ar C=C); UV λ_{max}^{MeOH} nm 292, 328: $-AlCl_3$ 315; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2; EIMS: *m/z* (rel. int.): 354 $[M]^+$ (100), 353 $[M-H]^+$ (6.6), 299 $[M-C_4H_7]^+$ (35), 234 $[M-120]^+$ (17.9), 206 $[M-(B\ ring+C_4H_7)]^+$ (39.7), 120 $[M-234]^+$ (17.9).

Munetone (**3**). Mp 198–200°; IR and UV identical with the published data [5]; ^{1}H NMR: Table 3; ^{13}C NMR: Table 4; EIMS: *m/z* (rel. int.): 416 $[M]^+$ (40.2), 401 (100), 385 (14.5), 371 (9.5), 193 (26.6).

Mundulone (**4**). Mp 194–196°; $[\alpha]_D^{25}$ −9.18° (MeOH: *c* 0.34); IR and UV identical with the published data [8]; ^{1}H NMR: Table 3; ^{13}C NMR: Table 4; EIMS: *m/z*

(rel. int.): 434 $[M]^+$ (33.2), 419 (100), 403 (7.6), 348 (17.2), 333 (19.7), 305 (8.2), 199 (7.0).

Mundulea lactone (**5**). Mp 103–105°; IR and UV identical with the published data [10]; ^1H NMR: Table 3; ^{13}C NMR: Table 4; EIMS: *m/z* (rel. int.): 296 $[M]^+$ (43), 281 (75), 253 (100), 193 (8), 165 (13), 131 (100), 103 (71), 91 (28), 77 (47).

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