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FLAVONOIDS IN ROOTS OF *SOPHORA PROSTRATA*

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Key Word Index—*Sophora prostrata*; Leguminosae; roots; pterocarpan; flavanone; prostratols D–G.

Abstract—Further investigation of the phenolic constituents in the roots of *Sophora prostrata* gave 14 phenolic compounds, including four new ones, prostratols D–G. Structures were characterized by means of spectral data involving 2D NMR techniques.

INTRODUCTION

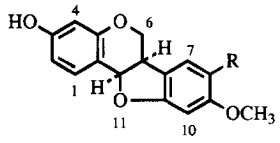
In studies on the chemosystematics of the genus *Sophora*, we have already reported the isolation and characterization of flavonoid compounds [1–13]. In our previous paper [14], we described three new isoflavanones, prostratols A–C, isolated from the root of *S. prostrata* native to New Zealand. Further chemical investigation of the roots of this species afforded 14 phenolic compounds, including four new compounds, named prostratols D–G. In the present paper, we describe the isolation and the structural determination of these new compounds.

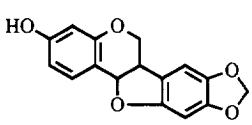
RESULTS AND DISCUSSION

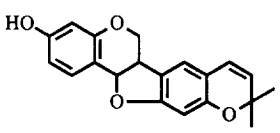
An acetone extract of the roots of *S. prostrata* was subjected to silica gel column chromatography eluting with a *n*-hexane–acetone system. Each fraction was further purified by vacuum liquid chromatography (VLC) and preparative TLC to give **1**–**14** in a pure form.

Compound **1** (prostratol D), obtained as an oil, gave a $[M]^+$ at *m/z* 338 in the EI mass spectrum. The UV spectral data and a set of four protons [δ3.55 (*m*), 3.59 (*t*, J = 9.8 Hz), 4.24 (*dd*, J = 9.8, 3.4 Hz) and 5.46 (*d*, J = 6.4 Hz)] in the ^{1}H NMR spectrum indicated that **1** was a pterocarpan derivative. ^{1}H and ^{13}C NMR spectra showed the presence of a γ,γ-dimethylallyl group which was located at a position where one of the *ortho*-positions is occupied by an oxygen function [15] (Fig. 1), a methoxyl (δ3.77) and a hydroxyl group (δ8.48). The ^{1}H NMR spectrum further exhibited three protons in an ABX spin system [δ6.35 (*d*, J = 2.0 Hz), 6.55 (*dd*, J = 8.3, 2.0 Hz) and 7.31 (*d*, J = 8.3 Hz)] and two aromatic singlets (δ6.43 and 7.06) [Fig. 1]. In the phase-sensitive NOESY (Fig. 2), NOEs were observed between the aromatic singlet (δ6.43) and the methoxyl group, and between the other singlet (δ7.06) and a methylene (δ3.22) of the γ,γ-dimethylallyl group. The partial structures of **1** are shown in Fig. 1; the whole structure would lead to a homospecific pterocarpan, either **1** or **1a** (Fig. 3) [16]. In the phase-sensitive NOESY (Fig. 2), NOEs were observed between H-11a (δ5.46) and the *ortho*-coupled aromatic proton (δ7.31), and between H-6a (δ3.55) and the aromatic singlet (δ7.06), which indicated that **1** was preferable to **1a** as the structure for prostratol D. The final decision was made by ^{13}C–^{1}H long-range correlation in the HMBC spectrum (Fig. 4). The optical rotation (see Experimental) indicated that both C-6a and C-11a had a *R*-configuration [17, 18]. Consequently, the structure of prostratol D was determined to be (6a*R*, 11a*R*)-8-γ,γ-dimethylallyl-3-hydroxy-9-methoxypterocarpan (8-γ,γ-dimethylallylmedicalpin) [**1**].

Compound **2** (prostratol E), obtained as an oil, gave a $[M]^+$ at *m/z* 406 in the EI mass spectrum. The UV and the ^{1}H NMR (Table 1) spectral data showed that **2** also had a pterocarpan skeleton. The ^{1}H and ^{13}C NMR spectrum (Table 1) exhibited the presence of a geranyl, methoxyl and hydroxyl group. The ^{1}H NMR spectrum further showed three protons in an ABX spin system [δ6.35 (*d*, J = 2.4 Hz), 6.55 (*dd*, J = 8.3, 2.4 Hz) and 7.31 (*d*, J = 8.3 Hz)] and two aromatic singlets (δ6.44 and 7.08), which were almost superimposable on those of **1**. The positions of the geranyl and methoxyl groups were confirmed at C-8 and C-9 on the bases of NOEs (Fig. 5). In the ^{1}H–^{1}H long-range COSY spectrum (Fig. 6), the proton at C-11a was correlated with *ortho*-coupled H-1 (δ7.31) and *meta*-coupled H-4 (δ6.35) aromatic protons through ^4J and ^5J, respectively. Furthermore, a proton at C-6a was correlated with an aromatic singlet (δ7.08) through ^4J. These results suggested that the methoxyl and geranyl group were substituted on the D-ring. Nevertheless, ^5J correlation was sometimes observed between a methoxyl and an adjacent aromatic proton (Fig. 6), which made it difficult to determine substitution only by long-range COSY. In the phase-sensitive NOESY spectrum (Fig. 5), NOEs were observed at H-6a and H-11a, the same as those in **1**. Substitution was thus determined to be 8-geranyl-3-hydroxy-9-methoxyl. The optical rotation of **2** (see Experimental) showed that the configurations of C-6a and C-11a were both *R*. Consequently, the structure for prostratol E was concluded to be (6a*R*,



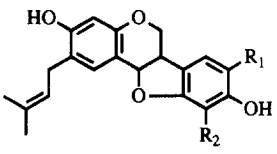


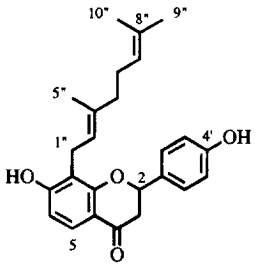


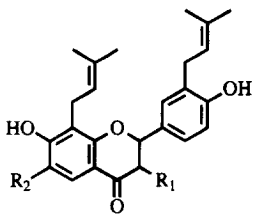
1: R = γ,γ-dimethylallyl
2: R = geranyl

3

4



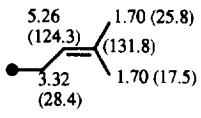


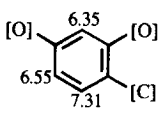


5: R_1 = γ,γ-dimethylallyl, R_2 = H
6: R_2 = γ,γ-dimethylallyl, R_1 = H

7

8: $R_1 = R_2$ = H
9: R_1 = OH, R_2 = H
10: R_1 = H, R_2 = γ,γ-dimethylallyl





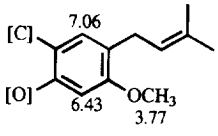


Fig. 1. Partial structures for **1** deduced by ^{1}H NMR.

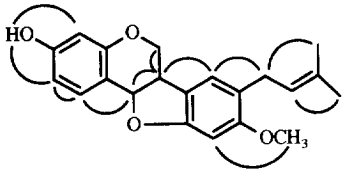


Fig. 2. NOEs observed in phase-sensitive NOESY of **1**.

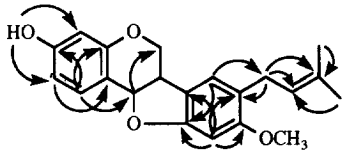
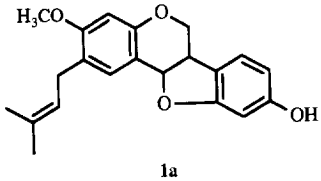


Fig. 4. Long-range correlations between C and H in HMBC spectrum (J = 10 Hz) of **1**.



1a

Fig. 3. Alternative structure for **1**.

11a*R*)-8-geranyl-3-hydroxy-9-methoxypterocarpan (8-geranylmedicalpin).

Compound **7** (prostratol F) obtained as an oil gave a $[M]^+$ at m/z 392 in the EI mass spectrum. In the ^{1}H NMR spectrum, three protons at δ2.71 (*dd*, J = 16.6, 2.9 Hz), 3.00 (*dd*, J = 16.6, 12.7 Hz) and 5.45 (*dd*, J = 12.7, 2.9 Hz) typically assignable to H-3 and H-2 of a flavanone skeleton, were observed. The ^{1}H and ^{13}C NMR spectral data (Table 2) exhibited the presence of a geranyl group. In the EI mass spectrum, the fragments at m/z 272, 203, 149 and 120, which were derived by RDA fragmentations, suggested that the geranyl and a hydroxyl group were located in the A-ring, and the second hydroxyl group in the B-ring. Furthermore, the ^{1}H NMR spectrum showed a set of one-proton doublets [δ6.63 and 7.60 (J = 8.5 Hz)] due to H-6 and H-5 of the A-ring, and a set of two-proton doublets [δ6.90 and 7.42 (J = 8.5 Hz)] assignable to those of the B-ring substituted with a hydroxyl group at C-4′. The configuration of C-2 was *S* from a consideration of the optical rotation (see Experimental). The structure of prostratol F was determined to be (2*S*)-8-geranyl-7,4′-dihydroxyflavanone (**7**).

Compound **10** (prostratol G), obtained as an oil, gave a $[M]^+$ at m/z 460. The ^{1}H NMR spectrum showed a set of three protons [δ2.68 (*dd*, J = 16.6, 2.9 Hz), 2.98 (*dd*, J = 16.6, 12.7 Hz) and 5.40 (*dd*, J = 12.7, 2.9 Hz)] assigned

Table 1. ^1H and ^{13}C NMR data of **1** and **2**

	1		**2**	
Position	δ_H	δ_C	δ_H	δ_C
1	7.31 (*d*, 8.3)	133.0 (*d*)	7.31 (*d*, 8.3)	133.0 (*d*)
2	6.55 (*dd*, 8.3, 2.0)	110.0 (*d*)	6.55 (*dd*, 8.3, 2.4)	110.4 (*d*)
3		159.6 (*s*)		159.6 (*s*)
4	6.35 (*d*, 2.0)	103.9 (*d*)	6.35 (*d*, 2.4)	103.9 (*d*)
4a		157.7 (*s*)		157.7 (*s*)
6	3.59 (*t*, 9.8)	67.1 (*t*)	3.59 (*m*)	67.1 (*t*)
	4.24 (*dd*, 9.8, 3.4)		4.25 (*m*)	
6a	3.55 (*m*)	40.7 (*d*)	3.56 (*m*)	40.7 (*d*)
6b		119.1 (*s*)		119.1 (*s*)
7	7.06 (*s*)	125.7 (*d*)	7.08 (*s*)	125.6 (*d*)
8		122.4 (*s*)		124.4 (*s*)
9		160.0 (*s*)		159.9 (*s*)
10	6.43 (*s*)	94.7 (*d*)	6.44 (*s*)	94.7 (*d*)
10a		159.0 (*s*)		159.1 (*s*)
11a	5.46 (*d*, 6.4)	79.1 (*d*)	5.49 (*d*, 6.8)	79.1 (*d*)
11b		113.0 (*s*)		112.9 (*s*)
1′	3.22 (*d*, 6.6)	28.9 (*t*)	3.19 (*dd*, 17.1, 7.6)	28.7 (*t*)
			3.26 (*dd*, 17.1, 7.6)	
2′	5.26 (*t*-like *m*)	124.3 (*d*)	5.29 (*br t*, 7.6)	124.1 (*d*)
3′		131.8 (*s*)		135.7 (*s*)
4′	1.70 (*br s*)	25.9 (*q*)	2.10 (*m*)	40.5 (*t*)
5′	1.70 (*br s*)	17.8 (*q*)	1.71 (*br s*)	16.1 (*q*)
6′			2.10 (*m*)	27.3 (*t*)
7′			5.12 (*t*-like *m*)	125.1 (*d*)
8′				132.0 (*s*)
9′			1.66 (*br s*)	25.8 (*q*)
10′			1.59 (*br s*)	17.7 (*q*)
OMe	3.77 (*s*)	55.9 (*q*)	3.79 (*s*)	55.9 (*q*)
OH	8.48 (*s*)		8.53 (*br s*)	

Measured in acetone-d_6 (100 MHz). All carbons of **1** were assigned by the aid of CH COSY, HMBC spectrum.

Carbons of **2** were assigned by comparison with those of **1**. Multiplicities and *J* are given in parentheses.

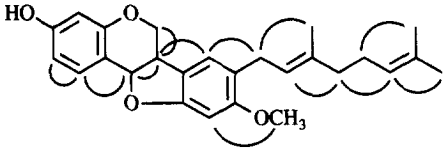


Fig. 5. NOEs of **2** observed in phase-sensitive NOESY of **2**.

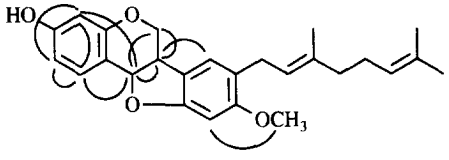


Fig. 6. Correlations in ^1H–^1H long range COSY spectrum of **2** (PI1 300 ms).

to H-3 and H-2 of a flavanone skeleton. The ^1H NMR also showed the presence of three γ,γ-dimethylallyls [δ1.63 (9H, Me × 3), 1.71, 1.72, 1.75 (each 3H, Me), 3.33–3.40 (6H, CH_2 × 3) and 5.30, 5.33, 5.35 (CH=)] and two hydroxyl groups [δ8.00 and 8.39]. In the EI mass spectrum, significant fragments at *m/z* 272, 188 and 133 were observed, indicating that two γ,γ-dimethylallyl groups and a hydroxyl were substituted at the A-ring, with the other γ,γ-dimethylallyl group and a hydroxyl on the B-ring. In the ^1H NMR spectrum, an aromatic singlet at δ7.49 and three protons in an ABM spin system [δ6.88 (*d*, *J* = 8.3 Hz), 7.20 (*dd*, *J* = 8.3, 2.2 Hz) and 7.30 (*d*, *J* = 2.2 Hz)] were observed. These data indicated that the A-ring moiety had a 6,8-di-γ,γ-dimethylallyl-7-hydroxy substitution, the B-ring, 3′-γ,γ-dimethylallyl-4′-hydroxy. The structure of prostratol G was therefore determined to be 7,4′-dihydroxy-6,8,3′-tri(γ,γ-dimethylallyl)flavanone (**7**).

Compounds **3**–**6** were all pterocarpan derivatives and characterized as maackiain (**3**), isoneorautenol (**4**) [19], ficifolinol (**5**) [20] and erythrabyssin II (**6**) [21] by means of spectral analysis. NMR spectra of **8** and **9**, obtained as

Table 2. ^1H and ^{13}C NMR data of flavanone **7**

Position	δ_H	δ_C
2	5.45 (*dd*, 12.7, 2.9)	80.3
3*eq*	2.71 (*dd*, 16.6, 2.9)	44.6
3*ax*	3.00 (*dd*, 16.6, 12.7)	
4		190.9
5	7.60 (*d*, 8.5)	131.6[b]
6	6.63 (*d*, 8.5)	110.4
7		162.2
8		115.4
9		162.0
10		116.6
1′		126.3
2′,6′	7.42 (*d*, 8.5)	128.8
3′,5′	6.90 (*d*, 8.5)	116.1
4′		158.5
1″	3.36 (*d*, 6.8)	22.7
2″	5.26 (*t*-like *m*)	123.1
3″		135.4
4″	1.94 (*m*)	40.5
5″	1.64 (*br s*)[a]	16.5
6″	2.05 (*m*)	27.4
7″	5.07 (*t*-like *m*)	125.1
8″		131.6[b]
9″	1.60 (*br s*)[a]	25.8
10″	1.55 (*br s*)	17.7
OH	8.45 (C-4′)	
	9.21 (C-7)	

Measured in acetone-d_6.
[a]Interchangeable.
[b]Overlapped.

oils suggested that both were flavanone derivatives possessing two γ,γ-dimethylallyl groups; they were identified as glabrol and 3-hydroxyglabrol [22], respectively. Compounds **11**–**13** were chalcone derivatives and identified as 3′-γ,γ-dimethylallyl-4,2′,4′-trihydroxychalcone (**11**), 3′-γ,γ-dimethylallyl-4,2′-dihydroxy-4′-methoxychalcone (**12**) and 4,2′-dihydroxy-6″,6″-dimethylpyrano[2″, 3″:4′,3′]-chalcone (**13**). Compound **14** was identified as caffeic acid octadecyl ester by means of spectral analysis.

EXPERIMENTAL

Plant material and extraction. As described in our previous paper [14].

Isolation. The Me_2CO extract (15 g) was subjected to CC on silica gel eluting with *n*-hexane–Me_2CO (10:1 to 1:1). The fr. (9:1) was subjected VLC with *n*-hexane–EtOH (10:1) to give **1** (29 mg), **2**, (20 mg) and **14** (8 mg). The fr. (7:1) was further purified by VLC with *n*-hexane–EtOH (10:1) and finally by prep. TLC with cyclohexane–Me_2CO–EtOH (10:2:1) to give **4** (10 mg), **5** (11 mg), **10** (3 mg), **12** (9 mg) and **13** (7 mg). The fr. (5:1) gave **3** (10 mg) and **6** (12 mg) by VLC eluted with *n*-hexane–EtOH (10:1). The fr. (3:1) was subjected to VLC ($CHCl_3$–$MeOH_3$, 20:1) and prep. TLC (cyclohexane–Me_2CO–EtOH, 8:2:1) to give **7** (5 mg), **8** (6 mg), **9** (4 mg) and **11** (6 mg), respectively.

Prostratol D (**1**). Oil. $[\alpha]_D$ −186° (MeOH; *c* 0.5). UV (nm, MeOH): 280sh, 288, 295sh, 313, 325sh. EIMS *m/z* (rel. int.): 338 ($[M]^+$, 100), 323 (23), 307 (59), 147 (24), 123 (31). ^1H and ^{13}C NMR: Table 1.

Prostratol E (**2**). Oil. $[\alpha]_D$ −170° (MeOH; *c* 0.18). UV (nm, MeOH): 280sh, 287, 295sh, 313, 325sh. EIMS *m/z* (rel. int.): 406 ($[M]^+$, 60), 390 (14), 307 (100), 283 (17), 149 (21), 147 (19), 124 (28).

Isoneorautenol (**4**). Solid. EIMS *m/z* (rel. int.): 322 ($[M]^+$, 47), 307 (100), 153 (16). ^1H NMR (400 MHz, acetone-d_6): δ 1.36, 1.37 (3H each, *s*, Me), 3.60 (2H, *m*, H-6 and 6a), 4.25 (1H, *d*-like *m*, H-6), 5.49 (1H, *d*, *J* = 5.5 Hz, H-11a), 5.52 (1H, *br d*, *J* = 9.8 Hz, H-5′), 6.19 (1H, *br s*, H-10), 6.32 (1H, *br d*, *J* = 9.8 Hz, H-4′), 6.35 (1H, *d*, *J* = 2.0 Hz, H-4), 6.55 (1H, *dd*, *J* = 8.3, 2.0 Hz, H-2), 7.01 (1H, *br s*, H-7), 7.30 (1H, *d*, *J* = 8.3 Hz, H-1), 8.25 (1H, *br s*, OH).

Ficifolinol (**5**) Solid. EIMS *m/z* (rel. int.): 392 ($[M]^+$, 100), 337 (44). ^1H NMR (400 MHz, acetone-d_6): δ 1.71, 1.73 (6H each, *br s*, Me × 2), 3.25 (4H, *m*, CH_2 × 2, H-1′ and 1″), 3.48 (2H, *m*, H-6 and 6a), 4.20 (1H, *d*-like *m*, H-6), 5.31 (2H, *m*, CH= × 2, H-2′ and 2″), 5.39 (1H, *d*, *J* = 6.6 Hz, H-11a), 6.32 (1H, *s*, H-10), 6.38 (1H, *s*, H-4), 7.02 (1H, *br s*, H-7), 7.16 (1H, *br s*, H-1), 8.23, 8.49 (1H each, *br s*, OH).

Prostratol F (**7**). Oil. $[\alpha]_D$ −42° (MeOH; *c* 0.05). EIMS *m/z* (rel. int.): 392 ($[M]^+$, 12), 377 (5), 354 (38), 349 (7), 323 (14), 307 (8) 281 (7), 273 (8), 272 (10), 271 (11) 270 (23), 269 (17), 229 (8), 218 (21), 203 (100), 187 (8), 149 (29), 137 (8), 123 (22), 120 (16). ^1H NMR (400 MHz, $CDCl_3$): δ 1.58, 1.66, 1.74 (3H each, *br s*, Me H-5″, 9″ and 10″), 1.94, 2.05 (2H each, *m*, CH_2CH_2, H-4″ and 6″), 2.71 (1H, *dd*, *J* = 16.6, 2.9 Hz, H-3*eq*), 3.00 (1H, *dd*, *J* = 16.6, 12.7 Hz, H-3*ax*), 3.36 (2H, *d*, *J* = 6.8 Hz, CH_2, H-1″), 5.07 (1H, *t*-like *m*, CH =, H-7″), 5.26 (1H, *t*-like *m*, CH =, H-2″), 5.45 (1H, *dd*, *J* = 12.7, 2.9 Hz, H-2), 6.63 (1H, *d*, *J* = 8.5 Hz, H-6), 6.90 (2H, *d*, *J* = 8.5 Hz, H-3′, 5′), 7.42 (2H, *d*, *J* = 8.5 Hz, H-2′, 6′), 7.60 (1H, *d*, *J* = 8.5 Hz, H-5), 8.45, 9.21 (1H each, *br s*, OH). ^1H and ^{13}C NMR: Table 2.

7,4′-Dihydroxy-8,3′-di(γ,γ-dimethylallyl)flavanonol (**9**). ^1H NMR (400 MHz, $CDCl_3$): δ 1.66, 1.69 (3H each, *br s*, Me), 1.77 (6H, *s*, Me × 2), 3.37 (4H, *m*, CH_2 × 2, H-1″ and 1‴), 4.54 (1H, *d*, *J* = 12 Hz, H-3), 4.98 (1H, *d*, *J* = 12 Hz, H-2), 5.22 (1H, *t*-like *m*, CH =, H-2″), 5.34 (1H, *t*-like *m*, CH =, H-2‴), 6.54 (1H, *d*, *J* = 9 Hz, H-6), 6.83 (1H, *d*, *J* = 9 Hz, H-5′), 7.28 (2H, *m*, H-2′ and 6′), 7.70 (1H, *d*, *J* = 9 Hz, H-5).

Prostratol G (**10**). Oil. EIMS *m/z* (rel. int.): 460 ($[M]^+$, 100), 445 (12), 417 (45), 405 (26), 272 (25), 217 (40), 188 (52), 173 (50), 171 (55), 133 (56). ^1H NMR (400 MHz, acetone-d_6): δ 1.63 (9H, *br s*, Me × 3), 1.71, 1.72, 1.75 (3H each, *br s*, Me), 2.68 (1H, *dd*, *J* = 16.6, 2.9 Hz, H-3*eq*), 2.98 (1H, *dd*, *J* = 16.6, 12.7 Hz, H-3*ax*), 3.33–3.40 (6H, *m*, CH_2 × 3, H-1″, 1‴ and 1⁗), 5.30 (1H, *t*-like *m*, CH =, H-2⁗), 5.33, 5.35 (1H each, *m*, CH=, H-2″ and 2⁗), 5.40 (1H, *dd*, *J* = 12.6, 2.9 Hz, H-2), 6.88 (1H, *d*, *J* = 8.3 Hz, H-6′), 7.20 (1H, *d*, *J* = 8.3, 2.2 Hz, H-6′), 7.30 (1H, *d*, *J* = 2.2 Hz, H-2′), 7.49 (1H, *s*, H-5), 8.00, 8.39 (1H each *br s*, OH).

Isobavachalcone (**11**). Yellow solid. EIMS *m/z* (rel. int.): 324 ($[M]^+$, 71), 309 (7), 281 (77), 269 (23), 205 (10), 204 (13), 189 (19), 176 (29), 161 (44), 149 (100), 147 (10), 120

(31), 91 (20), 77 (11). ^{1}H NMR (400 MHz, $CDCl_3$): δ1.77, 1.84 (3H each, *br s*, Me, H-4″, 5″), 3.48 (2H, *br d*, J = 7.3 Hz, CH_2, H-1″), 5.30 (1H, *t*-like *m*, CH =, H-2″), 6.42 (1H, *d*, J = 8.8 Hz, H-5′), 6.88 (2H, *d*, J = 8.4 Hz, H-3, 5), 7.46 (1H, *d*, J = 15.4 Hz, H-α), 7.57 (2H, *d*, J = 8.4 Hz, H-2 and 6), 7.72 (1H, *d*, J = 8.8 Hz, H-6′), 7.84 (1H, *d*, J = 15.4 Hz, H-β), 13.86 (1H, *s*, C-2′-OH).

Bavachalcone (**12**). Yellow solids. EIMS *m/z* (rel. int.): 338 ([M]$^+$, 80), 323 (12), 295 (100), 284 (28), 283 (35), 282 (25), 253 (9), 218 (9), 203 (22), 190 (15), 189 (17), 175 (20), 163 (42), 147 (36), 120 (9), 119 (10), 91 (15). ^{1}H NMR (400 MHz, $CDCl_3$): δ1.68, 1.80 (3H each, *br s*, Me, H-4″, 5″), 3.39 (2H, *br d*, J = 7.3 Hz, CH_2, H-1″), 3.91 (3H, *s*, OMe), 5.23 (1H, *t*-like *m*, CH =, H-2″), 6.50 (1H, *d*, J = 9.0 Hz, H-5″), 6.88 (2H, *d*, J = 8.5 Hz, H-3, 5), 7.48 (1H, *d*, J = 15.4 Hz, H-α), 7.57 (2H, *d*, J = 8.5 Hz, H-2, 6), 7.79 (1H, *d*, J = 90 Hz, H-6′), 7.84 (1H, *d*, J = 15.4 Hz, H-β, 13.44 (1H, *s*, C-2′-OH).

4,2′-*Dihydroxy*-6″,6″-*dimethylpyrano* [2″,3″:4′,3′] *chalcone* (**13**). Yellow solid. EIMS *m/z* (rel. int.): 322 ([M]$^+$, 22), 307 (56), 187 (100). ^{1}H NMR (400 MHz, $CDCl_3$): δ1.47 (6H, *s*, Me × 2), 5.59 (1H, *d*, J = 9.6 Hz, H-5″), 6.37 (1H, *d*, J = 9.5 Hz, H-5′), 6.75 (1H, *d*, J = 9.6 Hz, H-4″), 6.88 (2H, *d*, J = 8.8 Hz, H-3, 5) 7.43 (1H, *d*, J = 15.5 Hz, H-α), 7.56 (2H, *d*, J = 8.8 Hz, H-2, 6), 7.71 (1H, *d*, J = 9.5 Hz, H-6′), 7.83 (1H, *d*, J = 15.5 Hz, H-β), 13.76 (1H, *s*, C-2′-OH).

Caffeic acid octadecyl ester (**14**). Solid. EIMS *m/z* (rel. int.): 432 ([M]$^+$, 80), 180 (100), 163 (61). ^{1}H NMR (270 MHz, acetone-d_6): δ0.80 (3H, *t*-like *m*, Me), 1.30 (*br s*, CH_2), 4.14 (2H, *t*, J = 6.6 Hz, OCH_2), 6.27 (1H, *d*, J = 16.1 Hz, H-8), 6.87 (1H, *d*, J = 8.1 Hz, H-5), 7.04 (1H, *dd*, J = 8.1, 1.8 Hz, H-6), 7.15 (1H, *d*, J = 1.8 Hz, H-2), 7.35 (1H, *d*, J = 16.1 Hz, H-7), 8.18, 1.46 (1H each, *br s*, OH).

REFERENCES

1. Iinuma, M., Tanaka, T., Mizuno, M., Shirataki, Y., Yokoe, I., Komatsu, M. and Lang, F. A. (1990) *Phytochemistry* **29**, 2667.
2. Iinuma, M., Ohyama, M., Tanaka, T., Mizuno, M. and Lang, F. A. (1991) *J. Nat. Prod.* **54**, 1144.
3. Iinuma, M., Ohyama, M., Tanaka, T., Mizuno, M. and Hong, S.-K. (1991) *Phytochemistry* **30**, 3153.
4. Iinuma M., Tanaka, T., Kawai, M., Mizuno, M. and Lang. F. A. (1991) *Phytochemistry* **30**, 3773.
5. Iinuma M., Tanaka, T., Mizuno, M. and Lang, F. A. (1992) *Phytochemistry* **31**, 721.
6. Iinuma M., Ohyama, M., Tanaka, T., Mizuno, M. and Hong, S.-K. (1992) *Phytochemistry* **31**, 665.
7. Ruangrungsi, N., Iinuma, M., Tanaka, T., Ohyama, M., Yokoyama, J. and Mizuno, M. (1992) *Phytochemistry* **31**, 999.
8. Iinuma M., Ohyama M., Tanaka, T., Mizuno, M. and Hong, S.-K. (1993) *Phytochemistry* **31**, 2855.
9. Iinuma M., Ohyama, M., Tanaka, T., Mizuno, M. and Hong, S.-K. (1993) *Phytochemistry* **33**, 1241.
10. Iinuma M., Ohyama, M., Tanaka, T. and Lang, F. A. (1993) *J. Nat. Prod.* **56**, 2212.
11. Iinuma M., Yokoyama, J., Ohyama, M., Tanaka, T., Mizuno, M. and Ruangrungsi, N. (1993) *Phytochemistry* **33**, 203.
12. Iinuma M., Yokoyama, J., Ohyama, M., Tanaka, T. and Ruangrungsi, N. (1994) *Phytochemistry* **35**, 785.
13. Iinuma M., Ohyama, M., Tanaka, T., Hegarty, M. P. and Hegarty, E. E. (1993) *Phytochemistry* **34**, 1654.
14. Iinuma M., Ohyama, M. and Tanaka, T. (1994) *Phytochemistry* (in press).
15. Fukai, T. and Nomura, T. (1989) *Heterocycles* **29**, 2379.
16. Iinuma M. and Mizuno, M. (1989) *Phytochemistry* **28**, 681.
17. Pelter, A. and Amnenechi, P. I. (1969) *J. Chem. Soc.* (*C*) 887.
18. Mitscher, L. A., Gollapudi, S. R., Gerlach, D. C., Drake, S. D., Veliz, E. A. and Ward, J. A. (1988) *Phytochemistry* **27**, 381.
19. Mitscher, L. A., Okwute, S. K., Gollapudi, S. R., Drake S. and Avona, E. (1988) *Phytochemistry* **27**, 3448.
20. Brink, C. M., Engelbrecht, J. P. and Graham, D. E. (1970) *J. South Afr. Inst.* **23**, 24.
21. Kamat, V. S., Chuo, F. Y., Kubo, I. and Nakanishi, K. (1981) *Heterocycles* **15**, 116.
22. Mitscher, L. A., Park, Y. H., Clark, D. and Beal, J. L. (1980) *J. Nat. Prod.* **43**, 259.