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GERANYLATED AND PRENYLATED FLAVONOIDS FROM THE TWIGS OF *DORSTENIA MANNII*

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Key Word Index—*Dorstenia mannii*; Moraceae; twigs; geranylated and prenylated flavonols; prenylated chalcones; flavones and flavonones.

Abstract—The twigs of *Dorstenia mannii* yielded three prenylated and one geranylated flavonoids: 3′,4′-(2,2-dimethylchromano)-2′,4-dihydroxychalcone, 3′,4′-6,7-*bis*-(2,2-dimethylchromano)-flavanone,7,8-(2,2-dimethylchromeno)-6-geranyl-3,5,3′,4′-tetrahydroxyflavonol and 6,8-*bis*-(3,3-dimethylallyl)-3,5,7,4′-tetrahydroxy-3′-methoxyflavonol for which the names dorsmanin A–D, respectively, are proposed. Also identified were the known flavonoids: 3′,4′-(2,2-dimethylchromeno)-2′,4-dihydroxychalcone,6-(3,3-dimethylallyl)-5,7,4′-trihydroxy-3′-methoxyflavone and 6,8-*bis*-(3,3-dimethylallyl)-5,7,3′,4′-tetrahydroxyflavanone.

INTRODUCTION

Dorstenia mannii Hook f. (Moraceae) is a perennial herb, reaching 2 m in height. It grows in the tropical rain forest of West Africa [1]. A decoction of the leaves is used for the treatment of many diseases, but mainly for rheumatism and stomach disorders [2]. There are no phytochemical or pharmacological studies reported on *D. mannii* in the literature. As part of our program to study the chemical constituents of Cameroonian *Dorstenia* species [3, 4] we have investigated the twigs of *D. mannii*. This paper reports the isolation and structural elucidation of three prenylated and one geranylated flavonoids for which the names dorsmanin A (**1**), B (**2**), C (**3**) and D (**4**) are proposed. The known compounds 4-hydroxylonchocarpin (**5**) [5], 6,8-diprenyleriodictyol (**6**) [6] and 6-prenylchrysoeriol (**7**) [7] were also found. Compound **7** has been reported under other names, for example, canniflavone 1 [8], as well as cannflavin B [9].

RESULTS AND DISCUSSION

The polar fraction of a twig extract containing flavonoids was passed through Sephadex LH-20 column followed by repeated silica gel column chromatography and preparative TLC separations (see Experimental) to give compounds **1–7**.

Compound **1** was obtained as yellow oil and its molecular formula was determined as $C_{20}H_{20}O_4$ from the EIMS and NMR spectra. The UV-visible absorptions at λ_{max} 208, 255 and 371 were suggestive of a chalcone skeleton. The aluminum chloride induced bathochromic shift [10], the IR absorption at 1650 cm^{-1} indicated that compound **1** was a 2′-hydroxychalcone. The chemical shift of the carbonyl function at δ 193.0 and the highly deshielded signal at δ_H 13.97 were noted as further evidence for the β-hydroxyl and conjugated carbonyl moiety. The ^1H NMR of compound **1** showed eight proton resonances from δ 6–8 and the presence of one 2,2-dimethylchroman group (see below). Two of the proton signals form an AB system at δ 7.47 and 7.84 (*d*, $J = 15.4$ Hz), the large coupling constant indicating the *trans* geometry of a double bond, and a set of four AA′BB′ proton signals at δ 6.88 (2H, *d*, $J = 8.6$ Hz) and 7.55 (2H, *d*, $J = 8.6$ Hz) located in ring B. The remaining two protons form an AX system at δ 6.39 and 7.70 (*d*, $J = 9.0$ Hz) and were assigned to H-5′ and H-6′, respectively. The signals that could be assigned to the 2,2-dimethylchroman group were: a benzylic proton at δ 2.73 coupled to a pair of methylene protons at δ 1.84 (*t*, $J = 6.8$ Hz), and the *gem*-dimethyl group resonances which were observed as a singlet at δ 1.37. The foregoing data is consistent with structure **1** for which the name dorsmanin A is

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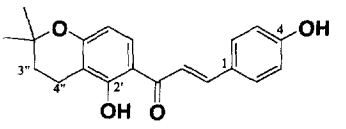

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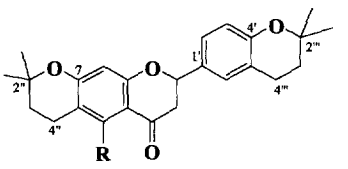
5 $\Delta^{3'',4''}$



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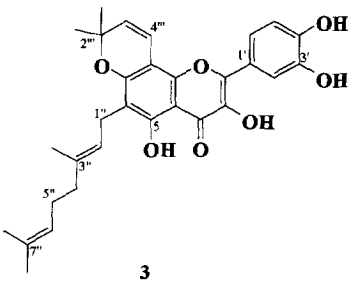

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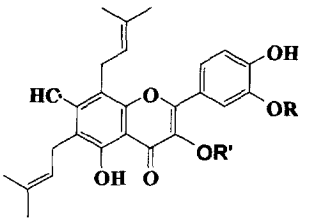

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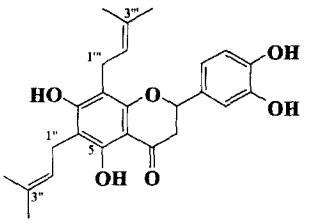

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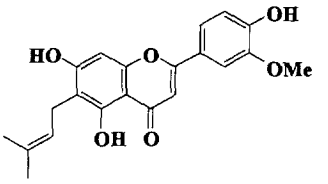

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proposed. An isomeric compound, called crotmadine, in which the β-hydroxyl function is involved in the formation of the chromano ring has been reported from *Crotalaria madurensis* (Fabaceae) [11]. The ^{13}C NMR data (Table 1) was fully assigned using DEPT spectra and by comparison of measured values with those reported for crotmadine [11].

Compound **2** (dorsmanin B) was isolated as yellow oil. Its molecular formula $C_{25}H_{28}O_4$ was derived from the EIMS and ^{13}C NMR spectra. It was clear from the NMR spectra that compound **2** was a flavanone. Thus, an oxymethine, a carbonyl group and a methylene at δ_C 79.4 (*d*), 191.5 (*s*), and 44.4 (*t*), respectively and an ABX system [δ_H 2.74 (*dd*, J = 17.0, 2.7 Hz), 3.04 (*dd*, J = 17.0, 13.2 Hz) and 5.31 (*dd*, J = 13.2, 2.7 Hz) typically assignable to H-3 and H-2 of a flavanone] could all be observed. Its ^1H NMR spectrum showed the presence of two 2,2-dimethylchroman groups (see below) and five aromatic proton signals. The two *para* protons at C-5 and C-8 appeared as singlets at δ 6.39 and 7.68. The three aryl protons in ring B formed an ABD system: δ 6.82 (*d*, J = 9.0 Hz), 7.17 (*br s*) and 7.19 (*br d*, J = 9.0 Hz). The signals that could be assigned to the two 2,2-dimethylchroman

Table 1. ^{13}C NMR data of compounds **1** and **5** (75 MHz, in $CDCl_3$ and CD_3COCD_3, respectively)

Carbon	1	5
1	127.7 (*s*)	127.4 (*s*)
2	130.6 (*d*)	131.9 (*d*)
3	116.1 (*d*)	116.8 (*d*)
4	160.8 (*s*)	160.3 (*s*)
5	116.1 (*d*)	116.8 (*d*)
6	130.6 (*d*)	131.9 (*d*)
α	118.0 (*d*)	117.9 (*d*)
β	143.9 (*d*)	145.6 (*d*)
β'	193.0 (*s*)	193.2 (*s*)
1′	113.0 (*s*)	109.8 (*s*)
2′	158.8 (*s*)	161.2 (*s*)
3′	109.4 (*s*)	114.9 (*s*)
4′	164.1 (*s*)	162.0 (*s*)
5′	109.2 (*d*)	108.8 (*d*)
6′	131.0 (*d*)	132.2 (*d*)
2″	75.9 (*s*)	78.5 (*s*)
3″	31.9 (*t*)	129.2 (*d*)
4″	16.4 (*t*)	116.3 (*d*)
Me	26.8 (*q*)	28.5 (*q*)
	26.8 (*q*)	28.5 (*q*)

Table 2. ^{13}C NMR spectral data of compounds **2**, **4**, **6**, and **7** at 75 MHz in $CDCl_3$ (**2** and **6**)*, DMSO-d_6 (**4***) and CD_3COCD_3 (**7**)

Carbon	2	4	6	7
2	79.4 (*d*)	147.3 (*s*)	78.5 (*d*)	164.7 (*s*)
3	44.4 (*t*)	135.8 (*s*)	43.2 (*t*)	104.3 (*d*)
4	191.5 (*s*)	176.0 (*s*)	196.9 (*s*)	183.1 (*s*)
5	127.8 (*d*)	155.0 (*s*)	159.4 (*s*)	156.5 (*s*)
6	114.5 (*s*)	110.8 (*s*)	107.5 (*s*)	112.2 (*s*)
7	161.7 (*s*)*	158.6 (*s*)	162.7 (*s*)	160.1 (*s*)
8	104.9 (*d*)	106.1 (*s*)	106.6 (*s*)	94.0 (*d*)
9	161.4 (*s*)*	155.2 (*s*)	157.8 (*s*)	162.5 (*s*)
10	115.8 (*s*)	103.5 (*s*)	102.8 (*s*)	105.0 (*s*)
1′	130.9 (*s*)	122.3 (*s*)	131.7 (*s*)	123.3 (*s*)
2′	128.3 (*d*)	111.5 (*d*)	113.3 (*d*)	110.4 (*d*)
3′	121.2 (*s*)	148.7 (*s*)	143.9 (*s*)	151.3 (*s*)
4′	154.5 (*s*)	146.4 (*s*)	144.0 (*s*)	148.8 (*s*)
5′	117.6 (*d*)	115.5 (*d*)	115.4 (*d*)	116.3 (*d*)
6′	125.7 (*d*)	121.7 (*d*)	119.0 (*d*)	121.2 (*d*)
1″	—	21.6 (*t*)†	21.9 (*t*)†	22.0 (*t*)
2″	74.6 (*s*)†	122.7 (*d*)‡	121.9 (*d*)‡	123.2 (*d*)
3″	32.7 (*t*)	131.2 (*s*)*	134.8 (*s*)*	131.6 (*s*)
4″	22.6 (*t*)‡	—	—	—
1‴	—	21.4 (*t*)†	21.3 (*t*)†	—
2‴	76.0 (*s*)†	122.4 (*d*)‡	121.7 (*d*‡	—
3‴	32.7 (*t*)	130.7 (*s*)*	134.3 (*s*)*	—
4‴	21.7 (*t*)‡	—	—	—
(*Z*)Me	—	17.9 (*q*)	17.9 (*q*)	17.9 (*q*)
(*Z*)Me	—	17.8 (*q*)	17.9 (*q*)	—
(*E*)Me	—	25.5 (*q*)	25.9 (*q*)	25.8 (*q*)
(*E*)Me	—	25.3 (*q*)	25.9 (*q*)	—
$C(Me)_2$	26.9 (*q*) × 2	—	—	—
	26.9 (*q*) × 2	—	—	—
OMe	—	55.5 (*q*)	—	56.5 (*q*)

*,†,‡ Signals with the same subscripts in the same column may be interchanged.

groups were as follows: four overlapping benzylic proton signals at δ 2.78 which form a *quintet* (4H, $J = 6.8$ Hz) coupled to two methylene protons at δ 1.82 (4H, *t*, $J = 6.8$ Hz) and four methyl proton signals at δ 1.35 (12H, *s*). Structure **2** was then assigned to dorsmanin B. This structure was confirmed by both ^{13}C NMR spectrum and the EIMS. The EIMS showed the RDA fragmentation at *m/z* 204 and 188. The ^{13}C NMR (see Table 2) was fully assigned using DEPT spectra and by comparison of measured values with those reported for paratocarpin J, **2a**, isolated from *Paratocarpus venenosa* (Moraceae) [12].

Dorsmanin C, the geranylated flavonol (**3**) was assumed to have the molecular formula $C_{30}H_{32}O_7$ from the EI mass spectrum and on the basis of ^{13}C DEPT analysis. Compound **3** showed a positive test with magnesium–conc. HCl. The UV spectral data employing shift reagents (Experimental) [10] and ^1H NMR signal at δ 12.62 indicated that dorsmanin C was a 5-hydroxyflavone. The aromatic region of the ^1H NMR spectrum displayed only five proton resonance signals, two of which were assigned to the chromen group (see below) and the remaining three form an ABD system: a doublet at δ 7.05 ($J = 8.5$ Hz), an *ortho* and *meta* coupled double doublet at δ 7.80 (1H, *dd*, $J = 8.5, 2.1$ Hz) and a *meta* coupled signal at δ 7.90 (*d*, 2.1 Hz), which were located in ring **B**. It was concluded that dorsmanin C contained a fully substituted ring A. It was also observed that the C-3 position should be substituted by an hydroxyl group because of the $\delta_{C=O}$ at 176.7. The ^1H NMR of dorsmanin C showed also one geranyl and one 2,2-dimethylchromen group [δ 1.49 (6H, *s*, 2 × Me), 5.77 (*d*, $J = 10.1$ Hz) and 7.00 (*d*, $J = 10.1$ Hz). The signals that could be assigned to the geranyl group were as follows: three vinyl methyls [δ_H 1.67, 1.70, 1.83, δ_C 17.7, 18.0, and 27.2] two methines [δ_H 5.16 (*t* like *m*), 5.27 (*t* like *m*), δ_C 124.8 (*d*), 122.9 (*d*)] three methylenes [δ_H 3.37 (*d*, $J = 6.8$ Hz), 1.90 (*m*), 2.38 (*m*), δ_C 21.8 (*t*), 23.5 (*t*) and 42.2 (*t*) and two quaternary sp^2 carbons at δ 132.1 and 131.7]. The geranyl and the 2,2-dimethylchromen groups are located in ring A. Two possibilities were considered regarding the position of the geranyl group, one with an angular chromen ring (**3**) or an alternative structure with a linear chromen ring and a geranyl substituent at C-8. The ^{13}C chemical shift of δ 112.0 for the geranyl-substituted carbon strongly favors the attachment of the geranyl group at C-6 [13].

The structure of dorsmanin C was determined to be 7,8-(2,2-dimethylchromeno)-6-geranyl-3,5,3′,4′-tetrahydroxyflavonol.

Compound **4** (dorsmanin D), obtained as yellow plates, gave a $[M]^+$ at *m/z* 452 in the EI mass spectrum. The NMR at **4** showed a chelated hydroxyl proton signal at δ 12.66 and an upfield carbonyl resonance at δ 176.0. The UV-visible spectral data (Experimental), including the bathochromic shifts induced by sodium acetate and aluminum chloride indicated that **4** was a 5,7-dihydroxyflavone substituted at C-3 either by an hydroxyl or an alkoxyl group [10, 13]. By similar arguments as those given for **3** above, we were able to conclude that both **3** and **4** have identical substitution pattern. Unlike **3**, the ^{1}H NMR of **4** showed the presence of two 3,3-dimethylallyl groups at 6 and 8 [δ 1.62 (6H, *s*, 2 × Me), 1.74 (6H, *s*, 2 × Me), 3.54 (4H, *d*, J = 6.0 Hz) and 5.60 (2H, *br t*, J = 6.0 Hz)]. A methoxyl group was observed at δ_H 3.81, which upon NOE irradiation caused a 2% enhancement of the *meta* coupled doublet at δ 7.73. This finding together with the observed chemical shift of the OMe group at δ_C 55.5 suggested that the methoxyl function was located at 3′. The structure of this new derivative, named dorsmanin D, was determined as: 6,8-*bis*-(3,3-dimethylallyl)-3,5,7,4′-tetrahydroxy-3′-methoxyflavonol (**4**). The proposed structure was further confirmed by the ^{13}C NMR data (Table 2) which was fully assigned using DEPT spectra and by comparison of measured values with those reported for its isomer broussoflavonol B (**4a**) isolated from *Broussonetia papyrifera* (Moraceae) [14].

Compound **5**, obtained as orange-red needles from hexane–ethyl acetate, gave a molecular ion $[M]^+$ at *m/z* 322 in the EIMS. Its UV-visible (Experimental) was consistent with a chalcone skeleton [10]. The ^{1}H NMR of compound **5** showed signals for one 2,2-dimethylchromen group and a set of four protons which form an AA′BB′ spin system. The data generated for **5** was identical to those reported by Delle Monache *et al.* [5] for a compound isolated from *Cordoa piaca* (*Lonchocarpus* sp.), Fabaceae.

Compound **6** has been reported from *Vellozia coronata* and *V. nanuzae* (Velloziaceae) by Harborne *et al.* [6]. These authors identified this compound on the basis of UV-visible, ^{1}H NMR and MS data. The data we generated were found to be identical. The ^{13}C NMR data (see Experimental) is presented here for the first time.

Compound **7** was found to be identical to a product reported from the leaves of *Cannabis sativa* (Cannabaceae) [7–9].

In conclusion it is found that *Dorstenia* elaborates a variety of prenylated flavonoids including chromano and chromeno rings attached to A and/or B rings. Although coumarin and furocoumarin derivatives are commonly found in other *Dorstenia* species [3, 4, 15–17], they are not detected in the present taxon. The few compounds that have been tested are biologically active (unpublished results), alluding credence to the use of these plants as medicinals in West Africa.

EXPERIMENTAL

General

Mps uncorr.; UV-visible: MeOH solution, EIMS: direct inlet, 70 eV; IR: KBr disk, ^{1}H and ^{13}C NMR ($CDCl_3$, Me_2CO-d_6 or DMSO-d_6) 300 MHz and 75 MHz, respectively, residual solvent peaks as internal references.

Plant material

Twigs of *Dorstenia mannii* Hook. f. were collected at Nkoljobe mountain (Yaounde in the Central Province of Cameroon) and a voucher specimen (No. 2135) is deposited at the National Herbarium.

Extraction, isolation and characterization

The air-dried and powdered plant material (2 kg) was extracted exhaustively with a cold mixture of CH_2Cl_2–MeOH (1:1), MeOH and water. Removal of the solvent from the combined organic extracts under reduced pressure gave 160 g of residue which was subjected to partition extraction with chloroform followed by EtOAc. The $CHCl_3$ and EtOAc soluble fractions, after concentration *in vacuo* furnished dark green residues (80 g and 10 g, respectively). The rest of the MeOH extract (65 g), was found to contain copious amounts of tannins and was not investigated further. The $CHCl_3$ and EtOAc extracts were monitored by TLC and combined. Part of this extract (60 g) was dissolved in EtOAc and chromatographed on a column of silica gel (600 g). Elution started with hexane and continued stepwise through hexane–EtOAc, EtOAc and EtOAc–MeOH mixtures. The eluate was collected in 250 ml frs which were analysed by TLC. Frs 1–15 (6 g) (TLC in hexane–EtOAc, 17:3) contained mainly mixtures of hydrocarbons and β-sitosterol (60 mg). Frs 16–25, (8 g), upon examination by TLC (hexane–EtOAc, 7:3) did not contain flavonoids and were not investigated further. Frs 26–36 (10 g) was passed through Sephadex LH-20 column and eluted with $CHCl_3$–MeOH (2:1). The post chlorophyll fraction was purified successively on CC and PTLC to yield compounds **1** (10 mg), **2** (12 mg) and **5** (30 mg). Frs 37–50 from the first column were combined on the basis of TLC and freed of solvent to give 16 g of dark green residue which were passed through Sephadex LH-20 column ($CHCl_3$–MeOH, 2:1). The post chlorophyll fraction (12 g) was subjected to CC on silica gel 60 (120 g) and eluted with $CHCl_3$, $CHCl_3$–MeOH mixture and MeOH. Frs of 100 ml were collected, monitored by TLC and ^{1}H NMR and similar frs were combined. From the chromatographic separation above and in some cases with the aid of

successive prep TLC, compounds **3** (30 mg), **4** (10 mg), **6** (180 mg) and **7** (15 mg) were obtained.

3′,4′-(2,2-*dimethylchromano*)-2′,4-*dihydroxychalcone—Dorsmannin A* (**1**). Yellow oil, EIMS *m/z* (rel. int): 324 (100, M^+), 279 (76), 167 (44), 149 (80); IR ν_{max}^{KBr} cm^{-1}: 3450–3400 (OH), 2950, 1650 (C=O), 1600, 1540; UV λ_{max}^{MeOH} nm log (ε): 208 (4.94), 255 (4.76), 371 (4.87), UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): 208 (4.94), 386 (4.93), 407 (4.86); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm log (ε): 209 (4.94), 386 (4.93), 405 (4.80); ^1H NMR (300 MHz, $CDCl_3$) δ: 1.37 (6H, *s*, 2 × Me), 1.84 (2H, *t*, J = 6.8 Hz, 2H-3″), 2.73 (2H, *t*, J = 6.8 Hz, 2H-4″), 6.39 (*d*, J = 9.0 Hz, H-5′), 6.88 (2H, *d*, J = 8.6 Hz, H-3, H-5), 7.47 (*d*, J = 15.4 Hz, H-α), 7.55 (2H, *d*, J = 8.6 Hz, H-2, H-6), 7.70 (*d*, J = 9.0 Hz, H-6′), 7.84 (*d*, J = 15.4 Hz, H-β), 13.97 (*br s*, 2′-OH); ^{13}C NMR Table 1.

3′,4′-6,7-*bis*(2,2-*dimethylchromano*)*flavanone—Dorsamin B* (**2**). Yellow oil, $[\alpha]_D$ 0° (MeOH, *c* 0.1). EIMS *m/z* (rel. int): 392 (100, M^+), 337 (20), 204 (15), 188 (40), 175 (44), 149 (22); IR ν_{max}^{KBr} cm^{-1}: 2950, 1645 (C=O), 1550, 1460, 1350. UV λ_{max}^{MeOH} nm log (ε): 221 (4.66), 235 (4.61), 282 (4.51), 322 (4.12); $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): 220 (4.68), 234 (4.61), 281 (4.50), 322 (4.11). ^1H NMR (300 MHz, $CDCl_3$) δ: 1.35 (12H, *s*, 4 × Me), 1.82 (4H, *t*, J = 6.8 Hz, 2H-3″, 2H-3‴), 2.74 (*dd*, J = 17.0, 2.7 Hz, H-3), 2.78 (4H, *quintet*, J = 6.8 Hz, 2H-4″, 2H-4‴), 3.04 (*dd*, J = 17.0, 13.2 Hz, H-3), 5.31 (*dd*, J = 13.2, 2.7 Hz, H-2), 6.39 (*s*, H-8), 6.82 (*d*, J = 9.0 Hz, H-5′), 7.17 (*br s*, H-2′), 7.19 (*br d*, J = 9.0 Hz, H-6′), 7.68 (*br s*, H-5). ^{13}C NMR Table 2.

7,8-(2,2-*dimethylchromeno*)-6-*geranyl*-3,5,3′,4′-*tetrahydroxyflavonol—Dorsmanin C* (**3**). Yellow plates in CH_2Cl_2, mp. 213–5°; EIMS *m/z* (rel. int): 504 (20, M^+), 489 (15), 461 (20), 449 (10), 435 (15), 421 (100), 381 (10), 354 (15), 231 (30), 156 (80), 150 (42). IR ν_{max}^{KBr} cm^{-1}: 3450–3400 (—OH), 1650 (C=O), 1610, 1540, 1450, 1400, 1300, 1240, 1180. UV λ_{max}^{MeOH} nm log (ε): 204 (4.55), 248 (4.61), 285 (4.52), 347 (4.33), 390 (4.32); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): 207 (4.55), 234 (4.64), 269 (4.55), 480 (4.65); UV $\lambda_{max}^{MeOH+AlCl_3HCl}$ nm log (ε): 204 (4.52), 232 (4.53), 252 (4.63), 295 (4.42), 383 (4.22), 455 (4.48); ^1H NMR (300 MHz, CD_3COCD_3) δ: 1.49 (6H, *s*, 2 × Me), 1.67, 1.70, 1.83, (3H each, *s*, Me), 1.90, 2.38 (2H each, *m*, 2H-4″, 2H-5″), 3.25 (*br s*, OH), 3.37 (2H, *d*, J = 6.8 Hz, 2H-1″), 5.16 (*t* like *m*, H-2″), 5.27 (*t* like *m*, H-6″), 5.77 (*d*, J = 10.1 Hz, H-3‴), 7.00 (*d*, J = 10.1 Hz, H-4‴), 7.05 (*d*, J = 8.5 Hz, H-5′), 7.80 (*dd*, J = 8.5, 2.1 Hz, H-6′), 7.90 (*d*, J = 2.1 Hz, H-2′), 12.62 (*br s*, chelated 5-OH). ^{13}C NMR (75 MHz, CD_3COCD_3) δ: 176.7 (*s*, C-4), 158.4 (*s*, C-7), 158.1 (*s*, C-5, C-9), 149.9 (*s*, C-2), 148.4 (*s*, C-4′), 145.9 (*s*, C-3′), 136.9 (*s*, C-3), 132.1, 131.7 (*s* each, C-3″, C-7″), 126.8 (*d*, C-3‴), 124.8, 122.9 (*d* each, C-2″, C-6″), 123.8 (*s*, C-1′), 121.5 (*d*, C-6′), 116.3, 116.2 (*d* each, C-2′, C-5′), 115.4 (*d*, C-4‴), 112.0 (*s*, C-6), 102.0 (*s*, C-10), 101.4 (*s*, C-8), 81.4 (*s*, C-2‴), 42.2 (*t*, C-4″), 27.2 [*q*, (E)-Me], 25.9 (*q*, 2 × Me), 23.5 (*t*, C-5″), 21.8 (*t*, C-1″), 18.0 [*q*, (Z)-Me], 17.7 [*q*, (Z)-Me].

6,8-*bis*-(3,3-*dimethylallyl*)-3,5,7,4′-*tetrahydroxy*-3′-*methoxyflavonol—Dorsmanin D* (**4**). Yellow plates, mp. 210–2°. EIMS *m/z* (rel. int): 452 (100 M^+) 164 (15), 187 (20), 188 (24). IR ν_{max}^{KBr} cm^{-1}: 3540–3400 (—OH), 1635 (C=O), 1600, 1540, 1480. UV λ_{max}^{MeOH} nm log (ε): 208 (5.08), 258 (4.74), 273 (4.73), 347 (4.67), 377 (4.73); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): 208 (5.01), 275 (4.70), 360 (4.55), 460 (4.47); ^1H NMR (300 MHz, DMSO-d_6) δ: 1.62 (6H, *s*, 2 × Me), 1.74 (6H, *s*, 2 × Me), 3.54 (4H, *d*, J = 6.0 Hz, 2H-1″, 2H-1‴), 3.81 (3H, *s*, OMe), 5.60 (2H, *br t*, J = 6.0 Hz, H-2″, H-2‴), 6.94 (*d*, J = 8.5 Hz, H-5′), 7.71 (*dd*, J = 8.5, 1.8 Hz, H-6′), 7.73 (*d*, J = 1.8 Hz, H-2′), 9.49 (*br s*, —OH), 9.80 (*br s*, —OH), 12.66 (*s*, 5-OH); ^{13}C NMR: Table 2.

3′,4′-(2,2-*dimethylchromeno*)-2′,4-*dihydroxychalcone* (**5**). Orange red needles from hexane–EtOAc, mp. 207–8° (lit. 203–5°, [5]). EIMS *m/z* (rel. int): 322 (66, M^+), 307 (92), 188 (23), 187 (100), 153 (24). IR ν_{max}^{KBr} cm^{-1}: 3350–3300 (—OH), 1650, (C=O), 1600, 1580, 1430, 1250, 1140. UV λ_{max}^{MeOH} nm log (ε): 202 (4.16), 230 (4.32), 280 (4.15), 375 (4.59); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): 201 (4.15), 231 (4.23), 258 (4.05), 285 (4.10), 409 (4.57); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm log (ε): 202 (4.15), 231 (4.26), 267 (4.06), 284 (4.11), 386 (4.50); ^1H NMR (300 MHz, CD_3COCD_3) δ: 1.48 (6H, *s*, 2 × Me), 5.68 (*d*, J = 10.0 Hz, H-3″), 6.33 (*br d*, J = 8.9 Hz, H-5′), 6.67 (*br d*, J = 10.0 Hz, H-4″), 6.89 (2H, *br d*, J = 8.6 Hz, H-3, H-5), 7.72 (2H, *br d*, J = 8.6 Hz, H-2, H-6), 7.73 (*d*, J = 15.2 Hz, H-α), 7.82 (*d*, J = 15.2 Hz, H-β), 8.02 (*d*, J = 8.9 Hz, H-6′). ^{13}C NMR: see Table 1.

6,8-*bis*-(3,3-*dimethylallyl*)-5,7,3′,4′-*tetrahydroxyflavanone* (**6**). Yellow plates from acetone, mp. 141–2°. EIMS *m/z* (rel. int): 424 (100, M^+), 369 (76), 353 (84), 233 (81), 220 (78), 189 (94), 176 (80). IR ν_{max}^{KBr} cm^{-1}: 3540–3400 (—OH), 2950, 1640 (C=O), 1600, 1450. UV λ_{max}^{MeOH} nm log (ε): 191 (3.41), 288 (4.01), 292 (3.87), 348 (3.35); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): 223 (4.00), 293 (3.89), 349 (3.26); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm log (ε): 232 (4.01), 278 (3.84), 289 (3.86), 350.2 (3.21). UV $\lambda_{max}^{MeOH+NaOAc}$ nm log (ε): 220 (3.99), 230 (4.03), 254 (3.77), 275 (3.75), 335 (4.03), 347 (4.01); ^1H NMR (300 MHz, $CDCl_3$) δ: 1.71 (6H, *s*, 2 × Me), 1.75 (3H, *s*, Me), 1.81 (3H, *s*, Me), 2.78 (*dd*, J = 17.1, 3.1 Hz, H-3a), 3.00 (*dd*, J = 17.1, 12.6 Hz, H-3b), 3.31 (4H, *d*, J = 7.2 Hz, 2H-1″, 2H-1‴), 5.20 (2H, *br t*, J = 7.2 Hz, H-2″, H-2‴), 5.26 (*dd*, J = 12.6, 3.1 Hz, H-2), 5.6–6.2 (—OH), 6.45 (—OH), 6.85 (*dd*, J = 8.2, 1.8 Hz, H-6′), 6.88 (*d*, J = 8.2 Hz, H-5′), 6.95 (*d*, J = 1.8 Hz, H-2′), 12.26 (*s*, 5-OH) ^{13}C NMR: Table 2.

6-(3,3-*dimethylallyl*)-5,7,4′-*trihydroxy*-3′-*methoxyflavone—Cannflavin B* (**7**). Yellow needles from $CHCl_3$, mp. 232–4° (lit 230–1° [8]). EIMS *m/z* (rel. int): 368 (64, M^+), 325 (100), 313 (82). IR ν_{max}^{KBr} cm^{-1}: 3350–3300 (—OH), 1645, (C=O), 1600, 1500, 1480, 1300, 1280. UV λ_{max}^{MeOH} nm log (ε): 216 (4.49), 274 (4.18), 343 (4.32); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log (ε): 216 (4.49), 259 (4.07), 286 (4.16), 368 (4.33); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm log (ε): 217 (4.49), 256 (4.07), 288 (4.18), 362 (4.32); UV $\lambda_{max}^{MeOH+NaOAc}$ nm log (ε): 224 (4.76), 275 (4.23), 401 (4.37); UV $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm log (ε): 224 (4.75), 274 (4.22), 352 (4.30). ^1H NMR (300 MHz,

CD_3COCD_3) δ: 1.60 (3H, *s*, Me), 1.78 (3H, *s*, Me), 3.30 (2H, *d*, $J = 7.0$ Hz, 2H-1″), 3.96 (3H, *s*, OMe), 5.23 (*br t*, $J = 7.0$ Hz, H-2″), 6.57 (*s*, H-3), 6.65 (*s*, H-8), 6.95 (*d*, $J = 8.2$ Hz, H-5′), 7.54 (*dd*, $J = 8.2$, 2.1 Hz, H-6′), 7.55 (*d*, $J = 2.1$ Hz, H-2′), 13.24 (*s*, 5-OH). ^{13}C NMR: Table 2.

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