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Prenylated flavonoids from the aerial parts of *Dorstenia mannii*

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Abstract

Four new prenylated flavanones, dorsmanins I, J and epi-dorsmanins F, G, identified, respectively, as 6,7-(2,2-dimethylpyrano)-8-prenyl-5,3′,4′-trihydroxyflavanone, 6,7-(2,2-dimethyldihydropyrano)-8-prenyl-5,3′,4′-trihydroxyflavanone, and 2''-epimers of dorsmanins F and G were isolated from the aerial parts of *Dorstenia mannii* together with 13 known flavonoids: 4-hydroxylonchocarpin, 4-methoxylonchocarpin, 6-prenylchrysoeriol, 6,8-diprenyleriodictyol, gancaonin P and dorsmanins A–H. The structures of these secondary metabolites were determined by spectroscopic means and by comparison with published data and with authentic specimens for some of the known compounds.

Keywords: *Dorstenia mannii*; Moraceae; Aerial parts; Pyranoflavanones; Furanoflavanones; Dorsmanins I, J; Epi-dorsmanins F, G; Isolation

1. Introduction

Dorstenia is a small and mostly tropical genus of Moraceae. It is represented by 23 species in the flora of Cameroon (Satabie, 1985). In the course of our systematic phytochemical studies of the genus *Dorstenia* (Abegaz et al., 1998; Ngadjui et al., 1998a,b), we have investigated *Dorstenia mannii* Hook. f. Recently, we have reported several prenylated and geranylated flavonoids from the organic extracts of the twigs of this plant (Ngadjui et al., 1998a,b; Ngadjui et al., 1999). As a continuation of the investigation of this species, we have harvested bulk quantities of the aerial parts of this plant in order to isolate minor constituents and now we wish to discuss the results of our findings. In addition to the previously reported flavonoids (Ngadjui et al., 1998a,b, 1999), we have isolated and characterized the known 4-methoxylonchocarpin (Singhal et al., 1983), gancaonin P (Fukai et al., 1990) together with the new prenylated flavanones: dorsmanins I (**9**), J (**10**), epidorsmanins F (**6/11**) and G (**7/12**). The structures of these secondary metabolites were established by spectroscopic means and by comparison with published information and/or with authentic specimens.

2. Results and discussion

The ethyl acetate soluble fraction of the dichloromethane/methanol extract of the aerial parts of *D. mannii* was subjected to flash chromatography. The non-polar portion was found to contain a mixture of hydrocarbons which were not investigated further. One of the polar fractions was passed through Sephadex LH-20 column and then subjected to silica gel chromatography and preparative TLC separations to give 4-methoxylonchocarpin (Singhal et al., 1983), gancaonin P (Fukai et al., 1990), 4-hydroxylonchocarpin (Delle Monache et al., 1974), 6,8-diprenyleriodictyol (Harborne et al., 1993), 6-prenylchrysoeriol (Crombie et al., 1980: Crombie & Crombie, 1982; Barrett et al., 1986), dorsmanins A-E (**1-5**) (Ngadjui et al., 1998a,b), H (**8**), I (**9**), J (**10**) (Ngadjui et al., 1999), dorsmanin F, epidorsmanin F (**6,11**) and dorsmanin G and epi-dorsmanin G (**7,12**).

The red colour produced on reaction of dorsmanins I (**9**) and J (**10**) with magnesium-hydrochloric acid together with the UV spectra data employing shift reagents

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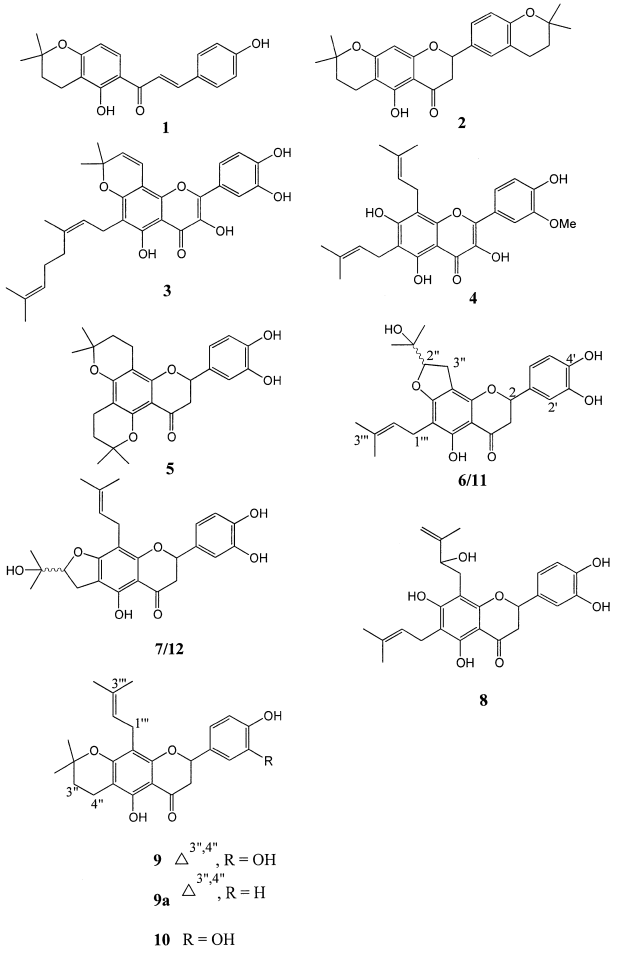
(Experimental) and the ^{1}H NMR signal at δ 12.46 for **9** and 12.47 for **10** indicated that these substances were 5-hydroxyflavanones (Mabry et al., 1970; Agrawal, 1989).



Compound **9** was obtained as yellow plates (mp 172–174°). Its EIMS gave a molecular ion at *m/z* 422 and the molecular formula $C_{25}H_{26}O_6$ was deduced from this together with its NMR and DEPT spectra. The flavanone nature of **9** was deduced from the NMR spectra which showed an oxymethine, a carbonyl group and a methylene at δ_C 79.9 (*d*), 198.2 (*s*) and 43.6 (*t*), respectively, and an ABX system [δ_H 2.78 (*dd*, *J* = 17.1, 3.0 Hz), 3.13 (*dd*, *J* = 17.1, 12.6 Hz) and 5.41 (*dd*, *J* = 12.6, 3.0 Hz), typically assignable to two H-3 and H-2 of a flavanone]. The spectrum of **9** also displayed six aryl/vinyl proton signals, two of which were assigned to the pyran ring (see below); one of the proton signals was consistent with a prenyl group (vide infra). The remaining three protons located in ring B were not resolved. They were indirectly deduced to be an ABC system from ^{13}C NMR data (see below) and by biogenetic considerations. It was then concluded that the ring A of compounds **9** is fully substituted. Signals that could be assigned to a 2,2-dimethylpyran group were as follows: two doublets of one proton each at δ5.62 and 6.58 *J* = 10.2 Hz and two singlets at δ 1.45 and 1.43 for the *gem* dimethyl groups. The fragment ion *m/z* 407 ([M-Me]$^+$, 92%) observed in the EI mass spectrum was taken as further evidence of the methyl substituents on the pyran group (Ingham et al., 1983). The ^{13}C NMR spectrum of dorsmanin I showed five oxygenated aromatic carbon signals, two of which were assigned to the *ortho* dihydroxyl carbons δ 146.4 (*s*) and 146.1 (*s*); the remaining three are *meta* oriented in a substituted benzene ring and their chemical shifts at δ 157.3 (*s*), 160.2 (*s*) and 160.7 (*s*) are consistent with the structure shown for **9**. The prenyl and the 2,2-dimethylpyran groups are located in ring A. Two possibilities were considered regarding the position of the prenyl group, one with a linear pyran and a prenyl group at C-8 (**9**) or an alternative structure with an angular pyran ring and the prenyl substituent at C-6. The prenyl group characterized by ^{1}H NMR chemical shift values 3.20 (*br d*, *J* = 7.5 Hz, methylene), 5.14 (*br dt*, *J* = 7.5, 1.2 Hz olefinic proton), 1.62 (3H, *br s*) and 1.66 (3H, *br s*) both olefinic methyls] and the 5-OH at δ 12.46 were similar to those given by the prenyl substituent of 8-prenylnaringenin obtained by regioselective synthesis from (2S)-naringenin (Tahara et al., 1991, 1994). Confirmation of the location of the prenyl group at position 8 was obtained from HMBC data which showed correlations of the benzylic proton signals of the prenyl substituent at δ 3.20 with two of the oxygenated Ar-C signals assigned to C7 and C9 (δ 160.7 and 160.2), but not to the C-5 signal at δ 157.3. The assignment of the latter signal to C-5 was established by observing the long range CH correlation to the only chelated-OH signal at δ12.46. Likewise, the vinyl proton signal of the pyran ring at C-4″ showed HMBC correlation to the C-5 signal at δ 157.3 From the foregoing spectroscopic data, the structure of dorsmanin I was deduced to be 8-prenyl-6,7-(2,2-dimethylpyrano)-5,3′,4′-trihydroxyflavanone (**9**). This structure was confirmed by both ^{13}C NMR spectrum and EIMS. The EIMS showed the RDA fragmentation at *m/z* 286 and 136. The ^{13}C NMR (Table 2) signals were fully assigned using DEPT spectra and by comparison of measured values with those reported for lupinifolin (**9a**) isolated from *Tephrosia lupinifolia* (Leguminosae) (Smalberger et al., 1974; Agrawal, 1989). A 3′-methyl-ether derivative of dorsmanin I (**9**) was isolated and characterized by Lin et al. (1991) from the root of *Derris laxiflora* (Leguminosae).

Compound **10** was isolated as a brown gum. Its IR spectrum showed absorption bands due to hydroxyl and carbonyl groups at ν_{max} 3350 and 1650 cm^{-1}, respectively; and aromatic ring at ν_{max} 1590. Compound **10** gave a molecular ion at *m/z* 424 in the EIMS, 2 amu higher than that of dorsmanin I (**9**). Its molecular formula was deduced to be $C_{25}H_{28}O_6$ on the basis of NMR and EIMS spectral data. The NMR spectra revealed the same flavanone nature as observed for compound **9**. Thus an oxymethine, a carbonyl and methylene signals at δ_C 79.7 (*d*), 198.0 (*s*) and 43.8 (*t*), respectively, and an

ABX system [δ_H 2.74 (*dd*, $J=17.2$, 3.1Hz), 3.07 (*dd*, $J=17.2$, 12.4 Hz) and 5.35 (*dd*, $J=12.6$, 3.1 Hz), typically assignable to 2H-3 and H-2 of a flavanone] were observed. The ^{1}H NMR of **10** showed also one 2,2-dimethyldihydropyran group [δ 2.57 (*br dt*, J = 6.9, 1.2 Hz, benzylic protons), 1.80 (*br t*, $J=6.9$ Hz, CH_2), 1.34 (*br s*) and 1.33 (*br s*) *gem*-dimethyl]. Like dorsmanin I (**9**), the NMR spectra of **10** displayed resonance signals for two carbons bearing *ortho* oxygenated substituents and one prenyl group. The NMR similarities of **9** and **10** together with two additional amu in the EIMS of **10**, led us to determine the structure of dorsmanin J a 8-prenyl-6,7-(2,2-dimethyldihydropyrano)-5,3′,4′-trihydroxyflavanone (**10**). This structure was confirmed by both ^{13}C NMR spectrum and the EIMS. The EIMS showed a fragment ion at *m/z* 369 diagnostic for the 2, 2-dimethyldihydropyran degradation (Drewes, 1973). The RDA fragments at *m/z* 288 and 136 were also observed. The ^{13}C NMR signals were fully assigned using DEPT spectra.

In our previous study (Ngadjui et al., 1999) we reported the isolation and characterization of dorsmanins F and G from the twigs of *D. mannii*. Chemical examination of the aerial parts of this plant resulted in the isolation of two compounds which each showed a single spot by TLC and were identical on TLC to dorsmanins F and G. The ^{1}H NMR of each of them showed duplicate resonances for the chelated 5-OH. This is also observed in the ^{13}C NMR spectra. Detailed NMR (Tables 1 and 2) analysis indicated that both consist of two pairs of diastereoisomers resulting from epimerisation of the asymmetric centre in the cyclic side attachment. Efforts to separate each set of diastereoisomers to dorsmanin F, epi-dorsmanin F (**6,11**) and dorsmanin G, epi-dorsmanin G (**7,12**) were unsuccessful. Each pair of diastereoisomers has been characterized as a mixture.

The results of this and the earlier investigation of *D. mannii* (Ngadjui et al., 1998a,b, 1999) indicated that this plant is a rich source of mono-and di-prenylated as well as geranylated chalcones, flavanones and flavones of considerable complexity in the modification of the prenyl substituent group. Noteworthy is the co-occurrence of epimeric pairs of C-2″ linear dihydrofurano flavanones and their corresponding angular isomers in reasonable yields. Moreover, this study identifies *D. mannii* as a most suitable source for obtaining multigram quantities of 6,8-diprenyleriodictyol which can be considered here as the biogenetic precursor of most of the diprenylated flavonoids isolated from this plant.

3. Experimental

3.1. General

Melting points were uncorrected. UV-visible spectra were recorded in MeOH on a Shimadzu-UV401PC spectrometer using analytical grade reagents; IR KBr disk; ^{1}H NMR (300 MHz, 600 MHz for HMBC data only), ^{13}C NMR (75 MHz) and DEPT spectra were determined on a Varian Gemini 2000 spectrometer in $CDCl_3$ or CD_3COCD_3, with residual solvent proton peaks as internal reference standards. EIMS: direct inlet, 70 eV.

3.2. Plant material

The aerial parts 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. The identity of the plant was established by Mr P. Mizili, botanist in the National Herbarium.

Table 1
^{1}H NMR data of dorsmanins I (**9**), J (**10**), dorsmanin F, epi-dorsmanin (**6/11**) and dorsmanin G, epi-dorsmanin G (**7/12**) (CD_3COCD_3, δ ppm, *J* in Hz, 300 MHz)

H	9	10	6/11	7/12
2	5.41 (*dd*, $J=12.6$, 3.0)	5.35(*dd*,$J=12.6$,3.1)	5.41(*dd*,$J=12.3$,3.2)	5.39/5.35(*dd*,$J=12.6$,33)
3a	3.13(*dd*,$J=17.1$,12.6)	3.07(*dd*,$J=17.2$,12.4)	3.10(*dd*,$J=17.0$,12.0)	3.15(*dd*,$J=17.0$,12.0)
3b	2.78(*dd*,$J=17.1$,3.0)	2.74(*dd*,$J=17.2$,3.1)	2.80(*dd*,$J=17.0$.3.0)	2.76/2.70(*dd*,$J=17.0$,3.0)
5-OH	12.46 (*br s*)	12.47(*br s*)	12.69/12.6(*br s*)	12.27/12.26(*br s*)
2′, 5′	6.88(*br s*)	6.87(*br s*)	6.86(*br s*)	6.86(*br s*)
6′	7.06(*br s*)	7.10(*br s*)	7.04(*br s*)	7.04(*br s*)
2″	–	–	4.75/4.74(*br t*, $J=9.0$)	4.76/4.74(*br t*, $J=8.0$)
3″	5.62(*br d*, $J=1.02$	1.80(*br t*, $J=6.9$)	3.05(*dd*, $J=15.0$,9.0)	3.10(*dd*, $J=15.0$,8.0)
4″	6.58(*br d*, $J=10.2$)	2.57(*br dt*, $J=6.9$,1.2)	–	–
Me_2C	1.45(*br s*), 1.43(*br s*)	1.34(*br s*), 1.33(*br s*)	–	–
Me_2C(OH)	–	–	1.25/1.23(*s*),1.21/1.20(*s*)	1.25/1.23(*s*),1.20(*s*)
1‴	3.20(*br d*,$J=7.5$)	3.17(*br d*,$J=7.2$)	3.12(*br d*,$J=7.2$)	3.15(*br d*,$J=7.0$)
2‴	5.14(*br dt*,$J=7.5$,1.2)	5.15(*br t*,$J=7.2$)	5.24(*br t*,$J=7.2$)	5.20/5.18(*br t*,$J=7.5$)
Me	1.62(*br s*)	1.60(*br s*)	1.75/1.74(*s*)	1.65/1.64(s)
Me	1.66(*br s*)	1.64(*br s*)	1.63(*s*)	1.63(*s*)

Table 2
^{13}C NMR spectra data of dorsmanins I (9), J (10), lupinifolin (9a), dorsmanin F, epi-dorsmanin F (6, 11), (δ ppm, CD_3COCD_3, 75 MHz)[a]

C	9	10	6/11
2	79.9 (*d*)	79.7 (*d*)	79.2/79.1(*d*)
3	43.6 (*t*)	43.8 (*t*)	43.0/42.9 (*t*)
4	198.1 (*s*)	198.0 (*s*)	196.3 (*s*)
5	157.3 (*s*)	158.2 (*s*)	156.6 (*s*)
6	109.1 (*s*)	108.8 (*s*)	104.5/104.4 (*s*)
7	160.7* (*s*)	161.2* (*s*)	167.2 (*s*)
8	103.4$^+$ (*s*)	102.8$^+$ (*s*)	103.8 (*s*)
9	160.2* (*s*)	160.2* (*s*)	161.9/161.8 (*s*)
10	103.3$^+$ (*s*)	102.3$^+$ (*s*)	102.8/102.7 (*s*)
1′	131.4 (*s*)	131.0 (*s*)	130.9 (*s*)
2′	116.1 (*d*)	116.1 (*d*)	114.0 (*d*)
3′	146.4 (*s*)	146.3 (*s*)	145.7 (*s*)
4′	146.1 (*s*)	146.1 (*s*)	145.3 (*s*)
5′	114.7 (*d*)	114.6 (*d*)	115.3 (*d*)
6′	119.1 (*d*)	119.0 (*d*)	118.4 (*d*)
2″	78.9 (*s*)	16.6 (*t*)	26.8/26.7 (*t*)
3″	127.1 (*d*)	32.3 (*t*)	91.5/91.4 (*d*)
4″	116.2 (*d*)	77.0 (*s*)	–
Me$_2$C	28.6 (*q*), 28.5(*q*)	27.2 (*q*), 27.0 (*q*)	25.5/25.4 (*q*), 25.2 (*q*)
Me$_2$C(OH)	—	—	71.0/70.9 (*s*)
1‴	22.1 (*t*)	22.3 (*t*)	21.4/21.3 (*t*)
2‴	123.5 (*d*)	123.9 (*d*)	122.4 (*d*)
3‴	131.7 (*s*)	132.1 (*s*)	131.0/130.9 (*s*)
4‴	18.1 (*q*)	18.2 (*q*)	17.2 (*q*)
5‴	26.0 (*q*)	26.0 (*q*)	24.6/24.5 (*q*)

[a] *,$^+$ Signals with the same signs in the same column may be interchanged.

3.3. Extraction, isolation and characterization

The air-dried and powdered aerial parts of *D. mannii* (4.2 kg) were soaked in CH_2Cl_2:MeOH (1:1) for 24 h, followed by MeOH for 2 h. Concentration of the combined organic extracts under reduced pressure gave a dark-green residue (290 g) which was re-extracted with EtOAc. Removal of the solvent yielded 162 g of EtOAc soluble material. The remaining gummy residue (100 g), was found to contain copious amounts of tannins and was not investigated further. Part of the EtOAc extract (110 g) was submitted to flash CC using hexane and introducing an EtOAc gradient and subsequently MeOH gradient in EtOAc. The eluate was collected in 250 ml fractions, which were monitored by TLC. Fractions containing components with the same retention times were combined. Frs 1–20 (10 g) were examined by TLC (hexane:EtOAc 9:1) and were found to contain mainly mixtures of hydrocarbons and phytosterols. Recrystallisation of the combined residues in hexane-EtOAc gave 120 mg of β-sitosterol. Frs 21-30 (2 g, hexane:EtOAc 17:3) were subjected to flash CC (Si gel, 60 g) and eluted with hexane:EtOAc (9:1) to give after preparative TLC, 4-methoxylonchocarpin (15 mg) and **2** (20 mg). Frs 31–45 (8 g, hexane:EtOAc 7:3) upon examination by TLC did not contain any flavonoids and were not investigated further. Frs 46–60 (23 g) were passed through Sephadex LH-20 column and eluted with CHCl3:MeOH (2:1). The post-chlorophyll fraction was separated and purified by CC and preparative TLC to yield **1** (15 mg), **3** (80 mg), **4** (20 mg), **5** (15 mg), 4-hydroxylonchocarpin (800 mg), **9** (30 mg), **10** (20 mg) and 6-prenylchrysoeriol (40 mg). Frs 61–70 yielded a precipitate (1.2 g) which was insoluble in the usual organic solvents and part of it (200 mg) was acetylated using boiling 8 ml of acetic anhydride for 2 h. The reaction mixture was evaporated in a petri dish to leave a residue which was chromatographed by CC (hexane: EtOAc 3:2) to give white crystalline tetraacetate of β-sitosterol 3-β-D-glucopyranoside (160 mg), mp 165–166°C. Frs 71–100 (20 g) from the first CC were passed through Sephadex LH-20 column. The post chlorophyll fraction (16 g) was subjected to CC on Si gel (150 g) and eluted with $CHCl_3$ introducing a MeOH gradient. 30 frs of 100 ml were collected, monitored by TLC, and similar frs were combined. From the chromatographic separation above, and in some cases with the aid of further CC or successive PTLC, the following compounds were obtained: 6,8-diprenyleriodictyol (2.5 g), gancaonin P (15 mg), **8** (20 mg), **6,11** (20 mg), and **7,12** (25 mg). Known compounds were identified by comparison (mp, ^1H, ^{13}C NMR) with published information or authentic specimens.

3.3.1. 6,7-(2,2-Dimethylpyrano)-8-prenyl-5,3′,4′-trihydroxyflavanone, dorsmanin I (**9**)

Yellow plates from hexane-EtOAc, mp 172–174°C; $[\alpha]_D$–27° (MeOH, c 0.12); UV λ_{max}^{MeOH} nm (log ε):205 (4.54), 220 (4.33), 275 (4.34), 354 (3.41); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε):205 (4.56), 286 (4.22), 320 (4.16), 412 (3.41); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ε):207 (4.48), 281 (4.42), 322 (4.26), 408 (3.50); UV $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε):220 (4.79), 274 (4.33), 318 (3.98), 341 (4.08); IR ν_{max}^{KBr} cm^{-1} :3400 (OH), 1645 (C=O), 1600, 1590, 1560, 1450, 1400, 1360, 1325, 1245, 125; EIMS *m/z* (rel. int.): 422 $[M]^+$ (82), 407 $[M\text{-}Me]^+$ (92), 379 $[M\text{-}Me\text{-}CO]^+$ (10), 367 $[M\text{-}C4H7]^+$ (12), 286 $[RDA]^+$ (10), 271 $[RDA\text{-}Me]^+$ (38), 243 $[RDA\text{-}Me\text{-}CO]^+$ (31), 215 $[RDA\text{-}C_4H_8\text{-}Me]^+$ (100), 136 (15); ^1H NMR (CD_3COCD_3, 300 MHz): Table1; ^{13}C NMR (CD_3COCD_3, 75 MHz):Table 2.

3.3.2. 6,7-(2,2-Dimethyldihydropyrano)-8-prenyl-5,3′,4′-trihydroxyflavanone, dorsmanin J (***10***)

Brown gum; $[\alpha]_D$–17° (MeOH, c 0.17); UV λ_{max}^{MeOH} nm (log ε):210 (4.43), 220 (4.33), 298 (4.25), 345 (3.52); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 210 (4.46), 221 (4.45), 320 (4.32), 402 (3.51); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ε): 209 (4.43), 219 (4.40), 322 (4.30), 400 (3.50); UV $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 220 (4.53), 298 (4.23), 344 (3.58); IR ν_{max}^{KBr} cm^{-1}:3350 (OH), 1650 (C=O), 1590, 1560, 1530, 1515, 1445, 1400, 1365, 1285, 1280, 1200. EIMS *m/z* (rel. int.):

424 $[M]^+$ (100), 409 $[M\text{-}Me]^+$ (18), 369 $[M\text{-}C_4H_7]^+$ (70), 288 [RDA] (10), 233 (22), 217 (18), 177 (20), 136 (43); ^1H NMR (CD_3COCD_3, 300 MHz): Table 1; ^{13}C NMR (CD_3COCD_3, 75 MHz): Table 2.

3.3.3. Dorsmanin F and 2″-epidorsmanin F (**6/11**)

Beige plates in CH2Cl2, mp.168–170°C; UV λ_{max}^{MeOH} nm (log ϵ): 222 (4.52), 300 (4.38), 352sh (3.69); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ϵ):220 (4.54), 320 (4.36), 392 (3.60); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ϵ):215 (4.50), 226 (4.54), 321 (4.46), 394 (3.63); nm (log ϵ):UV $\lambda_{max}^{MeOH+NaOAc}$ nm (log ϵ): 220 (4.51), 301 (4.36), 350 (3.70); IR ν_{max}^{KBr} cm^{-1}:3345–3350 (OH), 1645 (CO), 1600, 1580, 1565, 1450, 1380, 1300, 1250,1215, 1150; EIMS *m/z* (rel. int.):440 $[M]^+$ (100), 381 (35), 368 (30), 304 (10), 288 (60), 245 (32), 190 (40), 136 (25), 59 (20); ^1H NMR (CD_3COCD_3, 300 MHz): Table 1; ^{13}C NMR (CD_3COCD_3, 75 MHz): Table 2.

3.3.4. Dorsmanin G and 2″-epidorsmanin G (**7/12**)

Colorless powder, mp 148–150°C; UV λ_{max}^{MeOH} nm (log ϵ):223 (4.58), 301 (4.49), 347 (3.70); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ϵ 225 (4.60), 321 (4.55), 389 (3.65); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ϵ) 228 (4.58), 323 (4.60), 392 (3.71); UV $\lambda_{max}^{MeOH+NaOAc}$ nm (log ϵ):225 (4.59), 303 (4.52), 348 (3.81); IR ν_{max}^{KBr} cm^{-1}: 3340–3350 (OH), 1640 (C=O), 1600, 1580, 1565, 1540, 1500, 1475, 1425, 1320, 1280, 1200; EIMS *m/z* (rel.int.):440 $[M]^+$ (100), 423 (35), 381 (40), 304 (8), 288 (30), 245 (40), 136 (45), 59 (30); ^1H NMR (CD_3COCD_3, 300 MHz): Table 1.

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