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Prenylated flavanones from the twigs of *Dorstenia mannii*

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Abstract

Investigation of the twigs of *Dorstenia mannii* gave 6,8-diprenyl-5,7,3′4′-tetrahydroxyflavanone and four new prenylated flavanones, named dorsmanins E-H and characterized as 5,6-7,8-*bis*-(2,2-dimethylchromano)-3′,4′-dihydroxyflavanone, 7,8-[2″-(1-hydroxy-1-methylethyl)-dihydrofurano]-6-prenyl-5,3′,4′-trihydroxyflavanone, 6,7-[2″-(1-hydroxy-1-methylethyl)dihydrofurano]-8-prenyl-5,3′,4′-trihydroxyflavanone and 6-prenyl-8-(2-hydroxy-3-methylbut-3-enyl)-5,7,3′,4′-tetrahydroxyflavanone, respectively, on the basis of spectral analysis and chemical evidence for the chromano derivative.

Keywords: Dorstenia mannii; Moraceae; Twigs; Prenylated flavanones

1. Introduction

We recently reported (Ngadjui, Abegaz, Dongo, Tamboue & Fogue, 1998) the isolation, from the twigs of *Dorstenia mannii*, of three prenylated and one geranylated flavonoids named dorsmanins A-D. Their structures were established as 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′-tetrahydroxyflavone and 6,8-diprenyl-3,5,7,4′-tetrahydroxy-3′-methoxyflavone, respectively. In addition, the known compounds 6-prenyl-5,7,4′-trihydroxy-3′-methoxyflavone, 6,8-diprenyl-5,7,3′4′-tetrahydroxyflavanone, and 3′,4′-(2,2-dimethylchromeno)-2′,4-dihydroxychalcone were isolated and fully characterized. Further studies on the same plant have now led to the isolation of the known 6,8-diprenyleriodictyol (**1**), and four novel prenylated flavanones for which the names dorsmanins E-H are proposed. This paper deals with the isolation and characterization of these new prenylated flavanones.

2. Results and discussion

The polar fractions of the extract yielded five prenylated flavanones, four of which are new and identified as 5,6-7,8-*bis*-(2,2-dimethylchromano)-3′,4′-dihydroxyflavanone (**2**), 7,8-[2″-(1-hydroxy-1-methylethyl)-dihydrofurano]-6-prenyl-5,3′,4′-trihydroxyflavanone (**3**), 6,7-[2″-(1-hydroxy-1-methylethyl)dihydrofurano]-8-prenyl-5,3′,4′-trihydroxyflavanone (**4**) and 6-prenyl-8-(2-hydroxy-3-methylbut-3-enyl)-5,7,3′,4′-tetrahydroxyflavanone (**5**).

The flavanone nature of **1**–**5** was apparent from the red colours produced on reaction of these substances with magnesium-hydrochloric acid. Compound **2** (dorsmanin E) was obtained as beige powder. The EIMS showed a molecular ion at *m*/*z* 424 and the molecular formula $C_{25}H_{28}O_6$ was deduced from the MS and NMR data. In the ^{1}H NMR spectrum, three protons at δ 2.64 (*dd*, J = 16.5, 3.0 Hz), 2.90 (*dd*, J = 16.5,

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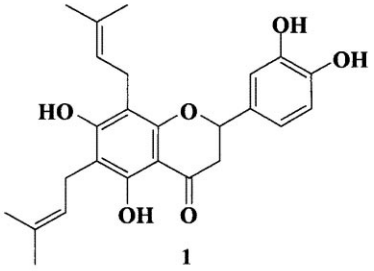

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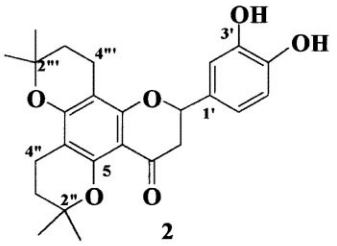

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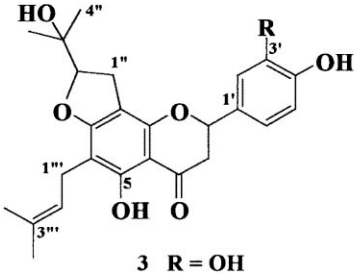

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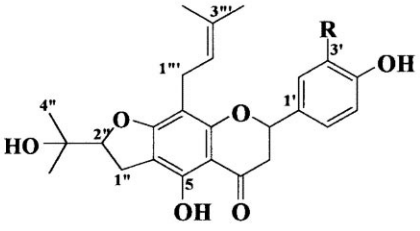

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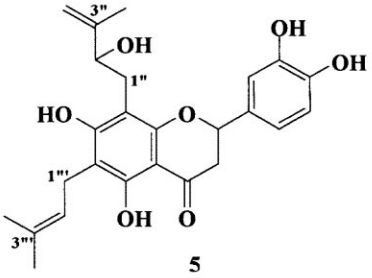

5

12.7 Hz) and 5.24 (*dd*, $J = 12.7$, 3.0 Hz) typically assignable to H–3 and H–2 of a flavanone system, were observed. The ^{1}H NMR of dorsmanin E also showed the presence of two 2,2-dimethylchroman groups (see below) and only three aromatic proton resonance signals indicating the highly substituted nature of the flavanone. The three Ar–H signals which were indirectly deduced to be an ABX system, from ^{13}C NMR data (two hydroxyls bearing *ortho* carbons at δ 146.5 and 146.6) and biogenetic considerations, were poorly resolved in methanol-d_4 and remained so when the spectrum was measured in acetone-d_6 as well. The signals assigned to the two 2,2-dimethylchroman groups were: four benzylic proton signals at δ 2.60 (2H, *t*, $J = 6.6$ Hz), 2.51 (2H, *t*, $J = 6.8$ Hz) each coupled to two methylene protons at δ 1.83 (2H, *t*, $J = 6.6$ Hz), 1.77 (2H, *t*, $J = 6.8$ Hz) and four methyl proton signals at δ 1.33, 1.35, 1.36 and 1.38. On the basis of the above data, structure **2** was proposed for dorsmanin E. The ^{13}C NMR (Table 1) was fully assigned using DEPT spectra and by comparison of measured values with those reported for 6,8-diprenyleriodictyol (**1**) isolated from *D. mannii* (Moraceae) (Ngadjui et al., 1998) and *Vellozia coronata* (Harborne, Greenham, Williams, Eagles & Markham, 1993). The EIMS showed the fragmentation at *m/z* 369 $[M\text{-}55]^+$ diagnostic for the 2,2-dimethylchroman degradation (Budzikiewicz, 1973). The structure of dorsmanin E as **2** was unequivocally established by its synthesis from **1** following a simple procedure reported by Hano, Itoh, Hanaoka & Nomura, 1995 for such interconversions Mahidol, Prawat, Ruchirawat, Lihkitwitayawuid, Lin, Ze & Cordell, 1997.

Compound **3** was isolated as beige plates. The IR spectrum displayed absorption bands due to hydroxyl, carbonyl and benzene ring protons at υ_{max} 3400–3350, 1640, 1580, respectively. Its molecular formula was determined as $C_{25}H_{28}O_7$ from NMR and EIMS data ($[M^+]$ at *m/z* 440). Like **2** above, the NMR spectra revealed the flavanone nature of **3**. Thus, an oxy-

Table 1
^{13}C NMR data of compounds **1**–**5** at 75 MHZ, in $CDCl_3$ (**1**) and CD_3OD (**2,3,4**) and CD_3COCD3 (**5**).

Carbon	1	2	3	4	5
2	78.5(*d*)	79.9(*d*)	80.4(*d*)	80.5(*d*)	79.7(*d*)
3	43.2(*t*)	46.5(*t*)	44.2(*t*)	43.9(*t*)	43.5(*t*)
4	196.9(*s*)	192.6(*s*)	197.6(*s*)	198.4(*s*)	197.5(*s*)
5	159.4(*s*)	155.6(*s*)	162.9(*s*)	161.8(*s*)	159.9(*s*)†
6	107.5(*s*)	105.9(*s*)	105.4(*s*)	104.7(*s*)	109.8(*s*)
7	162.7(*s*)	161.7(*s*)	168.5(*s*)	168.5(*s*)	165.4(*s*)
8	106.6(*s*)	104.2(*s*)	105.3(*s*)	106.3(*s*)	106.1(*s*)
9	157.8(*s*)	159.9(*s*)	156.7(*s*)	157.6(*s*)	160.7(*s*)†
10	102.8(*s*)	101.8(*s*)	103.8(*s*)	104.2(*s*)	102.8(*s*)
1′	131.7(*s*)	132.3(*s*)	131.8(*s*)	131.9(*s*)	131.7(*s*)
2′	113.3(*d*)	114.5(*d*)	114.7(*d*)	114.7(*d*)	114.6(*d*)
3′	143.9(*s*)*	146.5(*s*)†	146.9(*s*)†	146.8(*s*)†	146.4(*s*)‡
4′	144.0(*s*)*	146.6(*s*)†	146.5(*s*)†	146.5(*s*)†	146.6(*s*)‡
5′	115.4(*d*)	116.2(*d*)	116.3(*d*)	116.2 (*d*)	116.0(*d*)
6′	119.0(*d*)	118.9(*d*)	119.2(*d*)	119.2(*d*)	118.8(*d*)
1″	21.9(*t*)†	–	27.7(*t*)	27.4(*t*)	30.3(*t*)
2″	121.9(*d*)‡	77.0(*q*)‡	92.4(*d*)	92.4(*d*)	77.1(*d*)
3″	134.8(*s*)§	33.0(*t*)§	72.5(*s*)	72.4(*s*)	147.8(*s*)
4″	–	17.7(*t*)	25.9(*q*)	25.9(*q*)	110.2(*t*)
5″	–	–	25.9(*q*)	25.9(*q*)	18.9(*q*)
1‴	21.3(*t*)†	–	21.9(*t*)	23.0(*t*)	22.0(*t*)
2‴	121.7(*d*)‡	76.4(*s*)‡	123.3(*d*)	123.4(*d*)	124.0(*d*)
3‴	134.3(*s*)§	32.7(*t*)§	132.1(*s*)	132.2(*s*)	130.8(*s*)
4‴	–	17.7(*t*)	–	–	–
(E)Me	25.9(*q*)×2	–	24.6(*q*)	24.6(*q*)	25.9(*q*)
(Z)–Me	17.9(*q*)×2	–	17.9(*q*)	18.0(*q*)	17.9(*q*)
Me_2C		27.4(*q*)	–	–	–
		26.9(*q*)×2	–	–	–
		26.8(*q*)	–	–	–

Signals with the same subscripts in the same column may be interchanged. Multiplicities were determined from DEPT spectra.

methine, a carbonyl, and methylene signals at δ_C 80.4 (*d*), 197.6 (*s*) and 44.2 (*t*), respectively and an ABX system [δ_H 2.70 (*dd*, $J = 17.2$, 3.2 Hz), 3.05 (*dd*, $J = 17.2$, 12.6 Hz), and 5.28 (*dd*, $J = 12.6$, 3.2) typically assignable to H–3 and H–2 of a flavanone] could be observed. The ^1H NMR data (Experimental) also showed, like lonchocarpol C (**3a**) (Tahara, Katagiri, Ingham & Mizutani, 1994) proton resonance signals for a chelated 5-hydroxyl group at δ 12.74, a prenyl group [δ 5.21 (*t* like *m,* olefinic proton), 3.18 (2H, *br d*, $J = 7.4$ Hz methylene protons) and 1.68, 1.78 (3H, each olefinic methyl protons)] a 1-hydroxy-1-methylethyldihydrofuran ring [δ 1.27, 1.29 (each 3H, *s*, *gem* dimethyl protons), 3.04 (2H, *dd*, $J = 15.5$, 8.7 Hz, methylene protons), 4.67 (*t*, $J = 8.7$ Hz, oxymethine proton)]. However, the three aromatic proton signals were not well resolved in three solvents: acetonitrile-d_3, acetone-d_6 and methanol-d_4. The ^{13}C NMR (Table 1) displayed signals for two adjacent aromatic carbons bearing hydroxyl groups at δ 146.5 and 146.9, which should be located in ring B. Regarding the position of the prenyl group, two possibilities were considered, a linear and an alternative structure with an angular dihydrofuran ring (**3**) and a prenyl substituent at C–6. Tahara, Katagiri, Ingham & Mizutani, 1994; 1991 have shown that the chemical shift of the 5–OH signal is predictably influenced by the mode of cyclization of the dihydrofurano ring, *i.e.* cyclization of the 8-prenyl group ($8 \rightarrow 7$ [O]) shifts the signal of 5–OH to lower field, whereas 6-prenyl cyclization ($6 \rightarrow 7$[O]) shifts it to higher field. In 6,8-diprenyleriodictyol (**1**) (uncyclized) the 5–OH is reported to occur at *ca* δ 12.30 (Ngadju et al., 1998; Harborne et al., 1993). In dorsmanin *F* the corresponding signal is at δ12.74 consistent with the ($8 \rightarrow 7$ [O]) cyclization and the attachment of the other prenyl group at C–6. The structure of dorsmanin *F* was determined to be 7,8-[2″-(1-hydroxy-1-methylethyl)-dihydrofurano]-6-prenyl-5,3′,4′-trihydroxyflavanone (**3**).

Compound **4** (dorsmanin G), obtained as yellow oil, gave a $[M^+]$ at *m/z* 440 in the EIMS. Its molecular formula was assumed to be $C_{25}H_{28}O_7$ on the basis of NMR and EIMS data. The chelated 5-hydroxyl proton signal appeared at δ 12.04 and the carbonyl group signal at δ 198.4. Like compound **3**, the NMR spectra showed resonance signals for one prenyl group, a 1-hydroxy-1-methylethyldihydrofuran ring, and two aromatic carbons bearing *ortho* oxygenated substituents. Both **3** and **4** have the same molecular mass and the similarity of their NMR spectra led us to believe that they were isomers. This finding, together with the observed chemical shift of the chelated 5-hydroxyl group at δ 12.04, suggested the ($6 \rightarrow 7$ [O]) cyclization of the prenyl group to give a linear 1-hydroxy-1-methylethyldihydrofuran ring with the attachment of the other prenyl group at C–8. The structure of dorsmanin *G* was determined to be 6,7-[2″-(1-hydroxy-1-methylethyl)dihydrofurano]-8-prenyl-5,3′,4′-trihydroxyflavanone (**4**). Dorsmanins *F* (**3**) and *G* (**4**) are regioisomers. The ^{13}C NMR (Table 1) signals were fully assigned using DEPT spectra and by comparison of measured values with those reported for lonchocarpol C, (**3a**) (Roussis, Ampofo & Wiemer, 1987). The EIMS showed mass fragments at *m/z* 351 and 59 $[Me_2C{=}OH]^+$ typical for flavonoids possessing a 2-(1-hydroxy-1-methylethyl)dihydrofurano group (Tahara, Ingham, Nakahara, Mizatani & Harborne, 1984; Nakahara, Tahara, Mizutani & Ingham, 1986). Dorsmanins *F* (**3**) and *G* (**4**) are the 3′-hydroxyl derivatives of lonchocarpols C (**3a**) and D(**4a**), respectively, reported from the legumes *Lupinus luteus* (Tahara et al., 1994) and *Lonchocarpus minimiflorus* (Harborne et al., 1993).

Dorsmanin *H* (**5**), yellow oil, was assumed to have the molecular formula $C_{25}H_{28}O_7$ on the basis of NMR and EIMS. It contained a prenyl group characterized by ^{1}H NMR chemical shift values [δ 3.31 (*br d*, $J = 7.2$ Hz, CH_2), 5.27 (*br t*, $J = 7.2$ Hz olefinic proton), 1.66 (3H, *br s*) and 1.76 (3H, *brs*) both olefinic methyls)] similar to those given by the prenyl substituent of 6-prenylnaringenin (**6**) obtained by synthesis from (2S)-naringenin (Tahara et al., 1994). In addition, compound **5** gave ^{1}H NMR signals (Experimental) which could be assigned to a 2-hydroxy-3-methylbut-3-enyl side chain [2.83 (*dd*, $J = 14.8$, 7.8 Hz), 3.04 (*dd*, $J = 14.8$, 2.3 Hz) both benzyl methylene, 4.35 (*br t* like *ca* 6.5 Hz, oxymethine), 4.79, 4.90 (each *br s* olefinic methylene) and 1.75 (3H, *s*, olefinic methyl)]. The ^{13}C NMR (Table 1) was fully assigned using DEPT spectra and by comparison of measured values with those reported for similar compounds (Mahidol et al., 1997; Seo, Silva, Chai, Chagwedera, Farnsworth, Cordell, Pezzuto & Kinghorn, 1997). The EIMS showed characteristic mass fragments at *m/z* 369 and *m/z* 71 $[CH_2{=}C(CH_3){-}CH{=}OH]^+$, and at *m/z* 304 and 136 (RDA fragmentation).

6,8-diprenyleriodictyol (**1**) may very well be the biogenetic precursor of all the prenylated flavanones described in this report. The *bis*-chroman derivative **2** is almost undoubtedly a direct cyclization product of **1** and as mentioned earlier this has been done chemically in this study. Dorsmanins *F* (**3**), G(**4**) and H(**5**) may be derived from **1** *via* the 2″-3″ (or 2‴-3‴) epoxide and subsequent opening of the epoxide by the 7–OH group leading to (8 → 7[O] or (6 → 7[O]) cyclization to give **3** and **4**, respectively. The epoxy intermediate could also be transformed into **5** through enzymatic opening of the epoxide ring coupled with the loss of a proton from one of the 3‴-methyl groups. Although the biological activity of these compounds has not been investigated, it is reported recently that 6,8-diprenyleriodictyol (**1**) and other prenylated flavanones (Mahidol et al., 1997; Seo et al., 1997) were broadly cytotoxic (ED_{50} values $< 4\ \mu g\ ml^{-1}$) in several cell lines.

3. Experimental

3.1. General

M.ps. 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.

3.2. 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.

3.3. 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 as described previously (Ngadjui et al., 1998). The $CHCl_3$ and EtOAc soluble fractions, were monitored by TLC and combined. Part of this combined extract (60 g) was chromatographed on a column of silica gel (600 g) and eluted with hexane-EtOAc gradient. The polar fractions eluted with hexane-EtOAc (2:3) gave a dark green residue (8 g) which was passed through Sephadex LH-20 column ($CHCl_3$–MeOH 2:1). The post chlorophyll fraction (6 g) was subjected to further separation and purification using various chromatographic techniques (CC, MPLC, PTLC) and recrystallization to yield the flavanones **1** (70 mg), **2** (18 mg), **3** (20 mg), **4** (15 mg) and **5** (10 mg).

3.4. 6,8-Diprenyl-5,7,3′4′-tetrahydroxyflavanone (**1**)

Yellow plates from acetone, mp. 141–2°, $[\alpha]_D$-104° (MeOH, c 0.40); For EIMS, UV, IR and ^{1}H NMR see (Ngadjui et al., 1998) and (Harborne et al., 1993). ^{13}C NMR: Table 1.

3.5. 5,6-7,8-bis-(2,2-dimethylchromano)-3′,4′-dihydroxyflavanone (**2**)

Beige powder in hexane-EtOAc, m.p. 222–3°, $[\alpha]_D$ 0° (MeOH, c 0.12), EIMS *m/z* (rel. Int.): 424 (96, M^+), 369 (100, M-55), 340 (18), 314 (28), 313 (22), 259 (20), 233 (12), 203 (41), 137 (22), 136 (20), 123 (16), 55 (38); IR ν_{max}^{KBR} cm^{-1}:3450–3400 (OH), 1650 (C=O), 1600, 1580, 1550, 1450, 1330, 1240, 1150, 1120; UV λ_{max}^{MeOH} nm log(ϵ): 204 (4.46), 217 (4.31), 291 (4.18); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log(ϵ): 207 (4.56), 303 (4.22); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm log(ϵ): 216 (4.28), 294 (4.20); ^{1}H NMR (300 MHz, CD_3OD) δ: 1.33, 1.35, 1.36, 1.38 (3H each, *s*, 4×CH_3), 1.77 (2H, *t*, $J = 6.8$ Hz, 2H-3″), 1.83 (2H, *t*, $J = 6.6$ Hz, 2H-3‴), 2.51 (2H, *t*, $J = 6.8$ Hz, 2H-4″) 2.60 (2H, *t*, $J = 6.6$ Hz, 2H-4‴), 2.64 (*dd*, $J = 16.5$, 3.0 Hz, H-3β), 2.90 (*dd*, $J = 16.5$, 12.7 Hz,

H-3α), 5.24 (*dd*, $J = 12.7$, 3.0 Hz, H-2), 6.77 (2H, *br s*, H-5′, H-6′), 6.92(*br s*, H-2′).

3.6. Conversion of 6,8-diprenyleriodictyol (1) to 2

A mixture of **1** (200 mg) and 35% HCl (12 ml) - MeOH (40 ml) solution was refluxed for 2 h. The reaction mixture was poured into water (100 ml) and extracted with $CHCl_3$ (3×50 ml). The $CHCl_3$ ext. was washed with water, dried and evaporated under reduced pressure. The residue (180 mg) was separated and purified by prep. TLC to give **2** (20 mg). **2** was identified by comparing the physical and spectroscopic data (mp. NMR).

3.7. 7,8-[2″-(1-hydroxy-1-methylethyl)-dihydrofurano]-6-prenyl-5,3′,4′-trihydroxyflavanone (3)

Beige plates in CH_2 Cl_2, mp. 164–5°. $[\alpha]_D$ + 9° (MeOH, c 0.22); EIMS *m/z* (rel int): 440 (100, M^+), 381 (40), 368 (30), 288 (58), 245 (28), 230 (18), 190 (38), 136 (18), 59 (16); IR ν_{max}^{KBr} cm^{-1}: 3400–3350 (–OH), 1640 (C=O), 1600, 1580, 1450, 1380. UV λ_{max}^{MeOH} nm log(ε): 210 (4.43), 219 (4.43), 300 (4.23); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log(ε): 214 (4.51), 315 (4.24); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm log(ε): 212 (4.40), 312 (4.21); ^{1}H NMR (300 MHz, CD_3OD) δ: 1.27, 1.29 (3H each, *s*, 2×Me), 1.68, 1.78 (3H each, *s*, 2×olefinic Me), 2.70 (*dd*, $J = 17.2$, 3.2, H-3β) 3.05 (*dd*, $J = 17.2$, 12.6 Hz, H-3α), 3.04 (2H, *dd*, $J = 15.5$, 8.7Hz, 2H-1″), 3.18 (2H, *br d* like *t*, $J = 7.4$ Hz, 2H-1‴), 4.67 (*t*, $J = 8.7$ Hz, H-2″), 5.21 (*t* like *m*, $J = 7.4$ Hz, H-2‴), 5.28 (*dd*, $J = 12.6$, 3.2 Hz, H-2), 6.7–6.8 (2H, *m*, H-5′, H-6′), 6.91 (*br s*, H-2′). ^{1}H NMR (300 MHz, CD_3COCD_3) δ: 12.74 (5–OH), no change in the rest of the spectrum.

3.8. 6,7-[2″-(1-hydroxy-1-methylethyl)dihydrofurano]-8-prenyl-5,3′,4′-trihydroxyflavanone (4)

Yellow oil. $[\alpha]_D$-40° (MeOH, c 0.14). EIMS *m/z* (rel int): 440 (100, M^+), 423 (40), 381 (35), 366 (38), 338 (16), 288 (35), 249 (37), 245 (40), 230 (45), 202 (38), 177 (40), 136 (42), 123 (18), 59 (30); IR ν_{max}^{KBr} cm^{-1}: 3350–3300 (–OH), 1640 (C=O), 1600, 1500, 1350, 1240, 1200, 1100; UV λ_{max}^{MeOH} nm log(ε): 204 (4.43), 300 (4.08); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log(ε): 208 (4.56), 322 (4.10); UV $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm log(ε):205 (4.47), 224 (4.30), 323 (4.18), 394 (3.25); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.22, 1.34 (3H each, *s*, 4″-Me, 5″Me), 1.61(6H, *s*, 2×olefinic Me), 2.67 (*dd*, $J = 17.0$, 3.0 Hz, H-3β) 2.88 (*dd*, $J = 17.0$, 12.6 Hz, H-3α) 3.05 (*dd*, $J = 14.0$, 8.5 Hz, H-1″α), 3.08(*dd*, $J = 14.0$, 8.5 Hz, H-1″β), 3.13 (2H, *d*, $J = 7.0$ Hz, 2H-1‴), 4.71 (*t*, $J = 8.5$ Hz, H-2″), 5.12 (*t* like *m*, H-2‴), 5.16 (*dd*, $J = 12.6$, 3.0 Hz, H-2), 6.76(*dd*, $J = 8.3$, 2.2 Hz, H-6′), 6.83 (*d*, $J = 8.3$ Hz, H-5′), 6.89 (*d*, $J = 2.2$ Hz, H-2′), 12.04 (*br s*, 5–OH). ^{1}H NMR (300 MHz, CD_3OD) δ: 1.21, 1.24 (3H each, *s*, 4″-Me, 5″Me), 1.60, 1.62 (3H each, *s*, olefinic Me), 2.68 (*dd*, $J = 17.0$, 3.0 Hz, H-3β), 3.00 (*dd*, $J = 17.1$, 12.6 Hz, H-3α), 3.01–04 (2H, *br* d like *m*, 2H-1″), 3.14(2H, *d*, $J = 7.0$ Hz, H-1‴), 4.68 (*br t*, $J = 8.0$ Hz, H-2″), 5.15 (*t*, $J = 7.0$ Hz, H-2‴), 5.20 (*br d*, $J = 12.6$ Hz, H-2), 6.79 (2H, *br s*, H-5′, H-6′), 6.92 (*br s*, H-2′); ^{13}C NMR Table 1.

3.9. 6-Prenyl-8-(2-hydroxy-3-methylbut-3-enyl)-5,7,3′,4′-tetrahydroxyflavanone (5).

Yellow oil $[\alpha]_D$-176°(MeOH, c 0.5). EIMS *m/z* (rel int): 440 (8, M^+), 369 (100), 370 (44), 313 (88), 304(10), 233 (86), 177 (84), 136 (16), 71 (12); IR ν_{max}^{KBr} cm^{-1}: 3450–3400 (–OH), 1635 (C=O), 1600, 1440, 1330. UV λ_{max}^{MeOH} nm log(ε): 208 (4.36), 295 (4.04), 345 (3.35); UV $\lambda_{max}^{MeOH+AlCl_3}$ nm log(ε): 213 (4.43), 317 (4.04), 355 (4.21); ^{1}H NMR (300 MHz, CD_3COCD_3) δ: 1.66 (3H, *brs*, 3H-5‴), 1.75 (3H, *s*, 3H-4″), 1.76 (3H, *brs*, 3H-4‴), 2.74 (*dd*, $J = 16.8$, 3.0 Hz, H-3β), 2.83 (*dd*, $J = 14.8$, 7.8 Hz Ha-1″), 3.04 (*dd*, $J = 14.8$, 2.3 Hz, Hb-1″), 3.13 (*dd*, $J = 16.8$, 12.6 Hz, H-3α), 3.31 (2H, *brd*, $J = 7.2$ Hz, 2H-1‴), 4.35 (*br t* like *J ca* 6.5 Hz, H-2″), 4.79, 4.90 (*brs*, each, Ha-5″, Hb-5″), 5.27 (*br t*, $J = 7.2$ Hz, H-2‴), 5.36 (*dd*, $J = 12.6$, 3.0 Hz, H-2), 6.83 (2H, *br s*, H-5′, H-6′), 7.10 (*br s* H-2′) 12.50 (*br s*, 5–OH): ^{1}H NMR (300 MHZ, $CDCl_3$) δ: 6.79 (*br d*, $J = 8.5$ Hz, H-6′), 6.82(*d*, $J = 8.5$ Hz, H-5′), 6.86 (*br s*, H-2′), rest of the spectrum unchanged. ^{13}C NMR: Table 1.

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