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Dorsilurins C, D and E, three prenylated flavonoids from the roots of *Dorstenia psilurus*

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Abstract

The roots of *Dorstenia psilurus* yielded three phenolic compounds: 6,8-diprenyl-3′[O],4′-(2,2-dimethylpyrano)-3,5,7-trihydroxyflavone, 3,6-diprenyl-8-(2-hydroxy-3-methylbut-3-enyl)-5,7,2′,4′-tetrahydroxyflavone and an unusual B/C ring modified flavonoid derivative for which the names dorsilurins C, D and E, respectively, are proposed. Structures were elucidated on the basis of spectral analysis.

Keywords: *Dorstenia psilurus*; Moraceae; Roots; Prenylated flavonoids; Dorsilurins C, D and E

1. Introduction

As part of our continuing studies on Cameroonian *Dorstenia* species, we have already reported the isolation and characterization of some prenylated and geranylated flavonoids (Abegaz, Ngadjui, Dongo & Tamboue, 1998; Ngadjui, Abegaz, Dongo, Tamboue & Fogue, 1998; Ngadjui, Dongo, Happi, Bezabih, & Abegaz, 1998). In our previous paper Ngadjui et al., 1998, we described the isolation from the roots of *D. psilurus* Welw., of a new benzofuran derivative (**3**) and two prenylated flavones named dorsilurins A and B. Their structures were established as 6,8,3′-triprenyl-5,7,2′,4′-tetrahydroxyflavone (**1**) and 3,6-diprenyl-7,8-[2,2-dimethyl-3-hydroxydihydropyrano]-5,2′-4′-trihydroxyflavone (**2**), respectively. In addition, the known compounds stearyl ferulate, stearyl-*p*-coumarate and psoralen were identified Further chemical examination of the roots of this plant has now afforded three more triprenylated flavonoids for which we propose the names dorsilurins C (**4**), D (**5**) and E (**6**). In the present paper, we report the isolation and structural elucidation of these new prenylated flavonoids.

2. Results and discussion

The polar fractions of the CH_2Cl_2–MeOH extract of the roots of *Dorstenia psilurus* yielded three more prenylated flavonoids named as dorsilurin C, D and E. These were identified as 6,8-diprenyl-3′[O],4′-(2,2-dimethylpyrano)-3,5,7-trihydroxyflavone, 3,6-diprenyl-8-(2-hydroxy-3-methylbut-3-enyl)-5,7,2′,4′-tetrahydroxyflavone and an unusual B/C ring modified flavonoid derivative (**6**), respectively.

Dorsilurin C (**4**) was obtained as yellow gum. The EIMS showed a molecular ion at m/z 488 and the molecular formula $C_{30}H_{32}O_6$ was deduced from the HREIMS ($[M]^+$ m/z = 488.2193) and NMR spectra. The colour test with magnesium and concentrated hydrochloric acid (pink), together with the UV spectral data (Section 3) and the ^1H NMR signal at δ 13.19 indicated that dorsilurin C was a 5-hydroxyflavone (Markham, 1982). The bathochromic shift in the UV

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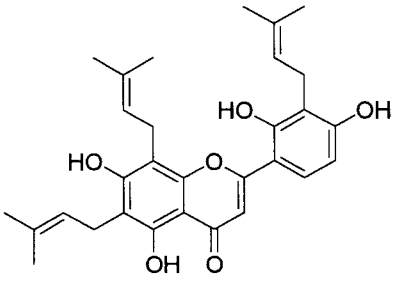

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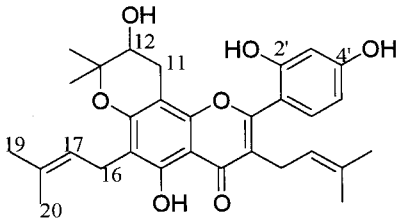

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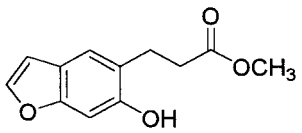

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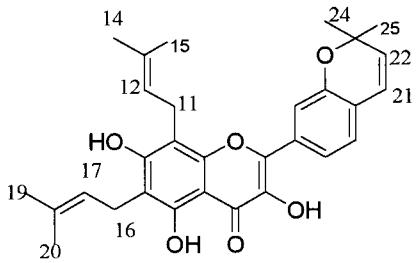

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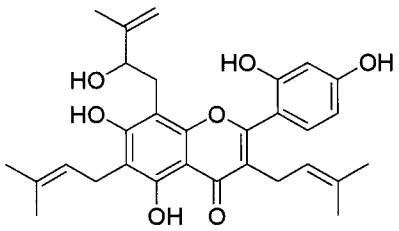

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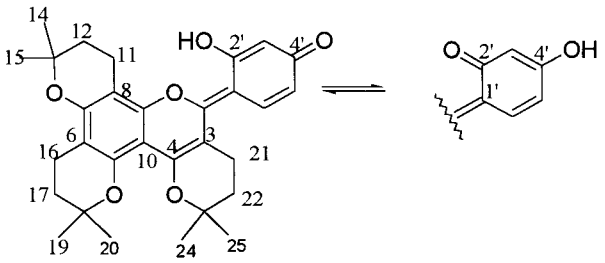

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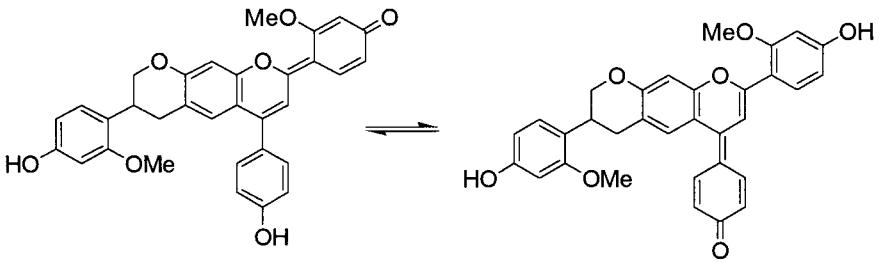

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spectrum of dorsilurin C induced by sodium acetate and aluminum chloride are consistent with its formulation as 5,7-dihydroxyflavone (Markham, 1982). The aromatic region of the ^{1}H NMR spectrum displayed only five proton resonance signals, two of which were assigned to the pyran group (see below) and the remaining three form an ABX system: a doublet at δ 7.73 (J = 8.5 Hz), an *ortho* and *meta* coupled double doublet at δ 6.67 (J = 8.5; 2.2 Hz) and a *meta* coupled signal at δ 6.47 (J = 2.2 Hz), which were located in ring B. The observed chemical shifts of the ring B protons are consistent with a 3′[O], 4′[C] substitution instead of the more common 3′[C],4′[O] pattern. However, 3,5,7,3′-tetraoxygenated flavonoids are not entirely uncommon Lin, Li, Li, Yu & Liang, 1992. It was concluded that dorsilurin C contained a fully sub-

stituted ring A. It was also observed that the C-3 position was substituted by an hydroxyl group because of the $\delta_{C=O}$ at 179.4 and 138.9 (s, C-3). The ^{1}H NMR of dorsilurin C showed two prenyl and one 2,2-dimethylpyran groups[1.72 (6H, s, 2 × Me), 5.50 (d, J = 9.5 Hz) and 6.25 (d, J = 9.5 Hz)]. The signals that could be assigned to the two prenyl groups at 6 and 8 were as follows: two overlapping olefinic proton signals at δ 5.27 (m, 2H), two methylene protons at δ 3.46 (br d, J = 6.8 Hz) and 3.66 (brd, J = 6.8 Hz) and four olefinic methyl protons at 1.63, 1.81, 1.88 and 1.98. The structure of this new derivative, named dorsilurin C was determined as 6,8-diprenyl-3′[O]-4′-(2,2-dimethylpyrano)-3,5,7-trihydroxyflavone (**4**). The proposed structure was further confirmed by the ^{13}C NMR data (Table 1) and the EIMS (Section 3).

Dorsilurin D (**5**), obtained as an oil, gave a molecular ion at m/z 506 in the EI mass spectrum and the molecular formula $C_{30}H_{34}O_7$ was deduced from the HREIMS ($[M]^+$ m/z = 506.2324) and the NMR spectra. The UV spectral pattern including the applications of shift reagents (Section 3) and the characteristic IR absorption at 1645 cm^{-1} indicated that dorsilurin D was also a 5,7-dihydroxyflavone (Markham, 1982). Since the aromatic region of the ^{1}H NMR spectrum displayed only three proton resonance signals, it was realized that dorsilurin D was also a highly substituted flavone. The three aromatic proton signals form a set of protons [7.16 (d, 1H, J = 8.5 Hz), 6.50 (br d, 2H, J = 8.5 Hz)] which were located in ring B. The ^{1}H NMR spectrum of this compound showed the presence of two prenyl groups [3.14 (br d, 2H, J = 6.4 Hz), 3.40 (br d, J = 6.8 Hz, 2H), 5.13 (m, 2H, olefinic protons), 1.47, 1.61, 1.63 and 1.65 (4 × Me olefinic)]. It was observed that the C-3 position must be substituted by one prenyl group since a singlet signal was not observed in the ^{1}H NMR spectrum. The ^{13}C NMR of dorsilurin D gave additional support to the attachment of a carbon residue and not an oxygen function at C-3 since the chemical shift of the latter was observed at δ 120.7. An oxygen substituent at this position would have led to a signal at ca. δ 139 ± 1 which is not observed Agrawal, 1989. Irradiation of one of the two methylene proton signals of the prenyl groups at δ 3.14 gave a 2% NOE enhancement of the doublet at δ 7.16. The above findings confirm that the C-3 position was substituted by a prenyl group. The ^{1}H NMR spectrum of **5** further showed proton resonance signals for a 2-hydroxy-3-methylbut-3-enyl side chain: δ 2.85 (dd, J = 14.6, 8.0 Hz, 2H, benzyl methylene), 4.37 (d, 1H, J = 8.0 Hz, oxymethine), 4.87, 4.99 (br s, 1H each, olefinic methylene) and 1.86 (br s, 3H, olefinic methyl). Regarding the position of this side chain and the second prenyl group, two possibilities were considered: one with the 2-hydroxy-3-methylbut-3-enyl side chain located at C-8 and the prenyl group at C-6 (**5**) or an alternative structure with the prenyl substituent at C-8. The co-occurrence of dorsilurins B (**2**) and D (**5**) and the ^{13}C chemical shift of 112.8 favors the attachment of the prenyl group at C-6 (Agrawal, 1989). An attractive biogenetic speculation would be that dorsilurin D (**5**) could arise from **2** through enzymatic opening of the 3-hydroxy-2,2-dimethyldihydropyran ring coupled with the loss of a proton from one of the methyl groups.

The HREIMS of dorsilurin E (**6**)gave a $[M]^+$ m/z = 490.2343 corresponding to a molecular formula of $C_{30}H_{34}O_6$. The UV spectrum showed absorptions at 208, 270 and 334 and these were not affected by the addition of shift reagents. The IR spectrum showed a strong hydroxyl absorption at 3400 and a carbonyl band at 1650 cm^{-1}. The above data established that dorsilurin E was a flavonoid derivative. The absence of a signal, in the ^{1}H NMR spectrum, attributable to a chelated hydroxyl group at the 5-position, and the failure to observe any change in the UV spectrum upon addition of the usual shift reagents led to the assumption that free hydroxyl groups were not present at the

Table 1
^{13}C NMR data of compounds **2**, **4**, **5** (75 MHz) and **6** (125 MHz) in CD_3OD (**2**), CD_3COCD_3 (**4**), $CDCl_3$ (**4** and **5**) and DMSO-d_6 (**6**)[a]

C	**2**, CD_3OD	**4**, $CDCl_3$	**4**, CD_3COCD_3	**5**, $CDCl_3$	**6**, DMSO-d_6
2	160.9(s)[a]	152.3(s)[a]	153.0(s)[a]	160.0(s)[a]	167.9(s)
3	123.5(s)	139.2(s)	138.9(s)	120.7(s)	110.0(s)
4	180.3(s)	179.0(s)	179.4(s)	182.7(s)	171.7(s)
5	157.3(s)[a]	158.1(s)[a]	159.0(s)[a]	155.4(s)[a]	151.3(s)
6	113.8(s)	110.1(s)	112.3(s)	112.8(s)	109.2(s)
7	161.5(s)[a]	160.9(s)[a]	164.2(s)[a]	160.4(s)[a]	159.6(s)
8	106.3(s)	105.5(s)	107.4(s)	104.6(s)	100.5(s)
9	152.9(s)[a]	157.2(s)[a]	158.0(s)[a]	154.0(s)[a]	154.7(s)
10	108.7(s)	105.3(s)	105.8(s)	106.9(s)	102.2(s)
1′	108.7(s)	109.2(s)	109.6(s)	108.8(s)	108.9(s)
2′	157.8(s)[a]	125.3(d)	126.1(d)	157.3(s)[a]	158.1(s)
3′	103.7(d)	109.2(s)	109.6(s)	104.0(d)	102.9(d)
4′	159.0(s)[a]	159.1(s)[a]	159.6(s)[a]	159.1(s)[a]	163.0(s)
5′	107.7(d)	104.6(d)	104.9(d)	108.3(d)	108.0(d)
6′	132.5(d)	121.8(d)	123.4(d)	131.6(d)	132.4(d)
11	27.8(t)	22.0(t)[b]	22.5(t)[b]	28.6(t)	15.6(t)
12	70.0(d)	121.5(d)[c]	122.9(d)[c]	77.5(d)	30.3(t)
13	79.0(s)	134.0(s)[d]	132.5(s)[d]	146.8(s)	78.0(s)
14	30.7 (q)	18.7 (q)[f]	18.6(q)[f]	110.4(t)	26.3(q)
15	20.4 (q)	25.9 (q)[e]	25.8 (q)[e]	17.7(q)	26.3(q)
16	25.9(t)[b]	21.7(t)[b]	22.2(t)[b]	22.0(t)[b]	16.7(t)
17	123.8(d)[c]	121.4(d)[c]	122.2(d)[c]	122.2(d)[c]	30.0(t)
18	132.3(s)[d]	134.5(s)[d]	132.5(s)[d]	132.7(s)[d]	76.4(s)
19	26.0(q)[e]	25.8(q)[e]	25.8(q)[e]	25.8(q)[e]	26.2(q)
20	17.8(q)[f]	18.1(q)[f]	18.6(q)[f]	18.5(q)[f]	26.2(q)
21	22.9(t) [b]	109.6(d)	110.8(d)	24.4(t)[b]	18.5(t)
22	123.3(d)[c]	125.3(d)	126.1(d)	121.1(d)[c]	29.9(t)
23	131.9(s)[d]	70.0(s)	70.4(s)	133.1(s)[d]	84.6(s)
24	25.9(q)[e]	29.7(q)	25.8(q)[e]	25.7(q)[e]	26.7(q)
25	17.7(q)[f]	29.6(q)	18.2(q)[f]	17.8(q)[f]	26.7(q)

[a] Signals with the same superscripts in the same column may be interchanged. Multiplicities were determined from DEPT spectra.

Table 2
^1J (from HSQC), ^2J and ^3J Gradient HMBC correlations optimized for 7 Hz

Proton	Position	^1J-correlated carbon	^3J- and ^2J-correlated carbons
6.54	3′	102.9	167.9 (C-2), 163.0 (C-4′), 158.1 (C-2′), 108.0 (C-5′), 108.9 (C-1′)
6.47	5′	108.0	108.9 (C-1′), 102.9 (C-3′)
7.49	6′	133.0	158.1 (C-2′), 163.0 (C-4′), 167.9 (C-2)
2.67	16	16.7	151.3 (C-5), 159.6 (C-7), 109.2 (C-6), 76.4 (C-18), 30.0 (C-17)
1.83	17	30.0	109.2 (C-6), 16.7 (C-16), 26.2 (C-19,20), 76.4 (C-18)
1.36	19, 20	26.2	30.0 (C-17), 16.7 (C-16)
2.74	21	18.5	167.9 (C-2), 171.7 (C-4), 110.0 (C-3), 29.9 (C-22), 84.6 (C-23)
1.96	22	29.9	110.0 (C-3), 18.5 (C-21), 26.7 (C-24,25), 84.6 (C-23)
1.55	24, 25	26.7	29.9 (C-22), 18.5 (C-21)
2.82	11	15.6	159.6 (C-7), 154.7 (C-9), 100.5 (C-8), 78.0 (C-13), 30.3 (C-12)
1.88	12	30.3	100.5 (C-8), 15.6 (C-11), 26.3 (C-14,15), 78.0 (C-13)
1.57	14, 15	26.3	30.3 (C-12)

5-, and 7-positions. The aromatic region in the ^{1}H NMR of **6** showed the presence of signals consistent with three protons. These signals were poorly resolved in $CDCl_3$ at high (70°C) as well as low (−16°) temperatures, but measuring the spectrum in DMSO-d_6 resulted in a well resolved spectrum clearly showing an ABX system: δ 7.49 (d, 1H, J = 8.6 Hz), 6.47 (dd, 1H, J = 8.6, 2.2 Hz) and 6.54 (d, 1H, J = 2.0 Hz). The highly substituted nature of this metabolite was deduced from the observation of three prenyl groups in the ^{1}H NMR and six oxygenated Ar–C signals in the ^{13}C NMR spectra. The absence of a singlet resonance signal attributable to H-3 and also to those of H-6 and H-8 led to the suggestion that ring A is fully substituted and also that a substituent is present at C-3. It was evident at this point that the structure consisted of a flavonoid skeleton with three prenyl groups at C-3, C-6 and C-8, with the former two cyclized ($8 \rightarrow 7$[O] and $6 \rightarrow 5$[O]) to form two dihydropyran rings. The prenyl group at C-3 was also cyclized but it was not clear at this stage if it had formed an eight membered ring with an oxygen functionality at C-2′ of ring B. Also the three Ar–H protons were located in ring B. An eight membered ring connecting C-3 through a prenyl chain to ring B was found to be inconsistent when the spectral properties of the compound, especially when the HMBC and HSQC, spectra were closely investigated. Instead, what was deduced was a structure in which the third 2,2-dimethyldihydropyran ring was formed between the prenyl group at C-3 and the oxygen at C-4 and that ring-B was present as a β-hydroxy-dienone moiety. An isomeric dienone having the keto-function at 2′ and an hydroxyl at 4′ would be an alternative structure which would be fully consistent with the observed spectroscopic data. The carbon chemical shift values of **6** were assigned by analysis of the 2D NMR experiments HSQC and HMBC (full ^{13}C- and ^{1}H-NMR assignments from HSQC experiments are given in Table 1 and connections through 2- and 3-bonds observed in HMBC are shown in Table 2). Finally, the question of *E–Z* stereochemistry with respect to the double bond connecting the two rings (B and C) was investigated. Preliminary investigations employing 2D NOESY experiments revealed small but noticeable enhancements of the signals due to the methylene protons at δ 2.74 upon irradiation of the aromatic proton signal at δ 7.49. This suggests a *Z* configuration for the double bond as shown in **6**. A search in the literature has revealed a related structure (**7**) in which a biflavonoid containing a similar dienone moiety has been identified from a legume, *Dalbergia candenatensis* (Prain Hamburger, Cordell, Ruangrungsi & Tantivatana, 1988). Interestingly, spectroscopic studies have revealed that this compound exists as a mixture of tautomers.

3. Experimental

3.1. General

UV-Visible: MeOH solution, EIMS: direct inlet, 70 eV; IR: KBr disk, ^{1}H and ^{13}C NMR ($CDCl_3$, CD_3OD, CD_3COCD_3) 300 or 500 MHz and 75 or 125 MHz, respectively, residual solvent peaks as internal references.

3.2. Plant material

Roots of *D. psilurus* Welwistsch were bought from Mbouda (West Province of Cameroon) market in 1996 and identified by Paul Mizili from the National Herbarium. A voucher specimen (No. 2109) is deposited at the National Herbarium in Yaounde.

3.3. Extraction, isolation and characterization

The air dried powdered root material (2 kg) of *D. psilurus* were macerated in a mixture of MeOH–CH_2Cl_2 (1:1). Removal of the solvent under red. press. yielded a dark brown extract (45 g) which was sub-

jected to repeated chromatographic separations on silica CC using CH_2Cl_2 and MeOH as eluants. Dorsilurins C (**4**, 30 mg) and D (**5**, 25 mg) were obtained from frs eluted with CH_2Cl_2–MeOH (9:1). Dorsilurin E (**6,** 35 mg) was obtained by repeated CC on the fractions eluted by CH_2Cl_2/MeOH (17:3).

*3.3.1. 6,8-Diprenyl)-3′[O],4′-(2,2-dimethylpyrano)-3,5,7-trihydroxyflavone, Dorsilurin C (**4**)*

Yellow gum, UV λ_{max}^{MeOH}nm (log ϵ): 207 (4.38), 250 (4.55), 280 (4.61), 350 (4.22); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ϵ): 207 (4.42), 245 (4.65), 275 (4.29), 380 (4.57); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ϵ): 209 (4.36), 245 (4.62), 270 (4.32), 382 (4.58); $\lambda_{max}^{MeOH+NaOAc}$ nm (log ϵ): 218 (4.50), 290 (4.65), 360 (4.37). IR ν_{max}^{KBr} cm^{-1}: 3480–3420 (OH), 1640 (C=O), 1600, 1550, 1475, 1420, 1350, 1310, 1260; ^{1}H NMR (300 MHz, CD_3COCD_3) δ: 1.72 (*br s*, 6H, 2 × Me), 1.63, 1.81, 1.88 and 1.98 (3H each, *br s*, 4 × Me olefinic), 3.46, 3.66 (2H, each *br d*, J = 6.8 Hz, 2H-11, 2H-16), 5.27 (2H, *m*, H-12, H-17), 5.50 (1H, *br d*, J = 9.5 Hz, H-22), 6.25 (1H, *d*, J = 9.5 Hz, H-21), 6.47 (1H, *d*, J = 2.2 Hz, H-2′), 6.67 (1H, *dd*, J = 8.5, 2.2 Hz, H-6′), 7.73 (1H, *d*, J = 8.5 Hz, H-5′) and 13.19 (1H, *br s*, 5-0H); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.75 (6H, *br s*, 2 × Me), 1.70, 1.84, 1.87, 1.98 (3H each, *br s*, 4 × Me olefinic), 3.44, 3.56 (2H each *br d*, J = 6.7 Hz, 2H-11, 2H-16), 5.26 (2H, *br t* like *m*, H-12, H-17), 5.43 (1H, *br d* like *m*, H-22), 6.28 (1H, *d*, J = 9.5 Hz, H-21), 6.3 (H, *br s*, OH), 6.43 (1H, *d*, J = 2.3 Hz, H-2′), 6.55 (1H, *dd*, J = 8.6, 2.3 Hz, H-6′), 7.65 (1H, *d*, J = 8.6 Hz, H-5′) and 13.05 (1H, *br s*, 5-0H); ^{13}C NMR (75 MHz, $CDCl_3$, CD_3COCD_3): see Table 1; HREIMS $[M]^+$ m/z = 488.2193 (calculated for $C_{30}H_{32}O_6$ 488.2199); EIMS m/z (rel. int.) 488 $[M]^+$ (70), 473 ($[M-15]^+$, 15) 433 ($[M-55]^+$, 68), 389 (20), 378 (15), 377 (36), 321 (25), 288 (10), 200 (16), 189 (40), 128 (10), 55 (12).

*3.3.2. 3,6-Diprenyl)-8-(2-hydroxy-3-methylbut-3-enyl)-5,7,2′,4′-tetrahydroxyflavone, dorsilurin D (**5**)*

Yellow oil $[\alpha]_D$ +28° (MeOH, *c* 0.02); UV λ_{max}^{MeOH} nm (log ϵ): 210 (4.82), 260 (4.88), 300 (4.61), 330 (4.55); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ϵ): 209 (4.83), 270 (4.80), 305 (4.67), 345 (4.60); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ϵ):209 (4.83), 270 (4.81), 306 (4.65), 345 (4.65); $\lambda_{max}^{MeOH+NaOAc}$ nm (log ϵ): 219 (4.90), 280 (4.65), 300 (4.68), 335 (4.60); IR ν_{max}^{KBr} cm^{-1}: 3450–3400 (OH), 1645 (C=O), 1580, 1550, 1500, 1470, 1420, 1350, 1200, 1130, 1090, 1040; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.47, 1.61, 1.63, 1.65 and 1.86 *br s*, each 5 × Me olefinic, 2.85 (2H, *dd*, J = 14.6, 8.0 Hz, 2H-11), 3.10 (*br s*, OH), 3.14 (2H, *br d*, J = 6.4 Hz, 2H-21), 3.40 (2H, *br d*, J = 6.8 Hz, 2H-16), 4.37 (1H, *d*, J = 8.0 Hz, H-12), 4.87, 4.99 (*br s*, each, H_a-15, H_b-15), 5.13 (2H, *m*, H-17, H-22), 6.50 (2H, *br d*, J = 8.5 Hz, H-3′, H-5′), 7.16 (1H, *d*, J = 8.5 Hz, H-6′), 9.15 (1H, *br s*, OH), 13.02 (1H, *br s*, 5-OH); ^{13}C NMR (75 MHz, $CDCl_3$): see Table 1; HREIMS $[M]^+$ m/z = 506.2314 (calculated for $C_{30}H_{34}O_7$ 506.2303); EIMS m/z (rel. int.) 506 $[M]^+$ (26), 488 $[M-H_2O]^+$ (15), 436 (22), 435 $[M-71]^+$ (100), 380 [M-71-55] (23), 379 (50), 233 (5), 202 (6), 178 (8), 137 (10), 71 (36).

*3.3.3. Dorsilurin E (**6**)*

Yellow solid, m.p. 205–207°C, UV λ_{max}^{MeOH} nm (log ϵ) 208(4.50), 270 (4.30) 334(4.12); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ϵ): 209(4.52), 271(4.40), 335(4.21); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ϵ): 209 (4.52), 271 (4.40), 335 (4.21); IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1650 (C=O), 1550, 1500, 1480, 1450, 1200, 1180, 1150; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 1.36 (*s*, 6H, Me-19, Me-20), 1.55 (*s*, 6H, Me-24, Me-25), 1.57 (*s*, 6H, Me-14, Me-15), 1.83 (*br t*, J = 6.8 Hz, 2H-17), 1.88 (*br t*, J = 6.8 Hz, 2H-12), 1.96 (*br t*, J = 6.6 Hz, 2H-22), 2.67 (*br t*, J = 6.8, 2H-16), 2.74 (*br t*, J = 6.6 Hz, 2H-21), 2.82 (*br t*, J = 6.6 Hz, 2H-11), 6.47 (*dd*, J = 8.6, 2.2 Hz, H-5′), 6.54 (*d*, J = 2.0 Hz, H-3′), 7.49 (*d*, J = 8.6 Hz, H-6′); ^{13}C NMR (125 MHz, DMSO-d_6): see Table 1; HREIMS $[M]^+$ m/z = 490.2343 (calculated for $C_{30}H_{32}O_6$ 490.2355); EIMS m/z (rel. int.) 490 $[M]^+$ (50), 447 (22), 435 $[M-55]^+$ (80), 380 [M-55-55]$^+$ (16), 379 (42), 289 (35), 288 (7), 233 (32), 177 (100), 137 (70), 55 (88).

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