Prenylated chalcones, flavone and other constituents of the twigs of *Dorstenia angusticornis* and *Dorstenia barteri* var. *subtriangularis* ☆

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Dedicated to Professor K. Hostettmann, University of Lausanne, Switzerland on the occasion of his 60th birthday

Abstract

The twigs of *Dorstenia angusticornis* and *Dorstenia barteri* var. *subtriangularis* yielded 16 compounds. Two novel diprenylated chalcones: 3,5′-di-(2-hydroxy-3-methylbut-3-enyl)-4,2′,4′-trihydroxychalcone, 3, 4-(2,2-dimethylpyrano)-3′-(2-hydroxy-3-methylbut-3-enyl)-2′,4′-dihydroxychalcone and the known stipulin were isolated from both species. 3-(2-Hydroxy-3-methylbut-3-enyl)-5′-(3,3-dimethylallyl)-4,2′,4′-trihydroxychalcone and the known compounds: 4-hydroxylonchocarpin, kanzonol B, bartericins A, B, C and 3′-(2-hydroxy -3-methylbut-3-enyl)-4,2′,4′-trihydroxychalcone were isolated from *D. barteri* while the known compounds: gancaonin Q, paratocarpins C, F, and lupeol were obtained from *Dorstenia angusticornis*. β-Sitosterol and its β-D-glucopyranoside were isolated from both species. Structures of these secondary metabolites were established using spectroscopic analysis, especially, NMR spectra in conjunction with 2D experiments, COSY, HMQC and HMBC.

Keywords: *Dorstenia angusticornis*; *Dorstenia barteri var. subtriangularis*; Moraceae; Twigs; Isolation; Prenylated chalcones; Bartericins A–D; Angusticornins A and B

1. Introduction

The genus *Dorstenia* (Moraceae) consisting of approximately 170 mostly tropical species (Mabberley, 1987) is indigenous to many countries in Africa, Central and South America. It is largely made up of herbaceous perennials with succulent and non-succulent scrambling rhizomes (Berg et al., 1989). The genus *Dorstenia* belongs to the fig and mulberry family and is characterized by impressive star-like flower arrangement, which are also referred to as "shield flowers" (Franke et al., 2001). The ripe seeds are expelled at distances of several feet. Besides fatty acids and the usual sterols this genus is recognised as a rich source of benzofuran derivatives, prenylated and geranylated coumarins, *C*-prenylated and *C*-geranylated flavonoids, styrenes and triterpenoids (Franke et al., 2001; Abegaz et al., 2000, 2002; Ngadjui and Abegaz, 2003). Many of these secondary metabolites are commonly known by their botanically derived trivial names. Previous investigations of the twigs of *Dorstenia barter* i var. *subtriangularis*, resulted in the isolation of four diprenylated chalcones: stipulin (**5**),

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bartericins A (**6**), B (**7**) and C(**8**) (Ngameni et al., 2004), while a subspecies of this same taxon, *D. barteri* var. *multiradiata* yielded: 5,7,4′-trihydroxy-8-prenylflavone, 4,2′,4′-trihydroxy-3′-prenylchalcone, stipulin and a bichalcone (Tsopmo et al., 1999). Because of the variation in the chemical constitution of the two *D. barteri* and the novelty of the secondary metabolites derived from them, we decided to undertake a more detailed examination of the twigs of *D. barteri* var. *subtriangularis* by extraction of more material than our previous study. As part of our continuing program to study the chemical constituents of African *Dorstenia* species (Abegaz et al., 2000; Ngadjui and Abegaz, 2003), we have also examined the extracts of the twigs of *Dorstenia angusticornis* Engl. To the best of our knowledge, no previous phytochemical or pharmacological studies have been reported on this taxon. The present paper describes the isolation and structure elucidation of three new prenylated chalcones bartericin D (**1**), angusticornins A (**2**) and B(**3**) from *D. barteri* var. *subtriangularis* and *D. angusticornis*.

2. Results and discussion

A combination of size exclusion chromatography (Sephadex LH-20), vacuum liquid chromatography (VLC) and preparative thin layer chromatography (PTLC) on the combined methylene chloride/methanol (1:1) and methanol extracts of the twigs of *D. barteri* var. *subtriangularis* resulted in the isolation of **1**–**8** and 4-hydroxylonchocarpin (Dagne et al., 1989) while the extracts of *D. angusticornis* yielded lupeol, **2**, **3**, **5**, **9**–**11**. β-Sitosterol and its β-D-glucopyranoside derivative were isolated from both species.

The molecular formula of compound **1** was deduced from the HREIMS *m/z* 408.1905 (Calc. 408.1917) as $C_{25}H_{28}O_5$. The UV–Vis absorption bands at 206, 248 and 378 were suggestive of a chalcone skeleton (Markham, 1982). The ^{1}H and ^{13}C NMR spectra data, especially, the aluminium chloride induced bathochromic shift (Mabry et al., 1970) and the IR absorption at 1635 (C=O) cm^{-1} indicated that compound **1** was a 2′-hydroxychalcone. The highly deshielded proton signal at δ 13.53 and the chemical shift of the carbonyl function at δ 192.2 were noted as further evidence for the chelated hydroxyl and conjugated carbonyl moieties, respectively. The ^{1}H NMR spectrum of this compound exhibited the presence of a 3,3-dimethylallyl group [a doublet signal of two protons at δ 3.30 (J = 7.1 Hz, 2H-1″), a triplet signal of a vinyl proton at δ 5.35 (J = 7.1 Hz, H-3″) and a singlet resonance of two vinyl methyls at δ 1.75 (6H)] and a 2-hydroxy-3-methylbut-3-enyl moiety {one methylene [δ 2.90 (*dd*, J = 4.8, 14.1 Hz, H-1‴ a), 2.96 (*dd*, J = 9.7, 14.1 Hz, H-1‴ b)], an oxymethine [δ 4.46 (*dd*, J = 4.8, 9.7 Hz, H-2‴)], a vinyl methyl [δ 1.85 (*s*)], and a vinyl methylene, δ 4.77, 4.96 both singlets}. It also showed an AB system at δ 7.73 and 7.82 (*d*, J = 15.4 Hz) and two singlets of one proton each at δ 6.41 and 7.92 assignable to two *p*-oriented aryl protons. Furthermore an ABX-system [an *ortho*-coupled doublet at δ 6.92 (J = 8.3 Hz), an *ortho*- and *meta*-coupled double doublet at δ 7.59 (J = 2.1, 8.3 Hz) and a *meta*-coupled signal at δ 7.62 (J = 2.1 Hz)] was observed. The ^{1}H and ^{13}C NMR spectra of **1** were remarkably similar to those of the positional isomer **6**, recently reported from *D. barteri* by Ngameni et al. (2004). It was only through examination of the HMBC spectrum that the position of the two prenyl substituents, and thus the isomeric relationship of the two compounds were established. The methylene proton signals (δ 2.90 and 2.96) of the hydroxymethylbutenyl moiety showed ^2J and ^3J correlations with C-4 (δ 159.3), C-2 (δ 133.0), C-3 (δ 127.1) and C-3‴ (δ 147.9). Also the downfield proton signal at δ 7.92 (H-6′) was correlated to the aromatic carbon at δ 131.6 (HMQC), the later showed long-range correlations (HMBC) to the two methylene proton signals of C-1″ (δ 3.30). These two sp^3 proton signals at C-1″ were also correlated to C-5′ (δ 120.7) and to one sp^2 oxygenated carbon signal at C-4′ (δ 163.0). The signal H-6′ (δ 7.92) further displayed interactions with C-2′, C-4′, C-5′ and C-β′. It is also noted that the mp of **1** (169–170°) differed significantly from what has been reported for isomer **6** (138–140 °C). From the foregoing data the structure of **1** was established as 3-(2-hydroxy-3-methylbut-3-enyl)-5′-(3,3-dimethylallyl)-4,2′,4′-trihydroxychalcone, a new compound, named bartericin D. The ^{13}C NMR signals (Table 2) were fully assigned on the basis of DEPT spectra, HMQC and HMBC experiments.

The mass spectrum of compound **2** showed the molecular ion peak at *m/z* 406, consistent with the molecular formula of $C_{25}H_{26}O_5$. Its ^{1}H NMR spectrum displayed a highly deshielded signal of a chelated hydroxyl group at δ 13.98, a chalcone *trans*-vinyl proton resonances constituting an AB system at δ 7.78 and 7.83; two aryl proton signals which appeared as doublets at δ 7.89 and 6.55 (J = 9.0 Hz) were assigned to the *ortho* oriented H-6′ and H-5′, respectively. An ABX-system: a doublet at δ 6.83, an *ortho*- and *meta*-coupled double doublet at δ 7.44 and a *meta*-coupled signal at δ 7.30 observed in the ^{1}H NMR spectrum of **2**, led to the deduction that the protons responsible for these signals could only be located in ring B. The NMR of **2** also indicated two prenyl units; one as 2-hydroxy-3-methylbut-3-enyl and another as dimethylpyrano moieties (Tables 1 and 2). From the foregoing data two structures can be proposed for this compound: one with the 2-hydroxy-3-methylbut-3-enyl group at C-3′ and the pyrano moiety in ring B (**2**) or the alternative with the pyrano group in ring A and the other prenyl unit at C-3. The 2-hydroxy-3-methylbut-3-enyl moiety was unambiguously established to be at C-3′ using HMBC and HMQC spectra.

Table 1
^{1}H NMR spectra data (300 MHz) of compounds **1–3**

H	**1** CD_3COCD_3	**2** $CDCl_3$	**3** CD_3COCD_3
2	7.62 (*d*, 2.1)	7.30 (*d*, 2.0)	7.57 (*d*, 2.2)
3	–	–	–
5	6.92 (*d*, 8.3)	6.83 (*d*, 8.4)	6.89 (*d*, 8.3)
6	7.59 (*dd*, 2.1, 8.3)	7.44 (*dd*, 2.0, 8.4)	7.58 (*dd*, 2.2, 8.3)
3′	6.41 (*s*)	–	6.34 (*brs*)
5′	–	6.55 (*d*, 9.0)	–
6′	7.92 (*s*)	7.89 (*d*, 9.0)	8.00 (*s*)
α	7.73 (*d*, 15.4)	7.78 (*d*, 15.3)	7.75 (*d*, 15.3)
β	7.82 (*d*, 15.4)	7.83 (*d*, 15.3)	7.80 (*d*, 15.3)
1″ a	3.30 (*d*, 7.1)	2.92 (*dd*, 8.4, 14.9)	2.91 (*dd*, 4.1, 13.6)
1″ b	3.30 (*d*, 7.1)	3.22 (dd, 2.0, 14.9)	3.50 (*dd*, 7.2, 13.6)
2″	5.35 (*brt*, 7.1)	4.44 (*brd*, 8.0)	4.44 (*dd*, 4.0, 7.8)
4″	1.75 (*s*)	4.90, 5.00 (*brs*)	4.97, 4.79 (*brs*)
5″	1.75 (*s*)	1.90 (*s*)	1.82 (*s*)
1‴ a	2.90 (*dd*, 4.8, 14.1)	–	2.91 (*dd*, 4.1, 13.6)
1‴ b	2.96 (*dd*, 9.7, 14.1)	–	3.50 (*dd*, 7.2, 13.6)
2‴	4.46 (*dd*, 4.8, 9.7)	–	4.44 (*dd*, 4.0, 7.8)
2‴-Me	–	1.48 (*s*)	–
3‴	–	5.70 (*d*, 10.0)	–
4‴ a	4.80 (*brs*)	6.38 (*d*, 10.0)	4.97 (*brs*)
4‴ b	4.99 (*brs*)	–	4.79 (*brs*)
5‴	1.84 (*s*)	–	1.82 (*s*)
2′-OH	13.53 (*brs*)	13.98 (*brs*)	13.51 (*brs*)
4′-OH	–	9.08 (*brs*)	–
2‴-OH	–	2.58 (*brs*)	–

Multiplicities and coupling constants in Hz are given in parentheses.

Table 2
^{13}C NMR spectra data (75 MHz) of compounds **1–3**. Multiplicities are given in parentheses

C	**1** CD_3COCD_3	**2** $CDCl_3$	**3** CD_3COCD_3
1	127.2 (*s*)	127.8 (*s*)	127.1 (*s*)
2	133.0 (*d*)	130.5 (*d*)	133.4 (*d*)
3	127.1 (*s*)	121.8 (*s*)	127.1 (*s*)
4	159.3 (*s*)	156.0 (*s*)	159.3 (*s*)
5	117.0 (*d*)	117.3 (*d*)	117.0 (*d*)
6	129.4 (*d*)	126.9 (*d*)	129.2 (*d*)
α	117.8 (*d*)	118.3 (*d*)	118.6 (*d*)
β	144.6 (*d*)	144.5 (*d*)	144.7 (*d*)
β′	192.2 (*s*)	192.4 (*s*)	192.2 (*s*)
1′	113.8 (*s*)	114.1 (*s*)	113.9 (*s*)
2′	165.4 (*s*)	164.8 (*s*)	165.8 (*s*)
3′	103.0 (*d*)	113.5 (*s*)	103.9 (*d*)
4′	163.0 (*s*)	163.6 (*s*)	164.1 (*s*)
5′	120.7 (*s*)	109.4 (*d*)	117.8 (*s*)
6′	131.6 (*d*)	130.2 (*d*)	133.8 (*d*)
1″	28.2 (*t*)	28.9 (*t*)	38.2 (*t*)[a]
2″	123.4 (*d*)	78.1 (*d*)	76.1 (*d*)[b]
3″	132.0 (*s*)	147.2 (*s*)	147.93 (*s*)[c]
4″	17.4 (*q*)	110.8 (*t*)	110.3 (*t*)
5″	25.4 (*q*)	18.9 (*q*)	17.8 (*q*)
1‴	38.2 (*t*)	–	37.6 (*t*)[a]
2‴	76.1 (*d*)	77.7 (*s*)	76.0 (*d*)[b]
3‴	147.9 (*s*)	131.8 (*d*)	147.88 (*s*)[c]
4‴	110.3 (*t*)	122.1 (*d*)	110.3 (*t*)
5‴	17.8 (*q*)	–	17.8 (*q*)
2‴-Me	–	28.7 (*s*)	–

Values with the same superscript letter in the same column may be interchanged.

The methylene proton signals (δ 2.92 and 3.22) of this prenyl group showed long range correlations with C-2′ (δ 164.8), C-4′ (δ 163.6) and C-3′ (δ 113.5); the latter carbon C-3′ also indicated interaction with the up field aryl proton signal at δ 6.55. Therefore the structure of the new compound, angusticornin A (**2**) was established as 3,4-(2,2-dimethylpyrano)-3′-(2-hydroxy-3-methylbut-3-enyl)-2′,4′-dihydroxychalcone. The ^{13}C NMR signals for **2** (Table 2) were fully assigned using DEPT spectra and by comparison of measured values with those reported for paratocarpin C (**9**) (Hano et al., 1995a) and the monoprenylated chalcone, kanzonol B (**8a**) (Fukai et al., 1994). The IR and UV spectra measurements with shift reagents (see Section 3) were fully in agreement with this structure.

Compound **3**, was assigned the molecular formula $C_{25}H_{28}O_6$ from HREIMS ($[M]^+$ at *m/z* 424.1925; Calc. 424.1930). The ^{1}H and ^{13}C NMR spectra were similar to those of bartericin D (**1**) clearly indicating a highly deshielded signal of a chelated hydroxyl group at δ 13.51 and an AB system at δ 7.75 and 7.80 (*d*, *J* = 15.3 Hz). The spectroscopic data of **1** and **3** mainly differed by the absence of the signals of the 3,3-dimethlallyl moiety. Instead signals of an additional 2-hydroxy-3-methylbut-3-enyl group appeared in the spectra. The NMR (Tables 1 and 2), ^{1}H–^{1}H COSY, HMBC, HMQC experiments were used to establish the structure of **3** as 3,5′-di-(2-hydroxy-3-methylbut-3-enyl)-4,2′,4′-trihydroxychalcone for which the name of angusticornin B was proposed. Its IR spectrum showed signals for hydroxyl and conjugated carbonyl vibrations at ν_{max} 3485–3419 and 1634 cm^{-1}, respectively, and the UV spectrum displayed absorption bands at λ_{max} 207, 249 and 382 nm, characteristic of a chalcone (Markham, 1982). The mass spectrum was also consistent with the proposed structure.

The spectroscopic data of compound **4** and **8a** were identical to those reported for 3′-(2-hydroxy-3-methylbut-3-enyl)-4,2′,4′-trihydroxychalcone and kanzonol B, respectively. Compound **4** has been obtained from *Maclura tinctoria* (Elsohly et al., 2001) while kanzonol B (**8a**) was isolated from the legume *Glycyrrhiza eurycarpa* (Fukai et al., 1994). Compounds **5–8** were identified as stipulin, bartericins A, B and C, respectively, from NMR spectroscopic analysis and direct comparison with authentic specimens obtained from our previous study (Ngameni et al., 2004).

Compound **9** was isolated as yellow oil and its spectroscopic data were in agreement with those generated for paratocarpin C previously isolated from the bark of *Artocarpus venonesa* (Hano et al., 1995a).

The NMR spectra of **10** and **11** were identical with those of gancaonin Q (Fukai et al., 1991) and paratocarpin F (Hano et al., 1995b), respectively. Paratocarpin F (**11**) was isolated from *Artocarpus venenosa* and gancaonin Q (**10**) from *Glycyrrhiza uralensis*.

Chalcones with 2-hydroxy-3-methylbut-3-enyl substituent in ring A undergo mass spectral fragmentation which for compounds **2**, **4** and **6** results in the appearance of a prominent ion at *m/z* 149 (100% for **5**). These compounds do carry the same substituents in ring A and the fragment **3a** is probably responsible for the appearance of this ion in the mass spectra. The formation of this ion results from the well known cleavage α to the carbonyl group on the one side and from scission of the benzylic carbon, on the other, which in this case is further facilitated by the hydroxyl group of the 2-hydroxy-3-methylbut-3-enyl side chain. An additional substitution of a methoxy group in ring A would result in the corresponding ion having a *m/z* value of 179, and indeed, Stevens et al. (2000) report the base peak of such a substituted chalcones, xanthohumol D, to be *m/z* 179.

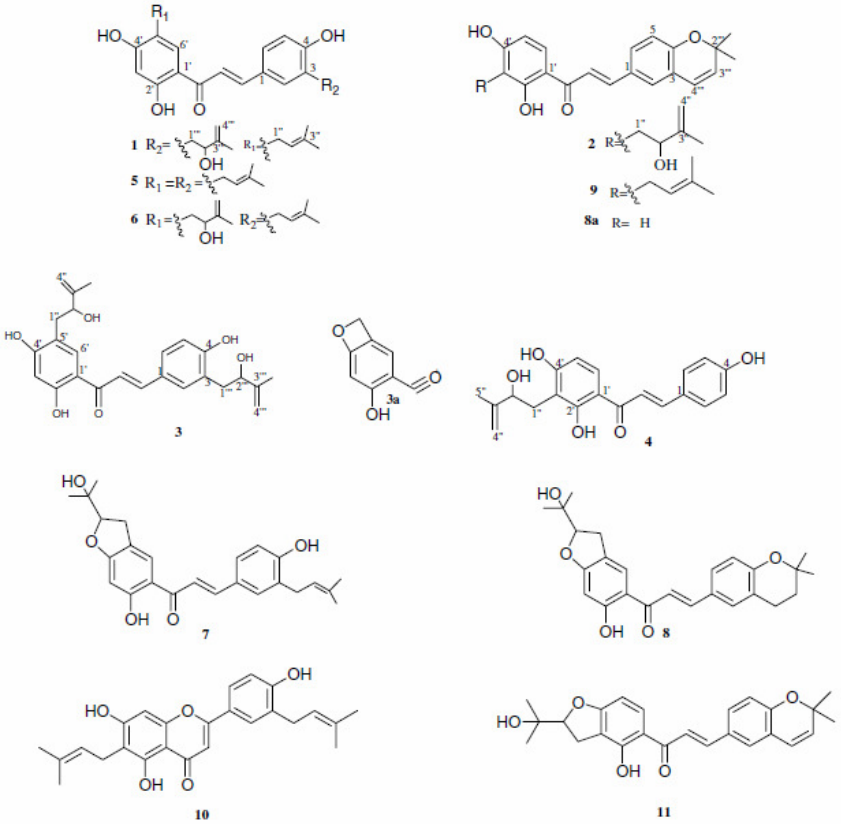
3. Experimental

3.1. General

Mps uncorr.; $CHCl_3$ for optical rotation, UV–Vis: MeOH solution; IR: KBr disk; EI and HREIMS: direct inlet 70 ev; ^1H and ^{13}C NMR: ambient temperature, 300 MHz (^1H) and 75 MHz (^{13}C) in $CDCl_3$, CD_3COCD_3; chemical shifts are given in δ values (ppm) with the residual solvent peaks as internal references. HMQC and HMBC experiments were performed with gradient enhancements.

3.2. Plant material

The twigs of *D. angusticornis* and *D. barteri* var. *subtriangularis* were collected from Kumba, Cameroon in



February 2002 and identified by Mr Victor Nana of the National Herbarium in Yaounde. Voucher specimens, 13456/srfcam (*D. barteri*) and 28165/sfcam (*D. angusticornis*) are deposited at the National Herbarium Yaounde, Cameroon.

3.3. Extraction and isolation from D. angusticornis

The air-dried and powdered twigs of *D. angusticornis* (1.05 kg) were successively macerated in CH_2Cl_2/MeOH (1:1) and MeOH for 24 and 4, respectively, at room temperature. The extracts were combined and solvents removed under reduced pressure to give a dark green residue (70 g). Part of the residue (65 g) was subjected to vacuum liquid chromatography (VLC, silica gel 60, 200 g) and eluted with petrol 40–60/ethyl acetate mixtures, EtOAc and EtOAc–MeOH mixtures to give 54 fractions of 250 ml each. Frs were monitored by TLC and ^{1}H NMR and similar frs were combined. Frs 1–7 (6 g), eluted with petrol–EtOAc (9:1) examined on TLC with the same solvent system contained mainly mixtures of hydrocarbons and phytosterols. Recryst. of the combined frs gave β-sitosterol (35 mg); frs 8–15 (2 g) eluted with petrol–EtOAc 20% gave lupeol (25 mg); frs 16–25 (8 g), obtained with 30% petrol–EtOAc, crystallized in the same solvent system to give **10** (40 mg); combined frs 26–45 (30 g) eluted with 60% petrol–EtOAc were passed through a Sephadex LH-20 column ($CHCl_3$/MeOH, 2:1). The post chlorophyll fractions were combined and subjected, successively to silica gel CC and PTLC to yield, **2** (20 mg), **3** (15 mg), **5** (10 mg), **9** (25 mg) and **11** (12 mg). Frs 46-50 (4 g) and 51–54 (3 g) eluted with EtOAc and EtOAc–MeOH 15%, respectively, gave precipitates which were recrystalised to yield β-sitosteryl-β-D-glucopyranoside (120 mg).

3.4. Extraction and isolation from D. barteri var. subtriangularis

Likewise the air-dried and powdered plant material of *D. barteri* var. *subtriangularis* (1 kg) was extracted with a mixture of CH_2Cl_2/MeOH (1:1) followed by MeOH. A dark green residue (80 g) was obtained after removal of the solvent of the combined organic extract. Part (50 g) of this was submitted to VLC on silica gel (180 g) using petrol followed by petrol–EtOAc gradient. A total of 40 fractions, 250 ml each, was collected and similar frs were combined on the TLC and ^{1}H NMR basis. Frs 1–10 (3 g) examined with petrol–EtOAc (9:1) contained mainly hydrocarbons and crystallized to give β-sitosterol (45 mg). Frs 11–15 (2 g) eluted with 20% EtOAc crystallized to give stipulin (**1**, 28 mg); fr 16–30 (27 g) obtained with 40% EtOAc were passed through a Sephadex LH-20 column and eluted with a mixture of $CHCl_3$–MeOH (2:1). The post chlorophyll fractions (15 g) were subjected to silica gel (175 g) CC separations and eluted with CH_2Cl_2 followed by CH_2Cl_2–MeOH gradient. Fractions eluted with CH_2Cl_2 gave, after repeated PTLC, 4-hydroxylonchocarpin (10 mg), **6** (10 mg), **7** (17 mg), **8** (8 mg) and **8a** (10 mg); those eluted with CH_2Cl_2–MeOH (96:4) gave **1** (15 mg), **2** (20 mg), **3** (21 mg) and **4** (20 mg), after repeated PTLC. Combined Frs 31–40 (7 g) of the VLC eluted with EtOAc gave a precipitate which was recrystalized in the mixture of petrol–EtOAc to yield β-sitosteryl-β-D-glucopyranoside (65 mg).

3.5. Characterization of compounds

3.5.1. (−)-3-(2-Hydroxy-3-methylbut-3-enyl)-5′-(3,3-dimethylallyl)-4,2′,4′-trihydroxychalcone: bartericin D (1)

Orange needles from hexa-EtOAc; m.p. 169–170 °C; $[\alpha]_D^{25}$ −75° ($CHCl_3$; *c* 0.25); UV λ_{max}^{MeOH} nm (log ε): 206 (4.32), 248 (4.18), 378 (4.23); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 205 (4.60), 280 sh (4.30), 324 (4.26), 440 (4.29); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ε): no change; $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 222 (4.85), 260 (4.82), 278 (4.24), 415 (4.23); IR ν_{max}^{KBr} cm^{-1}: 3477–3402 (OH), 2975, 1635 (C=O), 1600, 1560, 1540, 1373, 1246, 1119, 1100; ^{1}H NMR spectral data (300 MHz, CD_3COCD_3): Table 1; ^{13}C NMR spectral data (75 MHz, CD_3COCD_3): Table 2; EIMS 70 ev, *m/z* (rel. int.): 408 $[M]^+$(30), 338 $[M - CH_3C(=CH_2)\text{-}COH]^+$ (100), 322 (27), 307 (52), 205 (25), 149 (53), 71 $[CH_3\text{–}C(=CH_2)CH=OH]^+$ (20); HREIMS *m/z* 408.1905 (Calc. for $C_{25}H_{28}O_5$, 408.1917).

3.5.2. (−)-3,4-(2,2-Dimethylpyrano)-3′-(2-hydroxy-3-methylbut-3-enyl)-2′, 4′-dihydroxychalcone: angusticornin-A (2)

Yellow oil; $[\alpha]_D^{25}$ −95° ($CHCl_3$; *c* 0.15); UV λ_{max}^{MeOH} nm (log ε): 217 (4.22), 249 (4.20) 287 sh (4.25), 379 sh (4.23), 382 (4.28); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 205 (4.72), 288 (4.30), 323 (4.23), 449 (4.30); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ε): no change; $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 206 (5.16), 258 (4.80), 277 (4.19), 397 sh (4.33), 405 (4.33); IR ν_{max}^{KBr} cm^{-1}: 3544–3417 (OH), 2925, 1635 (C=O), 1545,1520, 1466, 1377, 1262, 1107; ^{1}H NMR spectral data (300 MHz, $CDCl_3$): Table 1; ^{13}C NMR spectral data (75 MHz, $CDCl_3$): Table 2. EIMS 70 ev, *m/z* (rel. int.): 406 $[M]^+$(10), 335 $[M - CH_3C(=CH_2)\text{-}CHOH]^+$(24), 322 (35), 221 (24), 149 (44), 71 $[CH_3\text{–}C(=CH_2)CH=OH]^+$ (10); HREIMS *m/z* 406.1815 (Calc. for $C_{25}H_{26}O_5$, 406.1820).

3.5.3. (−)-3,5′-Di-(2-hydroxy-3-methylbut-3-enyl)-4,2′,4′-trihydroxychalcone: angusticornin-B (3)

Yellow oil; $[\alpha]_D^{25}$ −112° ($CHCl_3$; *c* 0.12); UV λ_{max}^{MeOH} nm (log ε): 207 (4.13), 249 (4.21) 382 (4.26); $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 205 (4.72), 258 (4.30), 323 (4.23), 447 (4.32); $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm (log ε): no change; $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 206 (5.06), 263 (4.70), 400 sh (4.31), 450 (4.35);

IR ν_{max}^{KBr} cm^{-1}: 3485–3419 (OH), 2910, 1634 (C=O), 1556, 1500, 1421, 1371, 1252, 1171, 1120; ^1H NMR spectral data (300 MHz, CD_3COCD_3): Table 1; ^{13}C NMR spectral data (75 MHz, CD_3COCD_3): Table 2. EIMS 70 ev, *m/z* (rel. int.): 424$[M]^+$(10), 353 $[M - CH_3C(=CH_2)$-$CHOH]^+$(81), 336 (41), 231 (24), 221 (15), 149 (100), 71 $[CH_3–C(=CH_2)CH=OH]^+$ (23); HREIMS *m/z* 424.1925 (Calc. for $C_{25}H_{28}O_6$, 424.1930).

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