Eremophilenolide-Type Sesquiterpenes from *Hertia intermedia*

by **Abdul Malik***[a]), **Nighat Afza**[b]), **Shazia Yasmeen**[b]), **Mohammad Aijaz Anwer**[b]), **Muhammad Irfan Ali**[b]), and **Rasool Bakhsh Tareen**[c])

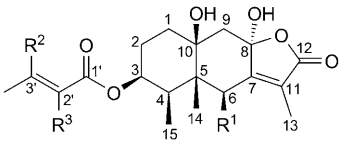
[a]) International Center for Chemical and Biological Sciences, HEJ Research Institute of Chemistry, University of Karachi, Karachi-75270, Pakistan (phone: +92-21-34824926; fax: +92-21-34819018: e-mail: abdul.malik@iccs.edu)

[b]) Pharmaceutical Research Centre, PCSIR Laboratories Complex Karachi, Karachi-75280, Pakistan

[c]) Department of Botany, Balochistan University, Sariab Road, Quetta, Pakistan

Hertidins A – E (**1** – **5**, resp.), new eremophilenolide-type sesquiterpenes, have been isolated from the AcOEt-soluble fraction of *Hertia intermedia*. Structures of **1** – **5** were elucidated on the basis of extensive spectroscopic studies.

Introduction. – The genus *Hertia* belongs to the family Compositae and comprises twelve species distributed all over South and North Africa, and Southwest Asia [1]. The crude $CHCl_3$-, AcOEt-, and MeOH-soluble extracts of *Hertia cheirifolia* have been reported to exhibit spasmolytic and anti-inflammatory activities. The antispasmodic effect of the sesquiterpenoid bakkenolide isolated from the $CHCl_3$-soluble extract was found in the same range as that of alverine, a standard musculotropic spasmolytic agent [2]. One of the species of the genus *Hertia* is *H. intermedia* BOISS. growing wildly in hilly regions of Balochistan and North West Frontier Provinces of Pakistan, and is also distributed westward towards Iran [3]. It is a small shrub with beautiful yellow flowers [4]. It is used as painkiller in the hilly areas of Pakistan [5]. A literature survey revealed that no biological studies have so far been carried out on this plant, while the phytochemical studies are confined to only two sesquiterpenes [6]. The ethnopharmacological and chemotaxonomic importance of the genus *Hertia* prompted us to carry out further phytochemical studies on *H. intermedia*, resulting in the isolation of five eremophilenolide-type sesquiterpenes, named hertidins A – E (**1** – **5**, resp.; *Fig. 1*), from the AcOEt-soluble fraction. Their structures have been elucidated through extensive spectroscopic analyses.



	R^1	R^2	R^3
1	H	Me	H
2	H	H	Me
3	OH	Me	H
4	OH	H	Me

Fig. 1. *Structures of hertidins A – D* (**1** – **4**, resp.)

Results and Discussion. – Hertidin A (**1**) was obtained as a white powder. Its molecular formula was deduced as $C_{20}H_{28}O_6$ from HR-EI-MS, which showed an M^+

peak at *m*/*z* 364.1882 (calc. 364.1886), representing seven degrees of unsaturation. The EI-MS showed, besides the M^+ peak at *m*/*z* 364, two prominent fragment peaks at *m*/*z* 346 and 328 due to successive losses of H_2O molecules, indicating the presence of two OH groups. The IR spectrum displayed absorption bands diagnostic of OH (3468 cm^{-1}), α,β-unsaturated lactone (1750 cm^{-1}), α,β-unsaturated ester (1696 cm^{-1}) and C=C bond (1620 cm^{-1}) functionalities. The ^{13}C-NMR (BB and DEPT) spectra exhibited 20 signals, ascribed to five Me, four CH_2, and three CH groups, and eight quaternary C-atoms. The CO C-atoms of the α,β-unsaturated lactone and α,β-unsaturated ester resonated downfield at δ(C) 173.1 and 165.9, while the corresponding olefinic C-atom signals were observed at δ(C) 158.2, 157.6, 122.8, and 115.9, respectively. Two O-bearing quaternary C-atoms gave rise to signals at δ(C) 102.5 and 74.1, while the O-bearing CH C-atom resonated at δ(C) 71.9. The Me signals were observed at δ(C) 27.4, 20.8, 17.9, 12.2, and 8.3.

The ^{1}H-NMR spectrum showed a *singlet* due to an olefinic H-atom of a trisubstituted C=C bond at δ(H) 5.63 and a *multiplet* of an O-bearing CH group at δ(H) 4.98. The broad peaks at δ(H) 5.01 and 3.37, which disappeared on shaking with D_2O, were assigned to the OH groups. Characteristic Me signals of an eremophilenolide-type sesquiterpene were observed at δ(H) 1.80 (*s*, 3 H), 1.20 (*d*, $J = 7.0$, 3 H), and 0.91 (*s*, 3 H) [7–9]. The Me groups attached to the olefinic C-atom resonated comparatively downfield at δ(H) 2.15 and 1.90 (2*s*, 3 H). The Me H-atom signals at δ(H) 1.80 showed interactions in the HMBC with signals of C(11) (δ(C) 122.8), C(7) (δ(C) 158.2), and C(12) (δ(C) 173.1), suggesting a Me-substituted α,β-unsaturated lactone. Another Me signal appearing at δ(H) 0.91 correlated with those of C(4) (δ(C) 36.4), C(6) (δ(C) 31.1), C(5) (δ(C) 46.0), and C(10) (δ(C) 74.1), allowing us to assign it to C(14). The remaining Me signal at δ(H) 1.20 correlated with signals of C(4) (δ(C) 36.4), C(3) (δ(C) 71.9), and C(5) (δ(C) 46.0) and could subsequently be assigned to C(15).

The ^{13}C-NMR data showed close similarities to those of herticin A [6], except for the downfield shifts of both C(3) and C(8). The presence of a OH group at C(8) could be inferred from the downfield shift of C(8) signal (δ(C) 102.5) and a well-defined *AX* pattern for the CH_2 H-atoms of C(9) appearing as *doublet*s at δ(H) 2.22 and 2.18 ($J =$ 11.1, 1 H). It was subsequently confirmed by HMBCs between the OH H-atom at δ(H) 5.01 and C(8) (δ(C) 102.5), C(7) (δ(C) 158.2), and C(9) (δ(C) 42.5). The presence of a 3-methylbut-2-enoyloxy moiety was evident from the EI-MS showing an intense peak at *m*/*z* 83 as well as other spectral data, and its location at C(3) could be confirmed by ^3J correlation of H–C(3) at δ(H) 4.98 with C(1′) (δ(C) 165.9). Its β-orientation was deduced by comparing chemical shifts, coupling pattern, and coupling constants with those of related compounds [10] and further confirmed by a NOESY correlation of H_α–C(3) with H_α–C(4), and H_α–C(6). The presence of a NOESY correlation between HO–C(10) (δ(H) 3.37) and Me(14) (δ(H) 0.91) confirmed the *cis*-fused *A*/*B* ring system. Another NOESY interaction between Me(14) (δ(H) 0.91) and Me(15) (δ(H) 1.20) allowed us to assign β-orientation to the Me group at C(4). The absence of a NOESY correlation between HO–C(8), and HO–C(10) and Me(14) provided evidence for their relative *trans*-orientation. The other NOESY correlations (*Fig. 2*) and HMQC were in complete agreement to the assigned structure of hertidin A (**1**) as 8α,10β-dihydroxy-3-[(3-methylbut-2-enoyl)oxy]eremophilenolide.

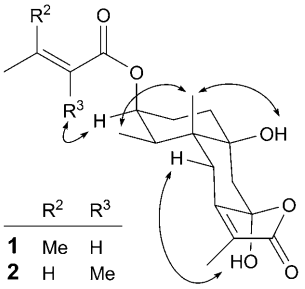


Fig. 2. *Key NOESY interactions in compounds* **1** *and* **2**

Hertidin B (**2**) was obtained as a white powder. The molecular formula was established as $C_{20}H_{28}O_6$ on the basis of the HR-EI-MS (M^+ peak at m/z 364.1884; calc. 364.1886). The EI-mass and IR spectra were similar to those of **1**. The ^{13}C-NMR spectrum (BB and DEPT) was also similar to that of **1** showing 20 signals for five Me, four CH_2, and three CH groups, and eight quaternary C-atoms. It was apparent that **2** is an isomer of **1**. The signals of rings *A*/*B* and Me-substituted α,β-unsaturated lactone were closely similar to those of **1**, showing a difference in the α,β-unsaturated ester moiety, *i.e.*, in the chemical shifts of the corresponding Me groups. The ^{1}H-NMR chemical shift of the H-atom of the trisubstituted C=C bond was shifted downfield to δ(H) 6.04 (*q*, $J = 7.0, 1.2$). The signal of one of the Me groups also shifted upfield to δ(H) 1.88, showing a *trans*-allylic coupling with the olefinic H-atoms (*d*, $J = 1.2$). The signal of the remaining Me group was observed at δ(H) 1.90 (*d*, $J = 7.0$, 3 H). These data confirmed the presence of a 2-methylbut-2-enoyloxy moiety. The (*E*)-configuration of the C=C bond was inferred through *trans* allylic coupling of olefinic H-atom with Me H-atoms at C(2′), as well as by NOESY correlations between Me H-atoms at C(2′), and C(4) and H_α–C(3) (*Fig. 2*). The HMBC and other NOESY correlations of **2** were similar to those of **1**. Therefore, the structure of hertidin B (**2**) could be assigned as 8α,10β-dihydroxy-3-[(*E*)-2-methylbut-2-enoyl)oxy]eremophilenolide.

Hertidin C (**3**) was obtained as white powder. The HR-EI-MS exhibited an M^+ peak at m/z 380.1830 consistent with a molecular formula $C_{20}H_{28}O_7$ (calc. 380.1835). The IR spectrum was similar to that of **1**. The ^{13}C-NMR spectrum (BB and DEPT) showed 20 signals comprising five Me, three CH_2, and four CH groups, and eight quaternary C-atoms. It was similar to **1** except the downfield shift of C(6) (δ(C) 72.0). The ^{1}H-NMR spectrum also showed the additional downfield O-bearing CH H-atom at δ(H) 4.70 (*s*, 1 H). It could be assigned to C(6) based on its HMBCs with C(5) (δ(C) 46.1), C(7) (δ(C) 158.2), C(11) (δ(C) 122.6), C(8) (δ(C) 102.7), C(4) (δ(C) 36.3), and C(10) (δ(C) 74.0). The compound **3** is, therefore, the 6-hydroxy derivative of **1**. The OH group at C(6) was assigned β-orientation based on a strong NOESY interaction between H_α–C(6) and HO–C(8). Hertidin C (**3**) could, therefore, be assigned the structure 6β,8α,10β-trihydroxy-3-[(3-methylbut-2-enoyl)oxy]eremophilenolide (*Fig. 1*).

Hertidin D (**4**) was obtained as a white powder. The molecular formula was established as $C_{20}H_{28}O_7$ by HR-EI-MS (M^+ at m/z 380.1831; calc. 380.1835). The IR spectrum was similar to that of **1**. The ^{13}C-NMR spectrum was very similar to that of **2** except for the downfield shift of the C(6) signal (δ(C) 72.0). Similarly, the ^{1}H-NMR

spectrum showed the downfield signal of the O-bearing CH H-atom at δ(H) 4.60 (*s*, 1 H), which could be assigned to C(6) based on its HMBCs with C(5) (δ(C) 45.8), C(7) (δ(C) 158.3), C(11) (δ(C) 122.7), C(8) (δ(C) 102.6), C(4) (δ(C) 36.4), and C(10) (δ(C) 74.2). It could be assigned α-orientation based on strong NOESY correlation with HO–C(8). The structure of hertidin D (**4**) was, therefore, deduced as 6β,8α,10β-trihydroxy-3-[(*E*)-2-methylbut-2-enoyl)oxy]eremophilenolide (*Fig. 1*).

Hertidin E (**5**; *Fig. 3*) was isolated as a white powder. The HR-EI-MS showed an M^+ peak at *m*/*z* 710.3165 consistent with molecular formula $C_{40}H_{54}O_{11}$ (calc. 710.3169). The molecular formula was confirmed by ^{13}C-NMR (BB and DEPT) spectrum showing 40 signals for ten Me, six CH_2, and eight CH groups, and 14 quaternary C-atoms. The spectra showed it to be a dimeric analogue of compounds **3** and **4** with a notable difference of the missing OH groups at C(8) and C(8′), of which the signals occurred together upfield at (δ(C) 75.9. In ^{1}H-NMR spectrum, the signals of H–C(8) and H–C(8′) were also observed together comparatively upfield at δ(H) 5.32 (*ddq*, J = 10.64, 4.8, 1.4, 2 H). The latter homoallylic coupling of smaller magnitude is due to coupling of the H-atoms at C(13) with H–C(8) and H–C(8′), characteristic for such compounds [1][6]. The signals of the geminal H-atoms at C(9) were now observed as double *doublet*s at δ(H) 2.34 (J = 13.0, 4.8, 2 H) and 1.81 (J = 13.0, 10.6, 2 H). Both H–C(8) and H–C(8′) showed a strong NOESY correlation with H_α–C(6) allowing us to assign α-orientation. Moreover, the ^{1}H-NMR spectrum showed the broad signals for two OH groups, *i.e.*, at C(6′) at δ(H) 4.60 and at C(10) at δ(H) 3.38, and a slight upfield shift of the H_α–C(6) signal, indicating that the OH groups at C(6) and C(10′) are involved in C–O–C bond-formation leading to a dimeric analogue. This could further be confirmed by HMBC of H–C(6) with C(10′) (δ(C) 77.1). Therefore, the structure of hertidin E (**5**) could be assigned as illustrated in *Fig. 3*.

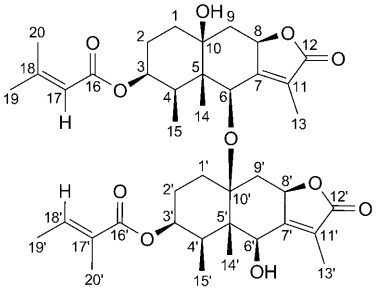


Fig. 3. *Structure of hertidin E* (**5**)

Experimental Part

General. Column chromatograpy (CC): silica gel (SiO_2; 230–400 mesh; *E. Merck*). TLC: Precoated silica gel F_{254} plates; detection at 254 nm and by spraying with ceric sulfate reagent. M.p.: *Gallenkamp* apparatus; uncorrected. Optical rotations: *Jasco-DIP-360* digital polarimeter. IR Spectra: *Jasco-302-A* spectrophotometer; in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker AMX 400* spectrometers at 400 and 100 MHz, resp.; δ in ppm, J in Hz; 2D-NMR Spectra: *Bruker AMX-500* spectrometer. EI-MS and HR-EI-MS: *Jeol JMS-DA-500* mass spectrometer; in *m*/*z* (rel.%).

Plant Material. The plant material of *H. intermedia* BOISS. was collected from Balochistan (Pakistan) in May 2006 and was identified by *R. B. T.*, Plant Taxonomist, Department of Botany, University of Balochistan, where a voucher specimen (No. HI-36-06) has been deposited.

Extraction and Isolation. The shade-dried whole plant (28.0 kg) was exhaustively extracted with MeOH (3 × 50 l) at r.t. The extract was evaporated to yield a residue (750 g), which was divided into hexane- (135 g), AcOEt- (150 g), BuOH- (68 g), and H_2O-soluble (38 g) fractions. The AcOEt-soluble fraction was subjected to CC (SiO_2; hexane, hexane/AcOEt, AcOEt, and AcOEt/MeOH). The fraction eluted with hexane/AcOEt 8.5: 2.5 were combined and resubjected to CC (SiO_2; hexane/AcOEt 8.5: 2.5) to afford fractions *FC-1*, *FC-2*, and *FC-3*. *FC-1* was purified by prep. TLC (SiO_2; hexane/AcOEt 8.0: 2.0) to afford **1** (4 mg) and **2** (4.3 mg). *FC-2* was also purified by prep. TLC (SiO_2; hexane/AcOEt 8.5: 1.5) to afford **3** (3.8 mg) and **4** (4.2 mg). *FC-3* was subjected to CC (SiO_2; hexane/AcOEt 8.5: 1.5) to afford **5** (4.5 mg).

Hertidin A (= *(4a*R,*5*R,*6*S,*8a*S,*9a*R*)-2,4,4a,5,6,7,8,8a,9,9a-Decahydro-8a,9a-dihydroxy-3,4a,5-trimethyl-2-oxonaphtho[2,3-*b*]furan-6-yl 3-Methylbut-2-enoate*; **1**). White solid. M.p. 150–151°. $[\alpha]_D^{26} = -118$ ($c = 0.015$, $CHCl_3$). IR (KBr): 3468, 1750, 1696, 1620. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.63 (*d*, *J* = 1.1 H–C(2′)); 5.01 (*s*, HO–C(8)); 4.98 (br. *d*, *J* = 2.2, H–C(3)); 3.37 (*s*, HO–C(10)); 2.61(*d*, *J* = 14.4, H_α–C(6)); 2.41 (*d*, *J* = 14.4, H_β–C(6)); 2.22 (*d*, *J* = 11.1, H_α–C(9)), 2.18 (*d*, *J* = 11.1, H_β–C(9)); 2.15 (*s*, Me(4′)); 1.90 (*d*, *J* = 1.1, Me(5′)); 1.80 (*s*, Me(13)); 1.65–1.69 (*m*, CH_2(2)); 1.46–1.49 (*m*, CH_2(4)); 1.35–1.38 (*m*, CH_2(1)); 1.20 (*d*, *J* = 7.0, Me(15)); 0.91 (*s*, Me(14)). ^{13}C-NMR (100 MHz, $CDCl_3$): 173.1 (C(12)); 165.9 (C(1′)); 158.2 (C(7)); 157.6 (C(3′)); 122.8 (C(11)); 115.9 (C(2′)); 102.5 (C(8)); 74.1 (C(10)); 71.9 (C(3)); 46.0 (C(5)); 42.5 (C(9)); 36.4 (C(4)); 31.1 (C(6)); 30.3 (C(1)); 27.5 (C(2)); 27.4 (C(5′)); 20.8 (C(4′)); 17.9 (C(14)); 12.2 (C(15)); 8.3 (C(13)). EI-MS: 364 (3, M^+), 346 (32), 328 (29), 264 (39), 246 (70), 95 (90), 83 (100). HR-EI-MS: 364.1882 (calc. 364.1886).

Hertidin B (= *(4a*R,*5*R,*6*S,*8a*S,*9a*R*)-2,4,4a,5,6,7,8,8a,9,9a-Decahydro-8a,9a-dihydroxy-3,4a,5-trimethyl-2-oxonaphtho[2,3-*b*]furan-6-yl (2*E*)-2-Methylbut-2-enoate*; **2**). White solid. M.p. 155–158°. $[\alpha]_D^{26} = -115$ ($c = 0.015$, $CHCl_3$). IR (KBr): 3468, 1750, 1696, 1620. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.04 (*q*, *J* = 7.0, 1.2, H–C(3′)); 5.02 (*s*, HO–C(8)); 4.91 (br. *d*, *J* = 2.1, H–C(3)); 3.36 (*s*, HO–C(10)); 2.62 (*d*, *J* = 14.0, H_α–C(6)); 2.42 (*d*, *J* = 14.0, H_β–C(6)); 2.21 (*d*, *J* = 11.0, H_α–C(9)), 2.19 (*d*, *J* = 11.0, H_β–C(9)); 1.90 (*d*, *J* = 7.0, Me(4′)); 1.88 (*d*, *J* = 1.2, Me(5′)); 1.82 (*s*, Me(13)); 1.66–1.70 (*m*, CH_2(2)); 1.46–1.49 (*m*, CH_2(4)); 1.35–1.37 (*m*, CH_2(1)); 1.21 (*d*, *J* = 7.2, Me(15)); 0.93 (*s*, Me(14)). ^{13}C-NMR (100 MHz, $CDCl_3$): 173.1 (C(12)); 167.2 (C(1′)); 158.1 (C(7)); 139.0 (C(3′)); 127.5 (C(2′)); 122.7 (C(11)); 102.5 (C(8)); 74.3 (C(10)); 71.2 (C(3)); 45.8 (C(5)); 42.5 (C(9)); 36.4 (C(4)); 31.1 (C(6)); 30.4 (C(1)); 27.5 (C(2)); 20.2 (C(4′)); 18.0 (C(14)); 12.3 (C(15)); 12.2 (C(5′)); 8.4 C(13). EI-MS: 364 (3, M^+), 346 (30), 328 (28), 264 (29), 246 (73), 95 (85), 83 (100). HR-EI-MS: 364.1884 (calc. 364.1886).

Hertidin C (= *(4*S,*4a*S,*5*R,*6*S,*8a*S,*9a*R*)-2,4,4a,5,6,7,8,8a,9,9a-Decahydro-4,8a,9a-trihydroxy-3,4a,5-trimethyl-2-oxonaphtho[2,3-*b*]furan-6-yl 3-Methylbut-2-enoate*; **3**). White solid. M.p. 146–148°. $[\alpha]_D^{26} = -120$ ($c = 0.015$, $CHCl_3$). IR (KBr): 3468, 1750, 1696, 1620. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.62 (*d*, *J* = 1.1, H–C(2′)); 5.10 (*s*, HO–C(8)); 4.97 (br. *d*, *J* = 2.3, H–C(3)); 4.60 (*s*, HO–C(6)); 4.70 (*s*, H–C(6)); 3.30 (*s*, HO–C(10)); 2.20 (*d*, *J* = 11.4, H_α–C(9)), 2.16 (*d*, *J* = 11.4, H_β–C(9)); 2.14 (*s*, Me(4′)); 1.90 (*d*, *J* = 1.1, Me(5′)); 1.80 (*s*, Me(13)); 1.66–1.70 (*m*, CH_2(2)); 1.45–1.49 (*m*, CH_2(4)); 1.35–1.39 (*m*, CH_2(1)); 1.20 (*d*, *J* = 7.0, Me(15)); 0.91 (*s*, Me(14)). ^{13}C-NMR (100 MHz, $CDCl_3$): 173.2 (C(12)); 165.9 (C(1′)); 158.2 (C(7)); 157.6 (C(3′)); 122.6 (C(11)); 115.9 (C(2′)); 102.7 (C(8)); 74.0 (C(10)); 72.0 (C(6)); 71.2 (C(3)); 46.1 (C(5)); 42.4 (C(9)); 36.3 (C(4)); 30.2 (C(1)); 27.5 (C(2)); 27.4 (C(5′)); 20.8 (C(4′)); 12.2 (C(14)); 10.5 (C(15)); 8.3 (C(13)). EI-MS: 380 (5, M^+), 362 (26), 344 (27), 280 (30), 262 (39), 95 (80), 83 (100). HR-EI-MS: 380.1830 (calc. 380.1835).

Hertidin D (= *(4*S,*4a*S,*5*R,*6*S,*8a*S,*9a*R*)-2,4,4a,5,6,7,8,8a,9,9a-Decahydro-4,8a,9a-trihydroxy-3,4a,5-trimethyl-2-oxonaphtho[2,3-*b*]furan-6-yl (2*E*)-2-Methylbut-2-enoate*; **4**). White solid. M.p. 141–143°. $[\alpha]_D^{26} = -125$ ($c = 0.015$, $CHCl_3$). IR (KBr): 3468, 1750, 1696, 1620. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.04 (*q*, *J* = 7.0, 1.2, H–C(3′)); 5.10 (*s*, HO–C(8)); 4.90 (br. *d*, *J* = 2.2, H–C(3)); 4.71 (*s*, H–C(6)); 4.60 (*s*, HO–C(6)); 3.2 (*s*, HO–C(10)); 2.22 (*d*, *J* = 11.0, H_α–C(9)); 2.18 (*d*, *J* = 11.0, H_β–C(9)); 1.96 (*d*, *J* = 7.0, Me(4′)); 1.87 (*d*, *J* = 1.2, Me(5′)); 1.83 (*s*, Me(13)); 1.58–1.61 (*m*, CH_2(2)); 1.46–1.49 (*m*, CH_2(4)); 1.33–1.37 (*m*, CH_2(1)); 1.23 (*d*, *J* = 7.2, Me(15)); 0.91 (*s*, Me(14)). ^{13}C-NMR (100 MHz, $CDCl_3$): 173.1 (C(12)); 167.2 (C(1′)); 158.3 (C(7)); 138.9 (C(3′)); 127.5 (C(2′)); 122.7 (C(11)); 102.6 (C(8)); 74.2 (C(10)); 72.0 (C(6)); 71.2 (C(3)); 45.8 (C(5)); 42.5 (C(9)); 36.4 (C(4)); 30.2 (C(1)); 27.4 (C(2)); 20.2 (C(4′)); 10.6 (C(14)); 12.2 (C(15)); 12.1 (C(5′)); 8.3 (C(13). EI-MS: 380 (3, M^+), 362 (29), 344 (28), 280 (29), 262 (40), 95 (90), 83 (100). HR-EI-MS: 380.1831 (calc. 380.1835).

Hertridin E (=*(4*R,*4a*S,*5*R,*6*S,*8a*S,*9a*R*)-2,4,4a,5,6,7,8,8a,9,9a-Decahydro-4-hydroxy-8a-({(4*R,*4a*S,*5*R,*6*S,*8a*S,*9a*R*)-2,4,4a,5,6,7,8,8a,9,9a-decahydro-8a-hydroxy-3,4a,5-trimethyl-6-[(3-methylbut-2-enoyl)oxy]-2-oxonaphtho[2,3-*b*]furan-4-yl}oxy)-3,4a,5-trimethyl-2-oxonaphtho[2,3-*b*]furan-6-yl (2*E*)-2-Methylbut-2-enoate*; **5**). White solid. M.p. 92–94°. $[\alpha]_D^{26} = -63$ ($c = 0.015$, $CHCl_3$). IR (KBr): 3468, 1750, 1696, 1620. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.07 (*q*, *J* = 7.0, 1.2, H–C(17′)); 5.65 (*J* = 1.2, H–C(17)); 5.32 (*ddq*, *J* = 10.6, 4.8, 1.6, H–C(8, 8′)); 4.96 (br. *d*, *J* = 2.1, H–C(3′)); 4.90 (br. *d*, *J* = 2.2, H–C(3)); 4.62 (*s*, H–C(6)); 4.60 (*s*, HO–C(6′)); 3.38 (*s*, HO–C(10)); 2.34 (*d*, *J* = 13.0, 4.8, H_α–C(9,9′)); 2.15 (*s*, H–C(19)); 1.86 (*d*, *J* = 1.5, Me(13,13′)); 1.81 (*d*, *J* = 13.0, 10.6, H_β–C(9,9′)); 1.66–1.69 (*m*, CH_2(2,2′)); 1.44–1.48 (*m*, CH_2(4,4′)); 1.42 (*d*, *J* = 7.0, Me(15,15′)); 1.35–1.39 (*m*, CH_2 (1,1′)); 1.97 (*d*, *J* = 7.2, Me(19′)); 1.90 (*J* = 1.2, Me(20)); 1.86 (*d*, *J* = 1.2, Me(20′)); 0.93 (*s*, Me(14, 14′)). ^{13}C-NMR (100 MHz, $CDCl_3$) 174.4 (C(12)); 174.5 (C(12′)); 167.6 (C(16)); 165.8 (C(16′)); 160.4 (C(7); 160.3 (C(7′)); 157.8 (C(18)); 139.0 (C(18′)); 127.5 (C(17′)); 122.3 (C(11)); 122.2 (C(11′)); 115.8 (C(17)); 77.1 (C(10′)); 75.9 (C(8, 8′)); 75.1 (C(6)); 74.1 (C(10)); 72.0 (C(6′)); 70.9 (C(3)); 71.7 (C(3′)); 46.0 (C(5)); 46.2 (C(5′)); 41.2 (C(9)); 41.1 (C(9′)); 36.5 (C(4)); 36.5(C(4′)); 31.3 (C(1)); 31.2 (C(1′)); 27.8 (C(2)); 27.4 (C(2′)); 27.2 (C(20)); 20.8 (C(19)); 20.0 (C(19′)); 12.5 (C(15)); 12.0 (C(15′)); 12.3 (C(14)); 12.2 (C(14′)); 12.0 (C(20′)); 8.7 (C(13)); 8.5 (13′)). EI-MS: 710 (5, M^+), 364 (29), 346 (35), 264 (32), 246 (30), 95 (90), 83 (100). HR-EI-MS: 710.3165 (calc. 710.3169).

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