New Secondary Metabolites from *Asphodelus tenuifolius*

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Asphorins A and B (**1** and **2**, resp.), two new triterpene glycosides, have been isolated along with a new chromone, **3**, from the AcOEt subfraction of the MeOH extract of the whole plant of *Asphodelus tenuifolius*. Their structures were elucidated by spectral analysis including 2D-NMR spectroscopic experiments.

Introduction. – Asphodelaceae is one of the subfamilies of Liliaceae, and comprises 15 genera and 780 species, which are distributed in tropical, subtropical, and temperate regions around the world, but mainly in Southern Africa. Among these, three genera and eleven species are native to Pakistan. One of the genera is *Asphodelus*, which comprises 20 species distributed from Mediterranean to western Asia. One of its species is *Asphodelus tenuifolius* CAV. (syn. *Asphodelus fistulosus* var.), which is found in northern Africa, and southwest regions of Asia and Europe. It commonly grows in the Cholistan desert of Pakistan. This plant is used by local population as a diuretic [1]. Literature survey revealed that only one triterpene has so far been reported from this plant [2]. The chemotaxonomic and ethnopharmacological importance of the genus *Asphodelus* prompted us to carry out further phytochemical studies on *A. tenuifolius*. As a result, we have isolated two new triterpenoid glycosides, named asphorins A and B (**1** and **2**, resp.), along with a new chromone (**3**).

Results and Discussion. – The MeOH extract of the whole plant of *A. tenuifolius* CAV. was suspended in H_2O and successively extracted with hexane, $CHCl_3$, AcOEt, and BuOH. The AcOEt-soluble subfraction was subjected to column chromatographic techniques (*cf.* the *Exper. Part*) to obtain compounds **1**–**3**, respectively.

Asphorin A (**1**) was obtained as colorless crystals and gave positive *Liebermann–Burchard* test for a triterpene and brisk effervescence with diluted $NaHCO_3$, indicating the presence of free carboxylic acid moiety. The HR-FAB-MS (negative-ion mode) of **1** showed a *quasi*-molecular-ion ($[M-H]^-$) peak at *m*/*z* 809.4324, consistent with the molecular formula $C_{42}H_{65}O_{15}$. The EI-MS exhibited a prominent peak at *m*/*z* 604 ($[M-CO_2-162]^+$). Its intensity allowed us to locate the hexose moiety at C(17). The loss of another hexose unit led to another fragment-ion peak at *m*/*z* 442. The peaks arising from the *retro-Diels–Alder* fragmentation at *m*/*z* 440 and 370 indicated the presence of a hexose moiety in rings *A*/*B* and two carboxylic moieties along with a

hexose unit in rings *C*/*D*. The IR spectrum evidenced the presence of a OH group (3425 cm^{-1}), ester and carboxylic acid CO functionalities (1732 cm^{-1}), an olefinic bond (1638 cm^{-1}), and C–O moiety (1103 cm^{-1}). The UV spectrum exhibited absorption maxima at 268 and 202 nm. The ^{13}C-NMR (H-BB decoupled) and DEPT spectra showed 42 well-resolved signals corresponding to six Me, eleven CH_2, 17 CH groups, and eight quaternary C-atoms (*Table 1*). The most downfield signals at δ(C) 178.0 and 176.5 were assigned to ester and carboxylic acid moieties, respectively. The olefinic C-atoms resonated at δ(C) 133.2 and 129.5, while the O-bearing CH C-atom signal appeared at δ(C) 88.7. The six Me groups resonated in the range of δ(C) 28.0 – 16.6. The signals at δ(C) 106.9 and 95.7 were assigned to two anomeric C-atoms of the hexose moieties, while the signals of their O-bearing CH_2 and CH C-atoms were observed in the range of δ(C) 79.3 – 62.3. In the ^{1}H-NMR spectrum, the signals of the olefinic H-atom of a trisubstituted C=C bond and an O-bearing CH H-atom were observed at δ(H) 5.97 (br. *s*) and 3.19 (*dd*, $J = 11.3, 4.5$), respectively. The signals of tertiary Me groups appeared as *singlet*s at δ(H) 1.21, 1.02, 0.93, and 0.87, and of two secondary Me groups as *doublet*s at δ(H) 1.17 (*d*, $J = 6.4$) and 0.73 (*d*, $J = 6.6$). The anomeric H-atoms gave rise also to *doublet*s at δ(H) 6.37 (*d*, $J = 7.8$) and 4.78 (*d*, $J = 5.3$). The O-bearing CH H-atoms of the sugar moieties resonated in the range of δ(H) 4.40 – 3.93, while the signals of the O-bearing CH_2 H-atoms were observed in the range of δ(H) 4.59 – 4.27. The above data corresponded to an ursene-type triterpene with two of the Me groups oxidized to carboxylic functions. The NMR data exhibited close resemblance to those previously reported for quinovic acid [3] except the downfield shifts of both H–C(3) and C(3) signals, and key HMBCs (*Fig. 1*), evidencing the presence of hexose moieties

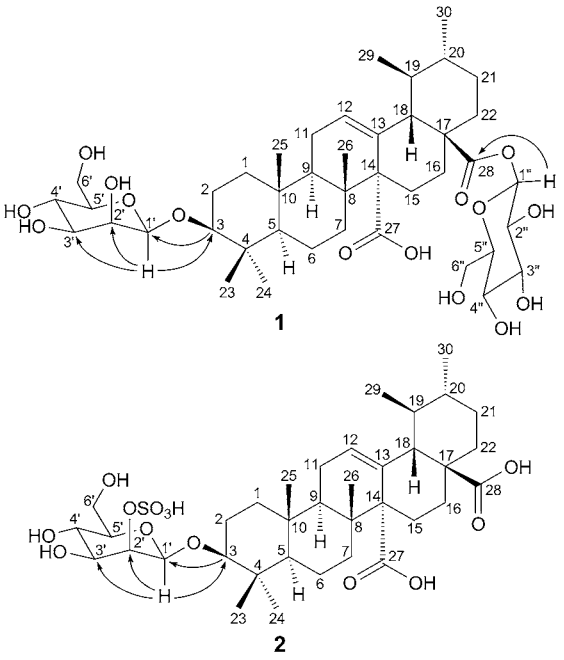

Fig. 1. *Structures and key HMBCs of asphorins A and B* (**1** and **2**, resp.)

at C(3) and C(28). The acid hydrolysis of compound **1** afforded a binary mixture of glycones, which could be identified as those of D-mannose and D-glucose by TLC as well as by comparison of retention times of their tetramethylsilane (TMS) ethers with corresponding standards in gas chromatography (GC). The large values of the coupling constant allowed us to assign β-configuration to both the hexose units. The aglycone could be identified as quinovic acid by comparison of its physical and spectral data with those reported in literature [3]. Thus, asphorin A (**1**) was assigned the structure (3β)-3-(β-D-mannopyranosyloxy)urs-12-ene-27,28-dioic acid 28-*O*-β-D-glucopyranosyl ester (*Fig. 1*).

Asphorin B (**2**) was obtained as colorless crystals which gave similar tests as those of **1**. The HR-FAB-MS (positive-ion mode) of **2** showed a *quasi*-molecular-ion ($[M + H]^+$) peak at *m*/*z* 729.3525, which corresponded to the molecular formula $C_{36}H_{57}O_{13}S$. The EI-MS exhibited prominent peaks at *m*/*z* 486 ($[M - SO_3\text{hexose}]^+$) and 468 ($[M - SO_3\text{hexose} - H_2O]^+$). The *retro-Diels–Alder* fragment-ion peaks at *m*/*z* 450 and 278 indicated the presence of a hexose moiety in rings *A*/*B* and two carboxy functionalities in rings *C*/*D*. The presence of sulfohexose moiety was further confirmed by fragment ions at *m*/*z* 97 and 80, respectively. The IR and UV spectra were similar to those of **1**. The ^{13}C-NMR (H-BB decoupled and DEPT) spectra showed 36 well-resolved signals corresponding to six CH_3, ten CH_2, twelve CH groups, and eight quaternary C-atoms (*Table 1*). The carboxy functions gave rise to downfield signals at δ(C) 177.8 and 176.8. The olefinic C-atom signals appeared at δ(C) 134.0 and 128.8, while those of the O-bearing CH group were at δ(C) 89.8. The six Me groups resonated in the range of δ(C) 28.1 – 16.5. The spectrum further exhibited the signals of the anomeric C-atom of a hexose moiety at δ(C) 104.1. The signal of the O-bearing CH_2 and O-bearing CH group C-atoms of the sugar moiety were observed in the range of δ(C) 81.0 – 62.7.

The ^{1}H-NMR spectrum showed signals of the olefinic H-atom and the O-bearing CH H-atom of the aglycone moiety at δ(H) 5.96 (br. *s*) and 3.12 (*dd*, $J = 11.1, 4.2$), respectively. The tertiary Me groups were attributed to *singlet*s at δ(H) 1.25, 1.11, 1.02, and 0.78, while the two secondary Me groups resonated as *doublet*s at δ(H) 1.19 (*d*, $J =$ 6.0) and 0.77 (*d*, $J = 6.4$). The spectrum also showed the *doublet* for an anomeric H-atom at δ(H) 4.80 (*d*, $J = 5.1$). The other O-bearing CH and O-bearing CH_2 H-atoms of hexose moiety resonated in the range of δ(H) 4.37 – 3.83 and 4.45 – 4.26, respectively. The NMR data exhibited a close resemblance to those reported for 3-(2-*O*-sulfo-β-D-glucopyranosyl)quinovic acid [4], except slight differences in the chemical shifts of the hexose unit. Acid hydrolysis of compound **2** gave quinovic acid and a glycone, the latter was identified as D-mannose by comparison of retention time of its TMS ether with that of a standard in GC. The large coupling constant of the anomeric H-atom allowed us to assign β-D-configuration to the sugar unit. One of the O-bearing CH H-atom of D-mannose resonated comparatively at δ(H) 5.00 (*dd*, $J = 5.2, 5.1$) due to the presence of a sulfate moiety and could subsequently be assigned to C(2′) (δ(C) 81.0) through HMBCs (*Fig. 1*). Comparison of ^{1}H- and ^{13}C-NMR data of compound **2** with that of quinovic acid revealed the downfield shifts of both C(3) and H–C(3), allowing us to assign the β-D-mannoside moiety to this position. On the basis of these evidences, the structure of asphorin B (**2**) could be assigned as (3β)-3-(2-*O*-sulfo-β-D-mannopyranosyloxy)urs-12-ene-27,28-dioic acid (*Fig. 1*).

Table 1. *^{1}H- and ^{13}C-NMR Data* (at 500 and 125 MHz, resp.)*, and Key HMBCs of Compounds* **1** *and* **2**. Recorded in C_5D_5N; δ in ppm, J in Hz.

	1			**2**		
	δ(H)	δ(C)	HMBC	δ(H)	δ(C)	HMBC
CH_2(1)	1.38–1.40 (*m*), 0.89–0.92 (*m*)	39.0	–	1.41–1.44 (*m*), 0.92–0.94 (*m*)	38.9	–
CH_2(2)	2.04–2.06 (*m*), 1.66–1.69 (*m*)	26.7	–	2.06–2.09 (*m*), 1.87–1.89 (*m*)	26.4	–
H–C(3)	3.19 (*dd*, *J* = 11.3, 4.5)	88.7	2, 4, 5, 1′	3.12 (*dd*, *J* = 11.1, 4.2)	89.8	2, 4, 5, 1′
C(4)	–	39.4	–	–	39.5	–
H–C(5)	0.86 (*d*, *J* = 10.6)	55.7	3, 4, 10	0.82 (*d*, *J* = 12.0)	55.7	3, 4, 10
CH_2(6)	1.50–1.53 (*m*), 1.30–1.33 (*m*)	18.5	–	1.37–1.41 (*m*)	18.5	–
CH_2(7)	1.88–1.92 (*m*), 1.68–1.73 (*m*)	37.5	–	1.79–1.85 (*m*), 1.64–1.66 (*m*)	37.5	–
C(8)	–	40.1	–	–	40.0	–
H–C(9)	2.49–2.53 (*m*)	47.2	8, 10, 11, 12	2.57–2.60 (*m*)	47.1	8, 10, 11, 12
C(10)	–	36.9	–	–	36.9	–
CH_2(11)	2.06–2.11 (*m*), 1.90–1.94 (*m*)	23.3	–	2.04–2.08 (*m*), 1.87–1.90 (*m*)	23.3	–
H–C(12)	5.97 (br. *s*)	129.5	11, 13, 14	5.96 (br. *s*)	128.8	11, 13, 14
C(13)	–	133.2	–	–	134.0	–
C(14)	–	56.7	–	–	56.8	–
CH_2(15)	2.60–2.64 (*m*), 2.50–2.54 (*m*)	25.5	13, 14, 17, 27	2.44–2.49 (*m*), 2.24–2.26 (*m*)	25.5	13, 14, 17, 27
CH_2(16)	2.25–2.30 (*m*), 2.00–2.04 (*m*)	26.1	–	2.18–2.22 (*m*), 1.76–1.78 (*m*)	26.5	–
C(17)	–	48.9	–	–	48.8	–
H–C(18)	2.68 (*d*, *J* = 11.3)	54.6	12, 13, 14, 17, 19, 28, 29	2.78 (*d*, *J* = 11.4)	55.0	12, 13, 14, 17, 19, 28, 29
H–C(19)	1.46–1.49 (*m*)	37.5	–	1.36–1.40 (*m*)	37.7	–
H–C(20)	0.87–0.91 (*m*)	39.0	–	0.77–0.80 (*m*)	39.4	–
CH_2(21)	1.39–1.42 (*m*), 1.26–1.30 (*m*)	30.2	–	1.36–1.39 (*m*), 1.30–1.34 (*m*)	30.6	–
CH_2(22)	1.98–2.02 (*m*), 1.77–1.80 (*m*)	36.4	–	1.93–1.96 (*m*)	37.1	–
Me(23)	1.21 (*s*)	28.0	3, 4, 5, 24	1.25 (*s*)	28.1	3, 4, 5, 24
Me(24)	0.93 (*s*)	17.0	3, 4, 5, 23	1.11 (*s*)	17.1	3, 4, 5, 23
Me(25)	0.87 (*s*)	16.6	1, 9, 10	0.78 (*s*)	16.5	1, 9, 10
Me(26)	1.02 (*s*)	19.2	7, 8, 9, 14	1.02 (*s*)	18.9	7, 8, 9, 14
C(27)	–	176.5	–	–	176.8	–
C(28)	–	178.0	–	–	177.8	–
Me(29)	1.17 (*d*, *J* = 6.4)	18.1	18, 19, 20	1.19 (*d*, *J* = 6.0)	18.3	18, 19, 20
Me(30)	0.73 (*d*, *J* = 6.6)	21.2	19, 20, 21	0.77 (*d*, *J* = 6.4)	21.3	19, 20, 21
H–C(1′)	4.78 (*d*, *J* = 5.3)	106.9	3, 2′, 3′	4.80 (*d*, *J* = 5.1)	104.1	3, 2′, 3′
H–C(2′)	3.96–3.99 (*m*)	75.7	1′, 3′, 4′	5.00 (*dd*, *J* = 5.4, 5.1)	81.0	1′, 3′, 4′
H–C(3′)	4.12–4.16 (*m*)	78.9	–	4.37–4.41 (*m*)	78.2	–
H–C(4′)	4.18–4.22 (*m*)	71.8	–	4.14 (*t*, *J* = 9.0)	71.6	–
H–C(5′)	3.93–3.95 (*m*)	79.3	–	3.83–3.88 (*m*)	77.7	–

Table 1 (cont.)

	1			**2**		
	δ(H)	δ(C)	HMBC	δ(H)	δ(C)	HMBC
CH_2(6′)	4.44–4.47 (*m*), 4.37–4.40 (*m*)	63.0	–	4.43–4.47 (*m*), 4.26 (*dd*, *J* = 5.1, 5.1)	62.7	–
H–C(1″)	6.37 (*d*, *J* = 7.8)	95.7	28	–	–	–
H–C(2″)	4.30–4.33 (*m*)	74.1	–	–	–	–
H–C(3″)	4.20–4.24 (*m*)	78.2	–	–	–	–
H–C(4″)	4.33–4.37 (*m*)	71.2	–	–	–	–
H–C(5″)	4.38–4.40 (*m*)	78.7	–	–	–	–
CH_2(6″)	4.55–5.59 (*m*), 4.27–4.30 (*m*)	62.3	–	–	–	–

Compound **3** (*Fig. 2*) was obtained as an amorphous powder, which gave purple coloration with $FeCl_3$, typical for a 5-hydroxychromone [5]. The HR-EI-MS showed the M^+ peak at *m*/*z* 626.5269, which corresponded to the molecular formula $C_{41}H_{70}O_4$. The IR spectrum indicated the presence of OH group (3411 cm^{-1}), conjugated CO functionality (1671 cm^{-1}), conjugated C=C bond (1630 cm^{-1}), and an aromatic moiety (1543, 1503 cm^{-1}). The UV spectrum showed absorption maxima at 336, 314, 290, 248, and 216, which were characteristic of a chromone [6]. The ^{13}C-NMR (H-BB decoupled and DEPT) spectra (*Table 2*) showed the signal of the CO C-atom at δ(C) 182.7. The O-bearing aromatic C-atoms exhibited signals at δ(C) 170.7, 162.2, 160.0, and 158.6. The aromatic quaternary C-atoms gave signals at δ(C) 108.8 and 106.1, and aromatic CH C-atoms resonated at δ(C) 107.9 and 93.2. A CH_2 group showed signal at δ(C) 34.2 indicating its association with the conjugated system, and the other CH_2 groups of the long chain resonated in the region of δ(C) 31.9–22.7. An aromatic Me group resonated at δ(C) 7.0. The ^{1}H-NMR spectrum (*Table 2*) showed a downfield signal at δ(H) 13.01 for a chelated OH group at C(5). The spectrum further displayed two *singlet*s at δ(H) 6.31 (*s*, 1 H) and 5.99 (*s*, 1 H), which were assigned to C(6) and C(3), respectively, on the basis of HMBCs. The Me group resonated at δ(H) 2.11 (*s*, 3 H) suggesting its attachment to the aromatic ring. The upfield region of the spectrum evidenced the presence of a long hydrocarbon chain with one of the CH_2 H-atoms resonating as a *triplet* at δ(H) 2.53 (*t*, *J* = 7.5). It showed COSY correlations with neighboring CH_2 H-atoms at δ(H) 1.61–1.64. Further 56 CH_2 H-atom signals were observed as a broad hump in the range of δ(H) 1.28–1.20. The terminal Me H-atoms gave a *triplet* at δ(H) 0.84 (*t*, *J* = 6.8). In the HMBC experiment, the H–C(6) signal at δ(H) 6.31 showed ^2J correlations with those of C(7) (δ(C) 162.2) and C(5) (δ(C) 158.6), as well as ^3J correlations with those of C(8) (δ(C) 106.1) and C(4a) (δ(C) 108.8). The H–C(3) signal at δ(H) 5.99 showed ^2J correlations with those of C(4) (δ(C) 182.7) and C(2) (δ(C) 170.7) as well as ^3J correlations with those of C(4a) (δ(C) 108.8) and C(1′) (δ(C) 34.2). The aromatic Me signal at δ(H) 2.11 showed ^2J correlation with those of C(8) (δ(C) 106.1), and ^3J correlations with those of C(7) (δ(C) 162.2) and C(8a) (δ(C) 160.0). The remaining HMBCs are compiled in *Table 2*. In the EI-MS spectrum, the peaks at *m*/*z* 219 and 206 [7] appeared due to the losses of nonacosanyl and triacontanyl moieties, respectively. The diagnostic peak at *m*/*z* 167, resulting from *retro-Diels–Alder*

fragmentation, confirmed the presence of the Me group in ring *A*. The spectrum also exhibited fragment-ion peaks, differing from each other by 14 a.m.u., of the hydrocarbon chain. On the basis of the spectral data, the structure of compound **3** was assigned as 2-hentriacontyl-5,7-dihydroxy-8-methyl-4*H*-1-benzopyran-4-one (*Fig. 2*).

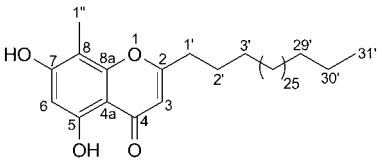

Fig. 2. *Structure of compound* **3**

Table 2. *^{1}H- and ^{13}C-NMR Data* (at 500 and 125 MHz, resp.)*, and HMBCs of Compound* **3**. Recorded in CD_3OD; δ in ppm, J in Hz.

	δ(H)	δ(C)	HMBC
C(2)	–	170.7	–
H–C(3)	5.99 (*s*)	107.9	1′, 2, 4, 4a
C(4)	–	182.7	–
C(4a)	–	108.8	–
C(5)	–	158.6	–
H–C(6)	6.31 (*s*)	93.2	5, 7, 8, 4a
C(7)	–	162.2	–
C(8)	–	106.1	–
C(8a)	–	160.0	–
CH_2(1′)	2.53 (*t*, J = 7.5)	34.2	2, 3, 2′, 3′
CH_2(2′)	1.61 – 1.64 (*m*)	26.8	2, 1′, 3′
CH_2(3′ – 28′)	1.28 – 1.20 (*m*)	29.7 – 28.9	–
CH_2(29′)	1.28 – 1.20 (*m*)	31.9	–
CH_2(30′)	1.28 – 1.20 (*m*)	22.7	29′, 31′
Me(31′)	0.84 (*t*, J = 6.8)	14.1	29′, 30′
Me(1″)	2.11 (*s*)	7.0	7, 8, 8a

The authors are grateful to *Higher Education Commission* of Pakistan for financial grant to *M. S.*

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 230 – 400 mesh; *E. Merck*, D-Darmstadt). TLC: silica gel *60-F_{254}* plates (*E. Merck*, D-Darmstadt). GC: *Schimadzu* gas chromatograph (*GC-9A*); *3% OV-1* silanized *Chromosorb* W column; column temp., 180°; injection port and detector temp., 275 – 300°; flow rate, 35 ml/min; flame-ionization detector. M.p.: *Gallenkemp* apparatus. Optical rotations: *JASCO P-2000* polarimeter. UV Spectra: *Hitachi UV-3200* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *JASCO 302-A* spectrometer; in KBr; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker AMX-500* instrument. EI-MS: *Finnigan MAT 312* mass spectrometer. HR-FAB-MS: *JEOL JMS-HX-110* mass spectrometer, glycerol as matrix.

Plant Material. The whole-plant material of *Asphodelus tenuifolius* CAV. (Asphodelaceae; 8 kg) was collected from Cholistan Desert (Bahawalpur) in 2006 and identified by Dr. *Muhammad Arshad*, Plant Taxonomist, Cholistan Institute of Desert Studies (CIDS), The Islamia University of Bahawalpur, Bahawalpur, where a voucher specimen has been deposited (Voucher specimen No. 28/CIDS/06).

Extraction and Isolation. The shade-dried whole-plant material (8 kg) was cut into small pieces and extracted with MeOH (3 × 30 l, 10 d each) at r.t. The combined extract was evaporated under reduced pressure to yield a residue (300 g), which was suspended in H_2O (1.0 l), and partitioned with hexane (45 g), $CHCl_3$ (85 g), AcOEt (75 g), and BuOH (45 g). The AcOEt-soluble subfraction (75 g) was subjected to CC (hexane/$CHCl_3$, $CHCl_3$, and $CHCl_3$/MeOH in increasing order of polarity) to yield ten fractions, *Frs. A–J.* The *Fr. B* (3 g), obtained with hexane/$CHCl_3$ 2:8, was re-chromatographed and eluted with same solvent system to yield a major compound with traces of impurities. It was purified by prep. TLC (hexane/$CHCl_3$ 0.5:9.5) to afford compound **3** (20 mg). *Fr. F* (4 g), which was obtained with $CHCl_3$/MeOH 9:1, was chromatographed ($CHCl_3$/MeOH 9.2:0.8) to give a semi-pure compound, which was further chromatographed ($CHCl_3$/MeOH 9:1) to provide compound **1** (18 mg). The *Fr. H* (3.5 g), obtained with $CHCl_3$/MeOH 8:2, was triturated with acetone, and the acetone-insoluble residue was chromatographed ($CHCl_3$/MeOH 8.2:1.8) to yield a semi-pure compound, which was purified by prep. TLC ($CHCl_3$/MeOH 7.5:2.5) to give compound **2** (15 mg).

Asphorin A (=*1-O-[(3β)-27-Hydroxy-3-(β-*D*-mannopyranosyloxy)-27,28-dioxours-12-en-28-yl]-β-*D*-glucopyranose*; **1**). Colorless crystals. M.p. 194–195°. $[\alpha]_D^{25} = +15$ ($c = 0.065$, MeOH). UV (MeOH): 268 (3.2), 202 (1.9). IR (KBr): 3425, 1732, 1638, 1103. ^{1}H- and ^{13}C-NMR: see *Table 1*. FAB-MS (neg.): 809 ($[M-H]^-$), 603 ($[M-H-hex-CO_2]^-$). EI-MS: 604 (4, $[M-hex-CO_2]^+$), 590 (4, $[M-hex-CO_2-Me]^+$), 440 (5), 425 (10), 409 (15), 370 (10), 287 (16), 261 (11), 247 (11), 207 (14), 203 (15), 189 (19), 135 (40), 95 (54), 81 (45), 73 (66), 69 (100), 55 (99). HR-FAB-MS (neg.): 809.4320 ($[M-H]^-$, $C_{42}H_{65}O_{15}^-$; calc. 809.4324).

Asphorin B (=*(3β)-3-[(2-*O*-Sulfo-β-*D*-mannopyranosyl)oxy]urs-12-ene-27,28-dioic Acid*; **2**). Colorless crystals. M.p. 270–271°. $[\alpha]_D^{25} = +26$ ($c = 0.09$, MeOH). UV (MeOH): 270 (4.2), 204 (1.3). IR (KBr): 3418, 1729, 1634. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 486 ($[M-SO_3hexose]^+$), 468 (4, $[M-SO_3hexose-H_2O]^+$), 450 (12), 442 (20), 427 (42), 409 (46), 287 (39), 278 (18), 273 (33), 261 (30), 247 (15), 207 (23), 203 (27), 189 (50), 135 (83), 97 (30), 95 (87), 83 (100), 80 (60), 69 (80), 55 (92). HR-FAB-MS (pos.): 729.3525 ($[M+H]^+$, $C_{36}H_{57}O_{13}S^+$; calc. 729.3520).

Compound **3** (=*2-Hentriacontyl-5,7-dihydroxy-8-methyl-4*H*-1-benzopyran-4-one*). Amorphous powder. M.p. 153–155°. UV (MeOH): 366 (4.1), 314 (4.3), 290 (3.8), 248 (3.9), 216 (2.4). IR (KBr): 3411, 1671 (CO), 1630, 1543, 1500. ^{1}H- and ^{13}C-NMR: see *Table 2*. EI-MS: 626 (5, M^+), 598 (73), 586 (12), 570 (52), 541 (11), 513 (11), 499 (10), 373 (13), 219 (100), 206 (36), 167 (20), 120 (28), 57 (13), 43 (16). HR-EI-MS: 626.5269 (M^+, $C_{41}H_{70}O_4^+$; calc. 626.5274).

Acid Hydrolysis of **1** *and* **2**. The MeOH soln. of each compound (5 mg) was hydrolyzed with 2N aq. CF_3COOH (8 ml) was refluxed for 4 h at 90° and extracted with CH_2Cl_2 (3 × 10 ml). Evaporation of the combined org. phase provided a pure crystalline compound (m.p. 297 (dec.) and $[\alpha]_D^{25} = +87$). It could be identified as quinovic acid by comparison of physical and spectral data with those reported in [3]. The aq. layer was repeatedly concentrated under reduced pressure with MeOH until neutral, and then analyzed by TLC (SiO_2; $CHCl_3$/MeOH/H_2O 8:5:1) by comparison with authentic sample. The sugar residue was dissolved in dry pyridine (1.0 ml) and stirred with L-cysteine methyl ester hydrochloride (1.5 mg) at 60° for 70 min. After concentration, 1-(trimethylsilyl)-1*H*-imidazole was added, and the mixture was stirred at 60° for 25 min. The supernatant was concentrated under N_2 and analyzed by GC. D-Glucose and D-mannose were detected from **1** by co-injection of the hydrolysate with standard silylated samples with t_R values of 14.1 and 13.2 min, resp. In case of **2**, only D-mannose was detected with a t_R value of 13.1 min [8].

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Received June 20, 2011