Three New Withanolides, Physagulins E, F and G from *Physalis angulata* L.[1)]

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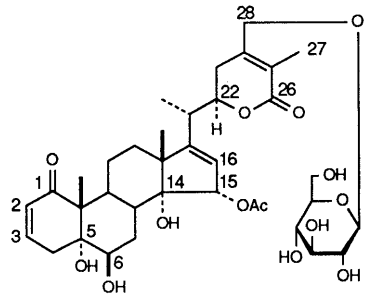
Three new withanolides, physagulins E (1), F (2) and G (3) were isolated from the fresh berries of *Physalis angulata* L. (Solanaceae). Their structures were established as (20*S*,22*R*)-15α-acetoxy-5α,6β,14α,28-tetrahydroxy-1-oxowitha-2,16,24-trienolide-28-*O*-D-glucopyranoside (1), (20*R*,22*R*)-15α-acetoxy-16β,17β-epoxy-5α,6β-14β-trihydroxy-1-oxo-witha-2,24-dienolide (2) and (20*R*,22*R*)-15α-acetoxy-16β,17β-epoxy-5α,6β,14β,28-tetrahydroxy-1-oxo-witha-2,24-dienolide 28-*O*-β-D-glucopyranoside (3) by spectroscopic means.

Keywords *Physalis angulata*; Solanaceae; withanolide; glycoside; physagulin

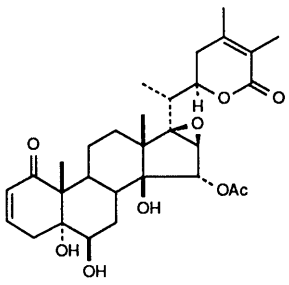
In our previous papers,[2)] we reported the structure elucidation of four withanolides, physagulins A (**4**), B (**5**), C (**6**) and D (**7**) obtained from the fresh leaves and stems of *Physalis angulata* L. Physagulins A (**4**) and B (**5**) were found to be the withanolides possessing a 15α-acetoxy-14α-hydroxy-16-ene system, and physagulin C (**6**) was shown to be a major component in this plant and to be the first withanolide substituted with oxygen atoms at C-14, -15, -16 and -17. Physagulin D (**7**) was revealed to be a withanolide glucoside carrying a fundamental simple framework.

As a continuing study of searching for the withanolides, we have now isolated three new withanolides, physagulins E, F and G, from the fresh berries of *Physalis angulata* L. Two of them, physagulins E (**1**) and G (**3**) were the first examples of withanolide glycosides which had a sugar moiety at the C-28 hydroxy group in the side chain.

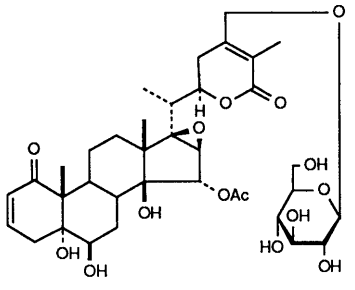
Physagulin E (**1**), a white powder, showed absorptions due to the hydroxy group (3464 cm^{-1}), the acetyl group (1733 cm^{-1}), α,β-unsaturated δ-lactone (1703 cm^{-1}) and α,β-unsaturated ketone (1678 cm^{-1}) in its infrared (IR) spectrum. The positive fast atom bombardment mass spectrum (FAB-MS) displayed peaks at *m/z* 799 $[M+glycerol+H]^+$, 707 $[M+H]^+$, 706 $[M]^+$, 689 $[M-H_2O+H]^+$, 647 $[M-AcOH+H]^+$, 629 $[M-H_2O-AcOH+H]^+$, 611 $[M-2H_2O-AcOH+H]^+$ and 544 [M − 162 (hexosyl unit) + H]$^+$. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum (Table I) of **1** gave a characteristic pattern for the structure of the withanolide: two singlet angular methyl signals [δ 1.36 (s, H_3-18), and 1.69 (s, H_3-19)], one secondary methyl signal [δ 1.22 (d, J = 7.0 Hz, H_3-21)], one vinyl methyl signal [δ 1.95 (s)] and an acetyl methyl signal [δ 2.16 (s)]. All other proton signals could be easily assigned by the proton–proton correlation spectroscopy (^{1}H–^{1}H COSY) of **1**. Strong cross-peaks appeared between the signals of H-2 [δ 6.15 (m)] and H-3 [δ 6.69 (ddd, J = 9.9, 5.0, 2.2 Hz)]; H-3 and H_2-4 [δ 3.78 (br d, J = 20.0 Hz) and 2.40 (dd, J = 20.0, 5.0 Hz)], indicating the presence of 1-one-2-ene system on ring A. Other cross peaks in the steroidal skeleton were also observed between the signals of H-6 [δ 4.18 (br s)] and H_2-7 [δ 2.58 (m) and



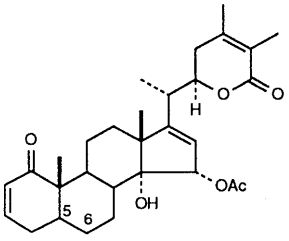
physagulin E (**1**)



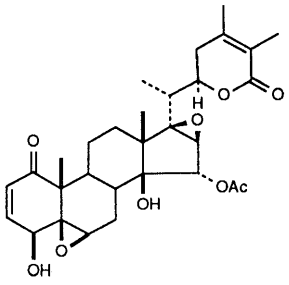
physagulin F (**2**)



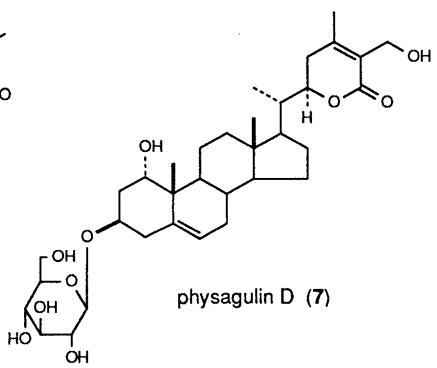
physagulin G (**3**)



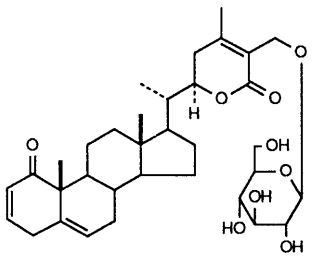
physagulin A : 5β,6β-epoxy (**4**)
physagulin B : 5α-Cl, 6β-OH (**5**)
withaminimin : 5α-OH, 6β-OH (**8**)



physagulin C (**6**)



physagulin D (**7**)



daturametelin A (**9**)

TABLE I. ^{1}H-NMR Data (in Pyridin-d_5, δ/ppm) for Physagulin E(**1**), Physagulin F(**2**), and Physagulin G(**3**)

Proton	**1**	**2**	**3**
2	6.15 m[a]	6.14 dd (9.9, 2.2)	6.14 dd (9.9, 2.9)
3	6.69 ddd (9.9, 5.0, 2.2)	6.69 ddd (9.9, 5.1, 2.2)	6.68 ddd (9.9, 5.1, 2.2)
4	3.78 br d (20.0) 2.40 dd (20.0, 5.0)	3.74 dt (22.2, 2.2) 2.38 dd (22.2, 5.1)	3.74 br d (19.8) 2.38 dd (19.8, 5.1)
6	4.18 br s	4.15 br s	4.14 br s
7	2.64 m	2.59 br dt (12.5, 2.8)	2.56 m
	2.58 m	2.38 br td (12.5, 2.7)	2.33 m
8	2.77 m	2.51 br td (12.8, 2.8)	2.50 br dd (15.8, 13.0)
9	3.38 br t (12.1)	3.18 br td (12.8, 2.6)	3.16 br t (13.0)
11	2.74 m	2.67 br td (13.0, 2.6)	2.67 br d (9.9)
	1.43 br d (8.1)	1.42 m	1.41 m
12	2.01 br t (13.2)	2.01 br t (13.0)	1.99 br t (12.8)
	1.89 br d (13.2)	1.71 br d (12.8)	1.69 br d (12.8)
15	5.95 d (2.6)	5.65 s	5.59 s
16	6.16 d[a] (2.6)	3.73 s	3.65 s
18	1.36 s	1.40 s	1.42 s
19	1.69 s	1.62 s	1.61 s
20	2.63 m	2.61 m	2.59 m
21	1.22 d (7.0)	1.02 d (7.0)	0.99 d (7.2)
22	4.48 br dt (13.6, 4.0)	4.51 ddd (12.8, 5.5, 3.7)	4.56[a]
23	2.93 br d (15.5)	2.33 br d (16.0)	2.98 br d (15.7)
	2.49 br d (15.5)	2.13 br dd (16.0, 3.0)	2.38 m
27	1.95 s	1.91 s	1.97 s
28	4.70 d (14.7)	1.74 s	4.76 d (13.6)
	4.33 d (14.7)		4.52 d (13.6)
–OAc	2.16 s	2.25 s	2.23 s
Glc-1	4.73 d (7.7)		4.85 d (7.7)
2	4.04 m		4.08 t (7.9)
3	4.21 m[b]		4.25 m[b]
4	4.21 m[b]		4.25 m[b]
5	3.94 m		3.98 m
6	4.58 dd (10.0, 2.6)		4.56 br d[a] (10.0)
	4.39 m		4.40 m

a, b) Its *J* value could not be calculated clearly owing to overlapping with each other signals.

TABLE II. ^{13}C-NMR Assignments (δ/ppm) of Physagulin E(**1**), Physagulin F(**2**), Physagulin G(**3**), Withaminimin (**8**), Daturametelin A(**9**) and Physagulin C(**6**)

	1 (C_5D_5N)	**8** ($CDCl_3$)	**9** (C_5D_5N)	**2** ($CDCl_3$)	**2** (C_5D_5N)	**6** (C_5D_5N)	**3** (C_5D_5N)
C-1	205.1	204.1	203.9	203.9	205.0	202.5	204.9
C-2	128.9	128.7	127.7	128.8	128.9	131.1	128.8
C-3	142.3	141.3	145.8	141.2	142.4	145.6	142.4
C-4	36.8	36.0	33.4	36.2	36.8	69.6	36.7
C-5	77.2	77.2	136.2	76.3	77.1	63.1	77.0
C-6	74.9	74.3	124.6	74.5	74.8	60.4	74.7
C-7	28.4	26.5	30.8	28.3	29.1	25.7	29.0
C-8	37.0	35.4	33.1	35.0	36.5	35.1	36.4
C-9	36.4	35.4	43.3	35.3	35.3	39.4	35.8
C-10	53.2	52.2	50.6	51.9	52.4	47.8	52.3
C-11	24.2	23.2	23.8	21.8	22.9	19.7	22.8
C-12	39.1	38.8	39.8	32.6	32.8	30.9	33.2
C-13	52.6	52.2	42.5	46.6	47.1	46.3	46.9
C-14	82.0	82.3	56.2	81.7	82.3	80.9	82.3
C-15	83.4	83.4	24.2	76.8	76.9	76.8	76.6
C-16	122.2	120.4	26.9	59.2	59.5	58.7	59.4
C-17	162.1	161.3	51.9	In solv.	76.7	75.9	77.2
C-18	17.1	16.8	11.7	15.9	16.0	16.4[a]	16.0
C-19	15.4	15.1	18.8	14.9	15.3	15.0[a]	15.2
C-20	35.3	36.1	38.9	33.1	33.6	34.0	33.8
C-21	17.9	17.2	13.3	13.5	14.0	13.8	14.2
C-22	79.9	78.5	78.2	76.7	77.3	77.9	77.8
C-23	27.6	32.4	29.9	32.4	33.3	32.7	28.3
C-24	148.5	150.3	157.0	149.1	149.3	In solv.	148.4
C-25	In solv.	121.4	122.8	121.9	121.8	121.3	124.2
C-26	166.2	167.5	166.0	166.3	166.0	165.6	165.9
C-27	12.3	12.4	63.2	12.4	12.6	12.2	12.3
C-28	66.5	20.6	20.4	20.5	20.0	20.6	66.9
–OAc	170.7	170.6		170.1	170.3	169.3	170.7
	21.4	21.4		21.1	21.1	19.8	21.1
Glc-1	102.9		104.6				103.4
Glc-2	74.9		75.0				74.9
Glc-3	78.3		78.3				78.4
Glc-4	71.6		71.5				71.5
Glc-5	78.7		78.3				78.7
Glc-6	62.6		62.6				62.7

a) Assignments for C-8 and C-9, C-18 and C-19 in Ref. 2*a*) should be revised as shown in this Table according to the several correlations of ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY and long range ^{13}C–^{1}H COSY.

2.64 (m)]; H_2-7 and H-8 [δ 2.77 (m)]; H-8 and H-9 [δ 3.38 (br t, J=12.1 Hz)]; H-9 and H_2-11 [δ 2.74 (m) and 1.43 (br d, J=8.1 Hz)]; H_2-11 and H_2-12 [δ 2.01 (br t, J=13.2 Hz) and 1.89 (br d, J=13.2 Hz)]; H-15 [δ 5.95 (d, J=2.6 Hz)] and H-16 [δ 6.16 (d, J=2.6 Hz)]. From the above COSY result, the presence of a 15α-acetoxy-5α,6β,14α-trihydroxy-2,16-diene-1-one system could be suggested in **1** as well as withaminimin (**8**).[3] On the other hand, as regards the structure of side chain moiety, the following correlations were observed in its ^{1}H–^{1}H COSY: between the signals of H_3-21 and H-20 [δ 2.63 (m)]; H-20 and H-22 [δ 4.48 (br dt, J=13.6, 4.0 Hz)]; H-22 and H_2-23 [δ 2.93 (br d, J=15.5 Hz) and 2.49 (br d, J=15.5 Hz)]; geminal protons in –CH_2O– [δ 4.70 (d, J=14.7 Hz) and 4.33 (d, J=14.7 Hz)]. Furthermore, among the remaining signals at δ 4—5 ppm, one sequence correlation due to the β-glucosyl moiety was observed. The carbon-13 and proton correlation spectroscopy (^{13}C–^{1}H COSY) also supported the occurrence of the glucosidic residue.

The ^{13}C-NMR data (Table II) for **1** were identical with those of withaminimin (**8**) except for the β-D-glucosyloxymethyl moiety in **1**. In comparing the ^{13}C-NMR data of the side chain moiety and β-glucopyranosyl part in **1** with those of daturametelin A (**9**)[4] having a 27-*O*-glucopyranosyl moiety, a vinylic methyl signal in **1** appeared at a higher field (at δ 12.3) than that (at δ 20.4) in **9**. The vinylic methyl signal appeared at δ_H 1.95 ppm and δ_C 12.3, and the –CH_2O– methylene signal at δ_H 4.33 and 4.70 (AB quartet) and δ_C 66.5, indicating that the hydroxymethyl group was located at C-28.[5] In addition, by the long range ^{13}C–^{1}H COSY of **1** between the C-26 lactone carbonyl carbon and C-27 vinyl methyl protons, the presence of an oxygen group at C-28 was supported. Furthermore, a correlation between the 28-hydroxymethyl carbon and an anomeric proton disclosed that the β-glucopyranosyl moiety linked to the C_{28} hydroxy group in the side chain. All assignments of proton and carbon signals in **1** could be attained by the several correlations of ^{1}H–^{1}H COSY, ^{13}C–^{1}H COSY and long range ^{13}C–^{1}H COSY.

The stereochemistries at C-14 and -15 have been established to be 14*R* and 15*S* by the reason that the ^{1}H-NMR and ^{13}C-NMR data of **1** were almost analogous with those of physagulin A (**4**) and withaminimin (**8**). The positive Cotton effect at 260 nm showed a 22*R* configuration.[5] Moreover, the negative Cotton effect at 335 nm

indicated *trans* fusion of rings A to B.[6] Besides, the ^{13}C-NMR chemical shift of the C-19 methyl group in the 5,6-dihydroxy or 4,5,6-trihydroxy derivatives indicated the relationships between the C-19 methyl and hydroxy group at C-5 to be gauche (*cis* fusion rings A to B) or not (*trans* fusion rings A to B). In the former, the chemical shift appears at around δ 10 ppm,[6,7] but in the latter, it appears at around δ 15 ppm.[8] This differences of chemical shift easily enabled us to discriminate the stereo compression effect between C-19 and the hydroxy group at C-5. In the case of **1**, the chemical shift due to C-19 was at δ 15.4 ppm, which corresponded to the latter case, *trans* fusion pattern. Furthermore, this *trans* conformation was verified by the observation of the nuclear Overhauser effect (NOE) experiment between H_3-19 and H-4. Thus, physagulin E could be formulated as **1**.

Physagulin F (**2**), a white powder, showed peaks due to $[M-H_2O+H]^+$ (*m/z* 527), $[M-AcOH+H]^+$ (*m/z* 485), $[M-2H_2O+H]^+$ (*m/z* 509), $[M-H_2O-AcOH+H]^+$ (*m/z* 467), $[M-2H_2O-AcOH+H]^+$ (*m/z* 449), $[M-3H_2O-AcOH+H]^+$ (*m/z* 431) and $[M-4H_2O-AcOH+H]^+$ (*m/z* 413) in the positive FAB-MS. Furthermore, the base peak at *m/z* 125 ($C_7H_9O_2$) characterized the presence of the lactone moiety of withanolide. The IR spectrum of **2** indicated the presence of the acetyl group (1740 cm^{-1}), α,β-unsaturated δ-lactone group (1714 cm^{-1}) and α,β-unsaturated carbonyl group (1684 cm^{-1}). Since the ^{1}H-NMR spectrum (Table I) of physagulin F (**2**) showed a similar signal pattern with that of physagulin C (**6**), that is, the following respective signals were assigned: six methyl groups [δ 1.40 (s, H_3-18), 1.62 (s, H_3-19), 1.02 (d, J=7.0 Hz, H_3-21), 1.74 (s, H_3-28), 1.91 (s, H_3-27) and 2.25 (s, 15-acetylmethyl)], two olefinic protons [δ 6.14 (1H, dd, J=9.9, 2.2 Hz, H-2) and 6.69 (1H, ddd, J=9.9, 5.1, 2.2 Hz, H-3)], one acetoxymethine proton [δ 5.65 (s, H-15)], one epoxy methine proton [δ 3.73 (s, H-16)] and a characteristic H-22 proton [δ 4.51 (ddd, J=12.8, 5.5, 3.7 Hz)]. These signals suggested the occurrence of the 1-one-2-ene system, 14β-hydroxy-15α-acetoxy-16β,17β-epoxy system and the normal withanolide side chain. The remaining signal at δ 4.15 (1H, br s) was assigned to H-6 by the similar proton–proton correlation set (H-6 to H_2-12) in **2** by comparing with those of **1**. In comparing the ^{13}C-NMR spectral data (Table II) for **2** with those of **1** (for rings A and B) and **6** (for rings C, D and the side chain moiety), **2** was found to possess the same rings A and B with that of **1**, and the same rings C, D and side chain moiety with those of **6**. Thus, the structure of physagulin F was established as shown in the formula **2**.

Physagulin G (**3**), a white powder, showed peaks due to $[M+glycerol+H]^+$ (*m/z* 815), $[M+H]^+$ (*m/z* 723), $[M-H_2O+H]^+$ (*m/z* 705), $[M-AcOH-H_2O+H]^+$ (*m/z* 645) and $[M-162$ (hexosyl unit)-$H_2O+H]^+$ (*m/z* 543) in the positive FAB-MS. These fragment ion peaks indicated the occurrence of the hexosyl group in the molecule as well as **1**. The IR spectrum of **3** indicated the presence of a hydroxy group (3464 cm^{-1}), an acetyl group (1740 cm^{-1}), α,β-unsaturated δ-lactone group (1710 cm^{-1}) and an α,β-unsaturated ketone group (1684 cm^{-1}). The ^{1}H-NMR spectrum (Table I) of **3** had a similar signal pattern with that of **2** except for signals in the proton region (δ 4—5 ppm) attached to the oxygen bearing carbon. Assignments were supported by comparison of the ^{1}H-NMR data of **3** with those of **2**, and by the ^{1}H–^{1}H COSY of **3**. Signals at δ 1.42, 1.61 (each 3H, s), 0.99 (3H, d, J=7.2 Hz) and 2.23 (3H, s) could be assigned to four methyl groups of H_3-18, H_3-19, H_3-21 and the 15-acetoxymethyl group. Two olefinic proton signals and an oxymethine proton signal at δ 6.14 (dd, J=9.9, 2.9 Hz), 6.68 (ddd, J=9.9, 5.1, 2.9 Hz) and 4.14 (br s) were assigned to H-2, H-3 and H-6, respectively, on the 1-one-2-ene-5α,6β-dihydroxy system. The signals at δ 5.59 (s) and 3.65 (s) were attributable to H-15 and H-16 on the 14β-hydroxy-15α-acetoxy-16β,17β-epoxy system. Moreover, the AB quartet signals at δ 4.76 (d, J=13.6 Hz) and 4.52 (d, J=13.6 Hz) and a vinyl methyl signal at δ 1.97 (s), which were assigned to H_2-28 and H_3-27, suggested the hydroxy group at C-28. Furthermore, the β-glucopyranosyl moiety was found to combine with the C-28 hydroxy group the same as with **1**. And then, by comparison of the ^{13}C-NMR spectral data (Table II) for **3** with those of **2** (for rings A to D) and **1** (for the side chain and sugar moiety), physagulin G (**3**) were found to have the identical rings A—D with **2** and the same side chain and sugar moiety as **1**. Thus, physagulin G was established as represented as formula **3**.

Physagulins E (**1**) and G (**3**) are the first examples of withanolide which have a C-28 hydroxy group and have the sugar moiety at the C-28 hydroxy group.

Experimental

Optical rotations were measured on a JASCO DIP-360 automatic digital polarimeter and circular dichroism (CD) spectrum on a JASCO J-50A spectropolarimeter. The IR spectra were recorded with a Hitachi IR spectrometer, model 270-30. The ^{1}H- and ^{13}C-NMR spectra were measured with a JEOL JNM-GX 400 NMR spectrometer and chemical shifts are given on a δ (ppm) scale with tetramethylsilane (TMS) as an internal standard. The FAB-MS were measured with JEOL DX-303 HF spectrometer and taken in a glycerol matrix containing NaI. Thin layer chromatography performed on precoated Kieselgel 60 F_{254} (Merck) and detection was achieved by spraying 10% H_2SO_4 followed by heating. Column chromatography was carried out on Kieselgel (70—230 and 230—400 mesh, Merck) and Sephadex LH-20 (Pharmacia Fine Chem. Co., Ltd.) using MeOH.

Extraction and Separation The fresh berries (2.1 kg) of *Physalis angulata* L. (Solanaceae), harvested at the botanical garden in Fukuoka University, in September 1988, were extracted with MeOH and the extract was partitioned between 1-BuOH and H_2O. The 1-BuOH layer (8.9 g) was subjected repeatedly to column chromatography over silica gel using $CHCl_3$–MeOH–H_2O=1:0:0→8:2:0.1→MeOH and Sephadex LH-20 using MeOH to give physagulins E (**1**, 5.8 mg), F (**2**, 11.4 mg) and G (**3**, 8.6 mg).

Physagulin E (**1**): A white powder, $[\alpha]_D$ +56.7° (c=0.66, MeOH). Positive FAB-MS (*m/z*): 799 $[M+glycerol+H]^+$, 707 $[M+H]^+$, 706 $[M]^+$. 689 $[M-H_2O+H]^+$, 647 $[M-AcOH+H]^+$, 629 $[M-AcOH-H_2O+H]^+$, 507 $[M-AcOH-2H_2O+H]^+$ and 544 $[M-162$ (hexosyl unit)$+H]^+$. IR (KBr): 3464, 2940, 1733, 1703, 1678, 1465, 1386, 1320, 1260 cm^{-1}. CD (c=0.66, MeOH) [θ] (nm): −30400 (335) (negative max), +55000 (260) (positive max).

Physagulin F (**2**): A white powder, $[\alpha]_D$ +70.7° (c=1.1, MeOH). Positive FAB-MS (*m/z*): 527 $[M-H_2O+H]^+$, 485 $[M-AcOH+H]^+$, 509 $[M-2H_2+H]^+$, 467 $[M-H_2O-AcOH+H]^+$, 449 $[M-2H_2O-AcOH+H]^+$, 431 $[M-3H_2O-AcOH+H]^+$, 413 $[M-4H_2O-AcOH+H]^+$. IR (KBr): 3528, 2980, 1740, 1714, 1684, 1470, 1390, 1320, 1240 cm^{-1}. CD (c=1.1, MeOH) [θ] (nm): −38500 (335) (negative max), +55300 (264) (positive max).

Physagulin G (**3**): A white powder, $[\alpha]_D$ +31.3° (c=0.76, MeOH). Positive FAB-MS (*m/z*): 815 $[M+glycerol+H]^+$, 723 $[M+H]^+$, 705 $[M-H_2O+H]^+$, 645 $[M-AcOH-H_2O+H]^+$, 543 $[M-162$ (hexosyl unit)-$H_2O+H]^+$. IR (KBr): 3464, 2940, 1740, 1710, 1684, 1386, 1254, 1130 cm^{-1}. CD (c=0.76, MeOH) [θ] (nm): −36100 (335) (negative max), +58400 (265) (positive max).

References and Notes

1) This work is Part XXIV in a series of studies on the constituents of solanaceous plants.
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