Triptexanthosides A—E: Xanthone Glycosides from Aerial Parts of *Tripterospermum japonicum*

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From the aerial parts of *Tripterospermum japonicum*, five new xanthone glycosides, named triptexanthosides A—E, were isolated along with a known xanthone C-glucoside, mangiferin. Their structures were elucidated as 1,2,6,8-tetrahydroxyxanthone (norswetianin) 1-*O*-*β*-D-glucopyranoside and 1-*O*-*β*-gentiobioside, and 1,2,8-trihydroxy-5,6-dimethoxyxanthone 2-*O*-*β*-D-glucopyranoside, 2-*O*-*β*-primeveroside and 1-*O*-gentiobioside, respectively, from spectroscopic evidence and acid hydrolysis.

Key words *Tripterospermum japonicum*; Gentianaceae; xanthone glycoside; triptexanthoside A—E; mangiferin; droplet counter-current chromatography

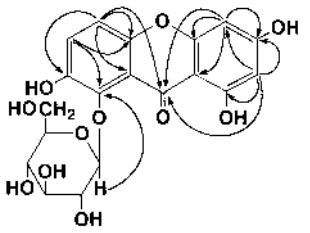
Gentianaceous plants are rich sources of xanthone glycosides[1] and *seco*-iridoid glucosides.[2] A xanthone glucoside, tripteroside, has been isolated from a tropical plant, *Tripterospermum taiwanense*.[3] A related plant, *T. japonicum* is a perennial herb with light blue flowers in early autumn and scarlet fruits in deep autumn, which grows in relatively shady places. Phytochemical investigation of the plant afforded five new xanthone glycosides, named triptexanthosides A—E (**1**—**5**), along with mangiferin (**6**). This paper deals with their structural elucidation.

Results and Discussion

A MeOH extract of the air-dried aerial parts of *T. japonicum* (SIEB. *et* ZUCC.) MAXIM. (1.30 kg) was partitioned between solvents to give 42.2 g of an *n*-BuOH-soluble fraction. Extensive isolation work was carried out on the fraction involving various kinds of column chromatography, such as highly porous synthetic resin (Diaion HP-20), silica-gel, reversed phase silica-gel and droplet counter-current chromatography, afforded six xanthone glycosides. The major compound was identified spectrometrically as mangiferin and the remaining five were found to be new xanthone glycosides.

Triptexanthoside A (**1**), $[\alpha]_D$ −115°, was obtained as yellow crystals (mp>300 °C), and its elemental composition was determined to be $C_{19}H_{18}O_{11}$ by negative ion high resolution (HR) FAB-MS. The IR spectrum indicated the presence of hydroxyl groups (3250 cm^{-1}), a ketone function (1645 cm^{-1}) and aromatic rings (1575, 1470 cm^{-1}). Of 19 signals observed in the ^{13}C-NMR spectrum, six were assigned as those of *β*-glucopyranose and the remaining 13 signals consisted of two aromatic rings, four of whose carbon signals were expected to carry hydroxyl groups from their chemical shifts, and a carbonyl function (Table 1). Two pairs of aromatic protons, coupled in the *ortho* and *meta* modes, one chelated hydroxyl proton (δ_H 12.94) and one anomeric (δ_H 4.97, J=8 Hz) proton were observed in the ^{1}H-NMR spectrum. From the combined physical data above, **1** was expected to be tetrahydroxyxanthone glucoside. In the UV spectrum, the significant bathochromic shift of a band I (318 nm→349 nm) on addition of AcONa implied that one of the free hydroxyl functions must be at the C-6 and/or C-3-position(s) of the xanthone skeleton. In the heteronuclear multiple bond correlation (HMBC) spectrum, the correlations observed between C-4a and H-3 and H-4 placed two hydroxyl functions at the 1- and 2-positions, and consequently the fourth hydroxyl group at the 8-position (Fig. 1). The HMBC spectrum also showed that the *β*-glucopyranose linkage was at the hydroxyl group at the 1-position. Therefore, the structure of **1** was concluded to be 1,2,6,8-tetrahydroxyxanthone 1-*O*-*β*-D-glucopyranoside.

Triptexanthoside B (**2**), $[\alpha]_D$ −98°, was obtained as yellow crystals (mp 196—201 °C), and its elemental composition was determined to be $C_{25}H_{28}O_{16}$ by negative ion HR-FAB-MS. The IR and UV spectra were essentially the same as those of **1**. The ^{13}C-NMR spectral data for the aglycone portion were essentially the same as those for **1**, and the sugar moiety was judged to be gentiobiose by comparison with reported data.[4] From this evidence, the structure of **2** was concluded to be 1,2,6,8-tetrahydroxyxanthone 1-*O*-gentiobioside, namely 1-*O*-(6′-*O*-*β*-D-glucopyranosyl)-*β*-D-glucopyranoside. To confirm the structure of the aglycone in **1** and **2**



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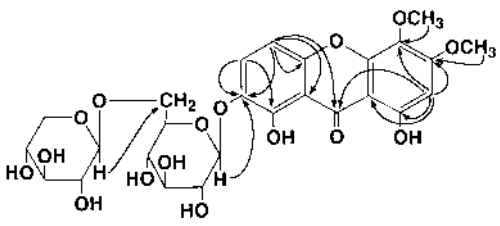

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Fig. 1. Diagnostic HMBC Correlations in Triptexanthosides A (**1**) and D (**4**)

Arrow heads indicate carbon atoms and arrow tails hydrogen atoms.

Table 1. ^{13}C-NMR Data for Triptexanthosides A—E (1—5) and Aglycones (**2a** and **3a**)

	1	2	2a	3	3a	4	5
C-1	141.6	141.6	147.0	148.9	147.0	148.8	141.6
2	146.3	146.1	140.3	140.5	140.5	140.2	146.2
3	125.1	124.9	123.8	124.2	124.2	125.2	125.1
4	114.3	114.2	105.9	106.2	106.2	106.4	114.3
4a	149.6	149.5	147.8	149.9	147.9	149.2	149.6
5	93.1	93.1	94.0	128.1	128.1	128.2	127.5
6	165.6	165.5	166.5	160.2	160.2	160.4	159.4
7	98.1	98.0	98.2	95.0	95.0	95.2	94.8
8	162.9	162.9	162.1	157.5	157.5	157.6	158.2
8a	102.5	102.4	100.7	101.1	101.1	101.2	102.7
9	180.4	180.3	183.8	184.5	184.5	184.3	180.9
9a	114.2	114.1	107.2	107.0	107.0	107.1	114.1
10a	156.8	156.7	157.7	149.1	148.8	149.9	148.0
1′	104.9	104.4		101.1		101.2	104.1
2′	73.7	73.4		73.0		73.4	73.4
3′	76.0	76.5		76.4		76.6	76.3
4′	69.5	69.8		69.4		69.7	69.7
5′	77.5	76.0		76.9		76.0	76.0
6′	60.7	68.0		60.5		68.3	69.0
1″		102.9				103.7	102.9
2″		73.6				73.2	73.4
3″		76.5				76.5	76.5
4″		69.6				69.5	69.6
5″		76.3				65.6	76.3
6″		60.8					60.8
OCH_3 on 5-C				60.9	60.9	60.9	60.8
OCH_3 on 6-C				56.6	56.4	56.6	56.5

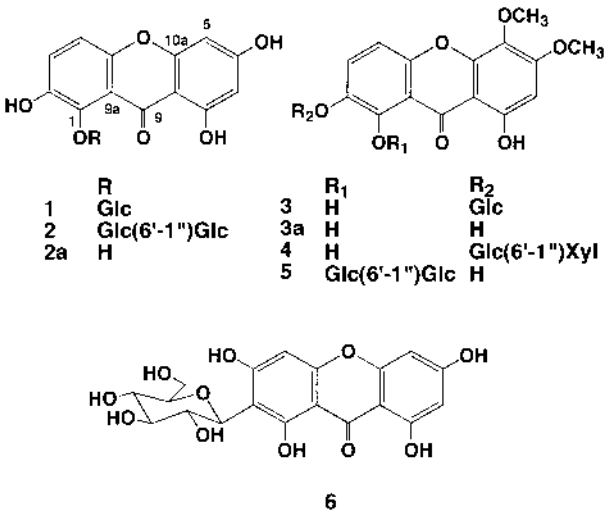

Chart 1. Structures

chemically, **2** was hydrolyzed with 2 N H_2SO_4 under reflux to give the aglycone (**2a**). The formation of a red precipitate with lead acetate suggested that two of the hydroxyl groups were in an *ortho* position. There were two possible *ortho* dispositions, *i.e.* 1,2- and 3,4-hydroxyl substitutions. Comparison of the reported ^{13}C-NMR data for such substitutions[5] with those of **2a** clearly eliminated the 3,4-substitution pattern, together with the evidence that two D_2O-exchangeable chelated protons were observed in the ^{1}H-NMR spectrum of **2a**. These data were consistent with a norswetianin (1,3,7,8-tetrahydroxyxanthone).[6]

Triptexanthosides C (**3**) and (**4**) were both obtained as yellow needles (mp 225—230 °C and 244—246 °C, respectively). On negative ion HR-FAB-MS, their elemental compositions were determined to be $C_{21}H_{22}O_{12}$ and $C_{26}H_{30}O_{16}$, respectively. The ^{13}C-NMR spectra indicated that **3** and **4** were also derivatives of xanthone, and their aglycones were expected to be the same, with two methoxyl and three hydroxyl functions, while the former had a β-glucopyranosyl unit, and the latter β-xylopyranose and 6-substituted β-glucopyranose units.[4] Since the ^{1}H-NMR spectra in DMSO-d_6 showed two D_2O exchangeable chelated protons (δ_H 11.74 and 11.79 in **3**, and δ_H 11.75 and 11.78 in **4**), two of the hydroxyl groups were placed at the 1- and 8-positions of the common aglycone. In the HMBC spectrum of **4**, the cross peaks observed between δ_H 6.59 (H-7) and δ_C 128.2 (C-5), 160.4 (C-6), 157.6 (C-8) and 101.2 (C-8a) placed two methoxyl groups at the 5 and 6-positions and consequently the remaining hydroxyl function at the 2-position (Fig. 1). Also, the HMBC correlations, δ_H 4.86 (H-1′) and δ_C 140.2 (C-2), and δ_H 4.17 (H-1″) and 68.3 (C-6′), confirmed that a biose was linked to the hydroxyl group at the 2-position. On acid hydrolysis of **3**, the aglycone (**3a**) was obtained as yellow crystals, together with D-glucose. Comparison of the ^{13}C-NMR signals (C-1, 2, 3, 4, 4a and 9a) with those of **2a** confirmed the conclusion that the substitution pattern of this ring was the same as that of **2a** (Table 1). Therefore, the structures of triptexanthoside C were elucidated as 1,2,8-trihydroxy-5,6-dimethoxyxanthone 2-*O*-β-D-glucopyranoside (**3**) and 2-*O*-(6′-*O*-β-D-xylopyranosyl)-β-D-glucopyranoside (primeveroside) (**4**), respectively, as shown in Chart 1.

Triptexanthoside E (**5**) was also obtained as yellow crystals (mp 245—250 °C). The elemental composition was determined to be $C_{27}H_{32}O_{17}$ by the same method. The ^{13}C-NMR spectrum showed that the signals for the sugar moiety were essentially the same as those of triptexanthoside B (**2**). The six signals (C-1, 2, 3, 4, 4a and 9a) for one of the aromatic rings were indistinguishable from those of triptexanthoside B (**2**), and those (C-5, 6, 7, 8, 8a and 10a) of the other ring those of triptexanthoside C (**3**). Therefore, the structure of triptexanthoside E (**5**) was concluded to be 1,2,8-trihydroxy-5,6-dimethoxyxanthone 1-*O*-(6′-*O*-β-D-glucopyranosyl)-β-D-glucopyranoside, as shown in Chart 1.

Experimental

Highly porous synthetic resin (Diaion HP-20) was purchased from Mitsubishi Kagaku (Tokyo). Silica-gel column chromatography (CC) and reversed phase [octadecyl silica gel (ODS)] open CC (RPCC) were performed on Silica-gel 60 (Merck) and Cosmosil 75C_{18}-OPN (Nacalai Tesque, Kyoto) [Φ=50 mm, L=25 cm, MeOH–H_2O (1 : 9, 1.5 l)→(7 : 3, 1.5 l), 10 g fractions were collected], respectively. Droplet counter-current chromatography (DCCC) was equipped with 500 glass columns (Φ=2 mm, L=40 cm), and the lower and upper layers of the solvent mixture of $CHCl_3$–MeOH–H_2O–*n*-PrOH (9 : 12 : 8 : 2) were used as the stationary and mobile phases, respectively. Five gram fractions were collected and numbered according to their order of elution.

All melting points were determined with a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured on a Union Giken PM-101 digital polarimeter. IR spectra were measured on a Shimadzu IR-408 spectrophotometer and UV spectra on a Shimadzu UV-160A spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were taken on a JEOL JNM α-400 spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane (TMS) as an internal standard. Negative ion high resolution (HR) FAB-MS were taken on a JEOL JMS SX-102 spectrometer.

Plant Material The aerial parts of *Tripterospermum japonicum* (Sieb. *et* Zucc.) Maxim. were collected in Kamo-gun, Hiroshima, in August 1993, and a voucher specimen was deposited in the Herbarium of the Institute of

Pharmaceutical Sciences, Hiroshima University School Medicine (JT-93-Hiroshima).

Extraction and Fractionation The air-dried parts of *T. japonicum* (1.30 kg) were extracted with MeOH three times. The MeOH extract was concentrated to 1.5 l, and then 75 ml H_2O was added to give a 95% aqueous solution. This solution was extracted with 1.5 l *n*-hexane and then the methanolic layer was concentrated to a viscous gum. The gummy residue was suspended in 1.5 l H_2O, and then extracted successively with 1.5 l both EtOAc and *n*-BuOH to give 42.4 g of an *n*-BuOH soluble fraction.

The *n*-BuOH-soluble fraction (42.0 g) was separated by Diaion HP-20 CC (Φ=55 mm, L=50 cm). The adsorbed materials were eluted with MeOH–H_2O following with a stepwise increase in the MeOH content [20% (2 l), 40% (4 l), 60% (4 l), 80% (4 l) and 100% (1 l)], and 500 ml fractions were collected. In many fractions, crystals of mangiferin (**6**) precipitated (more than 2.0 g). The residue (9.60 g, crystals were removed prior to evaporation) of fractions 9—15 was subjected to silica-gel (400 g) CC with $CHCl_3$ (2 l), $CHCl_3$–MeOH (99 : 1, 3 l), (49 : 1, 3 l), (24 : 1, 3 l), (47 : 3, 6 l), (23 : 2, 9 l), (9 : 1, 9 l), (17 : 3, 6 l), (4 : 1, 3 l), (3 : 1, 3 l) and (7 : 3, 3 l); 500 ml fractions were collected. The residue (1.47 g) of fractions 56—80 was separated by RPCC (517 mg in fractions 155—176) and then DCCC to give 35 mg of **2** as yellow crystals in fractions 29—34.

The residue (6.02 g, crystals were removed prior to evaporation) of fractions 16—23 was subjected to silica-gel (400 g) CC with $CHCl_3$ (1 l), $CHCl_3$–MeOH (39 : 1, 1 l), (19 : 1, 1 l), (37 : 3, 2 l), (9 : 1, 3 l), (17 : 3, 3 l), (4 : 1, 3 l), (3 : 1, 3 l) and (7 : 3, 3 l); 500 ml fractions were collected. Compound **5** (17 mg) crystallized from fractions 15—16. The residue (390 mg) of fractions 11—14 was purified by DCCC to give 17 mg of **1** as yellow crystals in fractions 77—89. The residue (1.46 g) of fractions 17—23 was subjected to RPCC. Compound **3** (42 mg) crystallized as yellow crystals from fractions 209—218. The residue (781 mg in fractions 155—185) of RPCC was separated by DCCC to give a further amount of **2** (24 mg in fractions 26—30). The residue (111 mg in fractions 197—208) from RPCC was similarly separated by DCCC to give 21 mg of yellow crystals (**4**) in fractions 146—166, and 5 mg of **3** was recovered from the stationary phase. A further amount of **4** (31 mg) was isolated from the residue (899 mg) on silica gel CC (fractions 24—30) by RPCC in fractions 179—186.

A Known Compound Isolated Mangiferin (**6**): Yellow crystals, $[\alpha]_D^{28}$ +32.8° (c=046, pyridine).[7]

Triptexanthoside A (1) Yellow crystals, mp >300 °C (MeOH), $[\alpha]_D^{28}$ −115° (c=0.39, pyridine). IR ν_{max} (KBr) cm^{-1}: 3250, 1645, 1575, 1470, 1315, 1280, 1170, 1075, 1035, 815. UV λ_{max} (MeOH) nm (log ε): 237 (4.37), 262 (4.49), 318 (4.16), 377 (3.67), λ_{max} (MeOH+AcONa) nm (log ε): 234 (4.48), 266 (4.31), 349 (4.19), 380sh (3.97), λ_{max} (MeOH+CH_3ONa) nm (log ε): 213 (4.69), 244 (4.46), 275 (4.48), 347 (4.33), 407 (3.81), λ_{max} (MeOH+$AlCl_3$) nm (log ε): 232 (4.61), 273 (4.64), 331 (4.37), 422 (3.95). ^{1}H-NMR (DMSO-d_6) δ: 3.50 (1H, t, J=8 Hz, 2′-H), 4.97 (1H, d, J=8 Hz, 1′-H), 6.18 (1H, d, J=2 Hz, 7-H), 6.31 (1H, d, J=2 Hz, 5-H), 7.30 (1H, d, J=9 Hz, 4-H), 7.42 (1H, d, J=9 Hz, 3-H), 12.94 (1H, s, 8-OH, exchangeable with D_2O). ^{13}C-NMR (DMSO-d_6); see Table 1. HR-FAB-MS (negative ion mode) m/z: 421.0750 (Calcd for M^-−H, $C_{19}H_{17}O_{11}$: 421.0771).

Triptexanthoside B (2) Yellow crystals, mp 198—201 °C (MeOH), $[\alpha]_D^{28}$ −98.0° (c=0.49, pyridine). IR ν_{max} (KBr) cm^{-1}: 3250, 1645, 1605, 1575, 1470, 1320, 1275, 1170, 1100—1000, 815. UV λ_{max} (MeOH) nm (log ε): 237 (4.37), 262 (4.47), 318 (4.15), 329sh (4.12), 376 (3.69), λ_{max} (MeOH+AcONa) nm (log ε): 207 (4.50), 235 (4.46), 264 (4.32), 349 (4.14), 378sh (3.97), λ_{max} (MeOH+CH_3ONa) nm (log ε): 210 (4.87), 244 (4.37), 274 (4.46), 349 (4.30), 403 (3.89), λ_{max} (MeOH+$AlCl_3$) nm (log ε): 212 (4.26), 234 (4.36), 275 (4.51), 334 (4.21), 344sh (4.18), 430 (3.70). ^{1}H-NMR (DMSO-d_6) δ: 4.12 (1H, d, J=8 Hz, 1″-H), 5.30 (1H, d, J=8 Hz, 1′-H), 6.18 (1H, d, J=2 Hz, 7-H), 6.31 (1H, d, J=2 Hz, 5-H), 7.29 (1H, d, J=9 Hz, 4-H), 7.39 (1H, d, J=9 Hz, 3-H), 9.18, 11.04 (each 1H, each br s, 2-, 6-OH, exchangeable with D_2O), 13.03 (1H, s,, 8-OH, exchangeable with D_2O). ^{13}C-NMR (DMSO-d_6); see Table 1. HR-FAB-MS (negative ion mode) m/z: 583.1305 (Calcd for M^-−H, $C_{25}H_{27}O_{16}$: 583.1311).

Triptexanthoside C (3) Yellow needles, mp 225—230°C (MeOH), $[\alpha]_D^{28}$ −42.9° (c=0.49, pyridine). IR ν_{max} (KBr) cm^{-1}: 3350, 1650, 1630, 1605, 1505, 1475, 1235, 1090, 1050, 815. UV λ_{max} (MeOH) nm (log ε): 236 (4.35), 267 (4.57), 345 (4.16), 383sh (3.69), λ_{max} (MeOH+AcONa) nm (log ε): 207 (4.51), 236 (4.37), 267 (4.47), 345 (4.15), 386sh (3.55), λ_{max} (MeOH+CH_3ONa) nm (log ε): 211 (4.76), 245 (4.48), 260sh (4.18), 349 (4.01), 388sh (3.81), λ_{max} (MeOH+$AlCl_3$) nm (log ε): 209 (4.31), 237 (4.31), 280 (4.52), 336 (3.87), 378 (4.01), 411sh (3.91). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 5-OCH_3), 3.95 (3H, s, 6-OCH_3), 4.93 (1H, d, J=8 Hz, 1′-H), 6.61 (1H, s, 7-H), 7.04 (1H, d, J=9 Hz, 4-H), 7.63 (1H, d, J=9 Hz, 3-H), 11.74, 11.79 (each 1H, each s, 1-, 8-OH, exchangeable with D_2O). ^{13}C-NMR (DMSO-d_6); see Table 1. HR-FAB-MS (negative ion mode) m/z: 465.1025 (Calcd for M^-−H, $C_{21}H_{21}O_{12}$: 465.1033).

Triptexanthoside D (4) Yellow crystals, mp 244—246°C (MeOH), $[\alpha]_D^{28}$ −51.8° (c=0.60, pyridine). IR ν_{max} (KBr) cm^{-1}: 3300, 1650, 1630, 1605, 1570, 1505, 1455, 1265, 1200, 1100—1000, 815. UV λ_{max} (MeOH) nm (log ε): 236 (4.36), 267 (4.58), 345 (4.18), 384 (3.59), λ_{max} (MeOH+AcONa) nm (log ε): 236 (4.39), 266 (4.52), 345 (4.14), 384 (3.64), λ_{max} (MeOH+CH_3ONa) nm (log ε): 214 (4.76), 245 (4.52), 265sh (4.33), 354 (4.08), 391sh (3.91), λ_{max} (MeOH+$AlCl_3$) nm (log ε): 218 (4.59), 233sh (4.58), 273 (4.66), 325 (4.15), 378 (4.23), 427sh (3.92). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 5-OCH_3), 3.94 (3H, s, 6-OCH_3), 4.17 (1H, d, J=7 Hz, 1″-H), 4.86 (1H, d, J=8 Hz, 1′-H), 6.59 (1H, s, 7-H), 7.05 (1H, d, J=9 Hz, 4-H), 7.73 (1H, d, J=9 Hz, 3-H), 11.75, 11.80 (each 1H, each s, 1-, 8-OH, exchangeable with D_2O). ^{13}C-NMR (DMSO-d_6); see Table 1. HR-FAB-MS (negative ion mode) m/z: 597.1465 (Calcd for M^-−H, $C_{26}H_{29}O_{16}$: 597.1456).

Triptexanthoside E (5) Yellow crystals, mp 245—250 °C (MeOH), $[\alpha]_D^{28}$ −84.9° (c=0.35, pyridine). IR ν_{max} (KBr) cm^{-1}: 3350, 1635, 1600, 1470, 1325, 1265, 1220, 1100—1000, 815. UV λ_{max} (MeOH) nm (log ε): 236 (4.32), 266 (4.50), 322 (4.05), 393 (3.59), λ_{max} (MeOH+AcONa) nm (log ε): 235 (4.61), 267 (4.48), 320 (4.01), 394 (3.61), λ_{max} (MeOH+CH_3ONa) nm (log ε): 213 (4.99), 246 (4.43), 276 (4.50), 347 (3.88), 412 (3.87), λ_{max} (MeOH+$AlCl_3$) nm (log ε): 213 (4.70), 236 (4.68), 281 (4.67), 331 (4.36), 439 (3.97). ^{1}H-NMR (DMSO-d_6) δ: 3.79 (3H, s, 5-OCH_3), 3.93 (3H, s, 6-OCH_3), 4.10 (1H, d, J=7 Hz, 1″-H), 5.06 (1H, d, J=7 Hz, 1′-H), 6.54 (1H, s, 7-H), 7.35 (1H, d, J=9 Hz, 4-H), 7.41 (1H, d, J=9 Hz, 3-H), 9.35 (1H, br s, 2-OH, exchangeable with D_2O), 12.95 (1H, s, 8-OH, exchangeable with D_2O). ^{13}C-NMR (DMSO-d_6); see Table 1. HR-FAB-MS (negative ion mode) m/z: 627.1572 (Calcd for M^-−H, $C_{27}H_{31}O_{17}$: 627.1561).

Acid Hydrolysis of Triptexanthoside B (2) to Norswetianin (2a) Compound **2** (8.0 mg) in 5 ml 2 N H_2SO_4 was refluxed for 30 min. The resultant crystals (**2a**) were collected by filtration (3.20 mg). Aglycone (**2a**), yellow crystals, mp>300 °C. UV λ_{max} (MeOH) nm (log ε): 238 (4.31), 265 (4.41), 329 (4.12), 387 (3.49), λ_{max} (MeOH+AcONa) nm (log ε): 235 (4.42), 268 (4.35), 356 (4.29), λ_{max} (MeOH+CH_3ONa) nm (log ε): 214 (4.55), 250 (4.35), 267sh (4.29), 355 (4.33), 415 (3.60), λ_{max} (MeOH+$AlCl_3$) nm (log ε): 244 (4.41), 276 (4.47), 326 (4.18), 360 (4.23), 445 (3.67). ^{1}H-NMR (DMSO-d_6) δ: 6.19 (1H, d, J=2 Hz, 7-H), 6.34 (1H, d, J=2 Hz, 5-H), 6.88 (1H, d, J=9 Hz, 3-H or 4-H), 7.26 (1H, d, J=9 Hz, 4-H or 3-H), 11.71, 11.88 (each 1H, each s, 1-, 8-OH, exchangeable with D_2O). ^{13}C-NMR (DMSO-d_6); see Table 1. HR-FAB-MS (negative ion mode) m/z: 259.0252 (Calcd for M^-−H, $C_{13}H_7O_6$: 259.0243).

Acid Hydrolysis of Triptexanthoside C (3) Compound **3** (15 mg) in 10 ml 2 N H_2SO_4 was refluxed for 2 h. The resultant crystals (**3a**) were collected by filtration (10 mg, quantitative). The filtrate was neutralized with $Ba(OH)_2$ and the precipitate was removed by filtration. The glucose liberated was recovered from the filtrate (3.95 mg). Aglycone (**3a**), Yellow needles, mp 233—235 °C (H_2O). UV λ_{max} (MeOH) nm (log ε): 238 (4.32), 268 (4.57), 312 (3.84), 343 (4.10), 402 (3.53), λ_{max} (MeOH+AcONa) nm (log ε): 238 (4.33), 267 (4.56), 311 (3.85), 343 (4.10), 402 (3.52), λ_{max} (MeOH+AcONa+H_3BO_3) nm (log ε): 255sh (4.37), 271 (4.57), 344 (4.09), 411 (3.52). ^{1}H-NMR (DMSO-d_6) δ: 3.78 (3H, s, 5-OCH_3), 3.94 (3H, s, 6-OCH_3), 6.56 (1H, s, 7-H), 6.95 (1H, d, J=9 Hz, 4-H), 7.29 (1H, d, J=9 Hz, 3-H), 9.34 (1H, s, 2-OH, exchangeable with D_2O), 11.61, 11.78 (each 1H, each s, 1-, 8-OH, exchangeable with D_2O). ^{13}C-NMR (DMSO-d_6); see Table 1. HR-FAB-MS (negative ion mode) m/z: 303.0494 (Calcd for M^-−H, $C_{15}H_{11}O_7$: 303.0501). D-Glucose, $[\alpha]_D^{22}$ +33.1° (c=0.26, H_2O), 24 h after being dissolved in the solvent.

Acknowledgments The author is grateful for access to the JEOL α-400 NMR spectrometer in the Research Center for Molecular Medicine at Hiroshima University Faculty of Medicine.

References and Notes

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