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晚香玉球茎中的一个新胆甾烷类配糖体*

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摘要: 从晚香玉 (*Polianthes tuberosa* L.) 球茎中分离到 3 个胆甾烷类配糖体。经波谱分析鉴定, 其中 1 个为新的胆甾烷类配糖体, 即 (22S)-胆甾烷-5-烯-1β, 3β, 16β, 22, 25-五醇 1-O-β-D-葡萄吡喃糖基-16-O-β-D-芹菜呋喃糖苷。

关键词: 晚香玉; 胆甾烷类配糖体; 晚香玉甙 A
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A New Cholestane Glycoside from the Tubers of *Polianthes tuberosa* *

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Abstract: A new cholestane glycoside, (22S)-cholest-5-en-1β, 3β, 16β, 22, 25-pentaol 1-O-β-D-glucopyranosyl-16-O-β-D-apiofuranoside, together with two known cholestane glycosides were isolated from the tubers of *Polianthes tuberosa*. Their structures were elucidated on the basis of spectroscopic data.

Key words: *Polianthes tuberosa*; Cholestane glycosides; Tuberoside A

The genus *Polianthes*, comprising about 12 species, is native to Mexico. *Polianthes tuberosa* L., a well-known ornamental plant, is widely cultivated in the south of China. Three steroidal sapogenins were isolated from the tubers of *P. tuberosa* (Zhou *et al*, 1965). But there is no report about steroidal glycosides in the tubers of *P. tuberosa*. During the investigation of steroidal constituents of *P. tuberosa*, three cholestane glycosides including a new cholestane glycoside were isolated from the tubers of *P. tuberosa*. Two known cholestane glycosides **1** and **2** were identified as (22S)-cholest-5-en-1β, 3β, 16β, 22-tetraol 1-O-β-D-glucopyranosyl-16-O-β-D-apiofuranoside (**1**) (Mimaki *et al*, 2000) and (22S)-cholest-5-en-1β, 3β, 16β, 22-tetraol 3, 16-di-O-β-D-glucopyranoside (**2**) (Mimaki *et al*, 1995), respectively.

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Results and Discussion

Compound **3** was obtained as an amorphous solid, $[\alpha]_D^{20.1}$ −24.51° (*c* 0.1489, pyridine). Its molecular formula was deduced as $C_{38}H_{64}O_{14}$ on the basis of ^{13}C DEPT NMR and the negative ion FAB-MS, which showed a quasi-molecular peak at *m/z* 743 $[M-H]^-$. The negative ion FAB-MS of **3** exhibited two fragment ion peaks at *m/z* 611 $[M-H-132]^-$ and 581 $[M-H-162]^-$, except the molecular ion peak at *m/z* 743 $[M-H]^-$. Its ^1H spectrum showed signals for three tertiary methyl groups at δ_H 0.96, 1.27 and 1.41, one secondary methyl groups at δ_H 1.02 (3H, d, J = 7.6 Hz). In addition, two anomeric proton signals were observed at δ_H 4.97 (1H, d, J = 7.0 Hz) and 5.46 (1H, br s).

Comparing the ^{13}C NMR data of **3** with those of **1** (table 1), the signals of the two compounds including the signals of sugar moieties were identical to each other, except for those of C − 23 to C − 27, indicating that the β-D-glucopyranosyl unit should be attached to C − 1 position of the aglycone and the β-D-apiofuranosyl unit should be attached to C − 16 position of the aglycone. DEPT spectrum of **3** indicated that it afforded one more quaternary carbon signal at δ_C 70.1, and lost one more carbon than those of **1**. By comparison of the chemical shifts of C − 26 and C − 27 (δ_C 29.9 and 30.2) of **3** with those of **1** (δ_C 23.1 and 23.1), the downfield shifts (+6.8 and 7.1 ppm) of C − 26 and C − 27 suggested the carbon signal at δ_C 70.1 should be assigned to C − 25 of the aglycone. These results indicated that there was a hydroxyl group was attached to C-25 of **3**.

Table 1 ^{13}C NMR data of compounds **1** − **3**

Aglycone	1	2	3	Sugar	1	2	3
1	83.0 (d)	83.0 (d)	82.9 (d)	Glc_1 1	101.3 (d)	101.4 (d)	101.4 (d)
2	37.6 (t)	37.6 (t)	37.6 (t)	2	75.5 (d)	75.6 (d)	75.5 (d)
3	68.2 (d)	68.2 (d)	68.1 (d)	3	78.7 (d)	78.8 (d)	78.7 (d)
4	43.8 (t)	43.8 (t)	43.8 (t)	4	72.5 (d)	72.5 (d)	72.5 (d)
5	139.7 (s)	139.6 (s)	139.6 (s)	5	78.2 (d)	78.3 (d)	78.4 (d)
6	125.0 (d)	125.1 (d)	124.8 (d)	6	63.7 (t)	63.7 (t)	63.7 (t)
7	31.9 (t)	32.0 (t)	31.8 (t)	Api_{16} 1	112.7 (d)		112.9 (d)
8	33.3 (d)	33.3 (d)	33.2 (d)	2	78.2 (d)		78.1 (d)
9	50.4 (d)	50.4 (d)	50.3 (d)	3	80.5 (s)		80.2 (s)
10	42.9 (s)	43.0 (s)	42.8 (s)	4	66.2 (t)		65.9 (t)
11	24.0 (t)	24.0 (t)	23.9 (t)	5	75.2 (t)		75.1 (t)
12	40.6 (t)	40.7 (t)	40.6 (t)	Glc_{16} 1		107.1 (d)	
13	42.1 (s)	42.3 (s)	42.0 (s)	2		75.8 (d)	
14	55.2 (d)	55.3 (d)	55.2 (d)	3		78.9 (d)	
15	36.6 (t)	37.4 (t)	36.6 (t)	4		71.8 (d)	
16	81.3 (d)	82.9 (d)	81.5 (d)	5		78.3 (d)	
17	58.0 (d)	58.3 (d)	58.1 (d)	6		63.0 (t)	
18	13.7 (q)	14.4 (q)	13.6 (q)				
19	14.9 (q)	14.9 (q)	14.8 (q)				
20	35.7 (d)	36.1 (d)	36.0 (d)				
21	12.0 (q)	12.7 (q)	12.1 (q)				
22	72.7 (d)	72.5 (d)	73.2 (d)				
23	34.5 (t)	34.0 (t)	35.8 (t)				
24	36.6 (t)	36.9 (t)	41.9 (t)				
25	28.9 (d)	29.1 (d)	70.1 (s)				
26	23.1 (q)	23.2 (q)	29.9 (q)				
27	23.1 (q)	23.3 (q)	30.2 (q)				

In HMBC spectrum, methyl proton signal at δ_H 1.41 (3H, s, H-26 and H-27) was correlated with carbon signals at δ_C 29.9 (CH_3, C-26), 30.2 (CH_3, C-27), 41.9 (CH_2, C-24) and 70.1 (C, C-25). In addition, Three-bond ^1H-^{13}C long-range correlations were observed that the anomeric proton signals were correlated with the carbon signals at δ_H 4.97 (H-Glc-1) and δ_C 82.9 (C-1 of aglycone), δ_H 5.46 (H-Api-1) and δ_C 81.5 (C-16 of aglycone) (Fig. 1). Thus, the chemical structure of **3** was determined as (22S)-cholest-5-en-1β, 3β, 16β, 22, 25-pentaol 1-O-β-D-glucopyranosyl-16-O-β-D-apiofuranoside, which was named as tuberoside A.

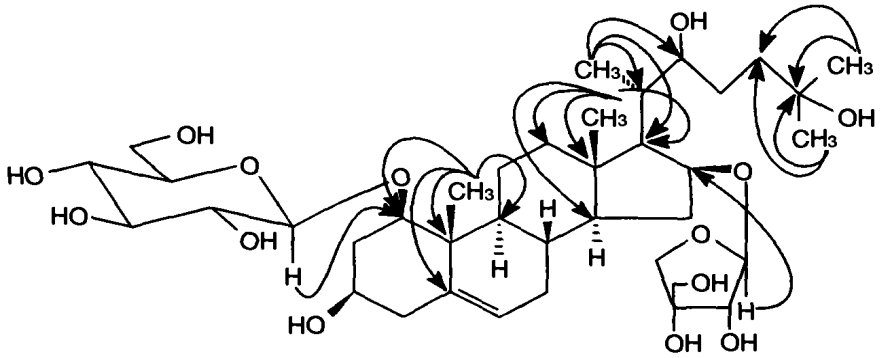

Fig. 1 The key $^1H-^{13}C$ long-range correlations of **3** in the HMBC spectrum

Experimental Section

General Optical rotations were measured with HORIBA SEPA-300 high-sensitive polarimeter. IR (KBr) spectra were measured on Bio-Rad FTS-135 spectrophotometer. NMR spectra were recorded on a Bruker DRX-500 instrument at 25℃, using TMS as an internal standard. The negative ion and high-resolution FAB mass spectra were recorded on a VG AutoSpec-3000 mass spectrometer using glycerol as matrix. Precoated silica gel plates (Qingdao Haiyang Chemical Co.) were used for TLC. Detection was done by spraying the plates with 5 % anisaldehyde-sulphric acid, followed by heating.

Plant material The fresh tubers of *P. tuberosa* L. cv Double were collected from Kunming Qianhui Seed and Seedling Limited Company at June 2001.

Extract and isolation The fresh tubers of *P. tuberosa* (24 kg) were extracted with hot 80% ethanol three times for 4 hours, the combined extract was concentrated under reduced pressure. Then concentrated extract was partitioned between *n*-butanol and water. Half the *n*-butanol layer (450 g) was repeatedly chromatographed on silica gel with $CHCl_3$: MeOH: H_2O and RP-8 with MeOH: H_2O to give **1** (345 mg), **2** (2.2 g) and **3** (50 mg).

Compound 1 A white amorphous powder: $[\alpha]_D^{17.1}$ −38.76° (*c* 0.0387, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3408 (OH), 2944 (CH), 1651, 1464, 1382, 1159, 1075, 1015, 988, 835. Negative ion FAB-MS *m/z*: 727 $[M-H]^-$; ^1H NMR (pyridine-d_5, 500 MHz): δ 3.92 (1H, m, H-1), 3.82 (1H, m, H-3), 5.55 (1H, br d, J = 4.7 Hz, H-6), 4.35 (1H, m, H-16), 1.03 (3H, s, H-18), 1.26 (3H, s, H-19), 1.18 (3H, d, J = 5.7 Hz, H-21), 4.20 (1H, H-22), 0.87 (3H × 2, d, J = 5.5 Hz, H-26 and H-27), 4.95 (1H, d, J = 7.0 Hz, H-Glc-1), 5.48 (1H, br s, H-Api-1); ^{13}C NMR data see table 1.

Compound 2 A white amorphous powder: $[\alpha]_D^{16.8}$ −14.43° (*c* 0.0537, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3369 (OH), 2951 (CH), 1699, 1652, 1382, 1163, 1071, 1020, 985, 932, 892, 839; Negative ion FAB-MS *m/z*: 757

$[M-H]^-$, 595 $[M-H-162]^-$; ^1H NMR (pyridine-d_5, 500 MHz): δ 3.93 (1H, m, H-1), 3.82 (1H, m, H-3), 5.48 (1H, br d, J=4.9 Hz, H-6), 4.31 (1H, m, H-16), 1.00 (3H, s, H-18), 1.23 (3H, s, H-19), 1.15 (3H, d, J=6.9 Hz, H-21), 4.20 (1H, H-22), 0.91 (6H, d, J=6.1 Hz, H-26 and H-27), 4.95 (1H, d, J=7.7 Hz, H-Glc_1-1); 4.73 (1H, d, J=7.8 Hz, H-Glc_{16}-1); ^{13}C NMR data see table 1.

Compound 3 A white amorphous powder: $[\alpha]_D^{20.1}$ −24.51° (*c* 0.1489, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3407 (OH), 2940, 2881, 1652, 1465, 1379, 1267, 1224, 1158, 1077, 1053, 990, 955, 909, 835; Negative ion FAB-MS *m/z*: 743 $[M-H]^-$, 611 $[M-H-132]^-$, 581 $[M-H-162]^-$; HR FAB-MS *m/z*: 743.4177 $[M-H]^-$ (calcd for $C_{38}H_{63}O_{14}$, 743.4218); ^1H NMR (pyridine-d_5, 500 MHz): δ 3.94 (1H, m, H-1), 3.82 (1H, m, H-3), 5.55 (1H, br d, J=4.6 Hz, H-6), 4.34 (1H, m, H-16), 0.96 (3H, s, H-18), 1.27 (3H, s, H-19), 1.02 (3H, d, J=7.6 Hz, H-21), 1.41 (6H, s, H-26 and H-27), 4.97 (1H, d, J=7.0 Hz, H-Glc-1), 5.46 (1H, br s, H-Api-1); ^{13}C NMR data see table 1.

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