Note

A new pentacyclic triterpene, gmeliniin A, from *Echinops gmelinii* Turcz

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Gmeliniin A, a new pentacyclic triterpene of ursane series isolated from the aerial parts of *Echinops gmelinii*, is elucidated structurally as 1 on the basis of 1D and 2D NMR spectroscopic studies.

Keywords *Echinops gmelinii*, compositae, triterpenoid

Introduction

Echinops gmelinii Turcz (Compositae) grows widely in China. The root of this plant is utilized as antipyretic, antidote, draining pus and promoting lactation by the native populations.[1] No phytochemical research has so far been reported on the title plant. A systematic study on the dried aerial parts has resulted in the isolation of a new pentacyclic triterpene, Gmeliniin A. Its structure has been elucidated as urs-20(30)-en-3β,21α-diol.

Results and discussion

EtOAc soluble fraction of *Echinops gmelinii* was subjected to repeated column chromatography and further purified by recrystallization to furnish Gmeliniin A(**1**) (Fig. 1) as colorless needles, mp: 122.5—124℃. It gave a positive response to Liebermann-Buchard test, suggesting the compound a triterpenoid. Compound **1** has molecular formula $C_{30}H_{50}O_2$ as determined by HREIMS and confirmed by ^{13}C NMR and DEPT analysis. The IR spectrum of **1** showed absorption bands at 3400, 3350, 1305 cm^{-1} (hydroxy groups) and 1640, 880 cm^{-1} (a methylene group). Its ^{13}C NMR spectrum (Table 1) revealed 30 carbon signals, which were assigned by DEPT as seven methyl, ten methylene, five methine, two alcoholic methine, and six quaternary (including an olefinic carbon) carbons. The ^1H NMR spectrum of **1** showed signals for vinyl protons (broad singlets at δ 4.89 and 4.98, 1H each), two oxygenated protons at δ 3.20 (dd, J = 11.0, 5.0 Hz, 1H) and δ 4.40 (dd, ^3J = 9.5, 5.3 Hz, 1H), one secondary methyl group (doublet at δ 1.20, d, J = 6.6 Hz), and six tertiary methyls (singlets at δ 0.77, 0.76, 0.85, 0.95, 0.97 and 1.01). These findings outlined a pentacyclic ursane-type triterpenoid skeleton, whereas in which the typical olefinic proton 12-H existed in most ursane triterpenes was absent. It only exhibited two exo-cyclic vinyl protons at δ 4.89, 4.98 (br. s, each 1H). Meanwhile the electron impact mass spectrum of **1** showed characteristic fragment peaks (m/z 207, 234, 273 and 289) indicating a pentacyclic triterpene of the ursane series in which rings A, B, C and D are saturated.[2] Furthermore, the significant peaks (m/z 207 and 234) arising from the typical C-ring cleavage of ursane triterpenes revealed that two hydroxyl groups were present in **1** with one located in ring A/B and another in ring D/E.[2-4] These fragment peaks also suggested the possible positions 19(29) or 20(30) for the exo-methylene, consisted with only one secondary methyl group observed in the ^1H NMR spectrum.

Conclusive evidence for the structure **1** was derived

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from the results of extensive 2D NMR experiments as shown in Fig. 2 that the presence of 3β-OH was supported and confirmed by NOE correlations of 3α-H with 23-Me and 5-H in its NOESY experiment. In ^2J and ^3J HMBC experiments, the alcoholic methine carbon at δ 71.4(d) showed correlation with exo-methylene proton at δ 4.98(br.s), while the quateary vinyl carbon at δ 158.5(s) was correlated with the secondary methyl protons at δ 1.20(d, J = 6.6 Hz), indicating that both the carbon bearing secondary methyl and the alcoholic methine carbon were adjacent to the vinyl carbon, so C-20 (30) was the only possible position for the exo-methylene.[2,4,5]

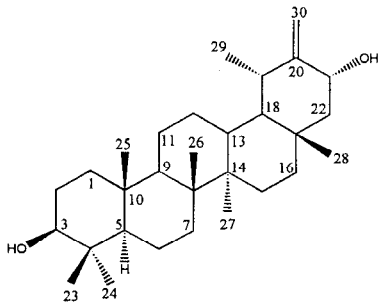

Fig. 1 Structure of gmeliniin A (**1**).

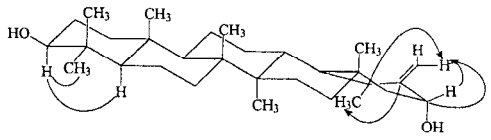

Fig. 2 Main NOESY and HMBC cross-peaks (curves represent NOE correlations while arrows stand for HMBC correlations from C to H).

The orientation of the hydroxy group at C-21 could be established as α-oriented from NOE correlation between 21-H and one of the vinyl proton in the NOESY spectrum (see Fig. 2). Therefore, the structure of **1** could be deduced as urs-20(30)-en-3β, 21α-diol, as shown in Fig. 1. Compound **1** is a 21α-hydroxy derivative of taraxasterol, which was isolated from *Euphorbia supina*.[4]

Experimental

General

Melting point was recorded on a Buchi-535 instrument and uncorrected. MS were recorded at 70 eV on a HP 5989A MS instrument. ^{1}H and ^{13}C NMR were recorded on a Bruker AM 400 NMR spectrometer using $CDCl_3$ as solvent and TMS as reference. Column Chromatography: silica gel (200—300 mesh).

Table 1 NMR assignments for compound **1** (δ with reference to the signal $CDCl_3$)

Atom	H	C
1	1.52—1.56(m), 1.68—1.71(m)	38.1
2		27.4
3	3.20(dd,11.0,5.0 Hz)	78.9
4		38.4
5	0.71(br.d, 9.0 Hz)	55.3
6	1.50—1.53(m), 1.30—1.33(m)	18.2
7		34.0
8		40.9
9	1.31—1.33(m) (overlap)	50.4
10		38.1
11	1.53—1.56(m), 1.58—1.61(m)	21.4
12		26.3
13		38.0
14		42.1
15		37.6
16		26.2
17		42.0
18	1.18(br.d, overlap)	48.4
19	2.19—2.21(m)	38.7
20		158.0
21	4.40(dd, 9.5,5.3 Hz)	71.4
22	1.95(dd, 9.0, 9.5 Hz), 2.20(m)	48.7
23	0.95(s, 3H)	15.9
24	0.77(s, 3H)	28.4
25	0.85(s, 3H)	15.4
26	0.97(s, 3H)	14.7
27	0.76(s, 3H)	16.3
28	1.01(s, 3H)	27.9
29	1.20(d, 6.6 Hz, 1H)	19.1
30	4.89,4.98(br.s, each 1H)	113.2

Plant material

The aerial parts of *E. Gemini* Turcz were collected from Ninxia province, China, in August 1997. A voucher specimen is deposited in the herbarium of Lanzhou Medical University.

Extraction and isolation

Dried and powdered whole herb (10 kg) were continuously extracted with 95% EtOH at room temperature. The EtOH extracts were combined and concentrated *in vacuo* to give crude extract (1.2 kg). This was fractionated into Petrol- and EtOAc-sol. The EtOAc-sol fraction (196 g) was subjected to column chromatography (silica gel, 600 g) with petrol-Me_2CO (9:1—1:1) as eluant. The fractions (9:1 and 8:2 parts) were further purified by silica gel CC and recrystallization to afford gmeliniin A (**1**, 26 mg) as white needles.

Gmeliniin A (**1**), colourless needles, mp: 122.5—124℃. ν_{max} (KBr): 3400, 3381, 1642, 1305 and 880 cm^{-1}. EIMS (*m/z*): 443$[M+1]^+$(4), 425(3), 289(2), 273(3), 234(4), 207(25), 189(33), 163(14), 149(16), 123(31), 109(37), 95(51), 69(74), 57(87) and 43(100). HREIMS (*m/z*): 442.3814 (Calcd. 442.3811). ^1H and ^{13}C NMR: see Table 1.

Acknowledgments

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