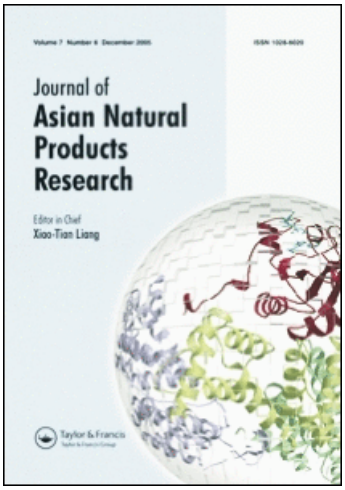

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

Note: A new cycloartane glycoside from *Comptosorus sibiricus* rupr.

Ning Li[a]; Xian Li[a]; Zhong-Jun[a]; Jin-Hui Wang[a]
[a] Research Department of Natural Medicine, Shenyang Pharmaceutical University, Shenyang, China

To cite this Article Li, Ning , Li, Xian , Zhong-Jun and Wang, Jin-Hui(2005) 'Note: A new cycloartane glycoside from *Comptosorus sibiricus* rupr.', Journal of Asian Natural Products Research, 7: 2, 161 — 164
To link to this Article: DOI: 10.1080/10286020310001617183
URL: http://dx.doi.org/10.1080/10286020310001617183

Journal of Asian Natural Products Research, Vol. 7, No. 2, April 2005, 161–164

Note

A new cycloartane glycoside from *Comptosorus sibiricus* rupr.

NING LI, XIAN LI*, ZHONG-JUN MA and JIN-HUI WANG

Research Department of Natural Medicine, Shenyang Pharmaceutical University, Shenyang 110016, China

(Received 9 May 2003; revised 11 June 2003; in final form 17 June 2003)

The structure of a new cycloartane glycoside isolated from the whole herbs of *Comptosorus sibiricus* Rupr. has been established, by chemical and spectroscopic methods (IR, 1D and 2D NMR, HRMS, ESI-MS), as 3β,7β,24β,25,30-pentahydroxycycloartane 24-*O*-β-D-glucopyranoside (**1**).

Keywords: *Comptosorus sibiricus*; Cycloartane glycoside

1. Introduction

Comptosorus sibiricus is a herbal medicine, widely distributed in the North of China, that has activity in the dilatation of blood vessels. Some flavonoids from the herb with such activity have been documented [1]. We report here the isolation and structural elucidation of a new cycloartane glycoside.

2. Results and discussion

A 70% ethanol extract of the air-dried whole herbs of *C. sibiricus* was separated by liquid–liquid extraction. Further purification of the resulting EtOAc fraction by repeated silica-gel column chromatography, eluting with $CHCl_3$–MeOH and EtOAc–MeOH, led to the isolation of compound **1** (figure 1).

Compound **1** was isolated as white powder, mp 230–233°C. It showed a positive reaction with the Molish reagent. The sugar was identified as glucose by acid hydrolysis and co-TLC with an authentic sample. The IR spectrum of **1** shows hydroxyl absorption bands at ν_{max} 3390 cm^{-1} (OH). The HRMS spectrum shows a molecular ion peak at *m/z* 677.4251, compatible with the molecular formula $C_{36}H_{62}O_{10}$. The ESI-MS spectrum

*Corresponding author. Tel.: +86-24-23902286. Fax: +86-24-23841116. E-mail: lixian@mail.sy.ln.cn

Journal of Asian Natural Products Research
ISSN 1028-6020 print/ISSN 1477-2213 online © 2005 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/10286020310001617183

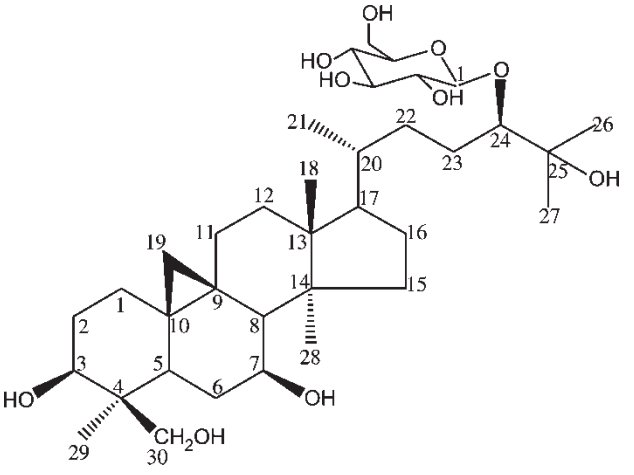

Figure 1. Structure of compound **1**.

shows a quasi-molecular ion peak $[M + H]^+$ at *m/z* 655.0 and the fragment $[M + 2H - 162]^+$ at *m/z* 494.4, represent the loss of 1 mole of hexose from the parent molecular ion. The ^{1}H NMR spectrum of **1** shows characteristic signals [2] of cyclopropane methylene protons at δ 0.30 (1H, br. s, H-19a) and 0.38 (1H, br. s, H-19b), five tertiary methyl and one secondary methyl groups at δ 0.92 (3H, s, 28-CH_3), 0.97 (3H, s, 18-CH_3), 1.76 (3H, s, 26-CH_3), 1.59 (3H, s, 27-CH_3), 1.52 (3H, s, 29-CH_3), and 1.12 (3H, d, $J = 6.3$ Hz, 21-CH_3). Additionally, the signal of the anomeric proton appears at δ 5.21 (1H d, $J = 7.8$ Hz, H-1′); thus, the anomeric center of the glucose was confirmed as having a β orientation. The signals at δ 3.71 (1H, t-like, H-3), 3.80 (1H, br. S, H-24), and 4.27 (1H, m, H-7) indicate protons with the carbon oxygenated. The ^{13}C NMR spectrum of **1** has 36 carbon signals, of which five oxygen-bearing carbons of the aglycone appear at δ 80.2 (C-3), 67.4 (C-7), 94.0 (C-24), 73.5 (C-25), and 64.6 (C-30),

Table 1. NMR data of **1**.

No.	δ_H	δ_C	*No.*	δ_H	δ_C
1		32.8	19	0.30, 0.38 (each 1H, br. s)	30.4
2		32.4	20		35.9
3	3.71 (1H, t-like, $J = 9.0$ Hz)	80.2	21	1.12 (3H, d, $J = 6.3$ Hz)	18.3
4		43.8	22		33.4
5	2.50 (1H, t, $J = 12.6$ Hz)	43.0	23		30.0
6		31.8	24	3.80 (1H, br. s)	94.0
7	4.27 (1H, m)	67.4	25		73.5
8	1.36 (1H, m)	48.3	26	1.76 (3H, s)	26.5
9		21.7	27	1.59 (3H, s)	26.7
10		26.1	28	0.92 (3H, s)	19.6
11		28.5	29	1.52 (3H, s)	21.2
12		35.9	30	3.82 (1H, d, $J = 10.6$ Hz) 4.70 (1H, d, $J = 10.6$ Hz)	64.6
13		45.7	1′	5.21 (1H, d, $J = 7.8$ Hz)	107.1
14		47.8	2′		76.0
15		33.4	3′		78.6
16		27.0	4′		71.7
17		53.8	5′		78.3
18	0.97 (3H, s)	18.6	6′		62.8

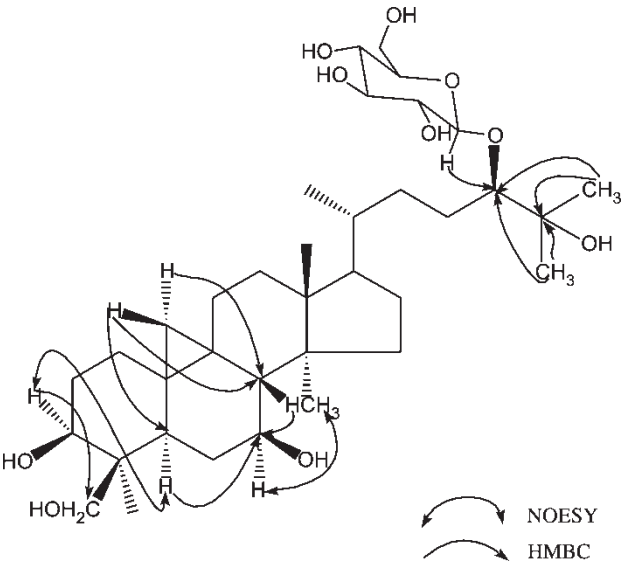

Figure 2. Important HMBC and NOSEY correlations of **1**.

along with the carbon signals ascribed to the sugar unit at δ 107.1 (C-1), 76.0 (C-2), 78.6 (C-3), 71.7 (C-4), 78.3 (C-5), and 62.8 (C-6) (table 1).

In the HMBC experiment (figure 2), the long-range correlations between δ 1.52 (H-29), 3.82 (H-30a), 4.70 (H-30b) and δ 80.2 (C-3), as well as δ 1.52 (H-29) and δ 64.6 (C-30), indicate that C-3 and C-30 are substituted by hydroxyl groups. In addition, δ 2.50 (H-5), 1.36 (H-8) shows long-range correlations with δ 67.4 (C-7), and in the NOESY spectrum of **1** there are correlations between proton H-5 and H-3, H-7 and H-28; thus, the 7-OH was determined. Furthermore, the configurations of 3- and 7-OH were determined as β. The partial fragments were also deduced from HMBC (figure 2), combined with HMQC, NOESY and ^{1}H–^{1}H COSY spectra; the aglycone of **1** was determined as 3β,7β,24,25,30-pentahydroxy-9,19-cycloartane. The anomeric proton of β-D-glucose at δ 5.21 (1H, d, J = 7.8 Hz) shows a long-range correlation to δ 94.0 (C-24), suggesting that the sugar is connected to C-24. The ^{1}H and ^{13}C NMR data for H-24 and C-24 of **1** are comparable with those reported for analogous compounds having a 24*R* configuration [3–5]. From the data above, the structure of **1** was established as 3β,7β,24β,25,30-pentahydroxycycloartane 24-*O*-β-D-glucopyranoside (**1**).

3. Experimental

3.1 General experimental procedures

The melting point was measured on a Yamaco-hot-stage and is uncorrected. NMR spectra were recorded on a Bruker ARX-300 spectrometer, using TMS as an internal standard. IR spectra were measured on a Perkin–Elmer 2000 FT–IR spectrometer as KBr pellets. ESI-MS was performed on a Finnigan LCQ mass spectrometer. HRMS was performed on a QSTAR LCQ mass spectrometer. The optical rotation was measured on Perkin–Elmer 241 polarimeter. Silica gel for chromatography was produced by the Qingdao Ocean Chemical Group Co. of China.

3.2 Plant material

The plant material was collected in Beining City, Liaoning Province, China, in July 2002, and was identified by Professor Qishi Sun (Shenyang Pharmaceutical University). A voucher specimen (No. 20020701) has been deposited in the Research Department of Natural Medicine, Shenyang Pharmaceutical University.

3.3 Extraction and isolation

Dried whole herbs (4.2 kg) of *Comptosorus sibiricus* were extracted with 70% ethanol. The extract was concentrated *in vacuo* and then partitioned with petroleum ether, EtOAc and n-BuOH successively. The EtOAc extract (38 g) was subjected to column chromatography on silica gel gradiently eluted with $CHCl_3$–MeOH; fraction 11 [$CHCl_3$–MeOH (100:15), 800 mg] was then chromatographed on a silica-gel column eluted with EtOAc–MeOH (100:7) to give compound **1** (6.0 mg).

Compound **1**: a white powder (MeOH), mp 230–233°C, $[\alpha]_D^{20} = +2.4$ (c 0.001, MeOH). IR (KBr pellet) ν_{max} (cm^{-1}): 3390 (OH), 2935 (CH), 1048 (C–O). ^1H (300 MHz, pyridine-d_5) and ^{13}C NMR (75 MHz, pyridine-d_5) data: see table 1. HRMS: m/z 677.4251 (calcd for $C_{36}H_{62}O_{10}$-Na, 677.4241). ESI-MS: m/z 655 $[M + H]^+$.

Acknowledgements

Special thanks are due to the Analytical Detective Center, Shenyang Pharmaceutical University, for recording IR, ESI-MS and NMR spectra.

References

[1] B.F. Zhang, S.J. Wang. *J. Shengyang Coll. Pharm.*, **11**, 29–35 (1979).
[2] H.M. Hua, X. Li, Y.H. Pei. *Nat. Prod. Res. Dev.*, **13**, 65–70 (2001).
[3] M.I. Isaev, M.B. Gorovits, N.K. Abubakirov. *Chem. Nat. Compd. (Engl. Transl.)*, 684–687 (1989).
[4] M.I. Isaev, B.A. Imomnazarov, Y.M. Fadaev, P.A. Kintya. *Chem. Nat. Compd. (Engl. Transl.)*, 315–320 (1992).
[5] I. Calis, M. Zor. *J. Nat. Prod.*, **59**, 1019–1023 (1996).