J. Basic Microbiol. **45** (2005) 4, 328–330 DOI: 10.1002/jobm.200410531

Short Note

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A new bitter diterpenoid from *Sarcodon scabrosus*

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(Received 17 November 2004/Accepted 29 November 2004)

The new cyathane-type diterpenoid sarcodonin I was isolated from the fruiting bodies of the basidiomycete *Sarcodon scabrosus*. Its structure was determined on the basis of spectroscopic means, including 2D-NMR (HMBC, HMQC, ROESY, ^{1}H, ^{1}H-COSY).

Sarcodon scabrosus is a mushroom belonging to the family *Thelephoraceae* and has a bitter taste. Diterpenoids, including sarcodonins A–H, scabronines A–F and scabronines L and M have previously been isolated from this mushroom as the bitter principles (SHIBATA *et al*. 1989, OHTA *et al*. 1998, KITA *et al*. 1998). All these diterpenoids posses a cyathane skeleton consisting of angularly condensed five-, six and seven-membered rings and show stimulating activity of nerve growth factor (NGF)-synthesis *in vitro*. In continuing our studies on basidiomycete-derived bioactive secondary metabolites, the chemical constituents of the mushroom *Sarcodon scabrosus* from Yunnan, China were investigated. This report describes the structural elucidation of a new compound named sarcodonin I.

The entire freshly collected fruiting bodies of *S. scabrosus* (dry weight after extraction 150 g) were immersed in 95% EtOH and left at room temperature for several days. Then the EtOH extract was decanted and evaporated *in vacuo*. The residue was extracted with $CHCl_3$ for 4 times. The extract (70 g) was fractionated by column chromatography (silica gel, eluted with petroleum ether/acetone 9:1, 8:2, 7:3, 6:4, v/v). The fraction eluted by petroleum ether/acetone (6:4, v/v) was submitted for further purification by reverse phase column chromatography (RP-8, MeOH/H_2O 6:4) to give sarcodonin I (6 mg).

Sarcodonin I was obtained as a yellow oil, $[\alpha]^{20}_D = +374.8°$ ($c = 0.2$, MeOH). High-resolution ESI-MS (pos.) gave an ion peak at *m/z* 355.1884 (*m/z* 355.1885 calculated for $C_{20}H_{28}O_4Na$). ^{1}H-NMR spectrum of sarcodonin I showed the hydrogens signals of two secondary methyls and two tertiary methyls at δ 0.94 (3H, d, $J = 6.8$ Hz) and δ 1.01 (3 H, s), respectively (Table 1). The former methyl hydrogen signal and another methylene protons (3.49, 2 H, m) were spin-coupled with a methine hydrogen signal at δ 3.12 (1 H, m), demonstrating the presence of an isolated system –CH(CH_3)–CH_2OH. ^{13}C-NMR of sarcodonin I showed one oxymethine and two oxymethylene carbons (δ 74.4, CH; 66.1, CH_2; 65.3, CH_2), and one tetrasubstituted doubled bond (δ 144.6, C; 142.7, C) and two trisubstituted double bonds (δ 139.7, C; 121.3, CH; 145.6, C; 153.9, CH). Based on the above partial structures, the construction of the molecular framework was deduced from ′H–′H COSY, HMQC and HMBC spectra. Compared with the NMR data of sarcodonin A (SHIBATA *et al*. 1989), the gross structure was given as shown in Fig. 1.

The relative stereochemistry of sarcodonin I was established by ROESY experiments. ROESY corrections at H-14/H-16, and H-14/H-7α,H-8α indicated that these protons were situated in the same side. In addition, ROESY correction at H-7β/H-8β confirmed the structure of sarcondonin I represented as Fig. 1.

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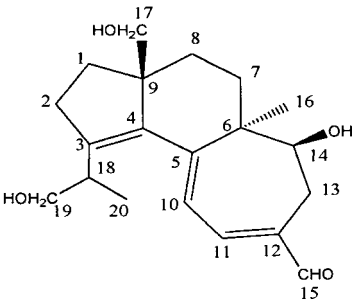
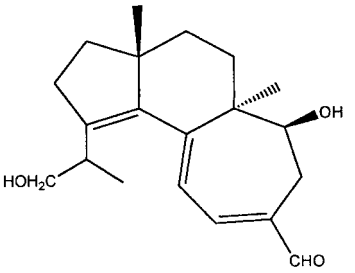
Table 1
NMR spectral data of sarcondonin I (δ ppm, CD_3OD, 400 MHz)

position	δ_H	δ_C
1	1.65 (m), 2.06 (m)	31.8
2	β 2.06 (m) α 2.38 (m)	29.8
3		144.6
4		142.7
5		139.7
6		48.5
7	β 1.50 (m) α 2.39 (m)	33.8
8	β 2.15 (m) α 1.35(m)	34.6
9		55.8
10	6.26 (d, J = 8.0 Hz)	121.3
11	6.78 (dd, J = 1.7, 8.0 Hz)	145.6
12		153.9
13	2.95 (dd, J = 7.2, 12.0 Hz)	29.9
14	3.68 (d, J = 7.2 Hz)	74.7
15	9.39 (s)	194.5
16	1.01 (s)	26.8
17	3.33 (d, J = 10.6 Hz) 3.40 (d, J = 10.6 Hz)	65.3
18	3.12 (m)	35.9
19	3.49 (m)	66.1
20	0.94 (d, J = 6.8 Hz)	16.2



sarcodonin I



sarcodonin A

Fig. 1
The structures of sarcodonins I and A

Acknowledgement

This project was supported by the National Natural Science Foundation of China (30470027 and 30225048).

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