SARCIDUMITOL, A NEW NATURALLY OCCURRING 2,6-DIDEOXY-DISACCHARIDITOL FROM *Sarcostemma acidum*

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*A new disaccharidito, sarcidumitol (**1**), has been isolated from the water-soluble fraction of the 95% ethanol extract of the plant* Sarcostemma acidum. *Its structure has been determined on the basis of spectroscopic methods, especially 2D NMR techniques. A 3D structure has been generated by computer molecular modeling, which satisfied all NOE correlations.*

Keywords: *Sarcostemma acidum*, sarcidumitol, NMR, disaccharidito.

Plants of the genus Sarcostemma are rich in disaccharides [1, 2] and pregnane glycosides [3, 4] (mostly cymarosides or diginosides), which have been proved to be the principle of their toxicity on the nervous system of livestock.

The plant *Sarcostemma acidum* (Roxb.), which grows in and over trees and shrubs near the seashore of Hainan Island of China, is a sturdy, succulent, and leafless creeper [5].

In our continuous chemical investigations on this medicinal plant [6], a new disaccharidito, sarcidumitol (**1**), has been isolated from the water-soluble fraction of the 95% ethanol extract. Herein we report the isolation and structure elucidation of this rarely occurring disaccharidito.

The molecular formula of **1** was determined to be $C_{14}H_{28}O_7$ on the basis of the HR-ESI-MS pseudo-ion peak at *m/z* 331.1725 $[M+Na]^+$ (calcd for $C_{14}H_{28}NaO_7^+$, 331.1727).

The IR spectrum of **1** had absorption bands for hydroxyls and glycoside C-O vibrations.

The ^{1}H NMR spectrum of **1** showed the presence of an anomeric proton at δ 4.92 (1H, d, J = 3.7 Hz), two OMe protons at δ 3.39 (3H, s), 3.38 (3H, s), and two methyls at δ 1.22 (3H, d, J = 6.4), 1.18 (3H, d, J = 6.4). The ^{13}C NMR spectrum (with DEPT) exhibited 14 signals, including one anomeric carbon signal at δ 98.7 d, two OMe carbon signals at δ 58.2 q, 56.9 q, and two methyl carbon signals at δ 19.7 q, 18.5 q, which corresponded to the five proton signals above, as well as 6 sp^3 methines and three sp^3 methylenes (one oxygenated). The 1D NMR spectra indicated that sarcidumitol had a 2,6-dideoxy-disaccharidito-like structure.

HMQC and HMBC experiments were carried out to determine the planar structure of **1**. The HMQC spectrum firstly allowed the assignments of all protons to their bonding carbons. In the HMBC spectrum (Fig. 1), long-range correlations of H-1/C-3, H-2α/C-4, OMe-3/C-3, H-3/C-5, H_3-6/C-5, and H_3-6/C-4 established the carbon skeleton of the hexounit, the correlations of H_2-1′/C-3′, H_2-2′/C-3′, OMe-3′/C-3′, H-4′/C-2′, H-4′/C-3′, H-4′/C-5′, and H_3-6′/C-4′ indicated the carbon skeleton of the hexitol unit, and the correlation H-1 and C-4′ showed the 1→4 linkage of the two units. Thus, the planar structure of sarcidumitol was unambiguously determined to be 2,6-dideoxy-3-*O*-methyl-ribo-hexo-(1→4)-2,6-dideoxy-3-*O*-methyl-ribo-hexitol (**1**).

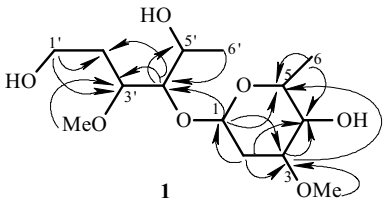

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Fig. 1. Planar structure and key HMBC correlations (H→C) of sarcidumitol (**1**).

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On the basis of ^{1}H coupling constants, NOESY spectrum, specific rotation, as well as literature support [7, 8] and the biological origin of **1**, we determined the stereochemical structure as 2,6-dideoxy-3-*O*-methyl-α-L-ribo-hexopyranosyl-(1→4)-2,6-dideoxy-3-*O*-methyl-D-ribo-hexitol (α-L-cymaropyranosyl-(1→4)-D-cymaritol), which has not been confirmed by classical methods for carbohydrate structure determination because of insufficient materials. Computer modeling gave an optimized 3D structure for **1**, which satisfied all NOE correlations.

Sarcidumitol (**1**) may be the first 2,6-dideoxy-disaccharidol isolated from nature.

EXPERIMENTAL

Optical rotation were measured on a JASCO p-1030 polarimeter. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. NMR spectra were measured on a Bruker AM-400 spectrometer with TMS as internal standard. ESI-MS were carried out on a Finnigan LC Q^{DECA} instrument.

Silica gel (200–300 mesh) was used for column chromatography, and precoated silica gel GF254 plates (Qingdao Haiyang Chemical Co. Ltd., Qingdao, People′s Republic of China) were used for TLC. C_{18} reverse-phased silica gel (150–200 mesh, Merck), and MCI gel (CHP20P, 75–150 μm, Mitsubishi Chemical Industries Ltd.) and Sephadex LH-20 gel (Amersham Biosciences) were used for column chromatography.

Extraction and Isolation. The air-dried and powdered whole plant of *S. acidum* (2.1 kg) was percolated with 95% EtOH at room temperature. After removal of the solvent under reduced pressure, the crude extract (198 g) was dissolved in 80% MeOH, which was partitioned with petroleum ether and EtOAc successively to give three fractions, SAP (116 g), SAE (50 g), and SAW (30 g). The SAW part was subjected to MCI gel column chromatography (0–60% MeOH in gradient) to give five subfractions, SAW1-SAW5. SAW 3 was subjected to Sephadex LH-20 gel column chromatography and later to a reverse-phased C-18 column (20% MeOH) to give sarcidumitol (**1**, 9 mg).

Sarcidumitol (1). Colorless gum. $[\alpha]_D^{20}$ –216° (*c* 1.6 MeOH). IR spectrum (film, ν_{max}, cm^{-1}): 3382 (OH), 2944, 2833, 1454, 1115, 1031 (glycoside C–O), 672. ^{1}H NMR spectrum (CD_3OD, δ, ppm, J/Hz): 4.92 (1H, br.d, J = 3.7, H-1), 4.20 (1H, dq, J = 9.4, 6.4, H-5), 3.82 (1H, dq, J = 6.4, 6.1, H-5′), 3.67 (2H, m, H-1′), 3.60 (1H, dd, J = 4.3, 5.6, H-4′), 3.57 (1H, m, H-3), 3.49 (1H, dt, J = 8.1, 3.3, H-3′), 3.39 (3H, s, 3′-OMe), 3.38 (3H, s, 3-OMe), 3.22 (1H, dd, J = 9.4, 3.2, H-4), 2.33 (1H, ddd, J = 14.9, 3.7, 1.4, H-2α), 1.83 (2H, m, H-2′), 1.69 (1H, ddd, J = 14.9, 4.6, 3.3, H-2β), 1.22 (3H, d, J = 6.4, H-6′), 1.18 (3H, d, J = 6.4, H-6). ^{13}C NMR spectrum (CD_3OD, δ, ppm, multi): 98.7 (d, C-1), 83.0 (d, C-4′), 80.5 (d, C-3′), 77.2 (d, C-3), 74.4 (d, C-4), 69.1 (d, C-5′), 66.5 (d, C-5), 60.5 (t, C-1′), 58.2 (q, 3′-OMe), 56.9 (q, 3-OMe), 34.6 (t, C-2′), 32.5 (t, C-2), 19.7 (q, C-6′), 18.5 (q, C-6). ESI-MS (positive) *m/z* (%): 331 $[M+Na]^+$ (100), 328 (27); HR-ESI-MS *m/z:* 331.1725 (calcd for $C_{14}H_{28}NaO_7^+$, 331.1727).

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