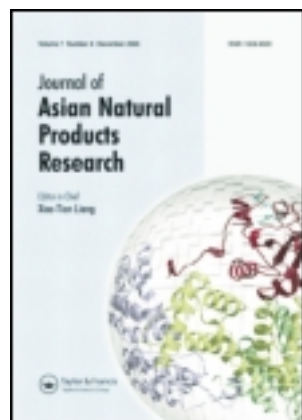


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## Two new triterpenoid glycosides from *Curculigo orchoides*

Ai-Xue Zuo<sup>ab</sup>, Yong Shen<sup>a</sup>, Zhi-Yong Jiang<sup>a</sup>, Xue-Mei Zhang<sup>a</sup>, Jun Zhou<sup>a</sup>, Jun Lü<sup>c</sup> and Ji-Jun Chen<sup>a\*</sup>

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Two new cycloartane triterpenoid glycosides, named curculigosaponin N and curculigosaponin O, were isolated from rhizomes of *Curculigo orchoides* Gaertn. Their structures were elucidated on the basis of comprehensive spectroscopic analysis including IR, MS, 1D, and 2D NMR (HSQC and HMBC).

**Keywords:** *Curculigo orchoides*; cycloartane triterpenoid glycoside; curculigosaponins N–O

### 1. Introduction

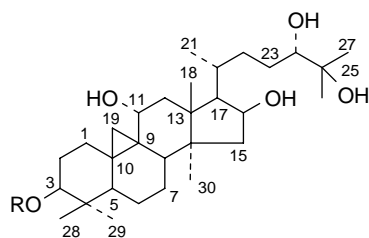
*Curculigo orchoides* Gaertn., belonged to the Hypoxidaceae family and named ‘Xian-Mao’ in Pharmacopoeia of China, mainly distributed in Japan, China, Malaysia, India, and Australia [1]. Its rhizomes have been employed as an analeptic agent for the treatment of decline in strength, against jaundice and asthma [1]. Previous investigation on this plant revealed that it contained cycloartane triterpenoid saponins [2–5], phenolic glycosides [6–8], and chlorophenyl glycosides [9]. Some compounds from *C. orchoides* exhibited biological activities including stimulation of the immune response [10,11], antioxidative activities [8], antidepressant activities [12], and cytotoxic activities [4,5]. Recently, several novel phenolic glycosides [13–16] in this genus have been elucidated by our group, meanwhile, some isolated phenolic derivatives displayed significant antidepressant effect [12] and anti-hepatitis B virus (HBV) activities [13]. To further

find structurally new chemical constituents from this medicinal plant, we explored its phytochemical composition. Our reinvestigation resulted in the isolation of two new cycloartane triterpenoid glycosides, named curculigosaponin N and curculigosaponin O. This paper deals with the isolation and structural elucidation of the two new compounds (**1** and **2**; Figure 1).

### 2. Results and discussion

Compound **1** was isolated as an amorphous powder with  $[\alpha]_D^{25} - 3.41$  (*c* 0.18, MeOH); its molecular formula was determined to be C<sub>42</sub>H<sub>72</sub>O<sub>14</sub> based on HR-ESI-MS at  $m/z$  799.4841 [M – H]<sup>–</sup>. Negative mode FAB-MS exhibited quasi-molecular ion and fragment ions at  $m/z$  799 [M – H]<sup>–</sup>, 653 [M – H – 146]<sup>–</sup>, and 491 [M – H – 146 – 162]<sup>–</sup>, suggesting the presence of hexose moiety in the molecule of compound **1**. Acid hydrolysis of compound **1** with 2 M H<sub>2</sub>SO<sub>4</sub> liberated rhamnose and glucose detected by comparison

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Curculigosaponin N (1) R = Rha(1-2)Glc

Curculigosaponin O (2) R = Glc(1-3)Glc(1-2)Glc

Figure 1. The structures of compounds **1** and **2**.

with authentic samples on paper chromatography (PC). IR showed the absorption bands for hydroxy ( $3438\text{ cm}^{-1}$ ), saturated methenes ( $2926\text{ cm}^{-1}$ ), and glycosidic bonds ( $1036\text{ cm}^{-1}$ ).  $^1\text{H}$  NMR spectrum of compound **1** revealed the presence of characteristic cyclopropane methylene proton resonances at  $\delta_{\text{H}}$  0.26 (1H, d,  $J = 3.2\text{ Hz}$ , H-19a) and 0.43 (1H, d,  $J = 3.2\text{ Hz}$ , H-19b), six singlet methyl resonances at  $\delta_{\text{H}}$  1.22, 1.26, 1.28, 1.30, 1.10, and 1.43 (each 3H, s, H-18, H-28, H-29, H-30, H-25, H-26) assignable to cycloartane-type aglycone, together with two anomeric proton signals at  $\delta_{\text{H}}$  4.93 (1H, d,  $J = 6.9\text{ Hz}$ , H-1') and 6.58 (1H, br. s, H-1''), implying the presence of one  $\beta$ -linked glucosyl moiety and one  $\alpha$ -linked rhamnosyl moiety. Rhamnosyl unit further supported by the methyl signal at  $\delta$  1.46 (3H, d,  $J = 6.1\text{ Hz}$ , H-6''). The  $^{13}\text{C}$  NMR spectrum of compound **1** exhibited 42 carbon signals, of which aglycone included seven methyl carbon signals at  $\delta_{\text{C}}$  15.7, 17.4, 18.8, 22.0, 25.7, 25.8, and 26.5 and five oxygen-bearing carbons at  $\delta_{\text{C}}$  72.1, 72.5, 72.6, 77.1, and 88.6. The  $^{13}\text{C}$  NMR data also confirmed the presence of two sugar moieties with anomeric carbons at  $\delta_{\text{C}}$  105.4 (d) and 101.8 (d), respectively. Above NMR data were similar to those of curculigosaponin L [2] except that C-25 in compound **1** was shifted downfield to  $\delta_{\text{C}}$  72.6, indicating that C-25 was substituted by a hydroxyl

group. This inference was further supported by the correlations observed from H-26 and H-27 to C-25 in HMBC experiment. In addition, the HMBC correlations observed from H-1' at  $\delta_{\text{H}}$  4.93 (1H, d,  $J = 6.9\text{ Hz}$ ) to C-3 and from H-1'' at  $\delta_{\text{H}}$  6.58 (1H, br.s) to C-2' demonstrated that the inner glucopyranosyl unit was attached to C-3 of aglycone, and the rhamnopyranosyl moiety was linked to C-2' of the inner glucose (Figure 2). Based on the above evidence, compound **1** was elucidated as 25-hydroxyl-curculigosaponin L, and named curculigosaponin N (**1**; Figure 1).

Compound **2**, obtained as an amorphous powder with  $[\alpha]_{\text{D}}^{17.8} + 4.62$  (c 0.15, MeOH), had the molecular formula  $\text{C}_{48}\text{H}_{82}\text{O}_{20}$  as established from the positive-mode HR-ESI-MS at  $m/z$  1001.5290  $[\text{M} + \text{Na}]^+$ . Negative-mode FAB-MS spectrum showed quasi-molecular ion and fragment ions at  $m/z$  977  $[\text{M} - \text{H}]^-$ , 815  $[\text{M} - 162]^-$ , 653  $[\text{M} - 162 - 162]^-$ , and 491  $[\text{M} - 162 - 162 - 162]^-$ , suggesting the presence of three hexoses in the molecule of compound **2**. Hydrolysis of **2** with 2 M  $\text{H}_2\text{SO}_4$  in MeOH revealed glucose as the only sugar moiety identified by comparison with authentic sample on PC. IR spectrum indicated the presence of hydroxyl ( $3423\text{ cm}^{-1}$ ) and glycosidic ( $1077\text{ cm}^{-1}$ ) groups. The  $^1\text{H}$  NMR spectrum displayed characteristic of the C-19 methylene protons of cyclopropane ring for a cycloartane triterpene at  $\delta_{\text{H}}$  0.47 (1H, d,  $J = 3.6\text{ Hz}$ , H-19a) and 0.56 (1H, d,  $J = 3.6\text{ Hz}$ , H-19b), seven methyl signals at  $\delta_{\text{H}}$  0.91, 1.00, 1.13, 1.17, 1.19 (each 3H, s, H-29, H-18, H-28, H-26, H-27), and 1.08–1.09 (6H, overlap, H-21, H-30) attributable to cycloartane-type aglycone, as well as three anomeric proton signals at  $\delta_{\text{H}}$  4.47 (1H, d,  $J = 7.0\text{ Hz}$ , H-1'), 4.58 (1H, d,  $J = 7.8\text{ Hz}$ , H-1''), and 4.76 (1H, d,  $J = 7.7\text{ Hz}$ , H-1') assigned to three  $\beta$ -linked sugar moieties.  $^{13}\text{C}$  NMR spectrum displayed 48 signals, of which the anomeric carbons of three sugar moieties at  $\delta_{\text{C}}$  105.2 (d), 105.2 (d), and 104.2 (d) were observed.

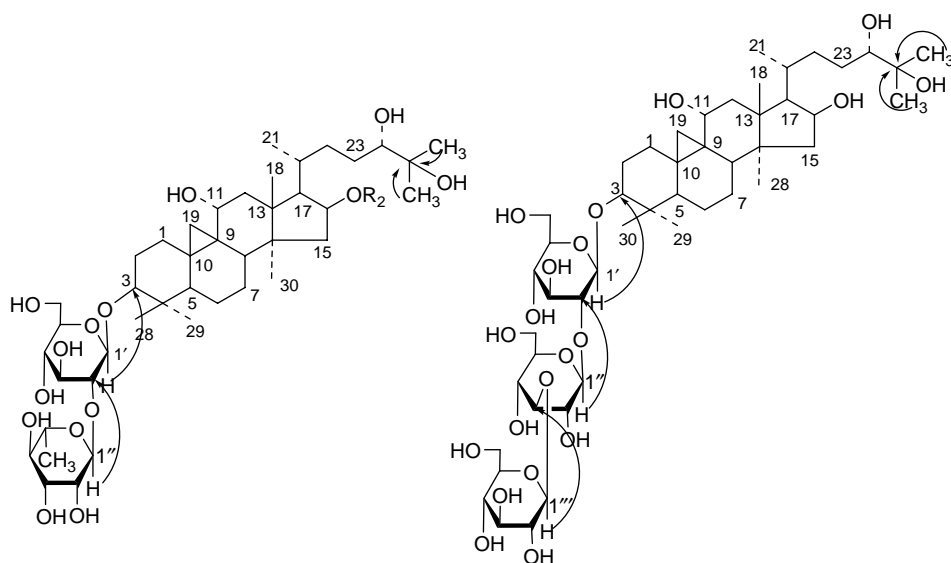


Figure 2. The key HMBC correlations of compounds **1** and **2**.

Comparing the NMR data of compound **2** with those of curculigosaponin K [2] indicated that they were analogous in structure except that C-25 was shifted downfield from  $\delta_C$  31.1 (d) to  $\delta_C$  73.8 (s), suggesting a hydroxyl linked to C-25; to further substantiate the location of the hydroxy group, HMBC experiment was conducted, in which the correlations from H-26 at  $\delta_H$  1.17 (3H, s) and H-27 at  $\delta_H$  1.19 (3H, s) to C-25 at  $\delta_C$  73.8 (s) were observed. Therefore, compound **2** was determined as 25-hydroxyl-curculigosaponin K and named curculigosaponin O (Figure 2).

### 3. Experimental

#### 3.1 General experimental procedures

Optical rotations were performed on a Horiba SEPA-300 polarimeter (Tokyo, Japan). IR spectra were recorded on a Bio-Rad FTS-135 spectrometer (Richmond, VA, USA) with KBr pellets,  $\nu$  in  $\text{cm}^{-1}$ . UV spectra were measured on a UV-210A spectrometer (Shimadzu, Japan); NMR spectra were conducted on Bruker AV-400 or DRX-500 spectrometer (Karlsruhe, Germany) with tetramethylsilane as internal

standard; chemical shifts ( $\delta$ ) were expressed in ppm and coupling constants ( $J$ ) in Hz. FAB-MS was recorded on a VG Autospec 3000 mass spectrometer (Manchester, England); ESI and HR-ESI-MS were taken on an API Qstar-Pulsar-1 mass spectrometer (Applied Biosystems/MDS Sciex, Vaughan, ON, Canada). Column chromatography (CC) separations were performed on silica gel (200–300 mesh, Qingdao Meigao Chemical Co., Ltd., Qingdao, China),  $\text{Al}_2\text{O}_3$  (Shanghai Wusi Chemical Reagents Company, Shanghai, China),  $\text{D}_{101}$  macroporous resins (Tianjin Pesticide Chemical Company, Tianjin, China), Sephadex LH-20 (Pharmacia Fine Chemical Co. Ltd., Uppsala, Sweden), and LiChroprep RP-18 (40–63  $\mu\text{m}$ ; Merck, Darmstadt, Germany). Fractions were monitored by thin-layer chromatography and visualized by spraying with 10%  $\text{H}_2\text{SO}_4$  in EtOH followed by heating.

#### 3.2 Plant material

The rhizomes of *C. orchoides* Gaertn. were collected in Wenshan county, Yunnan Province, China, in November 2005,

and authenticated by Prof. Dr Li-Gong Lei, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (No. 20051106) has been deposited in the Group of Anti-virus and Natural Medicinal Chemistry, Kunming Institute of Botany, Chinese Academy of Sciences.

### 3.3 Extraction and isolation

The air-dried, powdered rhizomes of *C. orchoides* (200 kg) were extracted with 70% EtOH (each 1000 liters, 2 h) three times under reflux to yield an extract which was combined and concentrated to a small volume (600 liters) and submitted to CC (macroporous resin D101, 200 kg), with gradient elution of H<sub>2</sub>O, 10% EtOH–H<sub>2</sub>O, 40% EtOH–H<sub>2</sub>O, 70% EtOH–H<sub>2</sub>O, and 90% EtOH–H<sub>2</sub>O to afford five fractions (1–5). The fraction 4 (70% EtOH–H<sub>2</sub>O eluted, 200 g) was subjected to Al<sub>2</sub>O<sub>3</sub> CC subsequently eluted with EtOAc–EtOH–H<sub>2</sub>O (8:2:0.2) and EtOAc–EtOH–H<sub>2</sub>O (7:3:0.5) to afford fractions A and B.

Fraction A (60.0 g) was successively subjected to RP-18 CC eluted with MeOH–H<sub>2</sub>O (4:6–7:3) to afford fractions A1–3. Fraction A2 (22.0 g) was performed on silica gel CC eluted with CHCl<sub>3</sub>–MeOH–H<sub>2</sub>O (8:2:0.3) to give a residue (2.0 g) that was submitted to Sephadex LH-20 CC developed with CHCl<sub>3</sub>–MeOH (1:1) and further purified by silica gel CC with EtOAc–EtOH–H<sub>2</sub>O (8:2:0.3) as solvent to yield compound **2** (290 mg). Fraction A3 (9.0 g) was applied to a silica gel CC eluted with CHCl<sub>3</sub>–MeOH–H<sub>2</sub>O (8.5:1.5:0.2) to give four portions. The fourth portion (1.3 g) was purified on RP-18 CC eluted with MeOH–H<sub>2</sub>O (5:5) to afford compound **1** (221 mg).

#### 3.3.1 *Curculigosaponin N* (**1**)

Amorphous powder; C<sub>42</sub>H<sub>72</sub>O<sub>14</sub>;  $[\alpha]_D^{15.3}$  –3.41 (*c* 1.78, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ): 250 (3.16) nm; IR (KBr)  $\nu_{\max}$ :

3438, 2926, 1629, 1429, 1036, 876, 537, 481 cm<sup>–1</sup>; <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N)  $\delta$ : 0.26 (1H, d, *J* = 3.2 Hz, H-19a), 0.43 (1H, d, *J* = 3.2 Hz, H-19b), 1.22, 1.26, 1.28, 1.30, 1.10, 1.43 (each 3H, s, H-18, H-28, H-29, H-30, H-25, H-26), 1.28–1.30 (3H, overlap, H-21), 4.93 (1H, d, *J* = 6.9 Hz, H-1'), 6.58 (1H, br. s, H-1''), 1.46 (3H, d, *J* = 6.1 Hz, H-6''), 3.41 (1H, dd, *J* = 11.2, 3.6 Hz, H-3), 3.95–3.97 (1H, m, H-11), 3.90–3.91 (1H, m, H-16), 4.26–4.29 (1H, m, H-24); for <sup>13</sup>C NMR (100 MHz, C<sub>5</sub>D<sub>5</sub>N) spectral data, see Table 1. (–) FAB-MS: *m/z* 799 [M – H]<sup>–</sup>, 653 [M – H – 146]<sup>–</sup>, 491 [M – H – 146 – 162]<sup>–</sup>; (–) HR-ESI-MS: *m/z* 799.4841 [M – H]<sup>–</sup> (calcd for C<sub>42</sub>H<sub>71</sub>O<sub>14</sub>, 799.4843).

#### 3.3.2 *Curculigosaponin O* (**2**)

Amorphous powder; C<sub>48</sub>H<sub>82</sub>O<sub>20</sub>;  $[\alpha]_D^{17.8}$  +4.62 (*c* 0.15, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ): 202 (3.73) nm; IR (KBr)  $\nu_{\max}$ : 3423, 2936, 1641, 1457, 1384, 1077, 635 cm<sup>–1</sup>; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$ : 0.47 (1H, d, *J* = 3.6 Hz, H-19a), 0.56 (1H, d, *J* = 3.6 Hz, H-19b), 0.91, 1.00, 1.13, 1.17, 1.19 (each 3H, s, H-29, H-18, H-28, H-26, H-27), 1.08–1.09 (6H, overlap, H-21, H-30), 4.47 (1H, d, *J* = 7.0 Hz, H-1'), 4.58 (1H, d, *J* = 7.8 Hz, H-1''), 4.76 (1H, d, *J* = 7.7 Hz, H-1'), 3.27–3.35 (1H, m, H-3), 4.47–4.49 (1H, m, H-11), 3.82–3.89 (1H, m, H-16), 3.27–3.32 (1H, m, H-24); for <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) spectral data, see Table 1; (–) FAB-MS: *m/z* 977 [M – H]<sup>–</sup>, 815 [M – 162]<sup>–</sup>, 653 [M – 162 – 162]<sup>–</sup>, 491 [M – 162 – 162 – 162]<sup>–</sup>; (+) HR-ESI-MS: *m/z* 1001.5290 [M + Na]<sup>+</sup> (calcd for C<sub>48</sub>H<sub>82</sub>O<sub>20</sub>Na, 1001.5297).

### 3.4 Acid hydrolysis

Compounds **1** and **2** (2.0 mg) were dissolved in MeOH (1.0 ml) and 2 M H<sub>2</sub>SO<sub>4</sub> (1.0 ml) solution and hydrolyzed under reflux for 2 h, respectively. The

Table 1. <sup>13</sup>C NMR (100 MHz) spectral data of compounds **1** and **2** (**1** in C<sub>5</sub>D<sub>5</sub>N, **2** in CD<sub>3</sub>OD, δ in ppm, and *J* in Hz).

| No. | 1        | 2        | No. | 1        | 2        | Glc | 1         | 2         |
|-----|----------|----------|-----|----------|----------|-----|-----------|-----------|
| 1   | 33.3 (t) | 33.0 (t) | 16  | 72.1 (d) | 73.8 (d) | 1'  | 105.4 (d) | 105.2 (d) |
| 2   | 30.4 (t) | 30.8 (t) | 17  | 49.3 (d) | 50.5 (d) | 2'  | 78.2 (d)  | 81.4 (d)  |
| 3   | 88.6 (d) | 90.9 (d) | 18  | 22.0 (q) | 21.9 (q) | 3'  | 77.7 (d)  | 75.5 (d)  |
| 4   | 40.3 (s) | 42.2 (s) | 19  | 30.1 (t) | 31.0 (t) | 4'  | 72.1 (d)  | 87.7 (d)  |
| 5   | 47.1 (d) | 47.6 (d) | 20  | 28.4 (d) | 29.3 (d) | 5'  | 80.0 (d)  | 71.5 (d)  |
| 6   | 21.5 (t) | 22.3 (t) | 21  | 17.4 (q) | 17.4 (q) | 6'  | 62.9 (t)  | 78.1 (d)  |
| 7   | 26.8 (t) | 27.5 (t) | 22  | 30.9 (t) | 33.2 (t) | Rha |           | 62.8 (t)  |
| 8   | 49.5 (d) | 49.9 (d) | 23  | 31.2 (t) | 31.1 (t) | 1'' | 101.8 (d) |           |
| 9   | 19.9 (s) | 20.9 (s) | 24  | 77.1 (d) | 77.7 (d) | 2'' | 72.2 (d)  |           |
| 10  | 26.1 (s) | 27.1 (s) | 25  | 72.6 (s) | 73.8 (s) | 3'' | 72.5 (d)  |           |
| 11  | 72.5 (d) | 73.2 (d) | 26  | 25.7 (q) | 25.4 (q) | 4'' | 74.2 (d)  |           |
| 12  | 40.9 (t) | 40.2 (t) | 27  | 25.8 (q) | 25.4 (q) | 5'' | 69.7 (d)  |           |
| 13  | 47.1 (s) | 47.6 (s) | 28  | 18.8 (q) | 18.6 (q) | 6'' | 18.6 (q)  |           |
| 14  | 49.8 (s) | 50.0 (s) | 29  | 26.5 (q) | 26.0 (q) |     |           |           |
| 15  | 50.1 (t) | 50.3 (t) | 30  | 15.7 (q) | 15.5 (q) |     |           |           |

hydrolysate was allowed to cool, diluted with 2.0 ml H<sub>2</sub>O, and extracted with 2.0 ml EtOAc. The aqueous layer was neutralized with aqueous Ba(OH)<sub>2</sub> and concentrated *in vacuo* to give a residue, in which glucose (from **1** and **2**) and rhamnose (from **1**) were identified by comparing with authentic samples on PC [BuOH–EtOAc–H<sub>2</sub>O 4:1:5, upper layer,  $R_f = 0.65$  (rhamnose); BuOH–EtOAc–H<sub>2</sub>O 4:1:5, upper layer,  $R_f = 0.45$  (glucose) on PC, respectively].

### Acknowledgements

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