# CORCHIOSIDE A, AN ORCINOL GLYCOSIDE FROM CURCULIGO ORCHIOIDES

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**Abstract**—The rhizomes of *Curculigo orchioides* yielded hentriacontanol, substerol, stigmasterol, cycloartenol, sucrose and a new phenolic glycoside, named corchioside A (orcinol-3- $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside). The structure was elucidated by spectroscopic methods and chemical transformations.

### **INTRODUCTION**

Curculigo orchioides Gaertn. is a small herb found in India in the sub-tropical Himalayas from Kumaon eastwards and in the Western ghats from Konkan southwards. Its tuberous roots are slightly bitter and mucilaginous and are considered tonic, alterative, demulcent, duretic and restorative [1] This is usually administered in combination with aromatics and bitters in piles, diarrhoea, jaundice, asthma and is used as a poultice for itch and skin diseases [2]. In China, it is also being used for the treatment of a decline in physical strength [3].

Despite its great importance in Indian and Chinese traditional medicines, *C. orchioides* had been the subject of limited investigations. Its rhizomes had yielded a phenolic glucoside, named curculigoside [3] and myricetin glycoside [4] in addition to few aliphatic compounds [5, 6]. Our investigation of the rhizomes has revealed the presence of a phenolic glycoside, named corchioside A along with hentriacontanol, sitosterol, stigmasterol, cycloartenol and sucrose.

#### **RESULTS AND DISCUSSION**

The chloroform extract of dried rhizomes of *C. orchioi*des yielded the earlier reported constituents hentriacontan-1-ol, sitosterol, stigmasterol and cycloartenol. The chloroform extracted rhizomes after re-extraction with methanol afforded appreciable amounts of corchioside A (1) and sucrose. The structure of 1 was elucidated mainly by spectroscopic methods. The mass spectrum of 1 showed  $[M]^+$  at m/z 418 (C<sub>18</sub>H<sub>26</sub>O<sub>11</sub>) with the base peak at m/z 124 (C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>). Its IR spectrum showed a fairly broad band at 3500-3200 and at  $830 \text{ cm}^{-1}$  suggesting the molecule to be a phenol derivative. Its <sup>1</sup>H NMR spectrum showed three doublets (J = 3 Hz) at  $\delta$ 7.10,  $\tilde{6.72}$  and 6.60 and singlet at 2.08 suggesting the presence of a 3,5-disubstituted toluene. Two singlets at  $\delta$ 160.0 and 1580 in its <sup>13</sup>C NMR spectrum further supported the oxygenation of the benzene ring at C-3 and C-5. The <sup>1</sup>H NMR spectrum showed two doublets (J = 7 Hz in each case) at  $\delta 4.95$  and 5 38 suggesting that the molecule consists of two sugar units. The large coupling constants (J = 7 Hz) of anomeric protons suggested the attachment of sugars as of  $\beta$ -type which was further supported by their chemical shifts in the <sup>13</sup>C NMR spectrum at  $\delta$ 102.4 and 103.2 [7]. The <sup>13</sup>C NMR spectrum showed nine additional signals in the range of  $\delta$ 80–67. This indicated that the sugar unit consisted of a hexose and a pentose. The absence of signals in the <sup>13</sup>C NMR spectrum at  $\delta$ 65–60 further indicated that the pentose is linked with hexose at C-6. After hydrolysis 1 gave orcinol- $\beta$ -D-glucoside and xylose which was comparable with D-xylose on paper chromato-



graphy This suggested that the  $\beta$ -D-xylopyranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside is attached at C-3. The <sup>1</sup>H NMR spectrum of 3 showed comparable signals and the mass spectrum had the molecular ion [M]<sup>+</sup> at m/z124 (see Experimental). Compound 1, after acetylation, afforded its acetate 2 which also supported its structure (see Experimental).

## **EXPERIMENTAL**

The mass spectra were recorded at 70 eV (direct inlet). Rhizomes of C. orchioides were obtained from the local market and identified by the taxonomists of our Institute The specimen voucher is deposited in the herbarium of our Institute. The powdered rhizome (2 5 kg) were extracted firstly with CHCl<sub>3</sub> and then with MeOH The CHCl<sub>3</sub> extract after CC on silica gel using petrol-Me<sub>2</sub>CO as solvent gave several fractions The petrol-Me<sub>2</sub>CO (99.1) fraction afforded hentriacontanol (50 mg) and petrol-Me<sub>2</sub>CO, (49 1) afforded stigmasterol (40 mg), sitosterol (200 mg) and cycloartenol (800 mg) On the other hand the MeOH extract after CC, using CHCl3-MeOH as solvent, afforded mainly three fractions Fraction 1 after further CC (CHCl<sub>3</sub>-MeOH, 5 1) afforded an unidentified compound (60 mg, R<sub>f</sub> 0 77 in CHCl<sub>3</sub>-MeOH, 3.1) and fraction 2 after CC (CHCl<sub>3</sub>-MeOH, 5 2) afforded 1 (200 mg, R<sub>f</sub> 0 27 in CHCl<sub>3</sub>-MeOH, 3.1). Fraction 3 yielded mainly sucrose (1 g)

 $(orcinol-3-\beta-D-xylopyranosyl-(1\rightarrow 6)-\beta-D-$ Corchioside A glucopyranoside, 1). Colourless crystals, mp 209–210°, IR  $v_{\text{max}}^{\text{KBr}}$  cm<sup>-1</sup> 3500–3200, 2900, 1630, 1600, 1465, 1310, 1170, 1075 and 830 MS m/z (rel int.) 418 [M<sup>+</sup>, C<sub>18</sub>H<sub>26</sub>O<sub>11</sub>] (19), 294  $[M-C_7H_8O_2]^+$  (17), 269  $[M-C_5H_9O_5]^+$  (25), 124  $[C_7H_8O_2]^+$  (100). <sup>1</sup>H NMR ( $C_5D_5N$ )  $\delta$ 7 10, 6 72 and 6.60 (d each, J = 3 Hz, H-2, H-4 and H-6), 2.08 (s, H-7), 4 95 (d, J = 7 Hz, H-1'), 4.25–4 00 (overlapping m, H-2' to 5'), 4.08 (dd, J = 7 and 12 Hz, H-6' a), 3 92 (t, J = 7 Hz, H-6'b), 5.38 (d, J = 7 Hz, H-1"), 4 25-4 00 (overlapping, m, H-2" to 4"), 4 13 (dd, J = 8 and 12 Hz, H-5"a), 3 45 (*dd*, J = 5 and 12 Hz, H-5"b) <sup>13</sup>C NMR (C<sub>5</sub>D<sub>5</sub>N)  $\delta$ 1600 and 158.0 (C-3 and C-5), 1410 (C-1), 111.8, 1099 and 1058 (C-2, C-4 and C-6), 21.5 (C-7), 1032 and 102.4 (C-1' and C-1"), 67.4 (C-6'), 75 3, 78 0, 71.4, 78 8, 74 6, 77 4, 71.6 and 70 9 (C-2' to 5' and C-2" to C-5")  $[\alpha]_{D}^{30} - 32^{\circ}$  (MeOH; c10)

Acetylation of 1 Compound 1 (80 mg) was taken in pyridine (2 ml) and kept overnight with  $Ac_2O$  (1 ml) at room temp After usual work-up and CC purification, 2 (60 mg) was obtained. Compound 2 on crystallization gave colourless crystals, mp

180°, IR  $v_{\text{max}}^{\text{KB7}}$  cm<sup>-1</sup> 2980–2950, 1760, 1600, 1380, 1260–1220, 1100–1055, 990 and 895 <sup>1</sup>H NMR(CDCl<sub>3</sub>).  $\delta 6.68, 6 66$  and 6.55 (*d* each, J = 3 Hz, H-2, H-4 and H-6), 2 34 (s, H-7), 4 48 and 5 07 (*d* each, J = 7 Hz, H-1' and H-1''), 3 62 (*dd*, J = 7 and 12 Hz, H-6'a), 3.88 (*t*, J = 7 Hz, H-6'b), 3 26 (*dd*, J = 8 and 12 Hz, H-5''a), 4 11 (*dd*, J = 5 and 12 Hz, H-5''b), 2 34 (s, H-7), 2 28 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 9H, 3 × OAc), 2 02 (s, 3H, OAc), 1 90 (s, 3H, OAc). [ $\alpha$ ]<sup>30</sup> –48 64° (CHCl<sub>3</sub>, *c* 2 5)

Hydrolysis of 1 Compound 1 (40 mg) was taken in MeOH (3 ml) and 5% HCl (2 ml) was added. The reaction mixture after refluxing over a water bath for 4 hr and usual work-up afforded 3 (8 mg from the Et<sub>2</sub>O phase) and glucose and xylose (from the aq phase) A similar experiment with 0 5% HCl and 1 hr refluxing gave orcinol- $\beta$ -D-glucoside (from the *n*-BuOH phase) and xylose (from the aq phase) The identity of glucose and xylose was substantiated by paper chromatography (n-BuOH-HOAc H<sub>2</sub>O, 4 1 5) using aniline phthalate in n-BuOH as the spray reagent, mp 105-107<sup>c</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta 6.20$ (br s, 3H, H-2, H-4 and H-6), 2 23 (s, 3H, H-7), 9 84 (br s, 2H, 2 ×OH) MS m/z (rel int) 124 [M<sup>+</sup>, C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>] (100), 106 [M -H<sub>2</sub>O]<sup>+</sup> (10), 95 (8)

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