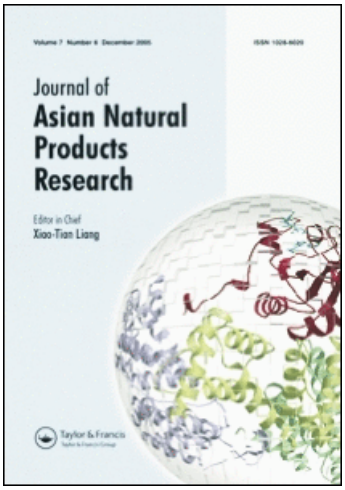

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NEW CHLORINE-CONTAINING PHENOLOID FROM *CURCULIGO CAPITULATA*

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A new chlorine-containing phenoloid, named capitulatin A, has been isolated from the rhizomes of *Curculigo capitulata*. Its structure was established as 2,4-dichloro-3-methyl-5-hydroxy-6-methoxylphenol-β-D-xylopyranosyl (1→6)-β-D-glucopyranoside (**1**) on the basis of the spectral data and chemical evidence.

Keywords: *Curculigo capitulata*; Hypoxidaceae; Chlorine-containing phenoloid; Capitulatin A

INTRODUCTION

The herb *Curculigo capitulata* (*Lour.*) *Ktze*, used as a tonic and a medicine for treating dysmenorrhea and rheumatism [1], is widely distributed in Southern and Southwestern China, Taiwan (China), Malaysia, India and Australia. Various compounds, including phenanthropyran [1], norneolignan and phenols [2], have been isolated from this plant. In this paper a new chlorine-containing phenoloid (**1**) was isolated from the rhizomes of *C. capitulata.* Chlorine-containing phenoloids of this kind, reported previously from the same genus, *C. orchioides* [3–5], are very scarce. Here we report the structural elucidation of **1**.

RESULTS AND DISCUSSION

Compound **1** was obtained as colorless needles (MeOH). Its HRFAB$^-$MS gave a quasi-molecular ion at *m/z* 515.0784 $[M-1]^-$ and fragment ions at *m/z* 517.0748 $[M-1+2]^-$, 519.0732 $[M-1+4]^-$, in which the relative abundance ratio for $[M-1]$:$[M-1+2]$:$[M-1+4]$ was 9:6:1, indicating that **1** contains two chlorines

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and a molecular formula of $C_{19}H_{26}O_{12}Cl_2$, which was confirmed by the ^{13}C NMR data. In the ^{13}C NMR spectrum, carbon signals at δ 145.1s, 144.5s, 142.5s, 125.9s, 125.6s and 125.0s confirmed the presence of hexa-substituted aromatic ring with three —OR, —C and two Cl groups. Furthermore, chemical shifts at δ 17.8 and 61.1 in ^{13}C NMR spectrum are in accordance with δ 2.69 (s, 3H) and 4.13 (s, 3H) in the ^1H NMR spectrum and indicate that **1** contains one CH_3 and one OCH_3 group. The correlation peaks between C-3 (δ 125.9) and protons of CH_3, C-6 (δ 145.1) and protons of OCH_3 in the HMBC spectra of **1** (Fig. 1) confirm that CH_3 is linked with C-3 and OCH_3 with C-6. Two quaternary carbon signals, at δ 125.6 and 125.0, correlate with the protons of CH_3 in HMBC, indicating the attachment of two chlorines in C-2 and C-4. In the ^{13}C NMR spectrum the carbon signals at δ 105.2, 74.8, 77.6, 71.1, 66.9 and δ 106.5, 75.3, 77.5, 70.9, 77.9, 69.4 indicated the presence of one xylose and 6-substituted glucose. Acid hydrolysis of compound **1** showed that it contains glucose and xylose. In the FAB-MS of **1**, the ion peaks at *m/z* 383$[M - 1 - xyl]^-$ and 221$[M - 1 - xyl - glc]^-$ suggested the presence of the two sugar moieties. Two doublets at δ 5.10 ($J = 7.60$ Hz) and 4.57 ($J = 7.30$ Hz) in the ^1H NMR spectrum also indicate the presence of a glucose unit and a xylose unit in **1**. From the coupling constants of the anomeric protons and the ^{13}C NMR chemical shifts, the two sugar moieties must be β-type sugars. The other positions of the two sugars were confirmed by $^1H-^1H$ COSY, HMQC-TOCSY and NOE spectroscopy. The cross signals at δ 142.5 (C − 1)/2.69 (proton of CH_3), δ 142.5 (C − 1)/5.10(H − 1′) and δ 69.4 (C − 6′)/4.57(H-1″) in the HMBC spectrum reveal a 1-*O*-glucoside and 1→6 linkage of the two sugars moieties. In the NOESY spectrum of **1**, cross-peaks were observed between the methoxyl protons (4.13) and H − 6′(4.30) of the glucose unit, indicating that the two quaternary carbons, attached by methoxyl group and glucose unit, are adjacent. On acetylation of **1**, the saponin acetate was subjected to FAB$^-$MS analysis, and showed *m/z* $515 + 7 \times 42([M - 1]^- + 7Ac - 7H)(809)$, which indicates the presence of an hydroxy group linked with the aromatic ring. A downfield chemical shift at δ 144.5 was due to C-5 linked with the hydroxy. From the above-mentioned evidence, compound **1** was determined to be 2,4-dichloro-3-methyl-5-hydroxy-6-methoxylphenol-β-D-xylopyranosyl (1→6)-β-D-glucopyranoside (Fig. 1).

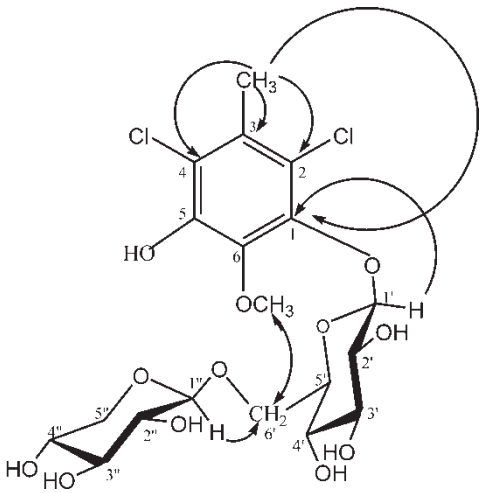

FIGURE 1 Structure of compound 1 (→ HMBC correlations; ↔ $^1H-^1H$ NOESY correlations).

EXPERIMENTAL

General Experimental Procedures

The mp was determined on an XRC-1 micro melting point apparatus and is uncorrected. $[\alpha]_D$ was determined with a JASCO-20. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectra were recorded on a UV 210A spectrometer. 1D and 2D NMR spectra were run on Bruker DRX-500 instruments with TMS as internal standard using CD_3OD as solvent. The FAB-MS was carried out on a VG Auto Spec-3000 spectrometer. TLC was carried on silica gel G (MEIJING) precoated plates. Spots were detected by spraying with 5% sulfuric acid–ethanol solution followed by heating.

Plant Material

Rhizomes of *C. capitulata* were collected from the west garden of Xi Shuang Ban Na Botanical Garden and identified by Professor Zhou Jun of the Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen was deposited in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation

The air-dried and powered rhizomes of *C. capitulata* (3 kg) were extracted with 85% EtOH (3×20 L) at room temperature, and the combined extracts were evaporated *in vacuo*. The residue was suspended in H_2O and then passed through a D101 resin column to eliminate sugars; the column was then eluted with 95% EtOH. The EtOH eluent was concentrated *in vacuo* to give a residue (240 g) that was chromatographed on silica gel column (200–300 mesh) with $CHCl_3$–MeOH (7:2) to give 8 fractions. Fraction 4 was subjected to column chromatography over silica gel eluted with $CHCl_3$–MeOH (10:1.5) to afford 1 (12 mg, yield 0.05%).

2,4-Dichloro-3-methyl-5-hydroxy-6-methoxylphenol-β-D-xylopyranosyl(1-6)-β-D-glucopyranoside (1)

Colorless needles (MeOH), mp 174–178°C, $[\alpha]_D^{21}$ −36.67 (*c* 0.30, MeOH); IR (KBr) ν_{max} (cm^{-1}): 3419, 2927, 1634, 1467, 1072, 1045, 994; UV(MeOH) λ_{max} (nm): 286, 205. ^1H NMR (CD_3OD, MHz) δ: 2.69 (3H, s, CH_3-3), 4.13 (3H, s, CH_3O-6), 4.57 (1H, d, $J =$ 7.30 Hz, H-1″), 5.10 (1H, d, $J = 7.60$ Hz, H-1′); ^{13}C NMR (CD_3OD, 125 MHz) data are shown in Table I. Molecular formula $C_{19}H_{26}O_{12}Cl_2$ (negative HRFAB MS 515.0732; calcd. 515.0723).

Acid Hydrolysis of 1

Compound **1** was dotted on a silica gel G plate, placed and hung in a sealed glass vessel with concentrated HCl (ca. 1 ml) at 70°C for 1 h for hydrolysis and then cooled for a few minutes; the plate was taken out, and the HCl volatilized with a ventilator. Authentic sugars were dotted to the plate, which was then developed with n-butanol–pyridine–water (6:4:3), and 5% sulfuric acid–ethanol solution used as spray reagent, followed by heating at 120°C. From compound **1** glucose and xylose were detected; R_f: glucose 0.40, xylose 0.52.

TABLE I ^{13}C NMR spectral data of compound **1** (CD_3OD, 125 MHz)

Aglycone			*Sugars*
1	142.5 s	Glucose	
2	125.0* s	1′	106.5 d
3	125.9 s	2′	75.3 d
4	125.6* s	3′	77.5 d
5	144.5 s	4′	70.9 d
6	145.1 s	5′	77.9 d
$-CH_3$	17.8 q	6′	69.4 t
$-OCH_3$	61.1 q	Xylose	
		1″	105.2 d
		2″	74.8 d
		3″	77.6 d
		4″	71.1 d
		5″	66.9 t

* Data are exchangeable.

Acetylation of 1

Compound **1** (1 mg) was dissolved in Ac_2O–pyridine (1:0.5) in a sealed micro-tube. After reacting at 60–70°C for 6 h, the acetate of **1** was subjected to FAB-MS analysis.

Acknowledgements

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