

A New Epoxynaphthoquinol from *Rumex japonicus*

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(Received April 3, 1998)

A new epoxynaphthoquinol derivative, 3-acetyl-2-methyl-1, 5-dihydroxy-2,3-epoxynaphthoquinol (**I**), was isolated from the root of *Rumex japonicus*. The structure was elucidated by high field 1D and 2D NMR techniques.

Key words : *Rumex japonicus*, Epoxynaphthoquinol

INTRODUCTION

Rumex japonicus Houtt. (Polygonaceae) has been used as a Chinese drug for the treatment of constipation, jaundice, uterine hemorrhage and hematemesis (Yook *et al.*, 1981). Earlier investigation on the chemical constituents of *R. japonicus* was mainly dealt with the isolation of flavonoids and anthraquinone derivatives (Demirezer, 1994; Rada and Hrochova, 1976; Sayed *et al.*, 1975). In the previous phytochemical study of this plant, we reported three anthraquinone derivatives and a naphthalene derivative as cytotoxic constituents (Kim *et al.*, 1998). Further investigation of the same extract afforded a new epoxy-naphthoquinol derivative (**I**). This paper reports its isolation and structural elucidation.

MATERIALS AND METHODS

General experimental procedures

¹H-NMR spectra were run at 500 MHz and ¹³C-NMR at 125 MHz and recorded by Bruker AMX-500 spectrometer. The EI/MS (70 eV) was determined on a VG-VSEQ mass spectrometer (VG Analytical, UK). The UV spectrum was recorded on Shimadzu UV 240 UV-Visible recording spectrophotometer. IR spectrum was measured on Shimadzu IR-435 Infrared spectrophotometer. TLC and column chromatography were carried out on Merck precoated silica gel F 254 plates. All other chemicals and solvents were analytical grade and used without further purification.

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Plant material

Rumex japonicus was collected in September 1995 at Changnyungkun, Kyungnam, Korea. A voucher specimen is deposited in the herbarium of College of Pharmacy, Sung Kyun Kwan University (SKKU-95-005).

Extraction and isolation

The air-dried plant materials (1 kg) was finely ground and extracted at room temperature with MeOH. The resultant MeOH extract (250 g) was followed by the successive solvent partition to give CH₂Cl₂ (15 g), n-BuOH (18 g) and H₂O (23 g) soluble fractions. The CH₂Cl₂ soluble fraction was chromatographed over silica gel using a solvent system of hexane-EtOAc (3:1) as eluent to give eight sub-fractions, whose sixth sub-fraction (1.8 g) was rechromatographed on silica gel eluting with CH₂Cl₂-EtOAc (8:1), followed by CH₂Cl₂-MeOH (40:1) to yield 10 mg of compound **I**.

Compound **I** (3-acetyl-2-methyl-1, 5-dihydroxy-2,3-epoxynaphthoquinol): IR $\lambda_{\max}^{\text{Nujol}}$ cm⁻¹: 3130 (OH), 1720 (free C=O), 1625 (chelated C=O), 1580 (arom. C=C); UV (MeOH) λ_{\max} : 268 nm, 342 nm; $[\alpha]_D^{25}$ = +54.93; EI-MS, m/z (rel. int.) 248 (M⁺, 60), 230 (12), 205 (13), 177 (65), 161 (78), 66 (100). ¹H- and ¹³C-NMR (DMSO-d₆): Table I.

RESULTS AND DISCUSSION

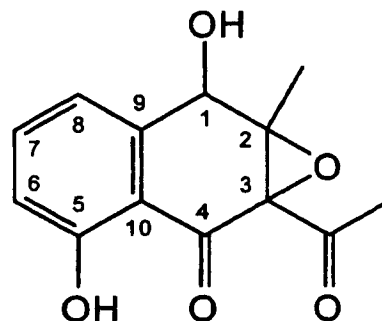
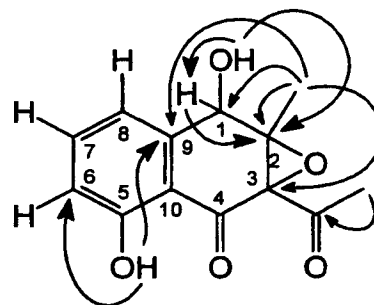
In the course of phytochemical study of the MeOH extract of *R. japonicus*, a new epoxynaphthoquinol derivative (**I**) was isolated in the CH₂Cl₂ soluble fraction.

Compound **I** was obtained as a brownish gum. Its IR spectrum displayed absorption bands at 3130, 1720 and 1625 cm⁻¹, indicating the presence of OH, C=O

Table I. ^1H - (500 MHz) and ^{13}C -NMR (125 MHz) data of compound **I** (DMSO-d_6).

position	δ_{C}	δ_{H}	^1H - ^1H COSY	HMBC
1	67.1	5.02 (1H, d, $J=8.5$)		2, 9, 10
2	65.0			
3	68.7			
4	196.5			
5	160.2			
6	116.1	6.92 (1H, dd, $J=8.2, 0.9$)	7	8, 9
7	137.1	7.62 (1H, m)	6, 8	5, 10
8	118.0	7.18 (1H, dd, $J=7.75, 0.9$)	7	1, 6, 9
9	112.9			
10	143.6			
C=O	200.7			
COCH_3	29.1	2.37 (3H, s, CH_3)		
CH_3	15.4	1.45 (3H, s, CH_3)		2, 3, 9
1-OH		6.41 (1H, d, $J=8.5$)	1	1, 2, 10
5-OH		10.89 (1H, s)		5, 6, 9

and aromatic C=C functionalities. UV spectrum gave the absorption bands of naphthoquinol derivatives at 268 and 342 nm. In the EI-MS spectrum of compound **I**, molecular ion and fragment ion appeared at m/z 248 [M^+], 230, 177, 161 and 66. The molecular formula, $\text{C}_{13}\text{H}_{12}\text{O}_5$, was determined by MS (M^+ m/z 248), ^1H -NMR, ^{13}C -NMR and DEPT data. ^{13}C -NMR spectrum showed two carbonyl (δ 200.7, 196.5) and six sp^2 carbon signals (δ 160.2, 143.6, 137.1, 118.0, 116.1, 112.9), hence the remaining 3 double bond equivalents should be tricyclic. In the ^1H -NMR spectrum (500 MHz, DMSO-d_6) of compound **I**, the signals due to three of olefinic (δ 7.62, 7.18, 6.92), two methyls (δ 2.37, 1.45) and a methine bearing oxygen (δ 5.02) protons were observed. In the ^{13}C -NMR spectrum (125 MHz, DMSO-d_6), thirteen carbon signals were observed, among which the presence of two methyls (δ 29.1, 15.4), two quaternary carbons bearing oxygen (δ 67.1, 65.0) and one tertiary carbinol carbon (δ 68.7) was confirmed by their chemical shifts and DEPT experiment. The ^{13}C -NMR chemical shifts of two carbonyl groups in naphthoquinone derivative are usually in the range of 180-190 ppm. The chemical shifts of δ 2.37 in the ^1H -NMR spectrum and δ 200.7 in the ^{13}C -NMR spectrum indicated that the compound **I** contained one acetyl group. The above results indicated that compound **I** was supposed to be a naphthoquinol (tetralone) derivative. And the presence of the epoxide ring was inferred by the chemical shifts (δ 67.1, 65.0) and eight degrees of unsaturation. The position of methyl group was determined by the correlation between methyl (δ 1.45) and C-2 (δ 65.0) in the HMBC spectra (Fig. 2). The chemical shift δ 10.89 of OH group in the ^1H -NMR spectrum indicated that the hydroxyl group could be placed at C-5. The other hydroxyl group must be placed at C-1 in consideration of the chemical shift of ^{13}C -NMR spectrum (δ 67.1)

**Fig. 1.** Structure of compound **I**.**Fig. 2.** Key HMBC correlations of compound **I**.

and naphthoquinol skeleton. The detailed analysis of 2D-NMR (^1H - ^1H COSY, ^{13}C - ^1H COSY, HMBC, NOESY) spectra provided the chemical structure of compound **I** (Fig. 1). The compound is optically active ($[\alpha]_{\text{D}}^{22} = +54.93$), but the configurations at C-1, C-2 and C-3 remain uncertain. This compound, 3-acetyl-2-methyl-1,5-dihydroxy-2,3-epoxynaphthoquinol (3-acetyl-2-methyl-1,5-dihydroxy-2,3-epoxy-4-tetralone) has not yet been reported in any other plant.

ACKNOWLEDGEMENT

This work was supported by the research grant from Kyungki Pharmaceutical Research Center (KPRC).

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