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Flavanone Glycoside from the Fruits of *Chaenomeles sinensis*

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Abstract – Investigation of the fruits of *Chaenomeles sinensis* (Rosaceae) resulted in the isolation of a minor flavonoid. The structure of flavanone glycoside was determined to be as 2-hydroxynaringenin-7-*O*-β-glucoside on the basis of FAB-MS and spectral evidence, especially by 2D-NMR (^{1}H-^{1}H COSY, HMQC, HMBC and NOESY).

Key words – *Chaenomeles sinensis*, Rosaceae, fruits, flavanone glycoside, 2-hydroxynaringenin-7-*O*-β-glucoside.

Introduction

Chaenomeles sinensis (Rosaceae) is widely distributed in Korea, Japan and China and used in traditional medicine for the treatment of cough, common cold, pain, and diarrhea (Lee, 1966; Namba, 1992). This plant showed a potent inhibition against the tyrosinase activity (Matsuda *et al.*, 1994), hitherto not studied phytochemically. To evalute anti-influenza A virus activity, we prepared various plant extracts and screened for a component which is effective for inhibition of influenza A virus. Of the various plant extracts, the methanolic extract of the fruits of *C. sinensis* showed anti-influenza A virus activity in haemagglutination inhibition test. This prompted us to carry out bioassay directed isolation studies on this species. In the present study, we report the isolation and structure elucidation of 2-hydroxynaringenin-7-*O*-β-glucoside for the first time from the fruits of this plant.

Experimental

Plant material – The fruits of *C. sinensis* (Rosaceae) were collected at Sangju, Kyeongbuk Province, Korea in October, 1998. A voucher specimen was deposited in the herbarium, Korea Institute of Oriental Medicine.

General – Spectra were recorded with the following instuments. Mp: Uncorr; IR (KBr, Bruker IFs 48); UV (MeOH, UV-1201); FAB-MS (negative mode, VG70-VSEQ): glycerol matrix; ^{1}H (500 MHz) and ^{13}C NMR (125 MHz): Bruker AM-500 spectrometer, CD_3OD with TMS as int. standard; TLC: Si gel (60 GF_{254}, Merck); Chromatography: Amberlite XAD-4 (Sigma), Sephadex LH-20 (Pharmacia), Silicagel [kieselgel 60 (70-230 mesh), Merck].

Extraction and isolation – The dried fruits (1 kg) were extracted with MeOH at room temp. and the extract was concentrated to dryness. 80 g of the MeOH extract (434.4 g) was fractionated on a Amberlite XAD-4 with a gradient MeOH in H_2O. The fraction MeOH-H_2O (4:6) gave a residue (5.3 g) was performed by CC on a Sephadex LH-20 with MeOH-H_2O (3:7). Seven fractions were collected. Fr. 6 was chromatographed on a silica gel column with $CHCl_3$-MeOH-H_2O (70:30:4), affording **1** (6.4 mg).

Compound 1: $C_{21}H_{22}O_{11}$, powder, mp 205°; IR (KBr) ν_{max} : 3309, (OH), 2922 (C-H), 1616 (C = O), 1515, 1384 (C = C), 1075 (glycosidic O), 835 (aromatic ring) cm^{-1}; UV (MeOH): λ_{max} 330, 291 nm; Negative FAB-MS: *m/z* = 449[M-H]$^-$, 287[M-(glc+H)]$^-$; ^{1}H-NMR and ^{13}C-NMR: see Table 1 (Lee *et al.*, 1995).

Acid hydrolysis of (1) – A solution of Compound **1** (3 mg) in 1N HCl (1 ml) was heated at 100°C for 5 h. After cooling, the reaction mixture was extracted with EtOAc. The water layer was neutralized with Dowex (Co_3^{2-}) and concentrated to obtain glucose which was identified by silica gel TLC comparison (EtOAc:EtOH:H_2O = 8:2:1, v/v, R_f = 0.2).

Results and Discussion

Compound **1** was obtained as a pale yellow amorphous powder, mp 205°. The negative FAB-MS showed a molecular ion peak at *m/z* 449[M-H]$^-$ and a

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fragment at *m/z* 287[M-(glc+H)]$^-$, suggesting the molecular formula to be $C_{21}H_{22}O_{11}$. Its UV absorption band (λ_{max} 330, 291 nm), ^{1}H NMR [δ3.08 (2H, *s*)] and ^{13}C NMR [δ107.6 (C-2) and δ42.2 (C-3)] spectral data indicated it to be a 2-hydroxyflavanone. In the ^{1}H NMR spectrum, the presence of two doublets at δ6.98 (2H, *d*, *J* = 8.4 Hz) and 6.56 (2H, *dd*, *J* = 2.0, 8.5 Hz) showed the presence of 4'-OH in the B-ring. Two singlets at δ6.04 and 5.92 could be assigned to two aromatic protons (H-8 and H-6) of the A-ring and revealed a hydroxyl group at the C-5 and C-7 position. The hydroxyl group at C-2 was deduced from the singlet signal observed at H-3 (δ3.08). Anomeric proton [δ4.84 (1H, *d*, *J* = 7.6 Hz)] was indicative of one glucose as sugar moiety.

In the ^{13}C-NMR spectra, anomeric carbon was observed at δ101.8 ppm, the signal due to C-7 (δ172.2) was shifted upfield and the signals due to C-6 (δ93.5) and C-8 (δ98.1) were shifted downfield. In addition, the quaternary carbon due to C-2 was showed at δ107.6 (Table 1).

Acid hydrolysis with HCl yielded glucose identified by direct TLC comparison with authentic samples.

In Fig. 1, selected long-range proton-carbon coupling constant connectivities are presented, especially correlation signals indicative of the sugar location and the hydroxyl substituent at C-2. The NOE's observed for H-3 and H-2', 6' confirmed the position of the hydroxyl group at C-2 (Fig. 2).

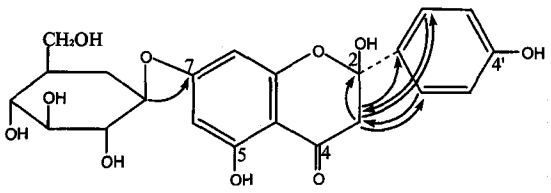

Fig. 1. The HMBC correlations of compound **1**.

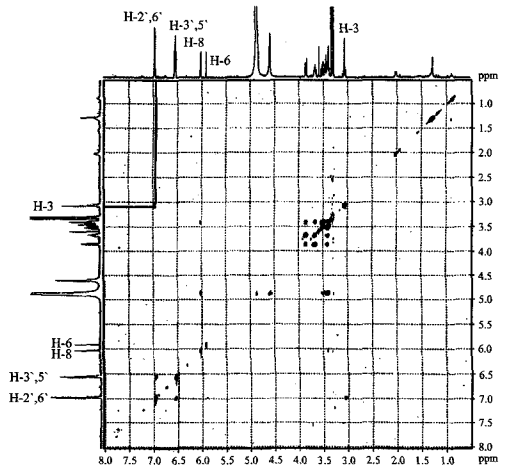

Fig. 2. The NOESY spectrum of compound **1**.

Table 1. ^{1}H-, ^{13}C-NMR and DEPT spectral data of compound **1**.

Carbon No.	^{1}H NMR	^{13}C NMR	DEPT
Aglycone			
2		107.6	C
3	3.08 (2H, s)	42.2	CH_2
4	–	196.8	C
5	–	174.6	C
6	5.92 (1H, s)	93.5	CH
7	–	172.2	C
8	6.04 (1H, s)	98.1	CH
9	–	158.5	C
10	–	103.5	C
1'	–	125.7	C
2', 6'	6.56 (2H, dd, J=2.0, 8.5 Hz)	132.5	CH
3', 5'	6.98 (2H, d, J = 8.4 Hz)	115.8	CH
4'	–	157.3	C
Glucose			
1"	4.84 (1H, d, J = 7.6 Hz)	101.8	CH
2"	3.51 (1H, t, J = 8.4 Hz)	74.1	CH
3"	3.46 (1H, t, J = 8.7 Hz)	77.4	CH
4"	3.40 (1H, m)	71.2	CH
5"	3.41 (1H, m)	78.4	CH
6"	3.68 (1H, dd, J = 5.2, 12.3 Hz) 3.86 (1H, dd, J = 2.4, 12.3 Hz)	62.1	CH_2

*In CD_3OD at 500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR and DEPT.

From these results, compound **1** was identified as 2-hydroxynaringenin-7-*O*-β-glucoside.

2-Hydroxyflavanones are rarely reported from nature although there are indications that they are, or at least could be, intermediates in the conversion of β-hydroxy-chalcones (dibenzoylmethanes) to flavones (Harborne, 1994). The finding of this compound from *C. sinensis* is thus of some future value for chemotaxonomy.

Acknowledgement

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