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A New Acetophenone of Aerial Parts from *Rumex aquatica*

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Abstract – A new acetophenone named rumexin (3-hydroxy-5-methyl-4-O-β-D-glucopyranosyl acetophenone) was isolated from methanolic extract of *Rumex aquatica* together with eight known compounds, quercetin-3-O-β-D-glucuropyranoside, musizin-8-O-β-D-glucopyranoside, quercetin-3-O-α-L-rhamnoside, emodin-8-O-β-D-glucopyra noside, caffeic acid, 1-O-caffeoyl-β-D-glucopyranoside, 1-methyl caffeic acid, kaempferol-3-O-β-D-glucuropyranoside. All of the above compounds were isolated from *Rumex aquatica* for the first time, and structures of compounds were established by spectroscopic means.
Keywords – *Rumex aquatica*, Polygonaceae, Rumexin, 3-hydroxy-5-methyl-4-O-β-D-glucopyranosyl acetophenone.

Introduction

Rumex aquatica (Polygonaceae) has been used as substitute for Rhubarb, and used for dermatitis as a folk medicine in Korea. There are a few reports about Rumex species; 3-acetyl-2-methyl-1,5-dihydroxy-2,3-epoxynaphthoquinol from *Rumex japonicus* (Zee OP *et al.*, 1998), 1-O-β-D-glucopyranosyl emodin from the root of *Rumex gmelini Turcz* (Kang Y *et al.*, 1996), quercetin-3-rhamnoside, kaempferol-3-rhamnopyranosyl(1→6)galactoside, quercetin-3-glycosyl(1 → 4)galactoside, emodin from *Rumex chalepensis* (Hasan A *et al.*, 1995), chrysophanol, physcion, emodin, chrysophanin, rheochrysin, emodin-8-O-glucoside, kaempferol-7-O-rhamnoside, quercimetrin, orientin from *Rumex luminiostrum* (Abdel-Fattah H *et al.*, 1994), essential oils from the aerial part of *Rumex japonicus Houtt* (Miyazawa M *et al.*, 1981), emodin from *Rumex hymenosepalus* (Bulchalter, 1969), and a lot of flavonoids from *Rumex acetosa* and *Rumex japonicus* (Aritomi M, 1965). But there's no report about constituent as well as pharmacological activity of *Rumex aquatica*. So, as a chemotaxonomic research of the Rumex species, we studied about its constituents.

Experimental

General procedures – Melting points were recorded on a Gallenkamp melting point apparatus. ^{1}H and ^{13}C-NMR spectra were measured on a Varian Gemini 2000, 300 MHz and 75.5 MHz, respecti vely, with 0.1% TMS as internal stnadard. FAB mass spectra were recorded on a Hewlet-Packard 5890-JMS AX505 WA. UV spectra were recorded on a Hitachi U-3300, IR on Magna-750, and Polarimeter and optical rotation on a Jasco DIP-370.

Plant material – The whole aerial parts of *Rumex aquaticus* were collected in April 1998 at medicinal plant garden of Chung-Ang University at Seoul, Korea. The plant was identified by Dr.Wan Kyunn Whang, College of Pharmacy Chung-Ang University.

Extraction and isolation – The aerial parts of the plant (4.2 kg) were washed and extracted for a week at room temperature with MeOH (3×18 l) three times to yield 127 g of extract. Then extract was suspended with water and partitioned by ether (5×4 l), and water-soluble part (86.8 g) for this study. Water-soluble part was filtrated and subjected into Diaion HP-20 gel and then eluted by gradient of water/MeOH mixture (0, 20, 40, 60, 80, 100 v/v% MeOH). 20% MeOH fraction (1.5 g) was separated by Sephadex LH-20 gel column chromatography (5×90 cm) with 10% MeOH and further separated by MCI gel column chromatography (3.5×60 cm) with 25% MeOH to obtain compound 6 (36 mg). 40% MeOH fraction (6 g) was recrystalized by Water to obtain Water soluble fraction and compound **1** (2.151 g). Water soluble fraction was separated by Sephadex LH-20 for several times (30%, 10% MeOH) to obtain compound **5** (48 mg) and further chromatography (MCI gel, 25% MeOH) of the other fraction afforded compound **9** (48 mg). 60% MeOH fraction (4.2 g) was subjected into Sephadex LH-

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Table 1. ^{13}C-NMR spectra of Compound 1, 3, 8

Carbon No.	Compound **1**	Compound **2**	Compound **3**
2	156.4	157.5	156.5
3	133.3	134.4	133.3
4	177.4	178.0	177.6
5	161.4	161.5	161.3
6	98.9	98.8	98.9
7	164.5	164.4	164.7
8	93.7	93.7	93.8
9	156.5	156.7	156.5
0	104.0	104.2	103.8
1'	121.0	121.3	120.9
2'	115.3	115.8	131.2
3'	145.1	145.4	115.2
4'	148.8	148.6	160.2
5'	116.2	115.6	115.2
6'	121.9	120.9	131.2
Glc-1	101.2	101.9	101.2
Glc-2	73.9	70.6	74.0
Glc-3	76.1	70.4	76.3
Glc-4	71.4	71.2	72.0
Glc-5	75.9	70.1	74.8
Glc-6	170.0	17.4	172.4

20 column chromatography to yield three fractions.

First fraction yield compound **2** (101 mg) by sephadex LH-20 with 30% MeOH, second fraction was separated by MCI gel chromatography with 50% MeOH to yield compound **4** (36 mg) and compound **8** (38 mg). And the last fraction was subjected into Sephadex LH-20 gel column chromatography with 40% MeOH to yield compound **3** (150 mg) and compound **7** (42 mg). The analytical data of isolated compounds were listed below.

Compound 1 – (Quercetin-3-O-β-D-glucuropyranoside)- Lemon yellow amorphous, mp : 193~195°C IR ν_{max}^{KBr} cm^{-1} : 3385 (OH), 1651, 1602, 1502 (Aromatic ring), 1657 (C = O), 1052 (Glycosidic -CO), 876 (Aromatic ring OH) Negative FAB MS : m/z 477[M-H]$^-$, 301[M-(GlcUA+H)]$^-$ ^{1}H-NMR (300MHz, DMSO-d_6) : δ5.48 (1H, d, J = 7.2Hz, anomeric proton), 6.19 (1H, d, J = 2.1Hz, H-6), 6.39 (1H, d, J = 2.1Hz, H-8), 6.82 (1H, d, J = 8.4Hz, H-5'), 7.51 (1H, s, H-2'), 7.59 (1H, dd, J = 2.4, 6.3Hz, H-6'), 12.55 (-OH) ^{13}C-NMR (75MHz, DMSO-d_6) : Table 1

Compound 2 – (Musizin-8-O-β-D-glucopyranoside)- Lemon yellow needle-shaped, mp : 203~204°C, IR ν_{max}^{KBr} cm^{-1} : 3391 (OH), 1631, 1621, 1508 (Aromatic ring), 1643 (C = O), 1075 (Glycosidic -CO), 870 (Aromatic ring OH) Negative FAB MS : m/z 377[M-H]$^-$, 215[M-(Glc-H)]$^-$ ^{1}H-NMR (300MHz, DMSO-d_6) : δ5.09 (1H, d, J = 7.2Mz, anomeric proton), 2.26 (3H, s, CH_3), 2.55 (3H, s, $COCH_3$), 7.23 (1H, s, H-4), 7.34 (1H, d, J = 8.1Mz, H-5), 7.41 (1H, dd, J = 8.1, 8.1Hz, H-6), 7.49 (1H, d, J = 8.1Hz, H-7), 9.62 (-OH) ^{13}C-NMR (75MHz, DMSO-d_6) : 19.3 (CH_3), 32.2 ($COCH_3$), 60.9 (C-6'), 70.0 (C-4'), 73.6 (C-2'), 76.5 (C-3'), 77.9 (C-5'), 102.9 (C-1'), 110.1 (C-9), 119.8 (C-4), 122.6 (C-5), 127.8 (C-6)

Compound 3 – (Quercetin-3-O-α-L-rhamnoside)-Lemon yellow amorphous powder, mp : 250~252°C, IR ν_{max}^{KBr} cm^{-1} : 3372 (OH), 1656, 1607, 1506 (Aromatic ring), 1607 (C = O), 1087 (Glycosidic -CO), 813 (Aromatic ring OH) Negative FAB MS : m/z 477[M-H]$^-$, 301[M-(Rha+H)]$^-$ ^{1}H-NMR (300MHz, DMSO-d_6) : δ5.23 (1H, d, J = 1.2Hz, anomeric proton), 6.19 (1H, d, J = 1.5Hz, H-6), 6.39 (1H, d, J = 2.1Hz, H-8), 6.85 (1H, d, J = 8.1Hz, H-5'), 7.24 (1H, dd, J = 2.1, 8.4Hz, H-6'), 7.28 (1H, s, H-2') ^{13}C-NMR (75MHz, DMSO-d_6) : Table 1

Compound 4 – (Emodin-8-O-β-D-glucopyranoside)- Orange color needle-shaped, mp : 210~211°C, IR ν_{max}^{KBr} cm^{-1} : 3420 (OH), 1620 (Chelated C = O), 1597, 1509, 1478 (Aromatic ring), 1071 (Glycosidic -CO), 1046 (Glycosidic -CO) Negative FAB MS : m/z 431[M-H]$^-$, 269[M-(Glc+H)]$^-$ ^{1}H-NMR (300MHz, DMSO-d_6) : δ5.06 (1H, d, J = 7.5Hz, anomeric proton), 2.40 (3H, s, CH_3), 7.00 (1H, d, J = 2.1Hz, H-7), 7.17 (1H, d, J = 2.7Hz, H-2), 7.28 (1H, d, J = 2.4Hz, H-5), 7.47 (1H, d, J = 2.4Hz, H-4), 13.23 (-OH) ^{13}C-NMR (75MHz, DMSO-d_6) : 26.5 (CH_3), 56.4 (C-6'), 65.3 (C-4'), 69.2 (C-2'), 72.3 (C-3'), 73.2 (C-5'), 96.8 (C-1'), 104.4 (C-7), 104.5 (C-5), 109.5 (C-9a), 110.5 (C-8a), 115.2 (C-4), 120.2 (C-2), 128.1 (C-4a), 132.5 (C-10a), 142.9 (C-3), 157.2 (C-8), 157.7 (C-1), 161.6 (C-6), 178.3 (C-10), 182.4 (C-9)

Compound 5 – (Caffeic acid)- Brown amorphous powder, mp : 223~225°C, IR ν_{max}^{KBr} cm^{-1} : 3435 (OH), 1647, 1619, 1510 (Aromatic ring) Negative FAB MS : m/z 179[M-H]$^-$ ^{1}H-NMR (300MHz, DMSO-d_6) : δ6.15 (1H, d, J = 15.9Hz, H-3), 6.74 (1H, d, J = 8.1Hz, H-6'), 6.94 (1H, d, J = 7.7Hz, H-2'), 7.00 (1H, d, J = 0.6Hz, H-5'), 7.38 (1H, d, J = 15.9Hz, H-2), ^{13}C-NMR (75MHz, DMSO-d_6) : Table 2

Compound 6 – (1-O-caffeoyl-β-D-glucopyranoside)- Brown amorphous powder, mp : 212°C, IR ν_{max}^{KBr} cm^{-1} :3385 (OH), 1651, 1602, 1502 (Aromatic ring), 1072 (Glycosidic -CO) Negative FAB MS : m/z 341[M-H]$^-$, 179[M-(Glc+H)]$^-$ ^{1}H-NMR (300MHz, DMSO-d_6) : δ5.59 (1H, d, J = 8.1Hz, anomeric proton), 6.39 (1H, d, J = 15.9Hz, H-3), 6.89 (1H, d, J = 8.4Hz, H-6'), 7.17 (1H, d, J = 8.1Hz, H-2'), 7.19 (1H, bs, H-5'), 7.68 (1H, d, J = 15.6Hz, H-2), 9.35, 9.77 (-OH) ^{13}C-NMR (75MHz, DMSO-d_6) : Table 2

Compound 7 – (1-methyl caffeic acid)-Brown amorphous powder, mp : 158~160°C, IR ν_{max}^{KBr} cm^{-1} : 3385 (OH), 1651, 1602, 1502 (Aromatic ring) Negative FAB MS : m/

Table 2. ^{13}C-NMR spectra of Compound 5, 6, 7

Carbon No.	Compound **5**	Compound **6**	Compound **7**
1	168.2	165.9	167.3
2	115.9	116.3	115.9
3	144.7	146.0	145.4
1'	125.8	125.9	125.7
2'	115.3	115.2	114.9
3'	145.7	146.9	145.8
4'	148.3	149.1	148.7
5'	114.7	113.8	113.9
6'	121.3	122.3	121.7
Glc-1		94.6	OCH_3 51.3
Glc-2		72.8	
Glc-3		78.1	
Glc-4		69.8	
Glc-5		76.8	
Glc-6		60.9	

z 193[M-H]$^-$ ^{1}H-NMR (300MHz, DMSO-d_6) : δ6.29 (1H, d, J = 16.2Hz, H-3), 6.78 (1H, d, J = 8.1Hz, H-6'), 7.02 (1H, d, J = 0.3, 2.1Hz, H-2'), 7.07 (1H, d, J = 2.1Hz, H-5'), 7.50 (1H, d, J = 16.2Hz, H-2), 9.21, 9.65 (-OH), 3.70 (3H, s, -OCH_3) ^{13}C-NMR (75MHz, DMSO-d_6) : Table 2

Compound 8 – (kaempferol-3-O-β-D-glucuropyranoside) -Brown amorphous powder, mp : 189~190.5°C, IR ν_{max}^{KBr} cm^{-1} :3372 (OH), 1656, 1607, 1506 (Aromatic ring), 1607 (C = O), 1087 (Glycosidic -CO), 813 (Aromatic ring OH) Negative FAB MS : m/z 461[M-H]$^-$, 285[M-(GlcUA +H)]$^-$ ^{1}H-NMR (300MHz, DMSO-d_6) : δ5.45 (1H, d, J = 6.6Hz, anomeric proton), 6.10 (1H, s, H-6), 6.32 (1H, s, H-8), 6.84 (2H, d, J = 8.7Hz, H-3', 5'), 8.01 (2H, d, J = 8.7Hz, H-2', 6'), 12.47 (-OH) ^{13}C-NMR (75MHz, DMSO -d_6) : Table 1

Compound 9 – (3-hydroxy-5-methyl-4-O-β-D-glucopyranosyl acetophenone, Rumexin)-Brown amorphous powder, m.p. 150-155°C [α]D: + 0.38° FAB-MS: *m/z* 327 [M]$^-$, 165 [M-Glc]$^-$ IR: Vmax 3365, 1621, 1074 cm^{-1} UV: λmax 238, 280 nm; ^{1}H-NMR (300 MHz, DMSO-d_6): δ4.78 (1 H, d, J = 7.7Hz, anomeric H), 6.39/6.36 (d, J = 2.1Hz, 1.8Hz, H-1, 3 respectively), 10.5 (-OH); ^{13}C-NMR (75MHz, DMSO-d_6): δ ppm 203.6, 32.2 (acetyl), 159.0 (C-4), 157.3 (C-5), 137.9 (C-1), 122.5 (C-3), 109.6 (C-2), 101.4 (C-6), 100.2, 77.0, 76.6, 73.1, 69.5, 60.5 (glycosidic signals), 20.1 (methyl)

Results and Discussion

Rumexin was obtained as a yellow powder from the aerial part of *Rumex aquatica* as through several phytochemical process and gel column chromatography.

Table 3. Isolated compounds from the aerial part of *Rumex aquatica*

No.	Name of the known compounds and the yields
1	Quercetin-3-O-β-D-glucuropyranoside (2.151 g)
2	Musizin-8-O-β-D-glucopyranoside (101 mg)
3	Quercetin-3-O-α-L-rhamnoside (150 mg)
4	Emodin-8-O-β-D-glucopyranoside (36 mg)
5	Caffeic acid (48 mg)
6	1-O-caffeoyl-β-D-glucopyranoside (36 mg)
7	1-methyl caffeic acid (42 mg)
8	kaempferol-3-O-β-D-glucuronopyranoside (38 mg)
9	3-hydroxy-5-methyl-4-O-β-D-glucopyranosyl acetophenone (48 mg)

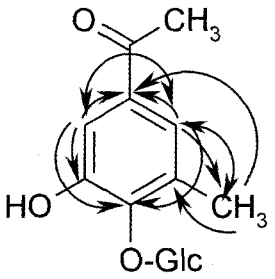

Fig. 1. Correlation of C-H in HMBC of Compound 9.

The UV spectrum in MeOH showed absorption at 238, 280 nm, and IR spectrum at 3365, 1621, and 1074cm^{-1}. Negative FAB-MS spectrum showed a molecular ion peak at *m/z* 327 [M]$^{-1}$, and a fragment ion peak that showed a loss of a hexose molecule at *m/z* 165 [M-Hexose]$^{-1}$.

^{1}H-NMR spectrum gave us doublet signals at δ6.39, 6.36 (J value = 2.1, 1.8Hz, respectively) which means meta-configuration of two aromatic proton. The other doublet signal at δ4.78 (J value = 7.7Hz) was an anomeric proton which shows a, β-configuration. And the signals at δ2.14, 2.44 by two methyl group were observed. In ^{13}C-NMR spectrum, signals at δ100.2, 77.0, 76.6, 73.1, 69.5, 60.5 indicated the existence of a glucose, and it was confirmed by usual acid-hydrolysis method and TLC with a D-glucose standard. There was a signal at δ203.6, a ketone signal. And two methyl signals at δ20.1, 32.2 but latter was low field shifted either. Put together these evidences, we could assume that there is an acetyl group on benzene ring. So, the structure of compound **9** is elucidated as below; a benzene ring which has two proton, an acetyl group, a methyl group, an O-glucose and a hydroxyl group. To confirm the structure, we used 2D-NMR technique such as H^1-H^{1}Cosy, HMQC, and HMBC. From HMQC, we found that aromatic proton siganls at δ6.39, 6.36 belongs to carbon siganls at δ101.4, 109.6, and from H^1-H^{1}Cosy, proton at δ6.36 is adjacent to methyl group. HMBC technique gave us inform that there

are two carbon signals (δ122.5, 159.0) that interact with two aromatic proton (δ6.39, 6.36) and the signal at δ159.0 also interacts with anomeric proton, so this carbon is ether-bonded with glucose. As for signal at δ122.5, it also interacts with methyl group's proton, so this carbon is between two protons. Carbon signal at δ109.6, 122.5, 137.9 interact with proton of methyl group, and δ20.1, 101.4, 122.5, 159.0 with δ6.36. The HMBC experiment confirmed the structure for the new compound **9** (3-hydroxy-5-methyl-4-O-β-D-glucopyranosyl acetophenone), which was then named Rumexin.

Other known compound **1,2,3,4,5,6,7,8** isolated and characterized by spectroscopic methods and by comparison with literature: Quercetin-3-O-β-D-glucuropyranoside (2.151 g) (Kashiwada. *et al.*, 2004), Musizin-8-O-β-D-glucopyranoside (101 mg) (Li *et al.*, 1989), Quercetin-3-O-α-L-rhamnoside (150 mg) (Shamuratov *et al.*, 2003) (Ko *et al.*, 1995), Emodin-8-O-β-D-glucopyranoside (36 mg) (Coskun *et al.*, 1990), Caffeic acid (48 mg) (Yang *et al.*, 2002) (Nishibe *et al.*, 1982), 1-O-caffeoyl-β-D-glucopyranoside (36 mg) (Warashina *et al.*, 1992), 1-methyl caffeic acid (42 mg) (Kunzemann *et al.*, 1997), and Kaempferol-3-O-β-D-glucuropyranoside (38 mg) (Dumknow *et al.*, 1969)

Among the compounds, Compound **1** was isolated in bulk volume (2.151 g from 4.2 kg of plant sample) and it seems that *Rumex aquatica* can be used as a resource material for it.

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