Natural Product Sciences
9(1) : 31-33 (2003)

A Triterpenoid Glucoside and Phenolic Compounds from *Rosa davurica*

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Abstract – A triterpenoid glucoside and five phenolic compounds have been isolated from the roots and leaves of *Rosa davurica*. They were elucidated as rosamultin and gallic acid from the roots, and methyl gallate, gallic acid, protocatechuic acid, quercetin and hyperoside from the leaves of this plant, respectively.
Key words – *Rosa davurica*, Rosaceae, rosamultin, triterpenoid glycoside, protocatechuic acid

Introduction

Fruits, roots and flowers of *Rosa davurica* Pall. have been used in traditional Chinese medicine for the treatment of inflammation of the stomach and indigestion. The fruit of this plant, which is rich in vitamine C, is used as a health drink (An, 1998; Yoshida *et al.*, 1989). *Rosa davurica* was reported that the extract had a promoting action on learning and memory in mice (Piao *et al.*, 1994), inhibition of immediate-type allergic reaction (Kim *et al.*, 1999) and anti-HIV protease activity (Park *et al.*, 2000). Hydrolysable tannins including davuriciin M_1, davuriciin T_1, davuriciin D_1, davuriciin D_2 and casuarictin from the roots of *Rosa davurica* (Yoshida *et al.*, 1989; 1991), and triterpenes such as betulinic acid, oleanolic acid, maslinic acid, ursolic acid and pomolic acid from the percarps (Kuang *et al.*, 1989) have been so far identified. In our continuing studies on rosaceous medicinal plants, we have examined the bioactive substances from the roots and leaves of *Rosa davurica,* and isolated a triterpenoid and six phenolic compounds.

Experimental

Plant material – *Rosa davurica* was collected in Jeongsun, Gangwon-do on October 7, 1998. The voucher specimen (No; NM-0353) is deposited at the Herbarium of Department of Oriental Medicine Resources, Sunchon National University.

Instrument – ^{1}H-(400 MHz) and ^{13}C-NMR (100.5 MHz) spectra were recorded on Bruker model AMX 400 spectrometer with TMS as internal standard.

Extraction and isolation – The dried and powdered roots (1.4 kg) and leaves (2.46 kg) of *Rosa davurica* were refluxed with methanol, respectively. These extracts have been partitioned with organic solvents of the different polarities to afford dichloromethane, ethyl acetate, *n*-butanol and aqueous fractions, respectively. The ethyl acetate fraction from the roots of this plant was subjected to chromatograph using silica gel with CH_2Cl_2-MeOH-H_2O (5:1:1, lower layer; 25:7:5, lower layer; 7:3:1, lower layer) as solvents to give RDRE 50-62 subfraction (compound **2**) and RDRE 204-213 subfraction (compound **1**). And compounds **3, 5, 4** and **2** were obtained from the subfractions RDLE 56-69, RDLE 76-82, RDLE 134-136 and RDLE 177-185, respectively, by silica gel column chromatography of ethyl acetate soluble fraction from the leaves with the elution of CH_2Cl_2-MeOH-H_2O (7:3:1, lower layer; 65:35:10, lower layer). The *n*-butanol fraction from the leaves was subjected to chromatograph using silica gel with CH_2Cl_2-MeOH-H_2O (65:35:10, lower layer) as solvents to give the subfraction RDLB 235-239 subfraction (compound **6**).

Compound 1 – ^{1}H-NMR (400 MHz, pyridine-d_5) δ1.03, 1.05, 1.14, 1.23, 1.37, 1.62 (each 3H, s, 6xCH_3), 1.10 (3H, d, J = 5.5 Hz, H-30), 2.86 (1H, s, H-18), 3.34 (1H, d, J = 9.4 Hz, H-3α), 3.75 (1H, m, H-2β), 5.51 (1H, brs, H-12), 6.16 (1H, d, J = 7.6 Hz, anomeric H); ^{13}C-NMR (100.5 MHz, pyridine-d_5) δ177.0 (C-28), 139.3 (C-13), 128.4 (C-12), 95.8 (C-1'), 83.9 (C-3), 79.1 (C-5'), 78.8 (C-3'), 74.0 (C-2'), 72.7 (C-19), 71.2 (C-4'), 68.7 (C-2), 62.4 (C-6'), 56.1 (C-5), 54.4 (C-18), 48.6 (C-17), 48.3 (C-1), 47.8 (C-9), 42.2

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(C-14 and 20), 40.8 (C-8), 39.8 (C-10), 38.5 (C-4), 37.8 (C-22), 33.5 (C-7), 29.3 (C-23), 29.1 (C-15), 27.1 (C-29), 26.7 (C-21), 26.1 (C-16), 24.5 (C-27), 24.1 (C-11), 19.1 (C-6), 17.6 (C-24), 17.4 (C-26), 16.9 (C-30), 16.6 (C-25)

Compound 1a – ^{1}H-NMR (400 MHz, pyridine-d_5) δ1.02, 1.09, 1.11, 1.28, 1.45, 1.73 (each 3H, s, 6 x C$\underline{H}_3$), 1.13 (3H, d, J = 6.2 Hz, H-30), 3.05 (1H, s, H-18), 3.40 (1H, d, J = 9.4 Hz, H-3α), 4.10 (1H, m, H-2β), 5.59 (1H, brs, H-12)

Compound 1b – ^{1}H-NMR (400 MHz, $CDCl_3$) δ0.72, 0.90, 0.97, 1.07, 1.21, 1.26 (each 3H, s, 6 x C$\underline{H}_3$), 0.94 (3H, d, J = 7.2 Hz, H-30), 1.98, 2.07 (each 3H, s, OAc), 2.55 (1H, s, H-18), 4.77 (1H, d, J = 10.2 Hz, H-3α), 5.12 (1H, m, H-2β), 5.34 (1H, brs, H-12)

Compound 2 – ^{1}H-NMR (400 MHz, DMSO-d_6) δ6.93 (2H, s, H-2 and 6); ^{13}C-NMR (100.5 MHz, DMSO-d_6) δ167.8 (C-7), 145.7 (C-3 and 5), 138.2 (C-4), 120.8 (C-1), 108.9 (C-2 and 6)

Compound 3 – ^{1}H-NMR (400 MHz, DMSO-d_6) δ3.75 (3H, s, $COOCH_3$), 6.94 (2H, s, H-2 and 6); ^{13}C-NMR (100.5 MHz, DMSO-d_6) δ166.5 (C-7), 145.7 (C-3 and 5), 138.5 (C-4), 119.5 (C-1), 108.6 (C-2 and 6), 51.7 (CH_3)

Compound 4 – ^{1}H-NMR (400 MHz, DMSO-d_6) δ6.79 (1H, d, J = 8.3 Hz, H-5), 7.29 (1H, dd, J=2.1 and 8.3 Hz, H-6), 7.34 (1H, d, J = 2.1 Hz, H-2); ^{13}C-NMR (100.5 MHz, DMSO-d_6) δ167.5 (C-7), 150.1 (C-4), 144.9 (C-3), 122.0 (C-1), 121.6 (C-6), 116.6 (C-2), 115.1 (C-5)

Compound 5 – ^{1}H-NMR (400 MHz, DMSO-d_6) δ6.18 (1H, d, J = 2.1 Hz, H-6), 6.41 (1H, d, J = 2.1 Hz, H-8), 6.88 (1H, d, J = 8.6 Hz, H-5'), 7.54 (1H, dd, J = 2.1 and 8.6 Hz, H-6'), 7.66 (1H, d, J = 2.1 Hz, H-2'); ^{13}C-NMR (100.5 MHz, DMSO-d_6) δ175.7 (C-4), 163.7 (C-7), 160.6 (C-5), 156.1 (C-9), 147.6 (C-4'), 146.7 (C-2), 145.0 (C-3'), 135.6 (C-3), 121.9 (C-1'), 119.8 (C-6'), 115.5 (C-5'), 115.0 (C-2'), 103.0 (C-10), 98.0 (C-6), 93.2 (C-8)

Compound 6 – ^{1}H-NMR (400 MHz, DMSO-d_6) δ5.33 (1H, d, J = 7.1 Hz, anomeric H), 6.18 (1H, d, J = 2.0 Hz, H-6), 6.40 (1H, d, J = 2.0 Hz, H-8), 6.86 (1H, d, J = 8.5 Hz, H-5'), 7.53 (1H, dd, J = 2.1 and 8.5 Hz, H-6'), 7.66 (1H, d, J = 2.1 Hz, H-2'); ^{13}C-NMR (100.5 MHz, DMSO-d_6) δ177.5 (C-4), 164.2 (C-7), 161.2 (C-5), 156.3 (C-2 and 9), 148.5 (C-4'), 144.8 (C-3'), 133.5 (C-3), 121.9 (C-6'), 121.0 (C-1'), 115.9 (C-5'), 115.2 (C-2'), 103.8 (C-10), 101.9 (C-1''), 98.6 (C-6), 93.5 (C-8), 75.8 (C-5''), 73.2 (C-3''), 71.2 (C-2''), 67.9 (C-4''), 60.1 (C-6'')

Results and Discussion

The ^{1}H-NMR spectrum of compound **1** exhibited the presence of six tertiary methyls (δ1.03, δ1.05, δ1.14, δ1.23, δ1.37, δ1.62), one secondary methyl (δ1.10, d, J = 5.5 Hz), an olefinic proton (δ5.51, brs), and one anomeric proton (δ6.16, d, J=7.6 Hz). Alkaline hydrolysis of compound **1** gave **1a** as a genin, then acetylation of **1a** with Ac_2-pyridine afforded **1b**. The ^{1}H-NMR spectrum of **1b** showed six tertiary methyl signals at 0.72-1.26, secondary methyl signal at δ0.94 (3H, d, J = 7.2 Hz), two acetyl signals at δ1.98 and δ2.07. The ^{1}H-NMR spectrum of **1b** also showed a doublet (1H, J = 10.2 Hz) centered at δ5.12 due to H-2β and a multiplet centered at δ4.77 due to H-3α, and a multiplet at δ5.34 for an olefinic proton. Thus, from the above evidence, **1a** was characterized as 2α,3β,19α-trihydroxy-urs-12-en-28-oic acid (tormentic acid) and ^{13}C-NMR analysis of this compound confirmed the above suggestion. From the above results, **1a** was characterized as tormentic acid, previously known from *Potentilla tormentilla* (Potier *et al.*, 1966), *Rosa multiflora* (Takahashi *et al.*, 1969) and *Trogopterus xanthipes* (Numata *et al.*, 1989). In the ^{13}C-NMR spectrum of compound **1**, a set of carbon signals due to β-glucopyranosyl ester moiety and an anomeric carbon signal (δ95.8) at rather highfield strongly indicated that one mole of glucose was linked to the 28-carboxylic acid of **1a** in the ester form. The relative large coupling constant (J = 7.6 Hz) of anomeric proton signal also indicated the β-configuration for glucoside linkage. Accordingly, the chemical structure of **1** was established as 28-β-D-glucopyranosyl tormentic acid (rosamultin). The ^{1}H-NMR and ^{13}C-NMR spectra of compound **1** were in agreement with those of reference (Young *et al.*, 1987). This compound had previously been isolated from *Rosa multiflora* (Du *et al.*, 1983), *Rosa rugosa* (Young *et al.*, 1987) and *Rosa maximowicziana* (Cho *et al.*, 1993), however was first found from this plant specimen. The ^{1}H-NMR spectra of compounds **2** and **3** showed one singlet at δ6.93 and two singlets at δ6.94 and δ3.75 attributable to galloyl and methoxyl protons, respectively. The comparison of the ^{13}C-NMR spectra of compounds **2** and **3** with literature data (Park *et al.*, 1993) showed them to be gallic acid and methyl gallate, respectively. The ^{1}H-NMR spectrum of compound **4** indicated the presence of aromatic signals at δ6.79 (J = 8.3 Hz), δ7.29 (J = 2.1 & 8.3 Hz) and δ7.34 (J = 2.1 Hz) assignable to H-5, H-6 and H-2, respectively. Its ^{13}C-NMR spectrum also showed the signals of two oxygen-bearing aromatic ring (δ150.1, δ144.9) and a ketone group (δ167.5). Compound **4** is characterized as protocatechuic acid (Pouchert and Behnke, 1993). Compound **5** was identified as quercetin by comparison of spectral data with published values (Markham *et al.*, 1978). The ^{1}H-NMR spectrum of compound **6** showed one anomeric proton signal at δ5.33 (J = 7.1 Hz), and an ortho-coupled doublet, a meta-coupled doublet and a ortho, meta-coupled doublet-doublet attributable to H-5', H-2' and H-6' of B-ring, respectively, and two meta-coupled doublets

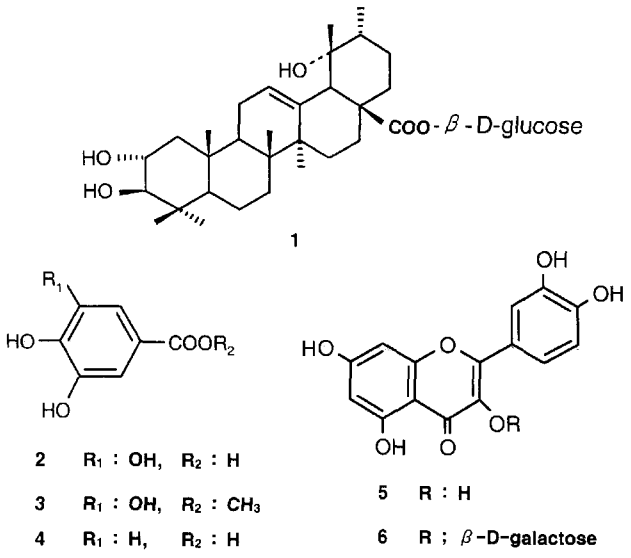

Fig. 1. The chemical structures isolated from *Rosa davurica.*

ascribable to H-6 and H-8 of A-ring in the flavonoid skeleton. The sugar moiety of compound **6** was determined to be β-D-galactopyranose by the *J* values of the anomeric proton signals and the ^{13}C-NMR spectrum. A comparison of the ^{13}C-NMR spectrum of compound **6** with literature data (Park *et al.*, 1993) showed it to be hyperoside.

From the above results, the compounds isolated from *Rosa davurica* were characterized as rosamultin, gallic acid, methyl gallate, protocatechuic acid, quercetin and hyperoside.

Acknowledgements

This work was supported by non directed research fund of Sunchon National University, Korea (2001). One of the authors (J.C.P.) wishes to thank S.N.U. for providing financial support.

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(Accepted February 19, 2002)