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Triterpenoids from Rubi Fructus (Bogbunja)

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The dried unripe fruits of *Rubus* sp. (Rubi Fructus, Bogbunja) have yielded β-sitosterol glucoside and four urs-12-en-28-oic acid derivatives, three of which were as their glucosides. They were identified as 23-hydroxytormentic acid, rosamultin, niga-ichigosides F_1 and F_2 on the basis of spectral data.

Key words: Rubi Fructus, Bogbunja, *Rubus* sp., Rosaceae, 23-Hydroxytormentic acid, Rosamultin, Niga-ichigosides F_1 and F_2

INTRODUCTION

The crude drug Rubi Fructus (Bogbunja) is designated as the dried unripe fruits of *Rubus coreanus* Miquel (Rosaceae) (Chi and Lee, 1988), and has been used as a tonic and to normalize renal functions (Perry, 1980). However, the botanical origin of the Rubi Fructus found in Korean crude drug markets are mostly derived from the fruits of *R. crataegifolius* and seems to be sometimes mixed fruits of *R. parvifolius* and *Rubus* sp. very close to *R. phoenicolasius* (Komatsu *et al.*, 1990). A number of terpenoids (Ganguly, 1972; Shaw *et al.*, 1987; Hattori *et al.*, 1988; Mukherjee *et al.*, 1984; Sarkar and Ganguly, 1978), and their glycosides from leaves (Zhou *et al.*, 1992; Seto *et al.*, 1984; Ohtani *et al.*, 1992), roots (Choi *et al.*, 1991; Gao *et al.*, 1985) and fruits (Chou *et al.*, 1987; Pabst *et al.*, 1991; 1992a; 1992b; Ohitani *et al.*, 1991; Kim and Kim, 1987) of *Rubus* spp. as well as flavonoids (Shamsizade and Novruzov, 1989; Ryan and Coffin, 1971; Wald *et al.*, 1986; Henning, 1981; Do *et al.*, 1988) have so far been reported.

In continuation of the work on the chemical consitutents of *Rubus* species (Do *et al.*, 1988) we report herein the isolation and structure elucidation of the components from the unripe fruits of *Rubus* sp., which have now been used as Bongbunja in Korean crude drug markets.

MATERIALS AND METHODS

General experimental procedures

Melting points were determined on a Mitamura-Riken apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 283B spectrophotometer. ^{1}H-NMR spectra were obtained on either a Varian FT-80A(80 MHz) or a Bruker AM-300 (300 MHz) spectrometer using TMS as an internal standard. ^{13}C-NMR spectra were recorded with a Bruker AM-300 (75.5 MHz) instrument. EI mass were determined on a Hewlett-Packard 5985B GC/MS System equipped with direct inlet system. For TLC, Kieselgel 60 F_{254} plates (Merck) were used.

Plant material

The dried unripe fruits of *Rubus* sp. were purchased at herbal drug store in Wonju city, Kangwon-do province in 1989. A voucher specimen was deposited at College of Natural Sciences, Sangji University.

Extraction and isolation

The dried fruits (500 g) were percolated with ether at room temperature. The extracts were combined and concentrated in vacuo to give a residue (20 g). The marc was refluxed with MeOH to afford MeOH extract which was in turn partitioned with EtOAc and then BuOH. The EtOAc and BuOH layers were separately combined and evaporated in vacuo to yield EtOAc (6.3 g) and BuOH (13 g) fractions. The EtOAc soluble fraction (6.3 g) was chromatographed with a flash column (Merck No. 9385, 750 g) by elution with EtOAc to yield 14 subfractions. Subfraction 7 (0.3 g) was rechromatographed over SiO_2 with $CHCl_3$-MeOH (9 : 1) to give 13 subfractions, among which subfraction No. 4 (50 mg) was subjected to column chromatography with $CHCl_3$-MeOH (gradient, 0 to 5%) to afford com-

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pounds **I** and **II**.

Compound I—recrystallized from MeOH as amorphous powder (50 mg).

mp. 288-292℃; [lit. (Seto *et al.*, 1984) mp. 283-5℃; $[a]_D^{17}$ +22.5° (MeOH)]; IR ν_{max}^{KBr} 3400 (OH), 1690 (COOH), 1047, 1032, 800 cm^{-1}, ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 1.05 (3H, s, CH_3), 1.08 (3H, s, CH_3), 1.09 (3H, d, J=7.7 Hz, 30-CH_3), 1.31 (3H, s, CH_3), 1.40 (3H, s, CH_3), 1.63 (3H, s, CH_3), 3.02 (1H, brs, H-18), 3.06 (1H, dt, J=4.6, 11.5, 11.5 Hz, H-16α), 3.70, 4.17 (1H each, d, J=10.4 Hz, H-23), 4.16 (1H, d, J=7.4 Hz, H-3), 4.23 (1H, m, H-2), 5.56 (1H, t-like, H-12); MS (30 eV), *m/z* (rel. int., %) 504 [M^+] (1.5), 486 [M-H_2O]$^+$ (1.4), 459 [M-COOH]$^+$ (4.3), 458 [M-(COOH+H)]$^+$ (12.4), 442 [M-(H_2O+CO_2)]$^+$ (3.2), 440 [M-(H_2O+COOH+H)]$^+$ (3.3), 386 (9.2), 368 [386-H_2O]$^+$ (1.4), 264 [a^+] (1.0), 246 [a-H_2O]$^+$ (6.8), 231 [a-(H_2O+CH_3)]$^+$ (9.0), 239 [b^+] (1.4), 221 [b-H_2O]$^+$ (5.3), 219 [a-COOH]$^+$ (9.0), 218 [c^+] (15.5), 201 [a-(COOH+H_2O)]$^+$ (32.5), 146 [d^+] (100).

Methylation of compound I—Compound I was methylated with CH_2N_2 at room temperature to afford a methylester.

Subfractions 9 and 10 were combined and methylated with CH_2N_2 at room temperature to afford a methylated product which was chromatographed by a SiO_2 column eluted with $CHCl_3$-MeOH (gradient) to give compound **I** methylester and compound **III**

Compound I methylester—crystallized from MeOH as amorphous white powder. mp. 167-170℃; IR ν_{max}^{KBr} 3420 (OH), 1717 (ester), 1650, 1150, 1049, 1035, 800, 765 cm^{-1}; ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 0.90 (3H, s, CH_3), 1.06 (3H, d, J=6.7 Hz, 30-CH_3), 1.08 (3H, s, CH_3), 1.12 (3H, s, CH_3), 1.34 (3H, s, CH_3), 1.57 (3H, s, CH_3), 2.81 (1H, brs, H-18), 3.00 (1H, dt, J=4.6, 11.5, 11.5 Hz, H-16α), 3.71 (3H, s, $COOCH_3$), 3.72, 4.19 (1H each, d, J=10.7 Hz, H-23), 4.17 (1H, d, J=9.4 Hz, H-3), 4.23 (1H, ddd, J=3.9, 10.5, 10.5 Hz, H-2), 5.46 (1H, t-like, H-12); MS (30 eV), *m/z* (rel. int., %) 518 [M^+] (6.2), 500 [M-H_2O]$^+$ (3.5), 482 [M-2H_2O]$^+$ (9.5), 459 [M-CH_3COO]$^+$ (13.9), 458 [M-HOAc]$^+$ (46.7), 386 (13.6), 278 [a^+] (6.1), 260 [a-H_2O]$^+$ (14.2), 250 [e^+] (9.0), 219 [a-CH_3COO]$^+$ (23.5), 218 [c^+] (31.2), 201 [a-(CH_3COO+H_2O)]$^+$ (48.5), 179 [f^+] (100), 146 [d^+] (86.4).

Compound II—crystallized from MeOH as amorphous powder (15 mg).

mp. 292-3℃; IR ν_{max}^{KBr} 3420, 1640, 1076, 1025 cm^{-1}; MS (30 eV) *m/z* (rel. int., %) 439 (0.6), 414 (21.0), 400 (3.2), 396 (100), 381 (15.4), 329 (4.9), 275 (6.7), 273 (5.6), 255 (24.0), 231 (12.3), 213 (29.3), 175 (19.7), 173 (17.4), 163 (33.1), 161 (49.9), 159 (31.7), 147 (68.2), 145 (66.6), 135 (42.4), 133 (36.1), 121 (42.7).

Acetylation of compound II—Compound **II** (10 mg) was acetylated with Ac_2O/pyridine at room temperature. The reaction product was blowed to dryness with a N_2 stream and then crystallized from MeOH to afford a acetate as colorless needles.

mp. 162-4℃; ^{1}H-NMR (80 MHz, $CDCl_3$) δ: 0.67 (3H, s, 18-CH_3), 0.98 (3H, s, 19-CH_3), 1.99 (3H, s, OAc), 2.01 (3H, s, OAc), 2.03 (3H, s, OAc), 2.06 (3H, s, OAc), 4.58 (1H, d, J=7.3 Hz, Glc H-1), 5.34 (1H, brd, J=3.4 Hz, H-6).

Compound III—crystallized from MeOH as amorphous powder (25 mg).

mp. 200-4℃ {lit. (Du *et al.*, 1983) mp. 208-210℃, $[\alpha]_D$=+10° (EtOH)}; ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 1.05 (3H, d, J=5.9 Hz, 30-CH_3), 1.05 (3H, s, CH_3), 1.08 (3H, s, CH_3), 1.20 (3H, s, CH_3), 1.24 (3H, s, CH_3), 1.45 (3H, s, CH_3), 1.66 (3H, s, CH_3), 2.92 (1H, brs, H-18), 3.08 (1H, dt, J=4.4, 11.7, 11. 7 Hz, H-16α), 3.36 (1H, d, J=9.3 Hz, H-3), 4.09 (1H, m, H-2), 5.53 (1H, t-like, H-12), 6.29 (1H, d, J=7.9 Hz, Glc H-1); MS (30 eV), *m/z* (rel. int., %) 488 [genin]$^+$ (4.0), 470 [488-H_2O]$^+$ (3.2), 442 [488-(COOH+H)]$^+$ (24.2), 424 [488-(COOH+H+H_2O)]$^+$ (6.3), 370 (8.6), 264 [a^+] (11.5), 246 [a-H_2O]$^+$ (21.9), 223 [b^+] (12.1), 219 [a-COOH]$^+$ (16.1), 218 [c^+] (17.0), 201 [a-COOH+H_2O)]$^+$ (42.4), 200 [a-(COOH+H+H_2O)]$^+$ (12.4), 146 [d^+] (84.7).

Subfraction No. 9 (100 mg) was purified with a SiO_2 column by elution with EtOAc-MeOH (98 : 2) to give compound **IV** (13 mg).

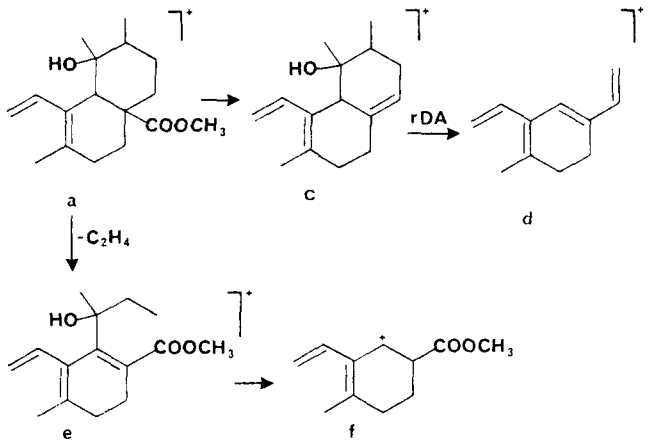
Compound IV—crystallized from MeOH as amorphous powder (20 mg).

mp. 214-6℃ {lit. (OHtani *et al.*, 1990) mp. 214-6℃, $[\alpha]_D^{18}$=+15.2° (MeOH)}; IR ν_{max}^{KBr} 3410 (OH), 1730 (ester), 1640, 1070, 1030, 810 cm^{-1}; ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 0.87 (3H, s, CH_3), 1.06 (3H, d, J=6.6 Hz, 30-CH_3), 1.08 (3H, s, CH_3), 1.23 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.63 (3H, s, CH_3), 2.92 (1H, brs, H-18), 3.06 (1H, dt, J=4.2, 11.7, 11.7 Hz, H-16α), 3.73, 3.90 (1H each, d, J=10.8 Hz, H-23), 5.55 (1H, brs, H-12), 6.29 (1H, d, J=7.9 Hz, Glc H-1); ^{13}C-NMR (75.5 MHz, pyridine-d_5) δ: 42.8, 66.3, 79.0, 41.9, 43.5, 18.6, 33.2, 40.8, 47.8, 38.5, 24.2, 128.4, 139.4, 42.3, 29.2, 26.1, 48.7, 54.5, 72.7, 42.1, 26.7, 37.7, 71.3, 17.2[a], 17.6[a], 17.8[a], 24.6, 177.0, 27.0, 16.7 (genin part C-1 to C-30), 95.9, 74.1, 79.0[b], 71.3, 79.2[b], 62.4 (glucose C-1 to C-6). [a,b]Assignements may be exchangeable.

Subfraction No. 11 (800 mg) was rechromatographed over SiO_2 with EtOAc saturated with H_2O-MeOH (gra-

dient, 0 to 6%) to afford compound **V**, which was crystallized from MeOH as colorless needles (230 mg).

Compound V—mp. 233-6℃ (Seto *et al.*, 1984) mp. 231-2℃, $[\alpha]_D^{26}$ = +11.2° (MeOH)}; IR ν_{max}^{KBr} 3430 (OH), 1730 (ester), 1640, 1075, 1035 cm^{-1}; ^{1}H-NMR (300 MHz, pyridine-d_5) δ: 1.06 (3H, d, *J*=6.7 Hz, 30-CH_3), 1.07 (3H, s, CH_3), 1.14 (3H, s, CH_3), 1.22 (3H, s, CH_3), 1.37 (3H, s, CH_3), 1.61 (3H, s, CH_3), 2.91 (1H, brs, H-18), 3.06 (1H, dt, *J*=4.3, 11.8, 11.8 Hz, H-16α), 3.70 (1H, d, *J*=10.5 Hz, H-23), 5.54 (1H, brs, H-12), 6.28 (1H, d, *J*=7.9 Hz, Glc H-1); ^{13}C-NMR (75.5 MHz, pyridine-d_5) δ: 47.9, 68.9, 78.3, 43.6, 48.0[a], 18.9, 33.1, 40.8, 47.8[a], 38.3, 24.2, 128.3, 139.2, 42.1, 29.2, 26.1, 48.6, 54.4, 72.6, 42.1, 26.6, 37.7, 66.6, 14.2, 17.4[b], 17.5[b], 24.5, 177.0, 26.9, 16.6 (genin part C-1 to C-30), 95.8, 74.0, 78.9[c], 71.2, 79.2[c], 62.3 (glucose C-1 to C-6). [a,b,c]Assignments may be exchangeable.



Scheme I. Characteristic mass fragment ions for 19α-hydroxy-urs-12-en-28-oic acid derivatives (in case of compounds **I** and **III**, the $COOCH_3$ group at C-17 was replaced by COOH).

RESULTS AND DISCUSSION

The MeOH extract of the fruits was subjected to solvent fractionation and repeated column chromatography to give compounds **I-V**.

Compound **I** was obtained as an amorphous powder. It gave a positive coloration in the Liebermann-Burchard test. The IR spectrum showed absorptions for hydroxyl groups, acid and trisubstituted double bond. The ^{1}H-NMR spectrum showed five angular methyl singlets, a secondary methyl doublet at δ 1.09 (*J*=7.7 Hz) and one proton t-like signal at δ 5.56 for a vinylic proton. The MS of **I** exhibited a molecular ion peak at *m/z* 504 and significant fragment peaks resulting from retro-Diels Alder cleavage of ring C at *m/z* 264(a) and *m/z* 239(b) indicating that three hydroxyl groups were located at rings A/B and a carboxylic acid and a hydroxyl group at rings D/E (Budzikiewicz *et al.*, 1963). Other important ions were at *m/z* 218 and 146, corresponding to c and d, respectively, and which are characteristic of the presence of a tertiary hydroxyl function at C-19 in the urs-12-en skeleton (Ngounou *et al.*, 1988; Aimi *et al.*, 1989; Delgado *et al.*, 1989). The occurrence of a broad singlet signal at δ 3.02 ppm for H-18 as well as a characterisitic double-triplet signal with coupling constants *J*=4.6, 11.5 and 11.5 Hz at δ 3.06 ppm assignable to H-16α which was caused downfield shift by the anisotropic effect due to 19 α-hydroxyl group supported that the basic skeleton of compound **I** was a urs-12-en-28-oic acid possessing one α-hydroxyl group at C-19 (Aimi *et al.*, 1989; Aquino *et al.*, 1990; Liang *et al.*, 1989). The presence of additional two oxymethine protons resonating at δ 4.23(m) and 4.16 (d, *J*=7.4 Hz) together with a hydroxymethyl protons at δ 3.70 (d, *J*=10.4 Hz) and 4.17 ppm (d, *J*=10.4 Hz) permitted the assignment of 2α,3β,23-trihydroxy functionalities (Ohtani *et al.*, 1990). Therefore, the structure of compound **I** was formulated as 2α,3β, 19α,23-tetrahydroxy-urs-12-en-28-oic acid (23-hydroxy-tormentic acid (Houghton and Lian, 1986; De Tommasi *et al.*, 1992; Reher *et al.*, 1991).

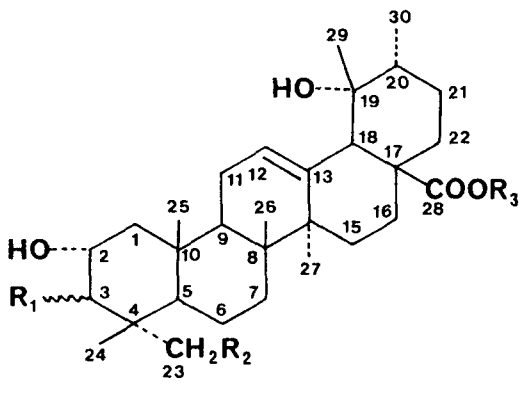
Compound **II** was identified as β-sitosterol 3-O-glucoside which was confirmed by direct comparison with an authentic sample.

The ^{1}H-NMR spectrum of compound **III** suggested ester glucoside because the anomeric proton signal was observed at δ 6.29 (d, *J*=7.9 Hz). The EI mass spectrum of **III** showed an ion peak at *m/z* 488 in the high mass region and other important fragment ions at *m/z* 370, 264(a), 223(b), and 146(d) diagnostic of retro-Diels Alder cleavage of the ring C of 19-hydroxyursolic acid derivatives carrying additional hydroxyl function on rings A/B (Budzikiewicz *et al.*, 1963; Aimi *et al.*, 1989). The presence of two carbinol protons at δ 4.09(m) and 3.36(d) with large coupling constant (*J*=9.3 Hz) was in agreement with the diaxial stereochemistry of the two carbinol protons at C-2 and 3 (Du *et al.*, 1983; De Tommasi *et al.*, 1992). Consequently, the structure of **III** was deduced to be 2α,3β,19α-trihydroxyurs-12-en(28→1)-β-D-glucopyranosyl ester [tormentic acid-(28→1)-glucopyranosyl ester], which was identical to rosamultin isolated from *Rosa multiflora* (Du *et al.*, 1983) and various Rosaceae plants (Rücker *et al.*, 1991; Reher *et al.*, 1991) as well as from Caulis Sargentodoxae (Sargentodoxaceae) (Rücker *et al.*, 1991), *Desfontainia spinosa* (Loganiaceae) (Houghton and Lian, 1986) and *Aphloia theiformis* (Flacourtiaceae) (Gopalsamy *et al.*, 1988).

The NMR spectra of **IV** and **V** indicated their similarity with β-glucosyl 19α-hydroxyurs-12-en-28-oate derivatives (Aimi *et al.*, 1989; Liang *et al.*, 1989), except for the signals ascribed to the ring A. The ^{13}C-NMR spectra showed that the signals of the aglycone of

IV were almost superimposable with those of the aglycone of **V**, the only significant differences being carbon signals of ring A. Both are revaled three carbinol carbon signals for 2,3,23(or 24)-trihydroxy functionalities. The 2α,3α,23-trihydroxy substitution for **IV** was evident from the chemical shift values of C-1 (δ 42.8) and C-5 (δ 43. 5) which could be explained as due to the γ-gauche shielding effect of axially oriented C-3 hydroxy group as well as the presence of hydroxymethyl group at C-23 (Kang, 1987). While it showed different chemical shifts in **V**. These on going from **IV** to **V** are shifted by +5.1 (C-1), +2.6 (C-2), +1.7 (C-4), +4.5 (C-5) and −3 (C-24) ppm, respectively. This trend can be explained by the presence of equatorially oriented C-3 hydroxy group in **V**. Furthermore the ^{13}C signals of **IV** and **V** [δ 177 and 95.9 in **IV**; δ 177 and 95.8 in **V**] together with a set of signals due to β-glucopyranosyl moiety indicated the location of β-glucopyranosyl group on C_{28} (Du *et al.*, 1983; Ohtani *et al.*, 1990). Therefore, the structures of **IV** and **V** were elucidated as 2α,3α,19α,23-tetrahydroxy urs-12-en-(28→1)-β-D-glucopyranosyl ester (niga-ichgoside F_2) and its 3β-hydroxy epimer, 23-hydroxytormentic acid (28→1)-β-D-glucopyranosyl ester (niga-ichgoside F_1) (Seto *et al.*, 1984), respectively.

Recently, Ohtani *et al.* reported the isolation and identificantion of niga-ichgosides F_1 and F_2, suavissimoside R_1 and coreanoside F_1 from *R. coreanus*. On the other hand, suavissimoside R_1, niga-ichgosides F_1 and F_2 from the fruits of *R. crataegifolius* and niga-ichgosides F_1 and F_2 from *R. parvifolius* were also identified. The HPLC analysis of commercial Bogbunja from crude drug market in Seoul showed very similar pattern to those of fruits of *R. coreanus* (Ohtani *et al.*, 1990). However, we could not detected suavissimoside R_1 as well as diterpene- and other triterpene glycosides from our sample. Therefore our sample is most likely a mixture of unripe fruits of *R. parvifolius* and those of other species from the chemotaxonomical point of view.



I	R_1 = β-OH	R_2 = OH	R_3 = H
III	R_1 = β-OH	R_2 = H	R_3 = Glucose
IV	R_1 = α-OH	R_2 = OH	R_3 = Glucose
V	R_1 = β-OH	R_2 = OH	R_3 = Glucose

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