Phytochemical Studies of Seeds of Medicinal Plants. III.[1] Ursolic Acid and Oleanolic Acid Glycosides from Seeds of *Patrinia scabiosaefolia* FISCHER

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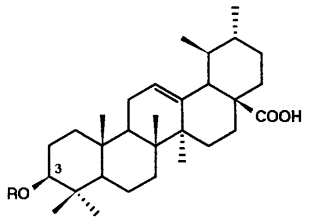
Three isomeric pairs of ursolic acid (1, 3, and 5) and oleanolic acid (2, 4, and 6) glycosides were isolated as predominant constituents from seeds of *Patrinia scabiosaefolia* FISCHER (Valerianaceae). Based on chemical and spectral evidence, their structures were established to be 3-*O*-[α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl] ursolic acid (1) and oleanolic acid (2), 3-*O*-[β-D-glucopyranosyl-(1→3)-α-L-arabinopyranosyl] ursolic acid (3) and oleanolic acid (4), and 3-*O*-{α-L-rhamnopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→3)]-α-L-arabinopyranosyl} ursolic acid (5) and oleanolic acid (6), respectively. Glycosides 1, 5, and 6 are new compounds and named as patrinia-glycosides A-I, B-I, and B-II, respectively. Glycoside 3 is a known but is the first naturally occurring product. Ursolic acid glycosides were first found from this plant specimen.

Keywords *Patrinia scabiosaefolia*; seed; ursolic acid glycoside; patrinia-glycoside A-I; patrinia-glycoside B-I; patrinia-glycoside B-II

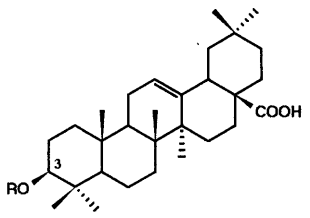
Whole plants of *Patrinia scabiosaefolia* FISCHER (Ominaeshi in Japanese) (Valerianaceae), a Chinese crude drug (Bai Jiang in Chinese; Haisho in Japanese), have been used in China as a diuretic and for "Qing Re Jie Du" (treatment of fever and inflamation along with detoxication), "Huo Xue Hua Yu" (mobilization of blood circulation and treatment of stasis), *etc.*[2]

To our knowledge, thirteen triterpenoid glycosides carrying hederagenin or oleanolic acid,[3] together with two coumarins[3b] and an iridoid glycoside,[4] have been so far identified from roots and rhizomes of *P. scabiosaefolia*. In the recent paper,[5] we characterized two novel sulfated triterpenoid glycosides, sulfapatrinosides I and II, from seeds of the plant. In our continuing research on additional chemical components of the same plant material, six triterpenoid glycosides (**1**—**6**) have been isolated as the predominant constituents and their structures have been established as shown in formulas **1**—**6**. Among these glycosides identified, **1**, **5**, and **6** were new compounds and thus, named as patrinia-glycosides A-I, B-I, and B-II, respectively. The structures of **2**, **3**, and **4** were already reported but **3** is the first naturally occurring product. In addition, it was also revealed that each of **1** and **2**, **3** and **4**, and **5** and **6** was a pair of isomeric glycosides having ursolic acid and oleanolic acid as aglycones. This paper gives a full account of the isolation and the structural elucidation.

The total glycoside mixture from the methanol extracts was purified by silica gel column chromatography and precipitation procedure to yield three kinds of isomeric mixtures, *i.e.*, an isomeric mixture of **1** and **2**, that of **3** and **4**, and that of **5** and **6**, respectively. Each of these mixtures was further subjected to repeated and painstaking separation by high-performance liquid chromatography (HPLC) to isolate each of **1**—**6** in a pure form.



1 : R=A
3 : R=B
5 : R=C



2 : R=A
4 : R=B
6 : R=C

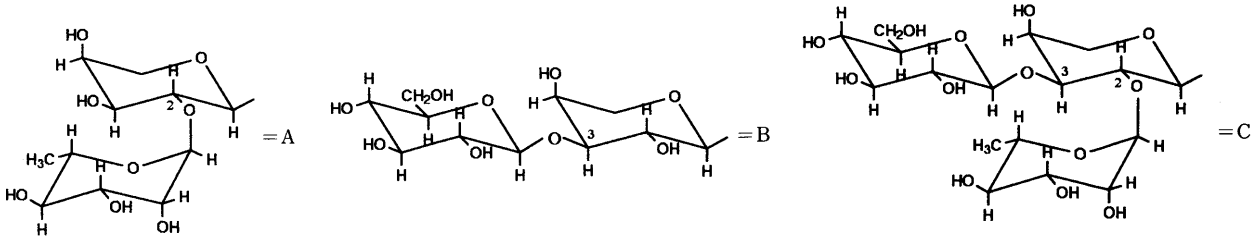


Fig. 1

Patrinia-glycoside A-I (**1**), mp 246—249 °C, $[\alpha]_D$ −5.8°, showed a carbonyl band (1690 cm^{-1}) due to a carboxyl and a hydroxy absorption in the infrared (IR) spectrum. The negative ion fast atom bombardment mass (FAB-MS) data ($[M-H]^-$, *m/z* 733), in conjunction with the result of the elemental analysis, suggested **1** to possess a molecular formula of $C_{41}H_{66}O_{11}$. In addition, **1** afforded two significant fragment ions at *m/z* 587 $[M-H-146]^-$ and 455 $[587-132]^-$, indicating that **1** carries a pentose as the inner sugar and a deoxyhexose as the terminal one. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum exhibited the presence of five tertiary methyls, two secondary methyls (δ 0.97, d, *J*=6.0 Hz, δ 1.01, d, *J*=6.2 Hz), an olefinic proton, and two anomeric protons (δ 4.92, d, *J*=5.3 Hz, δ 6.10, d, *J*=0.9 Hz). Methanolysis of **1** with 5% methanolic hydrogen chloride gave one mol each of ursolic acid, methyl arabinoside and rhamnoside. In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum, the C-3 signal (δ 88.9 ppm, see Table I) of the aglycone appeared at lower field[6] (by 10.7 ppm), compared with that of ursolic acid.[7] These lines of accumulated evidence indicate **1** to be ursolic acid 3-*O*-rhamnosylarabinoside.

With the aid of ^{1}H–^{1}H and ^{13}C–^{1}H shift-correlated spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY), all carbons on the disaccharide of **1** were assigned as shown in Table I. The arabinosyl C-2 in **1** resonated at lower field[6] (δ 76.0 ppm) than that (72.9 ppm) of ursolic acid 3-*O*-arabinoside[8] and two kinds of typical cross peaks between the 3α-H of the aglycone and the arabinosyl anomeric proton and between the arabinosyl 2-H and the rhamnosyl anomeric proton in the NOESY spectrum were observed. This evidence revealed that the rhamnosyl moiety was linked to C-2 of the arabinosyl moiety.

The large *J*-value (5.3 Hz) of the anomeric proton confirmed the presence of α-L-arabinopyranosyl moiety ($^4C_1$ conformation) in **1**. The $J_{C_1H_1}$ value[9] (170 Hz) of the rhamnosyl moiety suggested the presence of α-L-rhamnopyranoside ($^1C_4$ conformation) in **1**. This disaccharide structure deduced as above was further corroborated by the following ^{13}C-NMR evidence. Each of the carbons on the disaccharide in **1** coincided in chemical shift with the corresponding carbon reported for 3-*O*-[α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl] hederagenin.[10] Thus, patrinia-glycoside A-I (**1**) was determined to be 3-*O*-[α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl] ursolic acid.[11]

Based on the structural elucidation process analogous to that in the case of **1**, the structure for **2** has been elucidated to be 3-*O*-[α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl] oleanolic acid, an isomer of **1**. This structure is coincident with that reported for compound 4 obtained from roots of the same plant species.[3c]

The structures for glycosides **3** and **4** have also been established as 3-*O*-[β-D-glucopyranosyl-(1→3)-α-L-arabinopyranosyl] ursolic acid and oleanolic acid, respectively, on the basis of the combined proof by chemical (methanolysis of the corresponding methyl esters of **3** and **4**, *etc.*), physicochemical (mp, $[\alpha]_D$, thin layer chromatography (TLC), gas liquid chromatography (GLC), *etc.*), and spectral (IR, negative ion FAB-MS, ^{1}H- and ^{13}C-NMR, ^{1}H–^{1}H and ^{1}H–^{13}C COSY, NOESY, *etc.*) studies, analogous to the structural elucidation process for **1**, **5**, and **6**. Glycoside **3** was reported as a partial hydrolysate of matesaponin I obtained from *Ilex paraguariensis* St. Hil. (Aquifoliaceae).[8] However, **3** is the first naturally occurring compound. On the other hand, **4** gave the same structure as a glycoside isolated from *Thalictrum minus* (Ranunculaceae),[12] the structure of which was deduced based on only FAB-MS and ^{13}C-NMR data. However, significant difference in the ^{13}C-chemical shifts of the sugar carbons between **4** and the reported glycoside[12] are observed.[13]

The ^{13}C-NMR data of these known glycosides **2**—**4** are listed in Table I.

Table I. ^{13}C-NMR Spectral Data for **1**—**6** (100.5 MHz, in Pyridine-d_5, δ_C)

Carbon No.	1	2	3	4	5	6
Aglycone						
C- 1	39.0	38.9	39.0	38.8	39.2	39.0
C- 2	26.6	26.5	26.7	26.7	26.7	26.6
C- 3	88.9	88.8	88.8	88.7	88.3	88.2
C- 4	39.5	39.5	40.0	39.8[a]	39.8	39.6
C- 5	56.0	55.9	56.0	55.9	56.1	56.1
C- 6	18.6	18.5	18.5	18.6	18.6	18.6
C- 7	33.5	33.3	33.6	33.5[b]	33.5	33.4[a]
C- 8	40.0	39.8	40.0	39.7[a]	40.0	39.8
C- 9	48.1	48.1	48.1	48.2	48.1	48.1
C-10	37.0	37.1	37.0	37.1	37.0	37.1
C-11	23.6	23.8	23.7	24.0	23.6	23.8
C-12	125.4	122.4	125.5	122.1	125.5	122.3
C-13	139.5	144.9	139.5	145.5	139.4	145.2
C-14	42.6	42.2	42.6	42.3	42.5	42.2[b]
C-15	28.8	28.4	28.8	28.5	28.8	28.4
C-16	25.0	23.7	25.1	24.0	25.1	23.8
C-17	48.2	46.7	48.2	46.9	48.2	46.7
C-18	53.7	42.0	53.7	42.3	53.7	42.1[b]
C-19	39.6	46.6	39.6	46.9	39.6	46.8
C-20	39.5	31.0	39.5	31.1	39.4	31.0
C-21	31.2	34.3	31.2	34.5	31.2	34.4
C-22	37.6	33.3	37.6	33.3[b]	37.5	33.2[a]
C-23	28.2	28.1	28.2	28.2	28.2	28.1
C-24	17.0	17.0	17.0	17.0	17.1	17.1
C-25	15.7	15.5	15.7	15.6	15.8	15.6
C-26	17.6[a]	17.4	17.5[a]	17.6	17.5[a]	17.5
C-27	23.9	26.2	23.9	26.2	23.9	26.2
C-28	180.7	180.6	180.5	181.8	180.6	181.2
C-29	17.5[a]	33.3	17.6[a]	33.5	17.6[a]	33.4
C-30	21.5	23.8	21.5	23.9	21.5	23.9
Inner arabinose						
C- 1	104.8	104.6	107.4	107.4	104.8	104.8
C- 2	76.0	76.0	71.9	71.9	74.8	74.8
C- 3	74.0	74.0	84.2	84.3	82.2	82.2
C- 4	68.6	68.6	69.3	69.3	68.1	68.1
C- 5	64.6	64.5	66.9	67.0	64.8	64.9
Terminal rhamnose						
C- 1	101.8	101.7			101.9	101.9
C- 2	72.4	72.4			72.3	72.3
C- 3	72.6	72.6			72.5	72.5
C- 4	73.7	73.7			73.9	73.9
C- 5	69.9	69.9			70.0	70.0
C- 6	18.6	18.5			18.6	18.6
Terminal glucose						
C- 1			106.3	106.3	104.7	104.7
C- 2			75.7	75.7	74.9	74.9
C- 3			78.4	78.4	78.1	78.2
C- 4			71.6	71.6	71.4	71.4
C- 5			78.7	78.7	78.5	78.5
C- 6			62.7	62.7	62.5	62.5

a, b) Assignments with the same superscripts in each column may be interchanged.

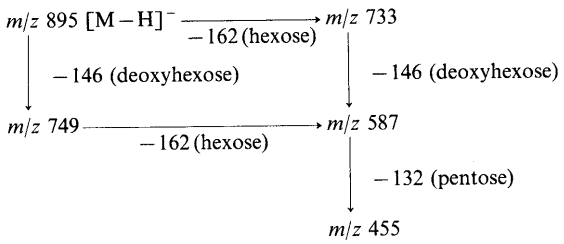


Chart 1. Negative Ion FAB-MS Spectrum of **5** and **6**

Patrinia-glycosides B-I (**5**), mp 260—263 °C, $[\alpha]_D$ −3.7°, and B-II (**6**), mp 259—262 °C (dec.), $[\alpha]_D$ −2.9°, showed bands due to a carboxyl (1690 cm^{-1} in both **5** and **6**) and a hydroxyl in the IR spectra and possessed the same molecular formula $C_{47}H_{76}O_{16}$, based on elemental analyses and the same ion $[M-H]^-$ (the base peak) at *m/z* 895 in the negative ion FAB-MS spectra. A common fragmentation (see Chart 1) in the negative ion FAB-MS of both glycosides showed both **5** and **6** to be a triglycoside composed of a pentose (the inner sugar), a hexose and a deoxyhexose (the terminal sugars). The ^{1}H-NMR spectrum of **5** showed signals due to five tertiary methyls, two secondary methyls (δ 0.97, d, J=5.8 Hz, δ 1.01, d, J=6.8 Hz), an olefinic proton, and three anomeric protons (δ 4.86, d, J=5.2 Hz, δ 5.08, d, J=7.6 Hz, δ 6.11, br s) and that of **6** exhibited the presence of seven tertiary methyls, an olefinic proton, and three anomric protons (δ 4.85, d, J=5.1 Hz, δ 5.08, d, J=7.7 Hz, δ 6.11, br s). Each of glycosides **5** and **6** was methanolyzed to give ursolic and oleanolic acids as the respective aglycones of **5** and **6**, and one mol each of methyl arabinoside, glucoside, and rhamnoside was confirmed as the common sugar components of **5** and **6**. In the ^{13}C-NMR spectra (see Table I), the C-3 signals (on the respective aglycones) of **5** and **6** (δ 88.3 and δ 88.2 ppm, respectively) appeared at lower field[6] (by 10.1 ppm in both) than those of ursolic[7] and oleanolic[14] acids, respectively. This accumulated evidence suggested that **5** and **6** were assigned to 3-*O*-rhamnosyl-[glucosyl]-arabinosides of ursolic and oleanolic acids, respectively.

All carbons on the respective trisaccharide parts were assigned with the aid of ^{1}H–^{1}H and ^{13}C–^{1}H COSY and NOESY experiments and these assignments are shown in Table I. The large J-values of the arabinosyl anomeric protons in **5** and **6** (5.2 Hz in **5** and 5.1 Hz in **6**) were indicative of the presence of a α-L-arabinopyranosyl moiety ($^4C_1$ conformation) in both **5** and **6**. Similarly, the glucosyl anomeric proton signals with large coupling constants (**5**, 7.6 Hz and **6**, 7.7 Hz) were in agreement with the presence of β-D-glucopyranoside ($^4C_1$ conformation) in both **5** and **6**. The anomeric configurations of the L-rhamnopyranosides ($^1C_4$ conformation) in **5** and **6** were decided to be α, based on the $J_{C_1H_1}$ values[9] (170 Hz) of the rhamnosides in **5** and **6**.

In the ^{13}C-NMR spectra (Table I), the arabinosyl C-2 atoms of **5** and **6** (both at δ 74.8 ppm) resonated at lower field[6] than those (both at δ 71.9 ppm) of **3** and **4**, respectively, and the arabinosyl C-3 atoms of **5** and **6** (both at δ 82.2 ppm) were also shifted downfield[6] compared with those of **1** and **2**, respectively. In addition, three significant cross peaks between the 3α-H of the aglycone and the arabinosyl anomeric proton, between the arabinosyl 2-H and the rhamnosyl anomeric proton, and between the arabinosyl 3-H and the glucosyl amomeric proton were observed in the NOESY spectra of **5** and **6**. Based on the combined evidence, the structures of patrinia-glycosides B-I (**5**) and B-II (**6**) are now defined as 3-*O*-{α-L-rhamnopyranosyl-(1→2)-[β-D-glucopyranosyl-(1→3)]-α-L-arabinopyranosyl} ursolic acid and oleanolic acid,[11] respectively.

Ursolic acid glycosides were first found from *P. scabiosaefolia*. To our knowledge, this is the first report on co-occurrence of many isomeric pairs of ursolic acid and oleanolic acid glycosides in a plant source.

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were run with a JASCO A-302 instrument. Unless otherwise stated, ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100.5 MHz) spectra were measured with a JEOL JNM-GX400 spectrometer with pyridine-d_5 as a solvent and tetramethylsilane as an internal standard. Negative ion FAB-MS spectra were obtained with a JEOL JNM-DX300 spectrometer under the following conditions: accelerating voltage, 3 kV; emission current, 30 mA; matrix, triethanolamine; collision gas, Xe. Optical rotations were determined on a JASCO DIP-140 digital polarimeter. GLC was carried out on a Shimadzu GC-7AG gas chromatograph under the following conditions: column, 1.5% SE-52 on Chromosorb WAW DMCS (2 m × 3 mm i.d.); detector, flame ionization detector (FID); column temperature, 180 °C; injection temperature, 250 °C; carrier N_2 gas, 30 ml/min. For column chromatography, Silica Gel 60 (nacalai tesque; 230—400 mesh) was used. TLC was performed by using precoated silica gel plates (Merk 60F-254) and the following developing solvent systems: No. 1, BuOH–AcOH–H_2O (4:1:2); No. 2, EtOH–28% aqueous NH_3–H_2O (20:1:4); NO. 3, $CHCl_3$–MeOH (60:1); No. 4, $CHCl_3$–acetone (15:1); No. 5, *n*-hexane–AcOEt (4:1); No. 6, $CHCl_3$–MeOH (30:1), No. 7, $CHCl_3$–acetone (10:1); No. 8, *n*-hexane–AcOEt (1:1). Preparative HPLC of the glycosides was carried out on a Waters 600E instrument with a U6K septum-less injector, a Lambda-Max Model 480 photospectrometer, and a reversed-phase TSK-GEL ODS-120T column (30 cm × 7.8 mm), and HPLC purification of the aglycone methyl esters, on a Waters instrument with an M 6000A pump and a series R-401 differential refractometer.

Plant Material Seeds of *P. scabiosaefolia*, cultivated at the Medicinal Plant Garden of Setsunan University (Faculty of Pharmaceutical Sciences), were harvested in 1985. The plant used in the present study was identified by one of us (H. M.).

Extraction and Isolation of Glycosides 1—6 The crushed seeds (171 g) were extracted three times with MeOH (1.0 l) at room temperature for two weeks, and the solvent was evaporated off under reduced pressure. The combined extracts (23.3 g) were washed twice with each 200 ml of Et_2O. The resultant insoluble precipitate (total glycoside mixture) (15.2 g) collected by filtration was chromatographed on silica gel (1 kg), eluting successively with each lower phase of $CHCl_3$–MeOH–H_2O (11:3:1), (7:3:1), (65:35:10), and a mixture of $CHCl_3$–MeOH–H_2O (6:4:1), and MeOH, to get the 12 separated fractions (Nos. 1 to 12). Fraction No. 4 (206 mg), a mixture of **1** and **2**, eluted with the lower phase of $CHCl_3$–MeOH–H_2O (11:3:1), was further purified by preparative HPLC separation with an eluant flow of 1.0 ml/min of H_2O–MeOH (13:87) to give pure **1** (27 mg) and **2** (91 mg), respectively.

Fraction No. 6 (386 mg) containing **3** and **4**, eluted with the lower layer of $CHCl_3$–MeOH–H_2O (11:3:1), was precipitated from MeOH to afford a white powder (170 mg), a mixture of **3** and **4**. A portion (43 mg) of it was subjected to preparative HPLC separation with gradient elution of H_2O–MeOH [from (17:83) to (20:80)] and with an eluant flow of 1.0 ml/min to isolate pure **3** (4.7 mg) and **4** (5.3 mg), respectively.

Fraction No. 8 (737 mg) containing **5** and **6**, eluted with the lower phase of $CHCl_3$–MeOH–H_2O (7:3:1), was precipitated from MeOH and the resulting white powder, a mixture (129 mg) of **5** and **6**, was collected by filtration and further purified on preparative HPLC with an eluant flow of 4.0 ml/min of H_2O–MeOH (11:89) to isolate **5** (36 mg) and **6** (26 mg) in a pure form, respectively.

Patrinia-glycoside A-I (**1**): Colorless fine crystals from MeOH, mp 246—249 °C, $[\alpha]_D$ −5.8° (c=0.30, pyridine). IR (KBr) cm^{-1}: 3420, 2920, 1690 (COOH), 1050. Negative ion FAB-MS *m/z* (%): 733 ($[M-H]^-$, 100), 587 ($[M-H]^-$ −146, 9), 455 ($[M-H]^-$ −146−132, 10). ^{1}H-NMR

δ: 0.86, 1.02, 1.07, 1.19, 1.27 (3H each, all s, 5 × *tert*-Me), 0.97, 1.01 (3H each, d, J=6.0, 6.2 Hz, respectively, 2 × *sec*-Me), 1.63 (3H, d, J=6.3 Hz, rham. Me), 2.65 (1H, d, J=11.2 Hz, 18β-H), 3.27 (1H, dd, J=11.5, 4.2 Hz, 3α-H), 5.47 (1H, m, 12-H), 4.92 (1H, d, J=5.3 Hz, anomeric H of ara.), 6.10 (1H, d, J=0.9 Hz, anomeric H of rham.). ^{13}C-NMR: Given in Table I. *Anal.* Calcd for $C_{41}H_{66}O_{11}\cdot 2H_2O$: C, 63.87; H, 9.15. Found: C, 63.78; H, 8.84.

Glycoside **2**: Colorless fine crystals from MeOH, mp 225—228 °C (lit.[3c] mp 242—244 °C), $[\alpha]_D$ −3.6° (c=0.28, pyridine) [lit.[3c] $[\alpha]_D$ +7.5° (c=0.4, MeOH)].[15] Negative ion FAB-MS (%): 733 ($[M-H]^-$, 100), 587 ($[M-H]^- - 146$, 18), 455 ($[M-H]^- - 146 - 132$, 34). ^{1}H-NMR δ: 0.85, 0.97, 0.99, 1.02, 1.06, 1.17, 1.31 (3H each, all s, 7 × *tert*-Me), 1.62 (3H, d, J=6.2 Hz, rham. Me), 3.25 (1H, dd, J=11.8, 4.3 Hz, 3α-H), 3.30 (1H, dd, J=13.9, 3.9 Hz, 18β-H), 5.47 (1H, m, 12-H), 4.90 (1H, d, J=5.0 Hz, anomeric H of ara.), 6.09 (1H, br s, anomeric H of rham.). The data on negative ion FAB-MS and ^{1}H-NMR are first reported here. ^{13}C-NMR: Given in Table I (on the sugar part data in DMSO-d_6, see lit.[3c]).

Glycoside **3**: A white powder from MeOH, mp 270—273 °C (dec.) [lit.[8] mp 274—277 °C (dec.)], $[\alpha]_D$ +39.2° (c=0.075, pyridine) [lit.[8] $[\alpha]_D$ +27.25° (c=1.89, pyridine)]. IR (KBr) cm^{-1}: 3410, 2920, 1690 (COOH), 1075. Negative ion FAB-MS: Essentially same to the reported data.[8] ^{1}H-NMR δ: 0.85, 0.99, 1.04, 1.28, 1.34 (3H each, all s, 5 × *tert*-Me), 0.97, 1.01 (both 3H, d, J=6.2 Hz, 2 × *sec*-Me), 2.67 (1H, d, J=10.5 Hz, 18β-H), 3.39 (1H, dd, J=11.5, 4.3 Hz, 3α-H), 5.49 (1H, m, 12-H), 4.77 (1H, d, J=7.3 Hz, anomeric H of ara.), 5.40 (1H, d, J=7.9 Hz, anomeric H of glc.). The IR and ^{1}H-NMR data are first reported here. ^{13}C-NMR: Given in Table I and consistent with the reported data.[8]

Glycoside **4**: A white powder from MeOH, mp 247—250 °C (dec.) (lit.[12] mp 262—264 °C), $[\alpha]_D$ +47.6° (c=0.12, pyridine). IR (KBr) cm^{-1}: 3410, 2920, 1690 (COOH), 1075. Negative ion FAB-MS m/z (%): 749 ($[M-H]^-$, 100), 587 ($[M-H]^- - 162$, 16), 455 ($[M-H]^- - 162 - 132$, 9). ^{1}H-NMR δ: 0.86, 0.98, 1.00, 1.04, 1.33 (3H, 3H, 6H, 3H, 6H, respectively all s, 7 × *tert*-Me), 3.34—3.42 (2H, m, 3α-, 18β-H), 5.49 (1H, m, 12-H), 4.77 (1H, d, J=7.4 Hz, anomeric H of ara.), 5.39 (1H, d, J=7.7 Hz, anomeric H of glc.). ^{13}C-NMR: Given in Table I.[13] *Anal.* Calcd for $C_{41}H_{66}O_{12}\cdot 2.5H_2O$: C, 61.86; H, 8.99. Found: C, 61.86; H, 8.69.

Patrinia-glycoside B-I (**5**): Colorless fine crystals from MeOH, mp 260—263 °C, $[\alpha]_D$ −3.7° (c=0.27, pyridine). IR (KBr) cm^{-1}: 3380, 2910, 1690 (COOH), 1075. Negative ion FAB-MS m/z: Given in Chart 1 and intensities (%) are as follows: 895 (100), 749 (23), 733 (24), 587 (15), 455 (22). ^{1}H-NMR δ: 0.85, 1.02, 1.11, 1.22, 1.26 (3H each, all s, 5 × *tert*-Me), 0.97, 1.01 (3H each, d, J=5.8, 6.8 Hz respectively, 2 × *sec*-Me), 1.61 (3H, d, J=6.0 Hz, rham. Me), 2.65 (1H, d, J=11.0 Hz, 18β-H), 3.32 (1H, dd, J=11.2, 3.6 Hz, 3α-H), 5.48 (1H, br s, 12-H), 4.86 (1H, d, J=5.2 Hz, anomeric H of ara.), 5.08 (1H, d, J=7.6 Hz, anomeric H of glc). 6.11 (1H, br s, anomeric H of rham.). ^{13}C-NMR: Given in Table I. *Anal.* Calcd for $C_{47}H_{76}O_{16}\cdot 3H_2O$: C, 59.35; H, 8.69. Found: C, 59.43; H, 8.34.

Patrinia-glycoside B-II (**6**): A white powder from MeOH, mp 259—262 °C (dec.), $[\alpha]_D$ −2.9° (c=0.29, pyridine). IR (KBr) cm^{-1}: 3380, 2910, 1690 (COOH), 1075. Negative ion FAB-MS: Given in Chart 1 and intensities (%) are as follows: 895 (100), 749 (24), 733 (30), 587 (19), 455 (34). ^{1}H-NMR δ: 0.85, 0.96, 0.99, 1.02, 1.12, 1.21, 1.31 (3H each all s, 7 × *tert*-Me), 1.62 (3H, d, J=6.2 Hz, rham. Me), 3.28—3.35 (2H, m, 3α-, 18β-H), 5.47 (1H, br s, 12-H), 4.85 (1H, d, J=5.1 Hz, anomeric H of ara.), 5.08 (1H, d, J=7.7 Hz, anomeric H of glc.), 6.11 (1H, br s, anomeric H of rham.). ^{13}C-NMR: Given in Table I. *Anal.* Calcd for $C_{47}H_{76}O_{16}\cdot 3.5H_2O$: C, 58.79; H, 8.71. Found: C, 58.67; H, 8.41.

Methanolysis of 1 A solution of **1** (3.0 mg) in 5% methanolic HCl (1.3 ml) was refluxed for 1.5 h, neutralized with Ag_2CO_3. The inorganic precipitate was filtered off. The resulting filtrate was concentrated *in vacuo*. The residue was subjected to TLC analyses to identify ursolic acid (in three different developing solvent systems, Nos. 6 to 8), methyl arabinoside and rhamnoside (in two different solvent systems, Nos. 1 and 2). The remaining residue was trimethylsilylated with *N,O*-bis(trimethylsilyl)-trifluoroacetamide in pyridine to demonstrate the presence of one mol each of arabinose and rhamnose in **1**. The t_R value of each sugar was 4 min 29 s (ara.) and 5 min 03 s (rham.).

Methanolysis of 5 and 6 Each (3 mg) of **5** and **6** was methanolyzed in the same manner as in methanolysis of **1**. On TLC analyses (in three developing solvent systems, Nos. 6 to 8) of the respective reaction products, the presence of ursolic acid from **5** and oleanolic acid from **6** was confirmed. In addition, the three common sugar components (methyl arabinoside, rhamnoside, and glucoside) were also identified by TLC and GLC in a similar manner as in the case of **1**. The t_R value of each sugar was 4 min 29 s (ara.), 5 min 03 s (rham.), and 20 min 30 s and 22 min 27 s (glc.) in the case of **5** and 4 min 30 s (ara.), 5 min 05 s (rham.), and 20 min 34 s and 22 min 25 s (glc.) in the case of **6**.

Methanolysis of Methyl Esters of 3 and 4 Each (16 mg and 14 mg, respectively) of the corresponding methyl esters of **3** and **4** was methanolyzed in a similar manner as in the methanolysis of **1**. The reaction product was partitioned between Et_2O and H_2O. The Et_2O layer was purified by HPLC [μ-Porasil semi prep column (30 cm × 7.8 mm); 1.0 ml/min flow rate of $CHCl_3$] to give each aglycone [methyl ursolate (6.6 mg) and oleanolate (5.6 mg), respectively], which was identified with respective authentic samples by comparison of IR ($CHCl_3$), ^{1}H-NMR ($CDCl_3$), and TLC (in developing systems of Nos. 3 to 5). From the aqueous layer of each reaction product, one mol each of arabinose and glucose was identified by GLC and TLC in similar manners as mentioned before.

References and Notes

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11) Both of the arabinose in glycosides **1**—**6** and the rhamnose in glycosides **1**, **2**, **5**, and **6** are assumed to be of L-configuration, because 3-*O*-α-L-arabinopyranosides of oleanolic acid and hederagenin[3b] and 3-*O*-[α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl] oleanolic acid[3c] (=**2**) have been already identified from the roots of *Patrinia scabiosaefolia*. With respect to the configuration of the glucose in glycosides **3**—**6**, the D form appear preferable from the viewpoint of natural occurrence of glucose.
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13) Both glycosides assigned to the structure **4**, *i.e.*, the glycoside **4** (see Table I) and a reported compound[12] (arabinosyl C-1, δ 106.9; C-2, 74.3; C-3, 79.2; C-4, 71.6; C-5, 65.7; glucosyl C-1, δ 106.5; C-2, 75.7; C-3, 78.5; C-4, 73.5; C-5, 78.4; C-6, 62.9), showed significant differences in their chemical shifts (both in pyridine-d_5) of arabinosyl C-2, C-3, C-4, C-5, and glucosyl C-4 carbons on the disaccharide part. As shown in Table I, the sugar part data for our specimen (glycoside **4**) are in agreement with those for glycoside **3** and thus, appear to be reasonable.
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