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Saponins from the Roots of *Pulsatilla koreana*

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Abstract □ From the roots of *Pulsatilla koreana,* three monodesmosides(pulsatilla saponins A, B and D) and two bisdesmosides(pulsatilla saponins F and H) were isolated. The structure of these saponins have been determined as hederagenin 3-O-α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranoside(A), hederagenin 3-O-β-D-glucopyranosyl(1→4)-α-L-arabinopyranoside(B), hederagenin 3-O-α-L-rhamnopyranosyl (1→2)-[β-D-glucopyranosyl(1→4)] -α-L-arabinopyranoside(D), 3-O-α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl ester (F) and 3-O-α-L-rhamnopyranosyl(1→2)-[β-D-glucopyranosyl(1→4)]-α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranosyl(1→6)-β-D-glucopyranosyl ester(H) on the basis of chemical and spectral studies. Pulsatilla saponin B is the first report of its presence in plants but saponins A, D, F, and H have recently been isolated from the same genus *P. cernua.*

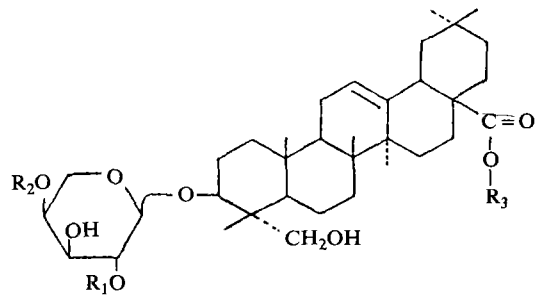
Keywords □ *Pulsatilla koreana,* Ranunculaceae, Hederagenin monodesmoside, Hederagenin bisdesmoside.

Pulsatillae Radix has been used in traditional medicine for hematochezia due to intense evil heat, malaria, chills and fever, epistaxis and internal hemorrhoids.[1] In Korea, the dried root of *Pulsatilla koreana* N. (Ranunculaceae) which is native to the Korean Peninsula and Manchuria has been used for Pulsatillae Radix. In previous studies in which hederagenin[2] and its glycosides[3] were isolated and detected, we have found that the MeOH extract showed strong sedative activities.[4] This paper describes the isolation and characterization of three monodesmosides and two bisdesmosides, which have been identified on the basis of spectral and chemical data.

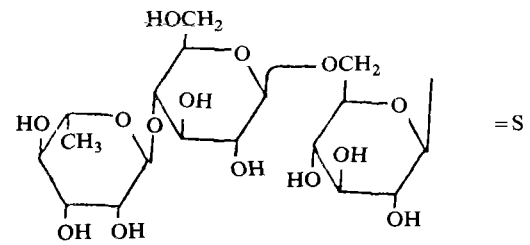
BuOH soluble fraction was subjected to silica gel column chromatography to obtain pure saponins. Five saponins, named pulsatilla saponins A(**I**), m.p. 264-5°, B(**II**), m.p. 263-4°, D(**III**), m.p. 239-41°, F(**IV**), m.p. 225-8°, and H(**V**), m.p. 205-8°, were isolated in pure forms. Acid hydrolysis of these saponins gave the same aglycone, hederagenin (**VI**), identified by comparison with an authentic sample, as well as rhamnose, and arabinose from **I**, rhamnose and glucose from **II**, and rhamnose, arabinose and glucose from **III**, **IV**, and **V** identified by tlc. The ^{1}H-NMR spectrum of saponin D(**III**) in pyridine-d_5 showed six tertiary methyl singlets at δ0.90-1.21 and a secondary methyl doublet (J = 6.1 Hz) at δ1.63 for rhamnosyl methyl together with three anomeric proton signals at δ4.96(1H, d, J = 6.6 Hz), 5.09(1H, d, J = 7.6Hz), and 6.25(1H, brs) ppm. These results suggested that saponin D(**III**) consisted of one mole each of arabinose, glucose and rhamnose. The SIMS spectrum of **III**[5] showed a protonated molecular ion at *m/z* 913 and two fragment ions at *m/z* 767 and 751 formed by the loss of a terminal methylpentose (rhamnose) and a terminal hexose (glucose) unit, respectively. A small quantity of NaI was added to enhance the response and a highly intense cationized molecular ion at *m/z* 935 was produced. Fragments corresponding to a loss of a terminal methyl pentose and a terminal hexose unit were also observed at *m/z* 789 and 773, respectively. These results may be proposed the attachment of arabinose with glucose on one side and with the rhamnose on the other side. Therefore **III** has a branched trisaccharide, rhamnosyl-[glucosyl]-arabinoside, combined with a hydroxyl group of hederagenin. When **III** was treated with dilute HCl in MeOH, two prosapogenins A(**I**) and B(**II**) together with hederagenin (**VI**) were obtained. Prosapogenin A and B were identified as pulsatilla saponins A(**I**) and B(**II**) by direct comparison with the authentic samples. The prosapo-

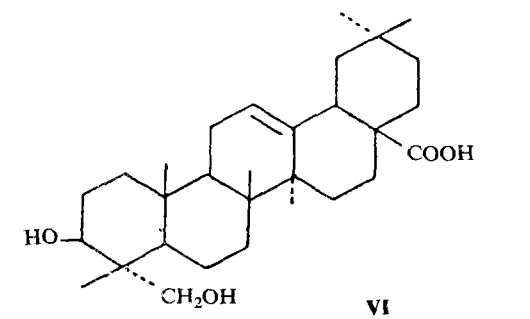
genin A(**I**), m.p. 264-5°, was hydrolyzed into the aglycone(**VI**) and rhamnose and arabinose and identified as hederagenin 3-O-α-L-rhamnopyranosyl (1 → 2)-α-L-arabinopyranoside by direct comparison with an authentic sample and ^{13}C-NMR spectrum (see Table I). The prosapogenin B(**II**), m.p. 263-4°, liberated on acid hydrolysis the aglycone(**VI**) and glucose and arabinose. The ^{1}H-NMR spectrum of **II** showed six tertiary methyl singlets at δ0.93-1.24, two anomeric proton signals at 4.91(1H, d, J=7.4Hz) and 5.27(1H, d, J=7.9Hz) and an olefinic proton signal at δ 5.49(1H, brs).

In the ^{13}C-NMR spectrum of **II**, significant glycosidation shift was observed for the C-4(+9.6 ppm) of the arabinopyranosyl moiety together with a set of signals for terminal glucose residue. These results indicated that the structure of **II** is hederagenin 3-O-β-D-glucopyranosyl(1 → 4)-α-L-arabinopyranoside. Therefore pulsatilla saponin D(**III**) was suggested to possess a β-glucopyranosyl residue attached to the hydroxyl function of arabinose in the prosapogenin A(**I**). The coupling constants of the three anomeric protons in the ^{1}H-NMR spectrum of **III** and of the two anomeric protons in that of **II** indicate α-configurations for arabinose and rhamnose, and β-configuration for glucose which further supported by the molecular rotation differences as shown in Table II. The molecular rotation differences between hederagenin 3-O-α-L-arabinopyranoside[6] and prosapogenin A(I), hederagenin 3-O-α-L-arabinopyranoside and prosapogenin B(**II**), and **II** and **III** were -274.9°, -14.9°, and -171.6°, respectively. By the Klyne's rule[7], the above results indicated that rhamnose was in the α-L form in each case and glucose was in the β-D form. From the above findings, the structure of pulsatilla saponins A, B and D were established as hederagenin 3-O-α-L-rhamnopyranosyl(1 → 2)-α-L-arabinopyranoside(**I**), hederagenin 3-O-β-D-glucopyranosyl(1 → 4)-α-L-arabinopyranoside(**II**), and hederagenin 3-O-α-L-rhamnopyranosyl(1 → 2)-[β-D-glucopyranosyl(1 → 4)]-α-L-arabinopyranoside (**III**), respectively. Pulsatilla saponin F(**IV**) appears an ester absorption band at 1735 cm^{-1} in its IR spectrum and gives **I** on alkaline hydrolysis with 3% KOH. The ^{13}C- and ^{1}H-NMR spectra of **IV** showed signals due to five anomeric carbons (δ_c95.3, 101.7, 102.7, 104.2, 104.8) and five anomeric protons (δ4.96, d, J = 7.8Hz; 5.10, d, J = 6.0Hz; 5.77, brs; 6.12, brs; 6.19, d, J = 7.8Hz). These data indicated that **IV** is a bisdesmoside of **VI** carrying a α-L-rhamnopyranosyl(1 → 2)-α-L-arabinopyranosyl moiety at C-3 and a trisaccharide moiety at C-28



I R_1 = Rha, R_2 = R_3 = H
II R_1 = R_3 = H, R_2 = Glc
III R_1 = Rha, R_2 = Glc, R_3 = H
IV R_1 = Rha, R_2 = H, R_3 = S
V R_1 = Rha, R_2 = Glc, R_3 = S





VI

comprising one mole of rhamnose and two moles of glucose. Comparison of ^{13}C-NMR data with those of **IV** and **I** has led to the assignments of the acylated trisaccharide moiety as indicated in Table I. There was a set of signals assignable to a terminal rhamnosyl unit. The chemical shifts for the acylated inner glucose is vertually identical to those of gentiobiosyl ester moiety.[8] Thus the innerglycosidic linkage in the glucosyl-glucose moiety is 1 → 6. The signals of C-4 and C-3 of the outer glucose in glucosyl-glucose moiety was displaced downfield by 6.9 ppm and upfield by 1.8 ppm, respectively. These indicated that the terminal rhamnosyl group is located at C-4 of the outer glucose. Therefore the interglycosidic linkage of the acylated sugar moiety is α-L-rhamnopyranosyl(1 → 4)-β-D-glucopyranosyl (1 → 6)-β-D-glucopyranosyl ester which is identical to that of prosapogenin **VI** obtained by partial

Table I. ^{13}C-NMR chemical shifts of pulsatilla saponins*

carbon No.	hederagenin 3-O-α-L-ara[9]	I	II	III	IV	V
C-3	82.0	81.1	82.3	81.5	81.2	81.5
C-23	64.6	64.0	64.9	64.9	64.1	64.9
C-28	180.4	180.4	180.2	180.7	176.5	176.6
3-O-sugar moiety						
ara-1	106.7	104.3	106.4[a]	104.8	104.2	104.8
2	73.1	75.8	73.5	80.7	76.0	80.7
3	74.8	74.6	74.5	75.9	74.3	75.8
4	69.6	69.4	79.2	76.7	69.3	76.7
5	67.0	65.7	62.6	64.4	65.4	64.4
rha-1		101.8		102.1	101.7	102.1
2		72.4[a]		72.7[a]	72.3[a]	72.7[a]
3		72.6[a]		72.9[a]	72.6[a]	73.0[a]
4		74.1		74.6	74.2	74.4
5		69.7		70.1	69.7	70.1
6		18.4		19.0	18.5	19.0
glc-1			106.5[a]	107.1		107.1
2			75.7	75.3		75.3
3			78.4[b]	78.9[b]		78.8[b]
4			71.6	71.7		71.7
5			78.5[b]	79.2[b]		79.1[b]
6			62.6	63.0		62.9
28-O-sugar moiety						
glc-1(inner)					95.3	96.1
2					73.9[b]	74.4
3					78.7[c]	79.1[b]
4					70.9	71.3
5					78.1[c]	78.5[b]
6					69.1	69.7
glc-1(outer)					104.8	105.2
2					75.3	75.8
3					76.6	76.9
4					78.5[c]	78.9[b]
5					77.1	77.6
6					61.3	61.8
rha-1					102.7	103.2
2					72.6[a]	73.0[a]
3					72.7[a]	73.2[a]
4					73.7[b]	74.4
5					70.3	70.7
6					18.2	18.9

*δppm from internal TMS in pyridine-d_5.
[a,b,c]Assignments may be reversed in each column.

Table II. Molecular Rotation Differences of Pulsatilla Saponins and Related Compounds.

Compounds	$[\alpha]_D$	$[M]_D$	$\Delta[M]_D$	ref.
I	+16.9°	+126.8°		
hederagenin-3-O-α-L-arabinopyranoside	+66.5°	+401.7°	-274.9°	
II	+50.5°	+386.8	- 14.9°	
III	+23.6°	+215.2°	-171.6°	(6)
methyl α-D-glucopyranoside		+309°		(17)
methyl β-D-glucopyranoside		- 66°		(17)
methyl α-L-rhamnopyranoside		-111°		(17)
methyl β-L-rhamnopyranoside		+170°		(17)

hydrolysis of Kizuta saponin K_{12}[9] and cussonoside A[10]. From the above results, the structure of pulsatilla saponin F(**IV**) was assigned as 3-O-α-L-rhamnopyranosyl (1 → 2)-α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl (1 → 4)-β-D-glucopyranosyl (1 → 6)-β-D-glucopyranosyl ester. The IR spectrum of **V** was very similar to that of **IV**. Alkaline hydrolysis of **V** yielded a prosapogenin which was identical to **III** confirmed by direct comparison with an authentic sample. Appearance of a cationized molecular ion at m/z 1405 in the SIMS spectrum[5] as well as comparison with the ^{13}C-NMR spectra of **V** and **III** permitted that **V** is also a bisdesmoside of **VI** having a α-L-rhamnopyranosyl (1 → 2)-[β-D-glucopyranosyl (1 → 4)]-α-L-arabinopyranosyl moiety at C-3 and an acylated trisaccharide moiety at C-28, which is identical with that of **IV**. Based on the above mentioned evidence, the structure of pulsatilla saponin **V** was determined to be 3-O-α-L-rhamnopyranosyl (1 → 2)-[β-D-glucopyranosyl (1 → 4)]-α-L-arabinopyranosyl hederagenin 28-O-α-L-rhamnopyranosyl (1 → 4)-β-D-glucopyranosyl (1 → 6)-β-D-glucopyranosyl ester.

Pulsatilla saponin A was earlier reported from *Akebia quinata*[11], *Hedera* plants[6,12-14], *Patrinia scabiosaefolia*[15], and *Caltha palustris*[16]. Pulsatilla saponins D, F, and H were also isolated from the same genus *P. cernua.*[3] However, the present communication further confirms the assigned structure for pulsatilla saponins D, F and H from spectral information. Pulsatilla saponin B(**II**) has been synthesized[3] but never reported in nature.

EXPERIMENTAL METHODS

Melting points were determined on a Mitamura-Riken apparatus and are uncorrected. IR spectra were measured on a Perkin-Elmer 283B IR spectrophotometer. ^{1}H-NMR spectra were recorded in pyridine-d_5 solution with a Bruker AM-200 (200 MHz) or a Bruker AM-300 (300 MHz) instrument using TMS as an internal reference. ^{13}C-NMR spectra were obtained on a Bruker AM-200 (50.3 MHz) or a Bruker AM-300 (75.5 MHz) spectrometer using TMS as an internal standard. Optical rotations were obtained on a Rudolph Autopol III autometic polarimeter.

Plant material

The plant material used was collected in early spring 1988, at Yangpyeong, Gyeonggi province and also purchased in Gyeongdong market.

Isolation

The plant material (600g) was refluxed with MeOH for 3 h (4 times) and concentrated *in vacuo*. The MeOH extract was partitioned between hexane and 10% aqueous MeOH to give hexane fraction (3.7g). The aqueous layer was partitioned with $CHCl_3$ and then BuOH to yield $CHCl_3$ (3.7g) and BuOH (56g) fractions, respectively. The BuOH fraction was chromatographed over silica gel and eluted with $CHCl_3$-MeOH-H_2O (520:280:80, lower phase; solvent A) to give 21 subfractions. Subfraction no. 1 and 2 (10g) was subjected to flash cloumn chromatography eluting with EtOAc-MeOH-H_2O (100:16.6:13.5; solvent B) to afford pure pulsatilla saponins A and B. Subfraction no. 4 was rechromatographed over a silica gel flash column and eluted with solvent B. The saponin D rich subfractions obtained from the above were pooled, concentrated and applied to rechromatography on silica gel column, eluted with EtOAc saturated with water-MeOH (gradient; solvent C) to yield pure saponin D. Subfractions no. 9 and 10 were combined and subjected to silica gel column chromatography eluted with solvent C to afford saponins E and F. Subfraction no. 18 was rechromatographed over silica gel in the same manner with saponins E and F to yield pure saponin H.

Pulsatilla saponin A(I)

Crystallized from MeOH as fine needles.

m.p. 264-5°, $[\alpha]_D^{25} = +16.9°$(c, 0.13, MeOH) [Lit.[3] m.p. 250-255°, $[\alpha]_D = +17.0°$]; IR ν_{max}^{KBr} cm^{-1} 3410(OH), 1698(COOH), 1640, 806(C=C), 1073, 1050, 1027(C-O); ^{13}C-NMR(50.3MHz): see Table I.

Pulsatilla saponin B(II)

Crystallized from MeOH as fine needles.

m.p. 263-4°, $[\alpha]_D^{22} = +50.5°$ (c, 0.2, MeOH) [Lit.[3] m.p. 260-1°, $[\alpha]_D = +58.3°$]; IR ν_{max}^{KBr} cm^{-1} 3400(OH), 1695(COOH), 1645, 812 (C=C), 1100-1000(C-O); ^{1}H-NMR (200MHz) δ: 0.93(6H, s, $2\times CH_3$), 0.96(3H, s, CH_3), 1.04(3H, s, CH_3), 1.11(3H, s, CH_3), 1.42 (3H, s, CH_3), 4.91(1H, d, J=7.4Hz, anomeric H), 5.27(1H, d, H=7.9Hz, anomeric H), 5.49(1H, brs, H-12); ^{13}C-NMR (50.3MHz): see Table I.

Pulsatilla saponin D(III)

Crystallized from MeOH-H_2O as amorphous white.

m.p. 239-41°, $[\alpha]_D^{22} = +23.6°$(c, 0.2, MeOH) [Lit.[3] m.p. 239-42°, $[\alpha]_D = +14.9°$]; IR ν_{max}^{KBr} cm^{-1} 3420(OH), 1697(COOH), 1640, 810 (C=C), 1075, 1047, 1030(C-O); ^{1}H-NMR(200MHz) δ: 0.90(6H, s, $2\times CH_3$), 0.97, 0.99, 1.06, 1.21(3H each, s, CH_3), 1.63(3H, d, J=6.1Hz, rha-CH_3), 4.96(1H, d, J=6.6Hz, anomeric H), 5.09 (1H, d, J=7.6Hz, anomeric H), 5.44(1H, brs, H-12), 6.25(1H, brs, anomeric H); ^{13}C-NMR(50.3MHz): see Table I; SIMS *m/z*: 913$(M+H)^+$, 767$[(M+H)-146]^+$, 751$[(M+H)-162]^+$; SIMS(NaI) *m/z*: 935$(M+Na)^+$, 889$[(M+Na)-(COOH+H)]^+$, 789$[(M+Na)-146]^+$, 773$[(M+Na)-162]^+$.

Pulsatilla saponin F(IV)

Crystallized from MeOH-H_2O as amorphous white.

m.p. 225-8°, $[\alpha]_D^{20} = -13.5°$(c, 0.3, MeOH)[Lit.[3] m.p. 215-6°, $[\alpha]_D = -8.0°$]; IR ν_{max}^{KBr} cm^{-1} 3400(OH), 1735(ester), 1645, 807(C=C), 1100-1000 (C-O); ^{1}H-NMR(300MHz) : 0.88, 0.98, 1.00, 1.03, 1.10, 1.16(3H each, s, CH_3), 1.61(3H, d, J=6.2Hz, rha-CH_3), 1.66 (3H, d, J=6.2Hz, rha-CH_3), 4.96(1H, d, J=7.8Hz, anomeric H), 5.10(1H, d, J=6.0Hz, anomeric H), 5.40(1H, t-like, H-12), 5.77(1H, brs, anomeric H), 6.12(1H, brs, anomeric H), 6.19 (1H, d, J=7.8Hz, anomeric H); ^{13}C-NMR(75.5MHz): see Table I.

Pulsatilla saponin H(V)

Crystallized from MeOH as amorphous white.

m.p. 205-8°, $[\alpha]_D^{21} = -17.1°$(c, 0.36, MeOH) [Lit.[3] m.p. 219-22°, $[\alpha]_D = -9.0°$]; IR ν_{max}^{KBr} cm^{-1} 3410(OH), 1735(ester), 1640, 806(C=O), 1100-1000 (C-O); ^{13}C-NMR(50.3MHz): see Table I; SIMS *m/z*: see text.

Acid hydrolysis of saponins

Acid hydrolysis of pulsatilla saponins A, B, D, F, and H was separately performed by refluxing each saponin with 5% H_2SO_4 in 60% dioxane for 5h. Hederagenin (**VI**) was identified as the genin in each case by direct comparison with an authentic sample. Rhamnose and arabinose from **I**, rhamnose and glucose from **II**, and rhamnose, arabinose and glucose from **III**, **IV**, and **V** were detected by tlc(precoated cellulose plate, pyridine-EtOAc-HOAc-H_2O=36:36:7:21, R_f 0.64 for arabinose, 0.53 for rhamnose and 0.41 for glucose).

Partial hydrolysis of III

A solution of **III**(380mg) in a mixture of MeOH(36m*l*) and c-HCl(0.5m*l*) was refluxed for 0.5h. The reaction mixture was poured into crushed ice and then filtered. The precipitate was subjected to silica gel column chromatography eluting with EtOAc saturated with water-MeOH(1% and then 2%) to yield hederagenin(**VI**, 45mg), prosapogenin A(**I**, 180mg), prosapogenin B(**II**, 70mg), and the starting material in the order of elution.

Prosapogenin A was crystallized from MeOH as needles, mp 263-5°, and identified as pulsatilla saponin A(**I**) by direct comparision with an authentic sample. In the same manner, prosapogenin B(**II**) was crystallized from MeOH as needles, m.p. 263-4°, and identified as pulsatilla saponin B(**II**).

Alkaline hydrolysis of saponins IV and V

Alkaline hydrolysis of **IV**(100mg) and **V**(80mg) was separately performed by refluxing each saponin with 3% KOH in MeOH for 0.5h. The reaction mixture from saponin **IV** was neutralized with 0.1N-H_2SO_4 and then extracted with BuOH. The BuOH layer was washed with water and concentrated to give a product, which was identified as saponin **I** by direct comparison with an authentic sample. In the same manner, the reaction product from saponin **V** was identified as saponin **III**.

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