Chemistry of Natural Compounds, Vol. 37, No. 3, 2001

TRITERPENE GLYCOSIDES OF *Fatsia japonica*. V. STRUCTURE OF GLYCOSIDES FROM FLOWER BUDS

E. A. Sobolev,[1]* V. I. Grishkovets,[1] V. V. Kachala,[2]
A. S. Shashkov,[2] and V. Ya. Chirva[1]

UDC 547.918:543.422

In continuation of investigation of the glycoside composition of *Fatsia japonica* Decne. et Planck (Araliaceae Juss.), we studied the glycosides of flower buds of this plant. It is noteworthy that the glycoside composition of the flower buds was previously studied by Japanese researchers [1, 2], who isolated and established the structure of six triterpene glycosides. However, our preliminary TLC analysis showed the presence of a large number of glycosides in these organs. Furthermore, our previous work on the leaves and fruit pericarp of *F. japonica* [3, 4] indicate that a more detailed study of the structure (bond types) of the isolated glycosides is advisable.

Glycosides were isolated from ground raw material (15 g) after defatting with benzene (3×150 mL) and three extractions (200 mL each) by isopropanol (80%). This afforded total extracted substances (9 g) that were dissolved in water-saturated butanol (400 mL) and washed twice (100 mL each) with cold aqueous ammonia (2.5%) to remove phenolic compounds, salts, and free sugars. Evaporation of the butanol layer gave purified total triterpene glycosides (3.7 g).

Glycosides were separated by chromatography over a silica-gel column with gradient elution by water-saturated $CHCl_3$—isopropanol (10:1→1:1) to give fractions A (30 mg), B (10 mg), C (60 mg), glycosides D (45 mg), E (450 mg), F (400 mg), G (610 mg), fractions H (723 mg), I (145 mg), glycoside J (158 mg), fractions K (500 mg), L (60 mg), M (50 mg), and N (100).

Fraction C was additionally separated by rechromatography over silica gel with elution by water-saturated $CHCl_3$—isopropanol (5:1) into glycosides C_1 (9 mg) and C_2 (45 mg).

Fractions G and H were separated analogously with elution by water-saturated $CHCl_3$—isopropanol (3:1→2:1) into pure glycosides G_1 (220 mg), G_2 (200 mg), G_3 (80 mg), H_1 (50 mg), and H_2 (600 mg).

Glycosides B (**1**), C_1 (**2**), and C_2 (**3**) were identical by TLC and acid hydrolysis with known samples of 3-O-α-L-arabinopyranosides of oleanolic and echinocystic acids and hederagenin. Their compositions were also confirmed by results from acid hydrolysis and the ^{13}C NMR, which were identical to those previously described [5]. These arabinosides were isolated in buds of *F. japonica* [1, 2]. However, we did not observe the 3-O-α-L-arabinopyranoside of 16-epi-echinocystic acid among the isolated monosides [2]. No additional signals of an isomeric aglycone were observed in the ^{13}C NMR spectrum.

Glycosides D (**4**) and E (**5**) were identified by TLC as 3-O-β-D-glucopyranosyl-(1→2)-O-α-L-arabinopyranosides of oleanolic acid and hederagenin, which we isolated from leaves of *F. japonica* [3]. Structures of these glycosides were confirmed by acid hydrolysis and ^{13}C NMR spectra, which were identical to those previously reported [3], where the 1→2 bond between monosaccharides was unambiguously proven. Therefore, the previously proposed [1, 2] 1→4 bond in glucosylarabinosides of oleanolic acid and hederagenin should be considered erroneous because we did not find other biosides in *F. japonica* buds.

Glycosides G_2 (**6**), H_1 (**7**), and H_2 (**8**) were identical by TLC to 3-O-α-L-arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl esters of oleanolic and echinocystic acids and hederagenin [5, 6]. The compositions of these glycosides were confirmed by total acid hydrolysis and alkaline hydrolysis to give the progenins, which are identical to those described above for glycosides **1-3**.

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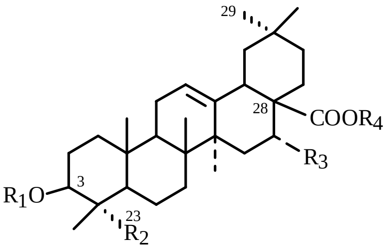
1) V. I. Vernadskii Tavricheskii National University, 95007, Simferopol′, ul. Yaltinskaya, 4, *e-mail: sobolevevg@mail.ru; 2) N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, 117913, Moscow, B-334, Leninskii pr., 47. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 248-249, May-June, 2001. Original article submitted June 20, 2001.

0009-3130/01/3703-0292$25.00



1 - 10

	R$_1$	R$_2$	R$_3$	R$_4$
1:	Ara*p*α→	CH_3	H	H
2:	Ara*p*α→	CH_3	OH	H
3:	Ara*p*α→	CH_2OH	H	H
4:	Glc*p*β-(1→2)-Ara*p*α→	CH_3	H	H
5:	Glc*p*β-(1→2)-Ara*p*α→	CH_2OH	H	H
6:	Ara*p*α→	CH_3	H	←β Glc*p*-(6←1)-β Glc*p*-(4←1)-α Rha*p*
7:	Ara*p*α→	CH_3	OH	←β Glc*p*-(6←1)-β Glc*p*-(4←1)-α Rha*p*
8:	Ara*p*α→	CH_2OH	H	←β Glc*p*-(6←1)-β Glc*p*-(4←1)-α Rha*p*
9:	Glc*p*β-(1→2)-Ara*p*α→	CH_3	H	←β Glc*p*-(6←1)-β Glc*p*-(4←1)-α Rha*p*
10:	Glc*p*β-(1→2)-Ara*p*α→	CH_2OH	H	←β Glc*p*-(6←1)-β Glc*p*-(4←1)-α Rha*p*

Glycosides J (**9**) and K (**10**) were identical by TLC and ^{13}C NMR to 3-O-β-D-glucopyranosyl-(1→2)-O-α-L-arabinopyranosyl-28-O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl esters of oleanolic acid and hederagenin, which we isolated previously from leaves of *F. japonica* [3]. Alkaline hydrolysis of **9** and **10** gave **4** and **5**, which were described above.

It is noteworthy that the glycoside composition of *F. japonica* buds is similar to that of the leaves [3] and fruit pericarp [4].

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