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TRITERPENOID GLYCOSIDES OF *Fatsia japonica*. III. ISOLATION AND STRUCTURE OF GLYCOSIDES FROM FRUIT PERICARP

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

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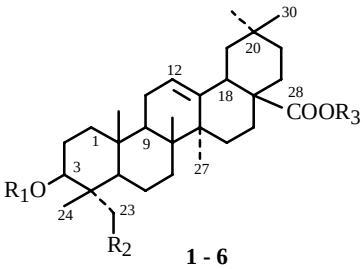
We have previously described triterpenoid glycosides from seeds of *Fatsia japonica* Decne. et Planch. (Araliaceae) [1]. In the present article, we report the isolation and identification of glycosides from fruit pericarp of this plant, the composition of which differs from that of the seeds. The composition of the fruit from *F. japonica* as a whole has been reported [2, 3]. Furthermore, the structures of the previously isolated glycosides were not confirmed by NMR.

For isolation and separation of glycosides from pericarp we used the same method as for the study of the composition of the seeds and leaves [1]. The pericarp remaining after removal of the seeds [1] from fruit of *F. japonica* (16 g) was ground, defatted with benzene (3×150 ml), and extracted with isopropanol (80%, 3×200 ml). The extract was evaporated to give the total extracted substances (8.1 g) that were dissolved in water-saturated butanol (400 ml) and washed (2×100 ml) with cooled aqueous ammonia (2.5%) to remove phenolic compounds, salts, and free sugars. The butanol layer was evaporated to give purified total triterpenoid glycosides (3.0 g) that were separated on silica gel with gradient elution by water-saturated $CHCl_3$—isopropanol mixtures (10:1→1:1). Yields of pure glycosides A (50 mg), B (**1**, 220 mg), C (**2**, 30 mg), D (**3**, 287 mg), fractions E (180 mg) and F (800 mg), glycoside G (**4**, 930 mg), fraction H (150 mg), glycosides I (**5**, 90 mg) and J (**6**, 590 mg) were measured.



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	R_1	R_2	R_3
1	Ara*p* α→	OH	H
2	Glc*p*β-(1→2)-Ara*p* α→	H	H
3	Glc*p*β-(1→2)-Ara*p* α→	OH	H
4	Ara*p* α→	OH	←βGlc*p*-(6←1)-βGlc*p*-(4←1)-α Rha*p*
5	Glc*p*β-(1→2)-Ara*p* α→	H	←βGlc*p*-(6←1)-βGlc*p*-(4←1)-α Rha*p*
6	Glc*p*β-(1→2)-Ara*p* α→	OH	←βGlc*p*-(6←1)-βGlc*p*-(4←1)-α Rha*p*

The isolated glycosides were identical according to TLC to the pricinpal glycosides contained in *F. japonica* leaves [4]. Thus, glycoside A was identified as β-sitosterol 3-O-β-D-glucopyranoside; B, hederagenin 3-O-α-L-arabinopyranoside; C and D, 3-O-β-D-glucopyranosyl-(1→2)-O-α-L-arabinopyranosides of oleanolic acid and hederagenin; G, I, and J, 28-O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-glucopyranosyl esters of hederagenin 3-O-α-L-arabinopyranoside and 3-O-β-D-glucopyranosyl-(1→2)-O-α-L-arabinopyranosides of oleanolic acid and hederagenin, respectively.

Total acid hydrolysis confirmed the qualitative composition of the isolated glycosides. Alkaline hydrolysis of glycosides G, I, and J produced glycosides B, C, and D, which are not affected by alkaline hydrolysis but are methylated by diazomethane in ether at the free carboxylic acid of the aglycone. This confirms that the carbohydrates are located on the C-3 hydroxyl of the aglycones. The ^{13}C NMR spectra are identical to those of the corresponding glycosides isolated from leaves of *F. japonica* [4]. It should be mentioned that the 1→6 bond between glucose residues in the trisaccharide chain on C-28 of the aglycone was unambiguously established (glycosides G, I, and J), like for glycosides of the leaves and in all other studied glycosides of

1) V. I. Vernadskii Tavricheskii National University, 95007, Simferopol, ul. Yaltinskaya, 4; 2) N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, 117913, Moscow, B-334, Leninskii prospekt, 47. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 426-427, September-October, 2000. Original article submitted November 14, 2000.

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Araliaceae species with a trisaccharide moiety on C-28 [5]. Therefore, the 1→4 bonding in the trisaccharide moiety that was proposed previously by Japanese researchers [3] for glycosides from fruits of *F. japonica* on the basis of methylation results should be considered to be incorrect.

We note that several glycosides, namely those with one or two glucoses on C-3 of the aglycone and a gentiobiose disaccharide on C-28 of the aglycone, which predominate in seeds of *F. japonica*, are not observed in fruit pericarp. This indicates that the glycoside compositions of the seeds and pericarp differ significantly whereas those of the leaves and pericarp are similar.

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