# TRITERPENE GLYCOSIDES OF THE LEAVES OF *Fatsia japonica*

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We have previously reported that the fresh leaves of *Fatsia japonica* (Thunb.) Decne et Planch., family Araliaceae (Japan fatsia) cultivated in the Georgian SSR Black Sea littora contain weakly polar, and the air-dry leaves more strongly polar, glycosides. In the fresh leaves by TLC in systems with various pH values at least four weakly polar compounds were detected [1] — fatsiasides $A_1$, $B_1$, $C_1$, and $D_1$ — and we give information on the study of their structures below.

The glycosides were isolated by extraction of the fresh leaves with ethanol followed by purification by repeated separation on a column of silica gel in the chloroform–methanol (7:1 and 5:1) and chloroform–methanol–water (82:32:6) systems.

The individual glycosides obtained consisted of crystalline substances. Complete acid hydrolysis showed that glycosides $A_1$ and $C_1$ were derivatives of oleanolic acid, while $B_1$ and $D_1$ were derivatives of hederagenin.

Using PC and TLC methods, arabinose was detected in the carbohydrate moieties of fatsiasides $A_1$ and $B_1$, and arabinose and glucose in those of fatsiasides $C_1$ and $D_1$.

On the basis of their physicochemical constants, the monosaccharides arabinose and glucose isolated by paper chromatography from acid hydrolysates belonged to the L and D configurations, respectively.

After reduction with $NaBH_4$ followed by acetylation in an $Ac_2O$/Py mixture of the hydrolysates obtained, by the GLC method the full acetate of arabitol was identified for fatsiasides $A_1$ and $B_1$, and the acetates of arabitol and sorbitol in a ratio of 1:1 for $C_1$ and $D_1$.

Methylation by Hakomori's method [2] followed by methanolysis of the fatsiasides under investigation permitted the identification by GLC of methyl 2,3,4-tri-O-methylarabinopyranoside for glycosides $A_1$ and $B_1$, and methyl 2,3,4,6-tetra-O-methylglucopyranoside and methyl 3,4,-di-O-methylarabinopyranoside in a ratio of 1:1 for $C_1$ and $D_1$. As a result of the methanolysis of the methylated fatsiasides, the methyl derivatives of oleanolic acid were also identified for fatsiasides $A_1$ and $C_1$ and those of hederagenin for fatsiasides $B_1$ and $D_1$, each with free C-3 positions, showing the site of attachment of the monosaccharide residue to the aglycone and the absence of ester bonds in the glycosides under investigation. The results obtained were confirmed by an analysis of the IR spectra of the compounds under investigation.

TABLE 1. Physicochemical Properties of the Glycosides from Fresh Leaves of *Fatsia japonica*

| Fatsiaside | mp, °C | $[\alpha]_D^{20}$, deg | Aglycone | Monosaccharide |
|---|---|---|---|---|
| $A_1$ | 234–239 | +56.1 (*c* 1; $CH_3OH$) | Oleanolic acid | Arabinose |
| $B_1$ | 240–242 | +82.1 (*c* 0,89 $C_5H_5N$) | Hederagenin | Glucose |
| $C_1$ | 262–263 | +41.6 (*c* 0,33 $C_5H_5N$) | Oleanolic acid | |
| $D_1$ | 237–238 | +44.4 (*c* 0,34 $C_5H_5N$) | Hederagenin | |

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The hydrolysis of the methylated fatsiasides followed by reduction and acetylation led to 1,5-di-O-acetyl-2,3,4-tri-O-methylarabitol identified by GLC, for both glycosides $A_1$ and $B_1$. For fatsiasides $C_1$ and $D_1$, 1,5-di-O-acetyl-2,3,4,6-tetra-O-methylsorbitol and 1,2,5-tri-O-acetyl-3,4-di-O-methylarabitol were found in a ratio of 1:1, which shows the sequence of the structure of the carbohydrate chain.

A summation of the results obtained and a comparison of them with literature information [3-6] permits the following structures to be suggested for them for the fatsiasides: $A_1$ [4] — oleanolic acid 3-O-α-L-arabinopyranoside; $B_1$ (corresponding to leontoside A) [5] — hederagenin 3-O-α-L-arabinopyranoside; $C_1$ [6] — oleanolic acid 3-O-[O-β-D-glucopyranosyl-(1 → 2)-α-L-arabinopyranoside]; and $D_1$ [6] hederagenin 3-O-[O-β-D-glucopyranosyl-(1 → 2)-α-L-arabinopyranoside].

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# GLYCOSIDES OF THE HOLOTHURIAN *Bohadschia graeffei*


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It has been shown previously that the chromatographic behavior of the glycosides of *Bohadschia graeffei* (Semper) does not coincide with that of the glycosides of other holothurians of this genus [1].

Continuing an investigation of the triterpene glycosides of holothurians, we have studied the glycoside fraction from *B. graeffei*. The animals were collected in July-August, 1974, on the coast of the Maldive islands. Glycoside (I) was isolated by a method described [2].

Glycoside (I) had mp 242–244°C (from ethanol), $[\alpha]_D^{25}$ –12.4° (c 0.01; pyridine). The acid hydrolysis of 45 mg of the glycoside (2 N HCl, 90°C, 2 h) yielded the sum of the artefact aglycones, from which, by column chromatography on silica gel in the benzene–ethyl acetate (8.5:1) system was isolated 16 mg of genin (II) [mp 280–282°C (from ethanol); UV spectrum, nm, $\lambda_{max}^{C_2H_5OH}$: 234, 243, 253 (log ε 4.21); mass spectrum ($M^+$ 170)] which was found to be identical with a known sample of holosta-7,9(11)-diene-3β,17α-diol by comparison of constants and mass spectra [3], together with a mixture of monosaccharides. With the aid of GLC, the monosaccharides, in the form of the aldononitrile acetates, were identified as quinovose, glucose, 3-O-methylglucose, and xylose (1:1:1:1). The hydrolysate gave a positive test with $BaCl_2$.

When the glycoside (I) was subjected to periodate oxidation followed by acid hydrolysis the quinovose residue was destroyed. The Smith degradation of glycoside (I) followed by desulfation performed by a method described previously [4] yielded a progenin (III) with mp 298–301°C (from methanol), $[\alpha]_D^{25}$ –9° (c 0.01; pyridine). The acid hydrolysis of (III) gave xylose. From its physical constants and the results of acid hydrolysis, (III) was identified as the known 3-O-β-D-xylopyranosylholost-9(11)-ene-3β,12α,17α-triol [4].


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