

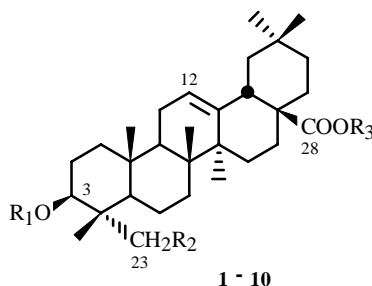
TRITERPENE GLYCOSIDES FROM *Kalopanax septemlobum*.IV. GLYCOSIDE COMPOSITION OF FRUIT FROM
PLANTS INTRODUCED INTO CRIMEA

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The present communication describes the isolation and identification of triterpene glycosides from fruit of *Kalopanax septemlobum* (Thunb.) Koidz. var. *typicum* (Nakai) Pojark. [1] that was introduced into Crimea (Nikitskii Botanical Garden). The glycoside composition of fruit from *K. septemlobum* has not been previously studied. Preparative TLC showed substantial qualitative differences in the glycoside composition of the pericarp and seeds.

Air-dried fruit (20 g) was separated into seeds (2.3 g) and pericarp (17.7 g) for glycoside isolation. Glycosides were isolated from individually selected seeds and pericarp by the usual method [2] that includes thorough grinding, defatting, and extraction of total glycosides by isopropanol (80%). Raw total glycosides were obtained from pericarp (1.8 g) and seeds (0.1 g). Glycosides were separated by chromatography on silica gel (L 40-100 μ m) with gradient elution by water-saturated $\text{CHCl}_3:(\text{CH}_3)_2\text{CHOH}$ (10:1 \rightarrow 1:1). Separation of total glycosides from pericarp eluted successively glycosides **1** (10 mg), **2** (80 mg), **3** (7 mg), **4** (90 mg), **5** (70 mg), and **6** (65 mg); of total glycosides from seeds, **2** (10 mg), **7** (20 mg), **8**, (5 mg), **9** (60 mg), **5** (20 mg), **10** (7 mg), and **6** (3 mg). Glycosides **1-8** and **10** were identified by TLC in various solvent systems as known glycosides that we isolated previously from leaves and fruit of *Hedera taurica* [3] and from leaves of *K. septemlobum* [2], by acid and alkaline hydrolysis, and by comparing their NMR spectra with those in the literature [2, 3].



R_1	R_2	R_3
1: $\alpha\text{-L-Rhap} \rightarrow^2 \alpha\text{-L-Arap} \rightarrow$	H	H
2: $\alpha\text{-L-Rhap} \rightarrow^2 \alpha\text{-L-Arap} \rightarrow$	OH	H
3: $\beta\text{-D-Xylp} \rightarrow^3 \alpha\text{-L-Rhap} \rightarrow^2 \alpha\text{-L-Arap} \rightarrow$	OH	H
4: $\alpha\text{-L-Rhap} \rightarrow^2 \alpha\text{-L-Arap} \rightarrow$	H	$\leftarrow \beta\text{-D-Glcp}^6 \leftarrow \beta\text{-D-Glcp}^4 \leftarrow \alpha\text{-L-Rhap}$
5: $\alpha\text{-L-Rhap} \rightarrow^2 \alpha\text{-L-Arap} \rightarrow$	OH	$\leftarrow \beta\text{-D-Glcp}^6 \leftarrow \beta\text{-D-Glcp}^4 \leftarrow \alpha\text{-L-Rhap}$
6: $\beta\text{-D-Xylp} \rightarrow^3 \alpha\text{-L-Rhap} \rightarrow^2 \alpha\text{-L-Arap} \rightarrow$	OH	$\leftarrow \beta\text{-D-Glcp}^6 \leftarrow \beta\text{-D-Glcp}^4 \leftarrow \alpha\text{-L-Rhap}$
7: $\beta\text{-D-Glcp} \rightarrow$	H	H
8: $\beta\text{-D-Glcp} \rightarrow^2 \beta\text{-D-Glcp} \rightarrow$	H	H
9: $\beta\text{-D-Glcp} \rightarrow$	H	$\leftarrow \beta\text{-D-Glcp}^6 \leftarrow \beta\text{-D-Glcp}$
10: $\beta\text{-D-Glcp} \rightarrow^2 \beta\text{-D-Glcp} \rightarrow$	H	$\leftarrow \beta\text{-D-Glcp}^6 \leftarrow \beta\text{-D-Glcp}$

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Glycoside **9** was not identified as any known glycoside. Total acid hydrolysis of **9** showed the presence of oleanolic acid and glucose. Alkaline hydrolysis of **9** gave **7**. A comparison of the chromatographic mobility of **9** with that of **10** led to the conclusion that **9** contained three glucose units. The results of alkaline hydrolysis indicated that the disaccharide Glu→Glu→ was located on the carboxyl in **9**. Treatment of **9** with emulsin (β -glucosidase from Rosales seeds, KF 3.2.1.21), which specifically cleaves a β -(1→6)-glycoside bond between glucose units, cleaved this glycoside (TLC monitoring) and confirmed the presence of a 1→6 bond (gentiobiose unit). The ^{13}C NMR spectrum of **9** confirmed the hypotheses because signals for the β -gentiobiose bound to the aglycon by an acylglycoside bond, for one β -glucopyranose bonded to aglycon C-3, and for the 3,28-disubstituted oleanolic acid aglycon were readily identified. Thus, **9** is the 3-O- β -D-glucopyranosyl-28-O- β -gentiobiosyl ester of oleanolic acid. This glycoside was isolated previously only from *Clematis montana* (Ranunculaceae) [5].

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