TRITERPENE GLYCOSIDES FROM Kalopanax septemlobum.

V. GLYCOSIDES FROM STEMS OF K. septemlobum VAR.

maximowiczii AND K. septemlobum VAR. typicum

D. A. Panov and V. I. Grishkovets

Udc 547.918

We have reported [1] on substantial qualitative differences in the glycoside composition of leaves from two varieties of *Kalopanax septemlobum* (Thunb.) Koidz. var. *maximowiczii* (Van Houtte) Hara and var. *typicum* (Nakai) Pojark. Despite the fact that triterpene glycosides from stems of *K. septemlobum* have been previously studied [2-5], we analyzed the glycoside composition of both varieties introduced into Nikitskii Botanical Garden (Crimea, Ukraine).

TLC of stem bark from both varieties showed differences in the glycoside composition. Glycosides were isolated from stem bark of each variety using the usual method [1], which includes grinding dried plant material, defatting, extracting glycosides with isopropanol (80%), and separating total glycosides by chromatography over silica gel (L 40-100 μ m) with gradient elution by water-saturated CHCl₃:(CH₃)₂CHOH (10:1 \rightarrow 1:1). Separation of the total glycosides eluted successively fractions A-J. Glycosides **1-6** in fractions A, C, D, H, I, and J were identified by TLC as glycosides of known structure that were isolated by us previously from leaves of *K. septemlobum* var. *maximowiczii* [1]. The structures of **1-6** were also confirmed by acid and alkaline hydrolyses and the complete agreement of ¹³C NMR spectra with those published [1].

R_1	R_2
1: α -L-Ara $p \rightarrow$	Н
2: α -L-Rha $p \rightarrow^2 \alpha$ -L-Ara $p \rightarrow$	Н
3: β -D-Xyl $p \rightarrow {}^{3}\alpha$ -L-Rha $p \rightarrow {}^{2}\alpha$ -L-Ara $p \rightarrow$	Н
4: α -L-Ara p \rightarrow	$\leftarrow \beta$ -D-Glc $p^6 \leftarrow \beta$ -D-Glc $p^4 \leftarrow \alpha$ -L-Rha p
5: α -L-Rha $p \rightarrow^2 \alpha$ -L-Ara $p \rightarrow$	$\leftarrow \beta$ -D-Glc $p^6 \leftarrow \beta$ -D-Glc $p^4 \leftarrow \alpha$ -L-Rha p
6: β -D-Xyl $p \rightarrow^3 \alpha$ -L-Rha $p \rightarrow^2 \alpha$ -L-Ara $p \rightarrow$	$\leftarrow \beta$ -D-Glc $p^6 \leftarrow \beta$ -D-Glc $p^4 \leftarrow \alpha$ -L-Rha p

Furthermore, we analyzed the distribution of triterpene glycosides along individual bands of the pith, wood (xylem), bark, and thorns of stems of both varieties. Their quantitative compositions were practically identical. It should be noted that significant variations in the relative contents of glycosides in fractions A-H were observed in stem bark from different plant parts whereas the contents in fractions I and J were stable. However, we did not find a direct connection between these variations and the age of the stem parts.

V. I. Vernadskii Tauric State University, 95007, Ukraine, Simferopol', prospekt Vernadskogo, 4, e-mail: vladgri@ukr.net. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 390-391, July-August, 2005. Original article submitted April 21, 2005.

TABLE 1. Content of Glycosides 1-6 in Stems of K. septemlobum var. maximowiczii and var. typicum

Fraction Glycoside	Classocials	Relative content, % of total glycosides	
	K. septemlobum var. maximowiczii	K. septemlobum var. typicum	
A	1	0.2	0.2
В		2.0	2.0
C	2	0.5	0.5
D	3	0.3	-
E		2.0	2.3
F		3.0	3.0
G		1.0	1.0
H	4	1.0	1.0
I	5	40.0	90
J	6	50.0	-

Total content of glycosides, ~7% of air-dried stems of both varieties.

According to TLC results and an estimate of the quantitative glycoside contents in bark of *K. septemlobum* var. *maximowiczii*, the principal glycosides are **5** and **6** (the content of **6** is slightly higher). On the other hand, **6** was detected only in trace amounts in var. *typicum*. Glycosides **1**, **2**, and **4** were present in bark of both varieties. However, their total contents were less than 2% (Table 1). It is interesting that the acetylated glycosides found by us in significant quantities in leaves of *K. septemlobum* var. *maximowiczii* were completely absent in stems of this and the other variety (var. *typicum*). Furthermore, glycosides of oleanolic acid, which occur in significant quantities in leaves of this variety, are absent in stems of *K. septemlobum* var. *typicum*.

Thus, significant differences in the glycoside compositions of both leaves and stems were observed in both *K. septemlobum* var. *maximowiczii* and var. *typicum*. Taking into account the substantial external morphological differences [6], an elevation of their taxonomic rank to that of species can be proposed, i.e., their description as independent species.

REFERENCES

- 1. V. I. Grishkovets, D. A. Panov, V. V. Kachala, and A. S. Shashkov, Khim. Prir. Soedin., 156 (2005).
- 2. D. R. Hahn, T. Oinaka, R. Kasai, and O. Tanaka, Chem. Pharm. Bull., 37, 2234 (1989).
- 3. S. H. Cho and D. R. Hahn, Arch. Pharm. Res., 14, 19 (1991).
- 4. K. Sano, S. Sanda, Y. Ida, and J. Shoji, *Chem. Pharm. Bull.*, **39**, 865 (1991).
- 5. A. Porzel, T. V. Sung, J. Schmidt, M. Lischewski, and G. Adam, *Planta Med.*, 58, 481 (1992).
- 6. Trees and Shrubs of the USSR. Wild, Cultivated, and Promising for Introduction [in Russian], in five vols., Izd. Akad. Nauk SSSR, Moscow-Leningrad (1960), Vol. 5: Angiosperms. Myrtaceae-Oleaceae Families.