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TRITERPENE GLYCOSIDES FROM LEAVES OF *Acanthopanax sieboldianus* INTRODUCED TO UKRAINE AND CRIMEA

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Acanthopanax sieboldianus Makino (synonyms *A. pentaphyllum* Marsh., *A. trichodon sensu* Zbl., *Aralia pentaphylla sensu* Sieb. et Zucc., *Eleutherococcus japonicus* Nakai) is one of the species of the genus *Acanthopanax* (Araliaceae) that grows in Japan (Shikoku, Honshu, Hokkaido) [1]. Like other *Acanthopanax* species, this plant is widely used in Eastern folk medicine to cure various illnesses [2]. This bush was successfully introduced in several districts of the European part of the CIS, in particular, in the Ukraine (L'vov, Kiev, Drogobych, Zakarpat'e) [1] and in the Crimea where a piedmont climate exists (e.g., Simferopol).

The glycoside composition of the plant was studied by Japanese researchers, who isolated from the leaves of *A. sieboldianus* collected in Japan seven triterpene glycosides of oleanic acid and hederagenin and the flavonoid glycoside kaempferol 3-rutinoside [3].

We studied the glycoside composition of leaves collected in Kiev, L'vov, and Simferopol and compared the results with the glycoside composition of leaves of *A. sieboldianus* from the natural habitat. Furthermore, we identified changes in the glycoside composition of the leaves as a function of plant age.

Preparative TLC of the alcohol extract of the leaves showed that, in contrast with the roots and stems, they are very rich in triterpene glycosides. The glycoside composition of the leaves of *A. sieboldianus* growing in Kiev, L'vov, and Simferopol is qualitatively and quantitatively practically the same. Total acid hydrolysis of the total extract and TLC analysis of the resulting aglycones showed the presence of mainly glycosides of hederagenin and only a small quantity of oleanolic and echinocystic acid glycosides.

Triterpene glycosides were isolated as follows. Dried ground leaves (22 g) obtained from the Botanical Garden of Kiev National University were defatted by benzene (3×200 ml) and extracted with aqueous isopropanol (80%, 3×200 ml). The combined alcohol extracts were evaporated. The solid was dissolved in water-saturated butanol and washed with aqueous ammonia (5%, 3×100 ml) to remove phenolic glycosides, salts, and free sugars. The butanol layer was evaporated to dryness. The solid (2 g) was chromatographed on silica gel (0.3 kg) with gradient elution by water-saturated $CHCl_3$—C_2H_5OH (10:1 · 1:1). The following compounds eluted successively: **1** (10 mg), **2** (25 mg), **3** (20 mg), **4** (170 mg), **5** (160 mg), **6** (25 mg), **7** (45 mg), **8** (35 mg), **9** (600 mg), and **10** (500 mg).

Glycosides **1-4** and **6-8** were identified with authentic samples isolated by us previously from Canary ivy *Hedera canariensis* [4] and common ivy *Hedera helix* [5] using TLC and NMR spectroscopy. Glycosides **5** and **10** were identified with previously described glycosides from leaves of *A. sieboldianus* [3] by comparison of ^{13}C NMR spectra.

The minor glycosides **1-3** and **6-8** have not previously been observed in leaves of *A. sieboldanus*. We note that glycosides of echinocystic acid (**3** and **8**) have not been previously observed in this plant.

Structural analysis of the minor glycosides and the pair of principal glycosides (**4** and **9**) indicates that the composition of triterpene glycosides in *A. sieboldianus* and Canary and common ivy are very similar [4, 5]. However, in contrast with these species, *A. sieboldianus* contains another pair of principal glycosides (**5** and **10**) with a trisaccharide fragment on the C-3 hydroxyl that were not found in the ivy species.

Comparative TLC analysis of leaves of *A. sieboldianus* with samples of different age indicates that leaves of young plants contain practically no **5** and **10** whereas they are some of the principal ones in old plants. On the other hand, the content of echinocystic acid glycosides in leaves decreases with age until they practically disappear. Furthermore, it can be concluded that the ecological conditions of the introduction sites have practically no influence on the qualitative and quantitative glycoside composition of *A. sieboldianus* leaves.

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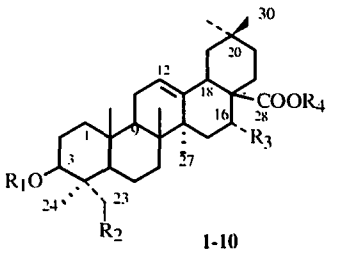

1-10

	R_1	R_2	R_3	R_4
1	Ara*p*α-	OH	H	H
2	Rha*p*α-(1-2)-Ara*p*α-	H	H	H
3	Rha*p*α-(1-2)-Ara*p*α-	H	OH	H
4	Rha*p*α-(1-2)-Ara*p*α-	OH	H	H
5	Xyl*p*β-(1-3)-Rha*p*α-(1-)Ara*p*α	H	H	H
6	Ara*p*α-	OH	H	- βGlc*p*-(6-1)-βGlc*p*-(4-1)-αRha*p*
7	Rha*p*α-(1-2)-Ara*p*α-	H	H	- βGlc*p*-(6-1)-βGlc*p*-(4-1)-αRha*p*
8	Rha*p*α-(1-2)-Ara*p*α-	H	OH	- βGlc*p*-(6-1)-βGlc*p*-(4-1)-αRha*p*
9	Rha*p*α-(1-2)-Ara*p*α-	OH	H	- βGlc*p*-(6-1)-βGlc*p*-(4-1)-αRha*p*
10	Xyl*p*β-(1-3)-Rha*p*α-(1-)Ara*p*α	H	H	- βGlc*p*-(6-1)-βGlc*p*-(4-1)-αRha*p*

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