

## Triterpene Glycosides of *Hedera Canariensis*

Vladimir I. Grishkovets<sup>1</sup>, Leonid A. Yakovishin<sup>1</sup>, Alexandr S. Shashkov<sup>2</sup>

<sup>1</sup>Simferopol State University, 33300, Yaltinskaya street 4, Simferopol, Crimea, Ukraine

<sup>2</sup>N.D. Zelinskiy Institute of Organic Chemistry, 117913, Leninsky Prospect 47, Moscow, Russia

It is known that plants of some species of *Hedera* genus are used in traditional and officinal medicine. We have studied the glycoside composition of leaves, stems and roots of *Hedera canariensis* Willd. (*Araliaceae*).

Triterpene glycosides were extracted by 80% isopropanol. Extracted compounds were separated by SiO<sub>2</sub> column chromatography with chloroform-ethanol-water eluent. 21 Individual pure triterpene glycosides were obtained after additional chromatographic separation and purification. Its complete structures were determined on the basis of chemical methods (acid, alkali and enzyme hydrolysis) and by use of different <sup>1</sup>H- and <sup>13</sup>C-NMR methods (COSY, HOHAHA, HETCOSY and APT).

It was found that aglycon moieties of glycosides from leaves are hederagenin, oleanolic and echinocystic acids (which glycosides are predominant), 30-norhederagenin and caulophyllogenin in minor glycosides. Carbohydrate chains of this glycosides are presented by 3-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-O- $\alpha$ -L-arabinopyranosides, 28-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 6)-O- $\beta$ -D-glucopyranosides and their degraded forms with less of one or more sugar residues. Moreover, it was found that in some glycosides 28-O-carbohydrate chain bears 6-O-acetyl group at the inner glucose residue. Location of this group was detected on the basis of chemical shifts in PMR and <sup>13</sup>C-NMR spectra.

From *Hedera canariensis* stems we have isolated 3-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-O- $\alpha$ -L-arabinopyranosides of hederagenin, oleanolic and echinocystic acids and their 28-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 6)-O- $\beta$ -D-glucopyranosides. The hederagenin glycosides are predominant. Glycoside composition of *Hedera canariensis* roots is significantly different from stems and presented by only two hederagenin glycosides, namely 3-O- $\alpha$ -L-arabinopyranoside and its 28-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 6)-O- $\beta$ -D-glucopyranosyl esters. But 30-norhederagenin glycosides presented in leaves were not found in stems and roots.

It is interesting to point out that the stems and roots of close species *Hedera taurica* and *Hedera helix* contain considerable amounts of acidic glycosides (glucuronides) and the glycoside composition of roots and stems is quite similar.

Some of isolated glycosides were found in other species of *Hedera* and other *Araliaceae* plants but 5 of them are new, namely: 3-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-O- $\alpha$ -L-arabinopyranosides of 30-norhederagenin and caulophyllogenin, their 28-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 6)-O- $\beta$ -D-glucopyranosides and 3-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 2)-O- $\alpha$ -L-arabinopyranosyl-28-O- $\alpha$ -L-rhamnopyranosyl-(1 $\rightarrow$ 4)-O-(6-O-acetyl- $\beta$ -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O- $\beta$ -D-glucopyranoside of echinocystic acid.