Chemistry of Natural Compounds, Vol. 35, No. 5, 1999

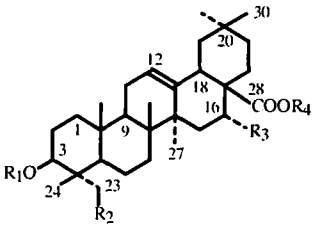
TRITERPENE GLYCOSIDES OF *Hedera canariensis.* V. STRUCTURE OF GLYCOSIDES FROM CANARY IVY STEMS

L. A. Yakovishin,[1] V. I. Grishkovets,[1] N. N. Arnautov,[2] and V. Ya. Chirva [1]

UDC 547.918

Triterpene glycosides from leaves of canary ivy Hedera canariensis *Willd. were previously isolated and characterized [1-4]. The glycosidic composition of the plant stems is reported in the present article.*

Glycosides from stems were isolated, separated, and purified according to the literature procedure [1]. The following compounds were obtained and identified by TLC with known glycosides from the leaves of canary ivy [1] and stems of Crimean ivy *Hedera taurica* [5-7] in various solvent systems: 3-O-α-*L*-arabinopyranoside of echinocystic acid (**1**, 0.02%) and hederagenin (**2**, 0.07%), 3-O-α-*L*-rhamnopyranosyl-(1→2)-O-α-*L*-arabinopyranoside of echinocystic acid (**3**, 0.02%) and hederagenin (**4**, 0.10%), 3-O-β-*D*-glucoronopyranoside of oleanolic acid (**5**, 0.04%) and hederagenin (**6**, 0.06%), and the 28-O-α-*L*-rhamnopyranosyl-(1→4)-O-β-*D*-glucopyranosyl-(1→6)-O-β-*D*-glucopyranosyl esters of **1-6** (**7**, 0.02%; **8**, 0.27%; **9**, 0.02%; **10**, 0.32%; **11**, 0.02%; **12**, 0.04%; respectively). The structures of the isolated glycosides were also confirmed by chemical methods (acid and alkaline hydrolysis) and identification of decomposition products.



№	R_1	R_2	R_3	R_4
1	Ara*p*α→	H	OH	H
2	Ara*p*α→	OH	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	GlcUA*p*β→	H	H	H
6	GlcUA*p*β→	OH	H	H
7	Ara*p*α→	H	OH	→β Glc*p*-(6→1)-β Glc*p*-(4→1)-α Rha*p*
8	Ara*p*α→	OH	H	→β Glc*p*-(6→1)-β Glc*p*-(4→1)-α Rha*p*
9	Rha*p*α-(1→2)-Ara*p*α	H	OH	→β Glc*p*-(6→1)-β Glc*p*-(4→1)-α Rha*p*
10	Rha*p*α-(1→2)-Ara*p*α	OH	H	→β Glc*p*-(6→1)-β Glc*p*-(4→1)-α Rha*p*
11	GlcUA*p*β→	H	H	→β Glc*p*-(6→1)-β Glc*p*-(4→1)-α Rha*p*
12	GlcUA*p*β→	OH	H	→β Glc*p*-(6→1)-β Glc*p*-(4→1)-α Rha*p*

1) Simferopol' State University; 2) Botanical Garden, Botanical Institute, Russian Academy of Sciences, St. Petersburg.
Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 676-678, September-October, 1999. Original article submitted July 30, 1999.

0009-3130/99/3505-0587$22.00

Glycosides of hederagenin predominate in the stems and leaves of canary ivy. Glycosides of oleanolic and echinocystic acids are minor components. The leaves contain mainly hederagenin 3-O-α-*L*-rhamnopyranosyl-(1→2)-O-α-*L*-arabinopyranoside and its 28-O-α-*L*-rhamnopyranosyl-(1→4)-O-β-*D*-glucopyranosyl-(1→6)-O-β-*D*-glucopyranosyl ester. The stems contain these and comparable amounts of the 3-O-α-*L*-arabinopyranoside and its 28-O-α-*L*-rhamnopyranosyl-(1→4)-O-β-*D*-glucopyranosyl-(1→6)-O-β-*D*-glucopyranoside. Furthermore, in contrast with the glycosidic content of the leaves [1], the stems do not contain neutral glycosides of oleanolic acid. However, the 3-O-β-*D*-glucuronopyranoside and the 28-O-α-*L*-rhamnopyranosyl-(1→4)-O-β-*D*-glucopyranosyl-(1→6)-O-β-*D*-glucopyranosyl ester of oleanolic acid in addition to acidic glycosides of hederagenin with the analogous carbohydrate chains were isolated.

Glycosides of 30-norhederagenin [2], caulophyllogenin [3], and acetylated glycosides [4], which are characteristic of the leaves, are not found in the stems of canary ivy.

The glycoside compositions of canary and Crimean ivy stems greatly differ in the content of several common glycosides. Thus, stems of *H. taurica* do not contain glycosides of echinocystic acid whereas stems of *H. canariensis* contain no 3-O-β-*D*-glucopyranoside, 3-O-β-*D*-glucopyranosyl-(1→2)-O-α-*L*-arabinopyranoside, and 3-O-α-*L*-rhamnopyranosyl-(1→2)-O-β-*D*-glucopyranoside of hederagenin [6] and their 28-O-α-*L*-rhamnopyranosyl-(1→4)-O-β-*D*-glucopyranosyl-(1→6)-O-β-*D*-glucopyranosyl esters [7, 8].

The results confirm that *H. canariensis* belongs to the subgenus *Helix* Pojark. The designation of canary ivy as an individual species [9] and not a variety of common ivy *H. helix canariensis* DC is therefore justified.

REFERENCES

1. V. I. Grishkovets, D. Yu. Sidorov, L. A. Yakovishin, N. N. Arnautov, A. S. Shashkov, and V. Ya. Chirva, *Khim. Prir. Soedin.*, 377 (1996).
2. A. S. Shashkov, V. I. Grishkovets, L. A. Yakovishin, I. N. Shchipanova, and V. Ya. Chirva, *Khim. Prir. Soedin.*, 772 (1998).
3. V. I. Grishkovets, L. A. Yakovishin, I. N. Shchipanova, A. S. Shashkov, and V. Ya. Chirva, *Khim. Prir. Soedin.*, 777 (1998).
4. L. A. Yakovishin, V. I. Grishkovets, I. N. Shchapanova, A. S. Shashkov, and V. Ya. Chirva, *Khim. Prir. Soedin.*, 81 (1999).
5. V. I. Grishkovets, O. Ya. Tsvetkov, A. S. Shashkov, and V. Ya. Chirva, *Khim. Prir. Soedin.*, 397 (1997).
6. V. I. Grishkovets, S. V. Godin, O. Ya. Tsvetkov, A. S. Shashkov, and V. Ya. Chirva, *Khim. Prir. Soedin.*, 411 (1997).
7. A. S. Shashkov, V. I. Grishkovets, O. Ya. Tsvetkov, and V. Ya. Chirva, *Khim. Prir. Soedin.*, 571 (1993).
8. V. I. Grishkovets, O. Ya. Tsvetkov, A. S. Shashkov, and V. Ya. Chirva, *Bioorg. Khim.*, 468 (1995).
9. *Trees and Bushes of the USSR*, in 5 Vol., Akademiya Nauk SSSR, Moscow-Leningrad (1960), Vol. 5, p. 167.