

TRITERPENE GLYCOSIDES OF *Hedera canariensis*.

VII. STRUCTURES OF GLYCOSIDES

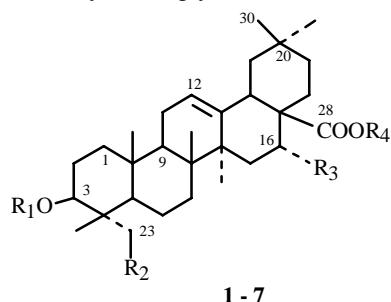
FROM ROOTS OF CANARY IVY

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We expanded the study of triterpene glycosides of the aerial parts, i.e., leaves [1-5] and stems [6], of canary ivy to an investigation of the glycoside composition of its roots.

Glycosides from the roots were isolated, separated by chromatography, and purified as before [1]. We obtained seven known triterpene glycosides: 3-O- α -L-arabinopyranosides of oleanolic acid (**1**, 0.005%), echinocystic acid (**2**, 0.004%), and hederagenin (**3**, 0.05%); hederagenin 3-O- α -L-arabinopyranosyl-28-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)-O- β -D-glucopyranosyl-(1 \rightarrow 6)-O- β -D-glucopyranosyl ester (**4**, 0.2%); hederagenin 3-O- β -D-glucopyranosyl-(1 \rightarrow 2)-O- α -L-arabinopyranosyl-28-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)-O- β -D-glucopyranosyl-(1 \rightarrow 6)-O- β -D-glucopyranosyl ester (**5**, 0.001%); and the 3-O- β -D-glucuronopyranosyl-28-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)-O- β -D-glucopyranosyl-(1 \rightarrow 6)-O- β -D-glucopyranosyl esters of oleanolic acid (**6**, 0.01%) and hederagenin (**7**, 0.015%). The yield of glycosides is calculated per dry mass of the plant material.



R ₁	R ₂	R ₃	R ₄
1: Arap α \rightarrow	H	H	H
2: Arap α \rightarrow	H	OH	H
3: Arap α \rightarrow	OH	H	H
4: Arap α \rightarrow	OH	H	$\leftarrow\beta$ Glcp-(6 \leftarrow 1)- β Glcp-(4 \leftarrow 1)- α Rhap
5: Glcp α -(1 \rightarrow 2)-Arap α \rightarrow	OH	H	$\leftarrow\beta$ Glcp-(6 \leftarrow 1)- β Glcp-(4 \leftarrow 1)- α Rhap
6: GlcUAp β \rightarrow	H	H	$\leftarrow\beta$ Glcp-(6 \leftarrow 1)- β Glcp-(4 \leftarrow 1)- α Rhap
7: GlcUAp β \rightarrow	OH	H	$\leftarrow\beta$ Glcp-(6 \leftarrow 1)- β Glcp-(4 \leftarrow 1)- α Rhap

Glycosides **1-7** were identified using TLC in various solvent systems with authentic samples of glycosides from leaves [1] and stems [6] of *Hedera canariensis*, stems of *H. taurica* [7], and leaves of *Fatsia japonica* [8]. Results of total and partial acid and alkaline hydrolysis, methylation by diazomethane, and identification of the resulting transformation products by TLC confirmed their structures.

It has been demonstrated that hederagenin glycosides dominate in roots of *H. canariensis*, like in the leaves and stems. Glycosides of 30-norhederagenin [2] and caulophyllogenin [3, 5] in addition to partially acetylated glycosides [4, 5] isolated from the leaves of canary ivy were not observed in the roots or stems [6]. An interesting feature of the glycoside composition

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of the roots of *H. canariensis* is the absence of hederagenin 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-O- α -L-arabinopyranosyl-28-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)-O- β -D-glucopyranosyl-(1 \rightarrow 6)-O- β -D-glucopyranosyl ester, the dominant glycoside of the leaves and stems of this plant.

The glycoside composition of the roots of other *Hedera* species is studied only partially for *Hedera helix* [9]. We did not observe in roots of *H. canariensis* 3-O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-O- α -L-arabinopyranosyl-28-O- α -L-rhamnopyranosyl-(1 \rightarrow 4)-O- β -D-glucopyranosyl-(1 \rightarrow 6)-O- β -D-glucopyranosyl esters of oleanolic acid and hederagenin, which were isolated from roots of *H. helix*.

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