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A TRITERPENE GLYCOSIDE AND FLAVONOIDS FROM LEAVES OF *Akebia quinata*

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We previously communicated the isolation from the polar fraction of leaves of *Akebia quinata* Decne. growing in Georgia of two triterpene glycosides 3-*O*-(α-L-Rha$_p$-1,2-L-Ara$_p$)-28-*O*-(α-L-Rha$_p$-1,4-β-D-Glc$_p$-1,6-β-D-Glc$_p$) of oleanolic acid and a second glycoside of hederagenin with the same sugar chain [1] that had the structure of the corresponding hederacolchisides B and C, which were isolated previously from *Hedera helix* and *H. caucasigena* [2] and from the pericarp of *A. quinata*. Both glycosides were found in the leaves of this plant and characterized for the first time.

In continuation of studies of the leaves of *A. quinata* growing in Georgia, we isolated three pure compounds from the slightly polar ethylacetate fraction by adsorption chromatography over a column of silica gel.

Compound 1, $C_{41}H_{66}O_{12}$. The ^{13}C NMR spectrum of glycoside **1** exhibited resonances for the aglycon part at 13.1, 15.9, 17.4, 26.1, 33.4, and 23.6 ppm, typical of the six methyls of hederagenin at C-24, C-25, C-26, C-27, C-29, and C-30. The C-12—C-13 double bond was recorded at δ 123.0 and 144.9 ppm; C-23 with a primary hydroxyl, at δ 64.2 ppm. A resonance at 81.7 ppm indicated that the C-3 genin hydroxyl was glycosylated; at δ 180.2 ppm, a free carboxyl on C-17.

The PMR spectrum of **1** showed resonances at δ 4.57 and 5.20 ppm that belonged to two anomeric protons of L-arabinose and L-rhamnose, respectively. The L-rhamnose methyl was recorded at δ 1.26 ppm. Resonances with integrated intensities corresponding to nine biose protons were found at δ 3-4 ppm. The resonance for C-2′ of L-arabinose was observed in the ^{13}C NMR spectrum at δ 76.3 ppm and indicated that the rhamnose was bonded to this sugar through the C-2 hydroxyl [3].

Based on the results and the literature, **1** was characterized as hederagenin-3-*O*-α-L-Rha$_p$-(1→2)-α-L-Ara$_p$, or α-hederin, which was isolated previously from *Clematis* sp. Osbeck [4].

Compound 2, $C_{27}H_{30}O_{16}$, mp 201-204°C and **3**, $C_{27}H_{30}O_{15}$, mp 180-182°C, were hydrolyzed by rhamnodiastase to give rutinose [5, 6]. The aglycon of **2** was kaempferol; of **3**, quercetin. The PMR and ^{13}C NMR spectra and TLC mobility compared with an authentic sample identified **2** as kaempferol-3-*O*-β-D-rutinoside or nicotiflorin [5]; **3**, quercetin-3-β-D-rutinoside, or rutin [6].

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