

IRIDOIDS FROM *Verbascum phlomoides* and *V. densiflorum*L. N. Gvazava^{1*} and V. S. Kikoladze²

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Plants of the family Scrophulariaceae, in particular the genus *Verbascum* L., are widely distributed in the wild flora of Georgia.

Various species of *Verbascum* have long been used in folk medicine and homeopathic practice [1, 2] as emollients, expectorants, and analgesics for acute respiratory infections and diseases of the digestive organs. Reports have appeared in the last 20–30 years [3] that their decoctions exhibit activity against flu A₂ and B viruses. The leading compound among all *Verbascum* species, aucubin, possesses neuroprotective activity for primary diabetic encephalopathy [4] and also protects human skin cells from photoaging caused by ultraviolet irradiation [5].

According to many studies [6], the species studied by us, *V. phlomoides* and *V. densiflorum*, contain a broad spectrum of biologically active compounds such as flavonoids, alkaloids, steroids, saponins, carbohydrates, phenylcarboxylic and fatty acids, and vitamins.

We have previously reported [7] on the non-flavonoid compound verbascoside, which was first isolated from *V. phlomoides*. Herein the chemical compositions of compounds from these plants that are classified as iridooids are given.

Aerial parts of both plants (300 g each) that were collected during flowering near Tbilisi (Georgia) were extracted exhaustively with MeOH. Subsequent chromatography of an aqueous solution of the MeOH extract that was washed with organic solvents and purified of phenolic compounds by Al₂O₃ [8] over columns of polyamide sorbent and silica gel isolated four pure compounds from *V. phlomoides*.

Compound **1**, C₁₅H₂₂O₉, yield 0.12% (here and henceforth, calculated per weight of air-dried raw material), *R_f* 0.50 (BAW, *n*-BuOH:CH₃CO₂H:H₂O, 4:1:5), mp 180–181°C (MeOH), [α]_D²⁰ –164.9° (*c* 0.01, H₂O), UV (EtOH, λ_{max}, nm): 240, 270 [9].

Compound **2**, C₁₅H₂₂O₁₀, yield 0.10%, *R_f* 0.43 (BAW), mp 202–204°C (MeOH), [α]_D²⁰ –119° (*c* 0.02, EtOH), UV (EtOH, λ_{max}, nm): 263 [9].

Compound **3**, C₂₀H₃₀O₁₃, yield 0.025%, mp 192–194°C (EtOH), [α]_D²⁰ –87° (*c* 1.1, H₂O), UV (MeOH, λ_{max}, nm): 204; IR (KBr, ν_{max}, cm^{–1}): 3400, 2910, 2860, 1652, 1385, 1240, 1165, 1050, 965 [10].

Compound **4**, C₃₀H₃₈O₁₆, yield 0.015%, *R_f* 0.77 (BAW), mp 266–268°C (EtOH:H₂O), [α]_D²⁰ –200° (*c* 0.2, MeOH), UV (EtOH, λ_{max}, nm): 206, 221, 312; IR (KBr, ν_{max}, cm^{–1}): 3430 (OH), 1706 (C=O), 1642 (C=C), 1605, 1540, 1515, 1363 (aromatic ring) [11].

Comparison of the NMR, IR, and UV spectra and physicochemical constants with the literature values identified **1–4** as aucubin, catalpol, 6-*O*-β-D-xylopyranosylaucubin, and 6-*O*-(2''-*O*-*trans*-*p*-coumaroyl)-α-L-rhamnopyranosylcatalpol or saccatoside, respectively.

The procedure for obtaining pure compounds from *V. densiflorum* was analogous to that for *V. phlomoides* [8]. In addition to the leading iridooids aucubin and catalpol, three additional compounds were isolated.

Compound **5**, C₁₅H₂₄O₁₀, *R_f* 0.42 (BAW), yield 0.015%, [α]_D²⁰ –136° (*c* 0.1, EtOH) [12]; IR (KBr, ν_{max}, cm^{–1}): 3500–3000, 1650, 1480, 1390, 1240 [13].

Compound **6**, C₁₇H₂₆O₁₁, *R_f* 0.51 (BAW), yield 0.009%, mp 153–155°C, [α]_D²⁰ –112° (*c* 0.1, EtOH); IR (KBr, ν_{max}, cm^{–1}): 3000–3500, 1720, 1630, 1480, 1390, 1240. The IR spectrum contained the main bands of **5** in addition to an ester band at 1720 cm^{–1} [13].

1) I. Kutateladze Institute of Pharmaceutical Chemistry, 0159, Tbilisi, ul. P. Saradzhishvili, 36, Georgia, e-mail: liligvazava@yahoo.com; 2) P. Melikishvili Institute of Physical and Organic Chemistry, 0186, Tbilisi, ul. Dzhikiya, 5, Georgia. Translated from Khimiya Prirodnikh Soedinenii, No. 5, pp. 627–628, September–October, 2009. Original article submitted March 26, 2009.

Compound **7**, C₃₁H₄₀O₁₆, *R_f* 0.76 (BAW), yield 0.011%, mp 269–270°C, $[\alpha]_D^{20}$ –214° (*c* 0.6, EtOH); UV (EtOH, λ_{\max} , nm): 206, 222, 312; IR (KBr, ν_{\max} , cm⁻¹): 3600–3200 (OH), 1700 (C=O), 1655, 1640, 1632 (CH=CH), 1600, 1514 (ArH) [14].

The spectral, chemical, and physical properties of compounds identified them as harpagide, harpagide acetate, and 6-*O*-(4''-*p*-methoxy-*trans*-cinnamoyl)- α -L-rhamnopyranosylcatalpol.

Compounds **4** and **7** were isolated for the first time from these *Verbascum* species.

The structures of the other compounds are under investigation.

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