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OROBANCHOSIDE AND FLAVONOIDS FROM *Verbascum phlomoides* AND *V. densiflorum*

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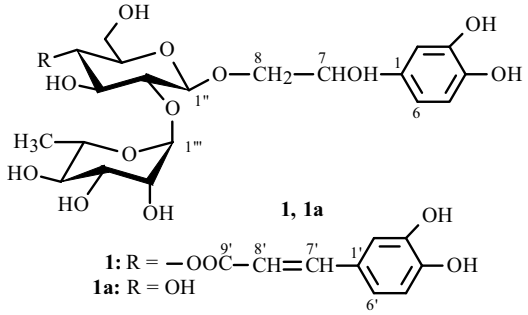
We established previously the presence of the iridoids aucubin, catalpol, and harpagide and their glycosides in the two mullein species *Verbascum phlomoides* and *V. densiflorum* [1]. Furthermore, the acylated phenylpropanoid glycoside verbascoside was also isolated from the first species [2].

In continuation of the phytochemical study of these plants, we isolated another phenolic compound of non-flavonoid nature (**1**) and five flavonoids (**2**, **4**, **5**, **6**, and **7**) from *V. densiflorum* and seven flavonoids (**2**–**8**) from *V. phlomoides*.

Compound **1** was isolated and its structure identified by methods analogous to those that were described for verbascoside [1].

Basic hydrolysis of **1** produced caffeic acid and glycoside **1a**, the mass spectrum of which exhibited a peak for a molecular ion with *m*/*z* 478 that corresponded to the formula $C_{20}H_{30}O_{13}$. Acetylation of **1a** by acetic anhydride gave its nonaacetate (*m*/*z* 856), which was hydrolyzed by 5% H_2SO_4. Acetates of the polyols sorbite and rhamnite were detected by GC in a 1:1 ratio in the hydrolysate after reduction of the carbohydrate part of the hydrolysate by $NaBH_4$ and acetylation.



Glycoside **1** (45 mg) was hydrolyzed by 5% H_2SO_4 in order to obtain the aglycon (17.2 mg). The mass, PMR, and ^{13}C NMR spectra of the aglycon identified it as *β*-hydroxy-*β*-(3,4-dihydroxyphenyl)ethanol.

The configurations of the glycoside bonds of the sugars and the site of attachment of the components of **1** were established using PMR and ^{13}C NMR spectroscopy and interpretation of COSY, NOESY, HMQC, and HMBC spectra.

Orobanchoside (1). PMR spectrum (DMSO-d_6 + CF_3CO_2H, δ, ppm, J/Hz, 0 = TMS): 7.48 (d, J = 15.8, H-7′), 7.05 (H-2′), 6.97 (d, J = 7.8, H-6′), 6.79 (d, J = 7.8, H-5′), 6.77 (H-2), 6.68 (d, J = 7.8, H-6), 6.59 (d, J = 7.8, H-5), 6.22 (d, J = 15.8, H-8′), 5.03 (br.s, H-1‴), 4.92 (t, J = 9.3, H-4″), 4.58 (d, J = 7.6, H-1″), 4.55 (m, J = 2.4, 9.1, H-7), 4.06 (m, H-3″), 3.96–3.72 (m, H-6″), 3.72 (m, H-5″), 3.59 (dd, J = 1.2, 2.8, H-2‴), 3.46 (m, H-5‴), 3.42 (m, H-8), 3.38 (dd, J = 7.6, 9.3, H-2″), 3.28 (dd, J = 2.8, 9.4, H-3‴), 3.14 (t, J = 9.4, H-4‴), 1.06 (d, J = 6.2, H-6‴).

^{13}C NMR spectrum (DMSO-d_6 + CF_3CO_2H, δ, ppm): 165.7 (C-9′), 148.7 (C-4′), 146.2 (C-7′), 145.8 (C-3′), 145.1 (C-3), 145.0 (C-4), 128.2 (C-1), 125.8 (C-1′), 121.6 (C-6′), 117.1 (C-6), 115.9 (C-8′), 115.3 (C-5), 114.7 (C-2′), 113.7 (C-2), 113.3 (C-5′), 100.4 (C-1‴), 97.3 (C-1″), 80.7 (C-2″), 76.3 (C-7), 76.2 (C-5″), 74.5 (C-3″), 71.6 (C-4‴), 71.2 (C-8), 70.5 (C-2‴), 70.5 (C-3‴), 68.9 (C-4), 68.8 (C-5‴), 60.9 (C-6″), 18.1 (C-6‴).

The results agreed with the literature [3]. This allowed **1** to be assigned the structure of *β*-hydroxy-*β*-(3,4-dihydroxyphenyl)ethyl-*O*-*α*-L-rhamnopyranosyl-(1→2)-*β*-D-(4-*O*-caffeoyl)glucopyranoside or orobanchoside. This compound was isolated for the first time from *V. densiflorum*.

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Fractions remaining after isolation of verbascoside from *V. phlomoides* and orobanchoside from *V. densiflorum* were combined and condensed to an aqueous residue that was extracted with EtOAc. The extract was evaporated. The total flavonoids were precipitated by $CHCl_3$.

Total flavonoids were separated by preparative chromatography over a column of polyamide with elution by $CHCl_3$ and $CHCl_3$:EtOH mixtures with an increasing concentration gradient of alcohol. Fractions containing mixtures of compounds were rechromatographed over a column of polyamide. Compounds **2**–**8** were purified additionally by recrystallization from MeOH.

Isolated compounds were identified by UV, IR, and PMR spectroscopy. Comparison of the results with the literature and with data for authentic samples of the flavonoids allowed **2** to be identified as quercetin [4, 5]; **3**, kaempferol [5, 6]; **4**, luteolin [4]; **5**, apigenin [4]; **6**, cinaroside [4, 7]; **7**, apigenin-7-*O*-glucopyranoside [7]; and **8**, rutin [8].

REFERENCES

1. L. N. Gvazava and V. S. Kikoladze, *Khim. Prir. Soedin.*, 627 (2009).
2. L. N. Gvazava and V. S. Kikoladze, *Khim. Prir. Soedin.*, 589 (2007).
3. C. Andary, R. Wylde, C. Laffite, G. Privat, and F. Winternitz, *Phytochemistry*, **21**, 1123 (1982).
4. M. P. Yuldashev, *Khim. Prir. Soedin.*, 242 (1998); M. P. Yuldashev and A. Karimov, *Khim. Prir. Soedin.*, 26 (2005).
5. Z. P. Xiao, H. K. Wu, T. Wu, H. Shi, B. Hang, and H. A. Aisa, *Khim. Prir. Soedin.*, 600 (2006).
6. G. Chen, H. Jin, X. Li, Q. Zhang, Y. Shen, S. Yan, and W. Zhang, *Khim. Prir. Soedin.*, 607 (2009).
7. X. F. Zhu and H. X. Zhang, *Khim. Prir. Soedin.*, 494 (2004); A. V. Simonyan, *Khim. Prir. Soedin.*, 810 (1972).
8. G. Zhang, M.-L. Guo, R.-P. Li, Y. Li, H.-M. Zhang, and Z.-W. Su, *Khim. Prir. Soedin.*, 341 (2009).