VERBASCOSIDE B — A MINOR IRIDOID OF *Verbascum georgicum*

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By preparative PC of the previously purified total iridoid material followed by chromatography on a column of silica, a new minor iridoid — verbascoside B (I) — has been isolated in the form of an amorphous substance with $[\alpha]_D$ −108 ± 4 (c 0.12; methanol). The structure of (I), corresponding to 6-α-L-rhamnopyranosyldecinnamoylglobularinin, has been shown on the basis of a passage from 6-α-L-rhamnopyranosylcatalpol and the spectral characteristics of (I) and of its nanoacetate (II). Characteristics of the IR and ^{1}H and ^{13}C spectra of (I) and (II) and of the mass spectrum of (II) are given.

Continuing a study of the iridoids of *Verbascum georgicum* Benth. [1], we have isolated with the aid of preparative PC a fifth, unidentified, minor component of the total iridoid material of the plant, consisting of a new substance with the composition $C_{21}H_{34}O_{15}$, which we have called verbascoside B (I). On acetylation, the iridoid (I) forms a nonaacetate (II) in the IR spectrum of which there is the absorption band of a free hydroxy group, which shows the presence in (I) of a difficultly acetylatable tertiary hydroxy group. In the mass spectrum of (II), together with the ions that are characteristic for triactylrhamnose (m/z 273, 213, 171, 153, 129, 111) and for tetraacetylglucose (m/z 331, 271, 229, 169, 109), there are also the peaks of ions with m/z 614, 556, 284, 267 belonging to fragments formed by the detachment of carbohydrate fragments from the molecular ion. These facts permitted the assumption that verbascoside B (I) is a diglycoside the aglycone moiety of which consists of pentahydroxy compound.

The ^{13}C NMR spectra of (I) and (II) confirm the validity of this hypothesis. In the spectrum of verbascoside B (I) with complete suppression of $^1H-^{13}C$ coupling the signals of 21 carbon atoms are observed. The multiplicities of the signals with incomplete $^1H-^{13}C$ decoupling and a comparison with the spectrum of known iridoids [2, 3] permitted an unambiguous assignment of the signals to be made (Table 1) and the positions of the substituents in the aglycone moiety of the molecule of verbascoside B corresponding to structure (I) to be made.

Finally, on continuing the alkaline hydrolysis of 6-α-L-rhamnopyranosylcatalpol (III), isolated previously from this plant [1], we effected a transition to verbascoside B and, thus thoroughly confirmed both the type of aglycone skeleton of (I) and the positions of the glycosyl and hydroxy groups. This transition also established the C1-αH, C5-βH, C6-αH, and C9-βH configurations of the asymmetric centers, which are not affected on the opening of the epoxide ring. On the other hand, the C1-αH, C8-αOH, and C9-βH configuration for (I) was established on the basis of the chemical shifts of the C9 and C1 signals in the ^{13}C NMR spectrum, the values of which play a diagnostic role in determining the configuration at C8 [2].

A comparison of the ^{13}C NMR spectra of verbascoside B (I) and that of a pair of iridoids stereoisomeric at C7 and C8 — globularinin (IV) and globularimin (V) — and their deacyl derivatives (VI) and (VII) [3] showed that (I) corresponds in structure to 6-α-L-rhamnopyranosyldecinnamoylglobularinin, which has not been described previously.

The PMR spectra of verbascoside B and its nonaacetate (II) do not contradict their structures deduced on the basis of the results of ^{13}C NMR spectroscopy and the alkaline hydrolysis of (III). The SSCCs for the protons at C1, C5, C6, C7, and C9, determined on the basis of results of double-resonance experiments, also correlate with the proposed configurations of the centers of asymmetry by analogy with globularinin [4].

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TABLE 1. ^{13}C NMR Spectra (δ, ppm, relative to TMS)

Carbon atom	I (in CD_3OD)	II (in $CDCl_3$)	IV*	VI	V	VII
			in CD_3OD			
C-1	96.10 d	94.44 d	96,29	95,16	93,48	93.34
C-3	141.89 d	141,19 d	14 ,61	141,61	140,45	149,39
C-4	106.05 d	103.38 d	106,40	105.27	105,84	106 54
C-5	37,19 d	35,95 d	38,86	37,16	38,38	37,32
C-6	83.10 d	78 33 d	78,63	78,34	83,76	83,14
C-7	78,13 d	81,64 d	78 63	79.34	85,38	86,42
C-8	82,29 s	79.34 s	81,36	81,03	80,23	80,33
C-9	44.13 d	43,04 d.	44.59	43.70	48.88	48 08
C-10	67,14 tr	68,90 tr	69,01	66,37	66,41	64.29
C-1′	100,67 d	97,42 d	100,87	99,20	99.68	99,55
C-2′	74.63 d	70,67 d	74.35	74,61	74,44	74,61
C-3′	77.76 d	72,41 d	77,78	77.99	77,59	77.94
C-4′	71,23 d	67,61 d	70,83	70,39	71,07	71.54
C-5′	76,85 d	72,16 d	77,43	78.34	77,59	77,71
C-6′	62,35 tr	61,80 tr	62,23	62.42	62,45	62.70
C-1″	100.77 d.	97,58 d				
C-2″	72,04 d	69,3 d				
C-3″	70,11 d	68,25 d				
C-4″	73,88 d	70,73 d				
C-5″	72,28 d	67,14 d				
C-6″	17,96 q	17,38 q				
$\underline{C}H_3CO$—	—	20,34 q 20.37 q 20,67 (7) q				
$CH_3\underline{C}O$	—	169.21 s 170,14 (2) q 170,68 s 170,76 (2) s 170,98 (2) s				

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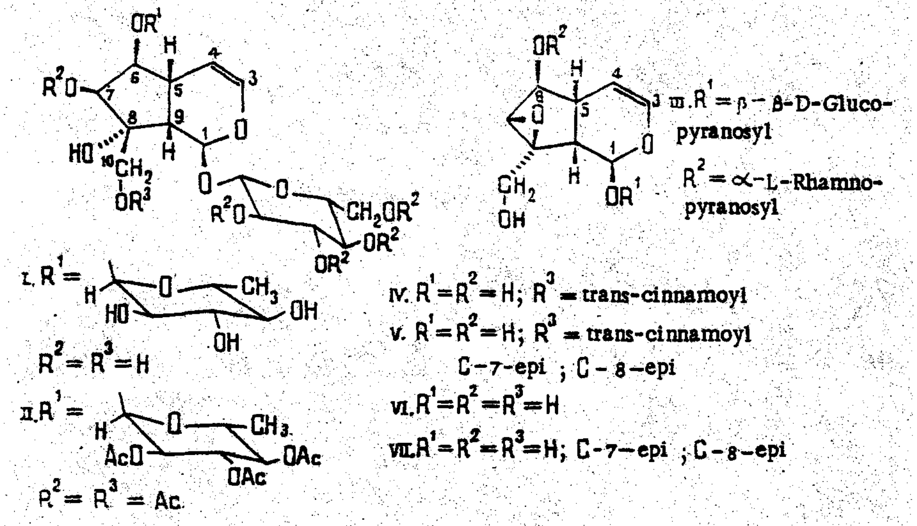
*The results for (IV)-(VII) have been taken from the literature [4]; the signals of the cinnamoyl fragment are not given.



EXPERIMENTAL

IR spectra were taken on a UR-20 instrument, NMR spectra on a Varian XL-200 instrument, and mass spectra on a MKh-1320 mass spectrometer, and optical activities were determined on a SM-1 instrument. Chromatography was carried out on type "C" ["medium"] paper (PC, in the butan-1-ol—acetic acid—water (4:1:5) system) and on Silufol 254 plates in the chloroform—methanol (30:1) system.

Verbascoside B (I). A mixture of fractions 1 and 2 (500 mg) obtained on the chromatography of the total iridoids of *Verbascum georgicum* Benth. [1] and consisting of a mixture of aucubin (R_f 0.50), catalpol (R_f 0.43), (III) (R_f 0.37), and a substance with R_f 0.30 (PC) were subjected to preparative chromatography three times on paper previously washed with methanol.

The substance with R_f 0.30 was additionally chromatographed on a column of silica gel (type KSK, 100/200 mesh) in the chloroform—methanol (1:1) system. This gave 14 mg of a substance with R_f 0.30 (I), $[\alpha]_D^{18}$ −108 ± 4° (c 0.12; methanol). PMR spectrum (in CD_3OD) (δ, ppm): 5.25 (1 H d, $J_{1,9}$ = 6 Hz, C1—H); 6.32 (1 H, dd, $J_{4,3}$ = 6.5 Hz, $J_{3,5}$ = 2 Hz, C3—H); 5.07 (1 H, dd, $J_{4,3}$ = 6.5 Hz, $J_{4,5}$ = 3 Hz, C4—H); 2.89-2.63 (1 H, m $J_{5,9}$ = 10 Hz, $J_{5,6}$ = 2 Hz, C5—H); 4.03 (1 H, dd, $J_{5,6}$ = 2 Hz, $J_{6,7}$ = 4 Hz, C6—H); 3.95 (1 H, d, $J_{6,7}$ = 4 Hz, C7—H); 2.32 (1 H, dd, $J_{9,5}$ = 10 Hz, $J_{1,9}$ = 6 Hz, C9—H); 4.70 (1 H, d, J = 7.5 Hz, C1'—H); 4.03 (1 H, dd, C2'—H); 3.20-4.10 (11 H, m, C10—2H, C3'—H, C4'—H, C5'—H, C6'—H, C2"—H, C3"—H, C4"—H, C5"—H); 4.76 (1 H, d, J = 2 Hz, C1"—H); 1.22 (3 H, d, J = 2.5 Hz, C6"—3H).

<u>Alkaline Hydrolysis of 6-α-Rhamnopyranosylcatalpol.</u> A solution of 240 mg of (III) in 5 ml of 10% caustic soda solution was heated in the boiling water bath for 24 h. The reaction mixture was cooled and transferred to a column of Sephadex LH-20 equilibrated with water. The substance was eluted from the column with 10 ml of water and the solution was evaporated. This gave 54 μg of (I).

<u>Nonacetate of Verbascoside B (II).</u> The acetylation of 50 mg of (I) by the usual method with a mixture of pyridine and acetic anhydride gave, after the purification of the product on a column of silica gel (in the chloroform—methanol (15:1) system), 55 mg of amorphous (II). R_f 0.28 (TLC). IR spectrum ($CHCl_3$): 1740-1770 cm^{-1} (CH_3COO) 3480 cm^{-1} (OH). PMR spectrum (in $CDCl_3$) 5.25 (1 H, d, $J_{1,9}$ = 6 Hz, C1—H); 6.31 (1 H, dd, $J_{3,4}$ = 6.5 Hz, $J_{3,5}$ = 2.5 Hz, C3—H); 4.95 (1 H, dd, $J_{4,3}$ = 6.5 Hz, $J_{4,5}$ = 3 Hz, C4—H); 2.70-2.83 (1 H, m, $J_{5,6}$ = 1.5 Hz, $J_{9,5}$ = 10 Hz, C5—H); 4.10 (1 H, dd, $J_{6,5}$ = 1.5 Hz, $J_{6,7}$ = 4 Hz, C6—H); 4.84 (1 H, d, $J_{7,6}$ = 4 Hz, C7—H); 2.47 (1 H, dd, $J_{1,9}$ = 6 Hz, $J_{9,5}$ = 10 Hz, C9—H); 4.33 and 4.20 (1 H each, d, J = 12 Hz, C10—2H); 4.92 (1 H, d, J = 8 Hz, C1'—H); 5.14 (1 H, d, J = 2 Hz, C1"—H); 4.92-5.25 (6 H, m, C2'—H, C3'—H, C4'—H, C2"—H, C3"—H, C4"—H); 3.77 (1 H, m, C5'—H); 4.11-4.29 (2 H, m, C6'—2H); 3.91 (1 H, m, C5"—H); 1.22 (3 H, d, J = 5.7 Hz, C6"—H); 1.99-2.14 ppm (9 × 3 H, s, 9 CH_3CO). Mass spectrum, m/z (%) (molecular peak with m/z 904 absent): 614(1.6) (M^+-290), 598(2.5), 556(2.7) ($M^+-17-331$), 538(1), 331(100), 284(29) ($M^+-347-273$), 273(70), 271(20), 267(17), ($M^+-290-347$), 256(51), 242(22), 231(9), 229(9), 223(27), 213(25), 211(15), 205(20), 200(16), 185(24), 171(30), 169(97), 153(40), 149(50), 145(34), 137(29), 129(51), 127(30), 111(70), 109(66).

SUMMARY

A new minor component of the total iridoid material of *Verbascum georgicum* Benth. has been isolated, and on the basis of passage from 6-α-L-rhamnopyranosylcatalpol and ^1H and ^{13}C NMR spectra its structure has been determined as 6-α-L-rhamnopyranosyldecinnamoylglobularinin.

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