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# IRIDOIDS OF *Verbascum georgicum*

É. Yu. Agababyan, L. S. Arutyunyan,
V. A. Mnatsakanyan, E. Gach-Baitts,
and L. Radich

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From the epigeal part of *Verbascum georgicum* Benth., in addition to aucubin, as the main component of the total iridoids a new iridoid has been isolated — 6-α-L-(4'-p-methoxy-trans-cinnamoyl)rhamnopyranosylcatalpol, the structure of which has been shown by UV, PMR, and mass spectroscopy and a comparison of the $^{13}C$ NMR spectrum with that of 6-α-L-rhamnopyranosylcatalpol (I). The presence of catalpol and (II) in the plant has been shown by PC and TLC.

The species of mullein *Verbascum georgicum* Benth. [1], which is widespread in the mesophytic grasslands of many regions of the Armenian SSR has not been studied chemically. By a qualitative chromatographic analysis of a methanolic extract of the epigeal part of this plant we detected in it the presence of at least five substances of iridoid nature. Two of them, forming the main components of the total iridoid material, have been isolated and characterized.

The first substance was identified by PMR and mass spectroscopy and from the constants of its acetyl derivative as the known iridoid aucubin, which is characteristic for *Verbascum* species [2]. The second substance, with the composition $C_{31}H_{40}O_{16}$, proved to be new and has been called verbascoside A (I). The iridoid nature of (I) was shown by qualitative reactions [3] and by absorption at 206 nm in the UV spectrum which is characteristic for an enol ether

A. L. Mndzhoyan Institute of Precision Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan. Central Research Institute of Chemistry, Academy of Sciences of the Hungarian People's Republic, Budapest. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 446-451, July-August, 1982. Original article submitted August 31, 1981.

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TABLE 1. PMR Spectra (δ, ppm) and SSCCs (Hz)*

| I | II | III | IV |
|---|---|---|---|
| C-1-H 4,98 d $J_{1,9}$=8 5 | 4,97 d $J_{1,9}$=8,8 | 5,16 d $J_{1,9}$=7,8 | 5,12 d $J_{1,9}$=9.0 |
| C-3-H 6,36 dd $J_{4,3}$=6,0 | 6,35 dd $J_{3,4}$=5,8 | 6,33 dd $J_{3,4}$=6.0 | 6.32 dd |
| C-4-H 5,01 dd | 5,04 dd | 5.05 dd | 5,01 dd |
| C-5-H 2,30 m $J_{5,3}$=1.6 | 2.28 m $J_{5,3}$=1,6 | 2,51 m | 2.52 m $J_{5,3}$=1,5 |
| $J_{5,4}$=4 5 | $J_{5,4}$=4,3; | | $J_{5,4}$=4,2; |
| $J_{5,9}$=8,0 | $J_{5,9}$=8 0 | | $J_{5,9}$=7,5 |
| $J_{5,6}$=7,5 | $J_{5,6}$=7,5 | | $J_{5,6}$=7,5 |
| C-6-H 3,9 br.d | 3,92 | 3,88 br. d | 3.91 br.d |
| C-7-H 3,64 br.s. $J_{7,6}$=1,0 | 3,57 br.s $J_{7,6}$=0.8 | 3,58 $J$=1 | 3.54 br.s $J_{7,6}$=1,0 |
| C-9-H 2,45 dd | 2,45 dd | 2,60 dd | 2,61 dd |
| C-10-2H 4.08–3,85 | 3,73 d ; 3,96 d $J_{A,B}$=13 | 4,80 d; 4,03 $J_{A,B}$=13 | 4,02 d; 4,79 $J_{A,B}$=12.5 |
| **β-Glucosyl** | | | |
| C-1′-H 4,97 d $J_{1,2}$=7.5 | 4,78 d $J_{1,2}$=7,5 | 4,79 d $J_{1,2}$=8.0 | 4,79 d $J_{1,2}$=8.2 |
| C-2′-H, C-3′-H, C-4′-H, C-5′-H 3 2—4 1 | 3,1—4,1 | 4.9–5,4; 3.6–3,8; 4,17 d ; 4,35 d $J_{A,B}$=12 | 4,9—5,4; $J_{4,5}$=9,5; 3,71 m $J_{5,6}$=3,5; 2,8; 4,16 d ; 4,33 d $J_{A,B}$=12 |
| C-6′-2H | | | |
| **α-Rhamnosyl** | | | |
| C-1″-H 4,96 d $J_{1,2}$=1,0 | 4.86 $J$ 1,2 | 5,0 d $J$=1 | 5 0 d $J$=0,9 |
| C-2″-H, C-3″-H 3,2—4,1 m | 3,1—4,1 | 4 9—5,4 | 4,9—5,4 |
| C-4″-H 4,97 5,15 | | 3,97 m | 3,97 m $J_{4,5}$=9,5 |
| C-5″-H 3,8 -4,1 | | | |
| C-6″-3H 1,16 d $J_{5,6}$=6 2 | 1,21 d $J$=6,2 | 1,26 d $J$=6,2 | 1,21 d $J$=6,2 |
| **Acyl** | | | |
| C-2‴ 7,00 d $J$=9; 6‴-2H $J$=2 | | 6,92 dd $J$=9; $J$=2 | |
| C-3‴,5‴-2H 7,63 dd $J$=9; $J$ 2 | | 7,58 dd $J$=9; $J$=2 | |
| α-H 6,40 d $J_{\alpha,\beta}$=15,5 | | 6,39 d $J_{\alpha,\beta}$=15,5 | |
| β-H 7,68 d | | 7,34 d | |
| $CH_3O$—Ar 3,83 s | | 3,83 br.s | |
| $CH_3CO$ | | 7×3H s: 2,17–1.96 | 8×3H; 2,13; 2.09; 2,07; 2.02; 2.01; 2,00; 1,99; 1,97 |

*The spectrum of (I) was taken in DMSO—$CDCl_3$ solution, that of (II) in $(CD_3)_2CO$—DMSO solution, and those of (III) and (IV) in $CDCl_3$ solution; d — doublet; dd — doublet of doublets; m — multiplet; s — singlet; br.s — broadened singlet; br.d — broadened doublet.

group of C-3,C-4-unsubstituted iridoids [4]. The alkaline hydrolysis of (I) led to p-methoxy-trans-cinnamic acid and a glycoside (II) the mass spectrum of which had a low-intensity peak of the molecular ion (m/z 508) corresponding to the composition $C_{21}H_{32}O_{14}$. This permitted the conclusion that (I) was an ester of p-methoxy-trans-cinnamic acid and (II). The acetylation of (I) and (II) gave the pentaacetate (III) and the octaacetate (IV), respectively.

The acid hydrolysis of (II) led to D-glucose, L-rhamnose, and a black decomposition product which is customary for iridoids in this reaction. The mass spectrum of (IV) showed strong peaks of the fragment of a tetraacetylglucose (with m/z 331, 271, 229, 169, 109) and of a triacetylrhamnose (with m/z, 273, 213, 171, 153, 129, 111), which excludes a biosidic nature for (II) and shows that the glucose and rhamnose residues are attached to different positions of the aglycone part of the molecule.

In the mass spectrum of the heptaacetate of verbascoside A (III), in addition to the fragments of a tetraacetylglucose there are only low-mass fragments of a triacetylrhamnose. The absence of an ion with m/z 273 and the simultaneous presence in the spectrum of the peaks of ions with m/z 391 and 241 (M — 330 — 391) shows that in (I) the p-methoxy-trans-

TABLE 2. $^{13}C$ NMR Spectra (chemical shifts, ppm, relative to TMS)*

| Carbon atom | I | IV | VI | 6-α-L-Rhamnopyranosylcatalpol | Octaacetate of 6-α-L-rhamnopyranosylcatalpol |
|---|---|---|---|---|---|
| C-1 | 93,30 d | 94,25 d | 94,22 | 93,22 | 94,30 |
| C-3 | 140,84 d | 141,15 d | 141,00 | 140,39 | 141,16 |
| C-4 | 102,30 d | 102,38 d | 101,98 | 102,50 | 103,24 |
| C-5 | 35,64 d | 35,47 d | 34,93 | 35,66 | 36,57 |
| C-6 | 82,12 d | 83,41 d | 79,56 | 81,49 | 82,42 |
| C-7 | 57,60 d | 57,95 d | 58,64 | 57,49 | 57,68 |
| C-8 | 65,31 s | 62,21 s | 62,63 | 65,30 | 62,47 |
| C-9 | 41,90 d | 41,71 d | 41,61 | 41,22 | 41,19 |
| C-10 | 59,38 t | 61,09 t | 61,23 | 58,91 | 61,19 |
| C-1′ | 97,99 d | 96,56 d | 96,59 | 97,91 | 95,97 |
| C-2′ | 73,55 d | 70,65 d | 70,72 | 73,45 | 70,64 |
| C-3′ | 77,23 d | 72,58 d | 72,55 | 77,43 | 71,77 |
| C-4′ | 70,76 d | 68,30 d | 68,34 | 70,33 | 68,03 |
| C-5′ | 76,42 d | 72,28 d | 72,33 | 76,45 | 70,64 |
| C-6′ | 61,42 t | 62,38 t | 62,31 | 61,41 | 61,09 |
| C-1″ | 98,83 d | 96,49 d | | 98,99 | 95,76 |
| C-2″ | 70,21 d | 69,96 d | | 70,64 | 68,98 |
| C-3″ | 68,43 d | 68,85 d | | 70,33 | 68,50 |
| C-4″ | 73,75 d | 71,03 d | | 71,97 | 70,01 |
| C-5″ | 66,57 d | 66,94 d | | 68,85 | 66,18 |
| C-6″ | 17,45 q | 17,38 q | | 17,85 | 17,08 |
| C-1‴ | 126,66 s | | | | |
| C-2‴,6‴ | 129,81 d(2) | | | | |
| C-3‴,5‴ | 114,32 d(2) | | | | |
| C-4‴ | 161,18 s | | | | |
| C-α | 144,30 d | | | | |
| C-β | 115,48 d | | | | |
| C=O | 196,17 s | | | | |
| $CH_3CO$ | | 20,57(2); 20,63(2); 20,68(2); 20,75, 20,86 q | | | |
| $CH_3CO$ | | 170,60; 170,72; 170,17; 169,98; 169,91; 169,82; 169,22; 168,99 s | | | |

*The spectrum of (I) was taken in DMSO—$CDCl_3$ solution, those of (IV)-(VI) in $CDCl_3$ solution, and those of 6-α-L-rhamnopyranosylcatalpol and of the octaacetate of 6-α-L-rhamnopyranosylcatalpol in DMSO solution [6]; d — doublet; s — singlet; t — triplet; q — quartet.

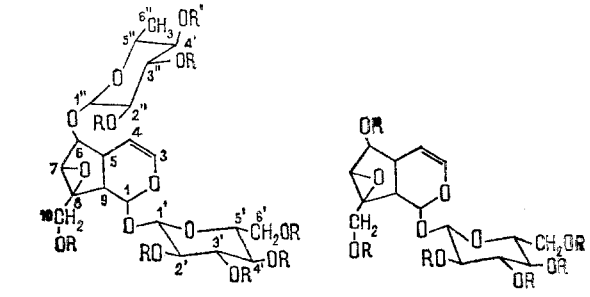
cinnamic acid esterifies one of the rhamnosyl hydroxy groups. Such a conclusion is in good agreement with the different behaviors of verbascoside A (I) and its derivative (II) on acid hydrolysis. While for the chromatographic detection of rhamnose and glucose in a hydrolysate of (II) (and of glucose in a hydrolysate of (I)) it is sufficient to heat their sulfuric acid solutions on the water bath for 1 hour; to detect rhamnose in a hydrolysate of (I) requires the reaction mixture to be boiled for 4-5 h.

In spite of the multiplicity of the pathways of mass-spectrometric fragmentation as the result of their polyfunctionality, the possibility that (I) and (II) were derivatives of catalpol (V) was shown by the detection of characteristic catalpol fragments in the mass spectra of (II)-(IV) (m/z 149 and 200) and the presence in the spectra of (III) and (IV) of medium-intensity ions with m/z 223 and 195, also showed the presence of an acetoxy group at C-10 [5].

The validity of these hypotheses and the precise position of the glycosyl and acid moieties in the molecule of (I) were shown by analysis of the PMR spectra of (I)-(IV) (Table 1) and of the $^{13}C$ NMR spectra of (I) and (IV) (Table 2). The assignment of the signals of the hydrogen and carbon atoms in the spectra was made on the basis of experiments with double resonance and with selective suppression of $^{1}H$-$^{13}C$ spin-spin coupling, and by a comparison of the $^{13}C$ NMR spectra of (I) and (IV) with the spectra of hexaacetylcatalpol (VI) and of 6-α-L-rhamnopyranosylcatalpol and its octaacetate [6].

The information given above and the results of a comparative analysis of the NMR spectra showed the intensity of the (II) with 6-α-L-rhamnopyranosylcatalpol, which has been isolated previously from *Scrophularia nodosa* L. [6]. The position of the acyl moiety in verbascoside A (I) was established from the effect of acylation on the $^{13}C$ chemical shifts of the atoms of the rhamosyl residue. A downfield displacement of the C-4" signal (+1.78 ppm) and an upfield displacement of the C-3" and C-5" signals (—1.99 and —2.32 ppm, respectively) in the $^{13}C$ NMR spectrum of (I) as compared with that of 6-α-L-rhamnopyranosylcatalpol showed that the acyl residue was attached at C-4" and, consequently, verbascoside A is 6-α-L(4"-p-methoxy-trans-cinnamoyl) rhamnopyranosylcatalpol.

Two of the remaining minor components of the combined iridoids of *V. georgicum* were identified chromatographically as catalpol and 6-α-rhamnosylcatalpol.



I R=H; R'=—C(=O)—CH=CH—C6H4—OCH3

II R=R'=H

III R=—C(=O)—CH3; R'=—C(=O)—CH=CH—C6H4—OCH3

IV R=R'=—C(=O)—CH3

V. R=H

VI. R=—C(=O)—CH3

## EXPERIMENTAL

UV spectra were taken on a Specord UV-VIS instrument in methanolic solution, the IR spectrum on a UR-20 instrument (tablets with KBr), NMR spectra on Varian A-60 and X-100-15GT spectrometers (δ scale), and mass spectra on a MKh-1320 instrument (70 eV), and optical activities were determined on a Polamat A instrument. Chromatography was performed on type S paper (PC, in the butan-1-ol—acetic acid—water (4:1:5) system) and on Silufol plates (TLC) in the chloroform—methanol (8:2) (1) and chloroform—methanol (30:1) (2) systems. The iridoids were detected on the chromatograms with the benzidine reagent (0.5 g of benzidine, 20 ml of acetic acid, 80 ml of ethanol) followed by heating at 100°C. Sugars were revealed with the aniline phthalate reagent.

Isolation of the Iridoid Fractions. The dry comminuted leaves and inflorescences of *Verbascum georgicum* (4 kg) were steeped with methanol in a percolator (8 × 20 liters). The combined methanolic extracts were concentrated in a vacuum apparatus to a volume of 0.6 liter, diluted with water to a volume of 1 liter, and washed successively with benzene (4 × 0.5 liter), chloroform (4 × 0.5 liter), ether (8 × 0.5 liter), and ethyl acetate (6 × 0.5 liter). The washed aqueous solution showed (PC) the presence of five substances of iridoid nature. The aqueous solution (100 ml) was passed through a layer of alumina (7.5 × 30 cm; neutral, activity grade III), which was then washed with water until the reaction of the eluate for iridoids was negative. The combined aqueous eluates were concentrated in vacuum to a volume of 50 ml, transferred to a column of Woelm polyamide (4.5 × 65 cm) and eluted with water. The fractions (100 ml each) were analyzed by PC and TLC. The first two fractions contained 7.4 g of a mixture of substances with $R_f$ 0.30 (orange), 0.37 (orange), 0.43 (orange), and 0.50 (grey) (PC). Fractions 3-8 were combined and evaporated to dryness. This gave 5.35 g of a yellow foam-like substance with $R_f$ 0.78 (orange) (PC).

Verbascoside A (I). The substance with $R_f$ 0.78 (5.35 g) was chromatographed on a column of silica gel (150 g, type KSK, 70/230 mesh) in system 1. This gave 3.21 g of white amorphous verbascoside A; $[\alpha]_D^{20}$ − 215° ± 1 (c 0.5; ethanol); $\lambda_{max}$ 206, 222, and 312 nm; $\nu_{max}$: 3200-3600 (OH), 1700 (CO), 1655, 1640, 1630 (CH=CH), 1600, 1515 (ArH). Found, %: C 55.47; H 6.46. $C_{13}H_{40}O_{16}$. Calculated, %: C 55.58; H 6.03.

Alkaline Hydrolysis of Verbascoside A. A solution of 0.2 g of (I) in 10 ml of 0.05 N caustic soda solution was heated at 30°C for 3 h and was then cooled and transferred to a column of Sephadex LH-20 (2 × 30 cm). The substances were eluted with water, 30-ml fractions being collected. Fractions 1-3 contained 55 mg of (II) with $R_f$ 0.37 (PC), 0.30 (TLC), ethanol—chloroform (1:1) system), $[\alpha]_D^{20}$ − 134 ± 5° (c 0.5; methanol); $\lambda_{max}$ 206 nm; mass spectrum, m/z (%): M+ 508 (0.3), 507 (0.2), 327 (0.4), 313 (0.9), 299 (0.5), 298 (0.5), 284 (0.7), 264 (1.5), 256 (1.5), 239 (1.2), 236 (1.0), 213 (1.0), 211 (1.0), 200 (1.0), 185 (1.5), 149 (2.5), 145 (2.5), 129 (3.0), 120 (3.5), 118 (3.5), 111 (3.0), 98 (4.0), 97 (4.0), 95 (4.0), 85 (56.0), 83 (100).

From fractions 5 and 6 by acidification with 0.1% hydrochloric acid and extraction with ether 20 mg of p-methoxy-trans-cinnamic acid was obtained with mp 186°C (from methanol). $\lambda_{max}$ 222, 312 nm; PMR spectrum: 7.66 (1 H, d, J = 16 Hz), 7.53 (2 H, d, J = 9 Hz), 6.93 (2 H, d, J = 9 Hz), 6.33 (1 H, d, J = 16 Hz), 3.81 (3 H, s). Found, $M^+$ 178 (mass spectrum), %: C 67.51; H 5.59. $C_{10}H_{10}O_3$. Calculated, M 178.18, %: C 67.40; H 5.65.

The Heptaacetate (III). A mixture of 120 mg of (I), 16 ml of anhydrous pyridine, and 16 ml of freshly distilled acetic anhydride was kept at room temperature for 24 h, and then 100 ml of ice water was added and the mixture was shaken for 30 min, after which the amorphous deposit that had precipitated was filtered off, washed with water and dried in a dessicator. The substance was dissolved in 5 ml of system 2 and chromatographed on a column of silica gel (2 × 60 ml) with elution by system 2. This gave 60 mg of (III) with mp 112°C (from ethanol), $R_f$ 0.80 (PC), 0.58 (TLC), system 2), $\nu_{max}^{CHCl_3}$ 1730 $cm^{-1}$ (broad band), mass spectrum, m/z (%): 632(0.5) ($M^+$ − 330), 631 (0.8), 603(1.0), 559(1.5), 511(1.0), 501(1.0), 497(1.0), 391(1.0), 331(31), 271(8.0), 241(18), 223(15), 211(10), 200(10), 195(10), 185(30), 178(40), 171(20), 169(100), 161(30), 159(10), 153(8.0), 151(25), 149(70), 139(15), 133(15), 131(10), 129(15), 127(10), 123(10), 121(10), 115(30), 111(10), 109(35), 95(30), 91(20), 83(35), 81(35).

The Octaacetate (IV). By the method described above, 58 mg of (II) yielded 34 mg of (IV) in the form of a white amorphous substance having $R_f$ 0.32 (PC), 0.23 (TLC, system 2); mass spectrum, m/z (%): $M^+$ 884(0.6), 786 (0.4), 654 (0.6), 571 (0.6), 554 (1.0), 506 (2.0), 505 (3.0), 496 (0.1), 429 (3.0), 386 (2.0), 368 (3.0), 355 (4.0), 344 (4.0), 331 (100), 285 (11), 284 (11), 273 (27), 271 (11), 256 (19), 242 (17), 229 (28), 223 (11), 213 (47), 204 (19), 202 (80), 201 (36), 200 (66), 199 (47), 198 (27), 194 (69), 185 (13.5), 183 (12), 182 (14), 182 (12), 173 (14), 171 (36), 169 (91), 167 (14), 165 (14), 158 (42), 153 (22), 149 (88), 129 (51), 125 (27), 115 (50), 111 (44), 109 (45).

Acid Hydrolysis of (I) and (II). A solution of 15 mg of (I) in 5 ml of 5% sulfuric acid solution was heated on the water bath for 1 h. The black-violet precipitate was filtered off, and the filtrate was neutralized with barium carbonate and filtered again. The filtrate was concentrated in vacuum to 0.5 ml and this concentrate was chromatographed on paper with glucose and rhamnose markers. Glucose, with $R_f$ 0.30, was detected in the hydrolysate.

A solution of 98 mg of (II) in 25 ml of 5% sulfuric acid was heated for 1 h, and the reaction mixture was worked up by the method described above. Glucose ($R_f$ 0.30) and rhamnose ($R_f$ 0.52) were detected in the hydrolysate. The hydrolysate (2 ml after concentration) was subjected to preparative chromatography on paper. The zones corresponding to glucose and rhamnose were cut out and the substances were eluted with methanol. Concentration of the eluate gave 21 mg of D-glucose, $[\alpha]_D^{20}$ 52° (c 2; $H_2O$) and 18 mg of L-rhamnose, $[\alpha]_D^{20}$ 8° (c 1.5; $H_2O$).

A solution of 20 mg of (I) in 5 ml of 10% sulfuric acid was boiled for 5 h and worked up as described above. Glucose and rhamnose were detected in the hydrolysate (PC).

Isolation of Aucubin. The preparative chromatography of 300 mg of the combined iridoids of fractions 1 and 2 on paper yielded 87 mg of a substance with $R_f$ 0.50 (PC), a solution of which in 2 ml of methanol was mixed with 1 g of silica gel, dried, and placed on a column containing 20 g of silica gel. Elution with system 1 gave 75 mg of aucubin with mp 181°C (from ethanol), $[\alpha]_D^{21} - 160° \pm 3$ (c 0.64; $H_2O$).

The acetyl derivative was obtained by keeping a mixture of 50 mg of aucubin, 2 ml of pyridine, and 2 ml of acetic anhydride at room temperature by the method described above. The yield was 45 mg of acicular crystals with mp 126-127°C (from aqueous methanol), $[\alpha]_D^{20}$ $-140° \pm 2$ (c 0.22); acetone), $R_f$ 0.92 (TLC, system 2). Found, $M^+$ 598, %: C 53.98; H 6.00. $C_{27}H_{34}O_{15}$. Calculated M 598.54, %: C 54.18; H 5.73. The PMR spectrum and the constants corresponded to those of aucubin hexaacetate [7].

Identification of (II) and (V) in the Total Iridoid Material. The combined fractions 1 and 2 were subjected to PC and TLC analysis with markers — samples of catalpol (V) and of 6-α-rhamnopyranosylcatalpol (II). Substances with $R_f$ 0.43 and 0.50 corresponded to their $R_f$ values and the coloration of their spots to (V) and (VI).

## SUMMARY

From the epigeal part of *Verbascum georgicum* Benth., together with aucubin as the main component of the combined iridoids, we have isolated and characterized a new iridoid — 6-α-L-(4"-p-methoxy-transcinnamoyl)rhamnopyranosylcatalpol. The presence in the combined material of catalpol and 6-α-L-rhamnopyranosylcatalpol, as well, has been shown by paper and thin-layer chromatography.

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