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Phenylethanoid Glycosides from *Verbascum sinaiticum*

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Two known phenylethanoid glycosides, 2′-acetylacteoside and arenarioside, and two new ones, β-(3,4-dihydroxyphenyl)-ethyl-O-α-L-rhamnopyranosyl (1→3)-β-D[β-D-xylopyranosyl (1→6)]-(4-O-isoferulyl)-gluco- pyranoside (**3**) and β-(3-hydrosy-4-methoxy phenyl)-ethyl-O-α-L-rhamnopyranosyl (1→ 3)-β-D[β-D-gluco-pyranosyl (1 → 6)]-4-O-isoferulyl)-glucopyranoside (**4**), were isolated and identified from aerial parts of *Vebascum sinaiticum*. The structures of all compounds were established by chromatographic and spectroscopic methods. This is the first report of phenylethanoid glycosides from *Verbascum sinaiticum*.

INTRODUCTION

Extracts of *Verbascum* species exhibit hypotensive and spasmolytic *effects*[1,2]. Phenylethanoid glycosides, iridoid glycosides and triterpenoid saponins have been previously reported from other species of *Verbascum*[3–7]. Here, we report from *V. sinaiticum* Benth. (Family *Scrophulariaceae*) four phenylethanoid glycosides, namely the known, 2′-acetylacteoside (**1**), arenarioside (**2**) and two new derivatives of isoferulic acid, β-(3,4-dihydroxyphenyl)-ethyl-O-α-L-rhamnopyranosyl (1 → 3)-β-D-[β-D-xylopyranosyl(1 → 6)]-(4-O-isoferulyl)-glucopyranoside (**3**) and β-(3-hydroxy-4-methoxyphenyl)-ethyl-O-α-L-rhamno-pyranosyl (1 → 3)-β-D[β-D-glucopyranosyl (1→6)]-(4-O-isoferulyl)-gluco-pyranoside (**4**). This report is a continuation of our current project on our chemical and biological investigations of plants from the *Scrophulariaceae*.

EXPERIMENTAL

Verbascum sinaiticum was obtained from South Sinai, Egypt, 1998, and was identified by Dr. M. El-Gebally, Department of Taxonomy and Flora, N.R.C., Cairo-Authentic reference compounds for caffeic, ferulic, isoferulic, *p*-coumaric acids and the sugars glucose, xylose, rhammose and apiose, were available in the School of Biological Sciences, University of Texas at Austin. ^{1}H NMR spectra were recorded at 500 MHz and ^{13}C NMR spectra at 100 MHz; all chemical shifts are given in ppm with TMS as an internal standard. UV spectra were measured with a Shimadzu 1601 UV-visible spectrophotometer.

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Isolation: Dried aerial parts of *Verbascum sinaiticum* were extracted with 70% aqueous ethanol, and the extract was concentrated under reduced pressure; the concentrate was extracted with ethyl acetate. The water soluble fraction was subjected to polyamide column chromatography using an aqueous methanol mixture. The eluted mixture was evaporated to dryness. The residue was rechromatographed on a silica gel column using chloroform and methanol. The isolated fractions were purified by TLC on cellulose plates using ethyl acetate-methanol-chloroform-water (60 : 16.5 : 13.5 : 5). Acid hydrolysis utilized refluxing in 10% H_2SO_4-EtOH for 1 h. After taking the solution to dryness, the reaction mixture was partitioned between ethyl acetate and water. The ethyl acetate layer was concentrated to dryness, and the residue was chromatographed on PC with *n*-BuOH-HOAc-H_2O (4 : 1 : 5 top layer) against standard hydroxycinnamic acids. The water residue components were co-chromatographed with standard sugars on PC.

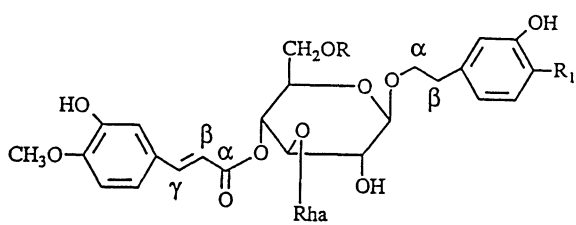
Spectral data for 1: ^{13}C NMR (CD_3OD); aglycone moiety: δ 131.6 (C-1), 117.2 (C-2), 145.9 (C-3), 144.6 (C-4), 116.2 (C-5), 121.3 (C-6), 72.0 (C-α), 36.4 (C-β); caffeic acid moiety: δ 127.6 (C-1), 115.3 (C-2), 149.8 (C-3), 146.6 (C-4), 116.6 (C-5), 123.1 (C-6), 168.20 (C-α), 114.7 (C-β), 148.1 (C-γ); glucose moiety: δ 101.6 (C-1), 75.1 (C-2), 80.2 (C-3), 70.5 (C-4), 75.9 (C-5), 62.3 (C-6), 171.5 (CO), 20.9 (CH_3); rhamnose moiety: δ 103.1 (C-1), 72.0 (C-2), 71.7 (C-3), 73.6 (C-4), 70.7 (C-5), 18.5 (C-6).

Spectral data for 2: ^{13}C NMR (CD_3OD); aglycone moiety: δ 131.2 (C-1), 117.1 (C-2), 146.0 (C-3), 144.9 (C-4), 115.9 (C-5), 121.3 (C-6), 72.2 (C-α), 36.5 (C-β); caffeic acid moiety: δ 127.4 (C-1), 114.9 (C-2), 149.7 (C-3), 146.7 (C-4), 116.3 (C-5), 123.2 (C-6), 168.2 (C-α), 114.9 (C-β), 148.1 (C-γ); glucose moety: δ 104.3 (C-1), 75.6 (C-2), 81.5 (C-3), 70.2 (C-4), 75.3 (C-5), 69.6 (C-6); rhamnose moiety: δ (103.1 (C-1), 72.0 (C-2), 72.1 (C-3) 73.6 (C-4), 70.3 (C-5), 17.9 (C-6); xylose moiety: δ 104.7 (C-1), 74.6 (C-2), 77.3 (C-3), 71.0 (C-4), 66.5 (C-5).

Spectral data for 3: ^1H NMR (DMSO-d_6): δ 7.45 (1H, d, J = 16 Hz,(H-γ isoferulic), 7.02 (1H, d, J = 2 Hz, H-2 isoferulic), 6.95 (1H, J = 8, 2 Hz, H-6 isoferulic), 6.72 (1H, d, J = 8 Hz, H-5 isoferulic), 6.65 (1H, d, J = 8 Hz, H-5 aglycone), 6.62 (1H, d, J = 2 Hz, H-2 aglycone), 6.49 (1H, dd, J = 8, 2 Hz, H-6 aglycone), 6.16 (1H, d, J = 16 Hz H-β isoferulic), 5.04 (1H, d, J = 1.5 Hz, H-1 rhamnosyl), 4.35 (1H, d, J = 8 Hz, H-1 glucosyl), 4.27 (1H, d, J = 7.5 Hz, H-1 xylosyl), 3.78 (3H, S, OCH_3), 2.7 (2H, m, H-β aglycone), 0.95 (3H, d, J = 6 Hz, Me rhamnosyl). ^{13}C NMR (DMSO-d_6); aglycone moiety: δ 128.9 (C-1), 116.3 (C-2), 146.0 (C-3), 145.3 (C-4), 115.8 (C-5), 119.4 (C-6), 70.3 (C-α), 34.9 (C-β); isoferulic acid moiety: δ 124.7 (C-1), 115.4 (C-2), 148.0 (C-3), 149.7 (C-4), 112.7 (C-5), 121.5 (C-6), 165-7 (C-α), 115.7 (C-β), 146.07 (C-γ), 55.8 (OCH_3); glucose moiety: δ 102.19 (C-1), 74.4 (C-2), 78.95 (C-3), 69.0 (C-4), 73.3 (C-5), 68.0 (C-6) ; rhamnose moiety: δ 101.1 (C-1), 70.4 (C-2) 70.2 (C-3), 71.6 (C-4) 68.6 (C-5), 18.05 (C-6); xylose moiety: δ 103.7 (C-1), 73.5 (C-2), 76.3 (C-3), 69.9 (C-4), 65.4 (C-5). Acid hydrolysis of **3** gave isoferulic acid, glucose, rhamnose and xylose by PC.

Spectral data for 4: ^1H NMR (CD_3OD): δ 7.65 (1H, d, J = 16 Hz, H-γ isoferulic), 7.18 (1H, d, J = 2Hz, H-2 isoferulic), 7.07 (1H, dd, J = 8, 2 Hz, H-6

isoferulic), 6.83 (1H, d, J = 8 Hz, H-5 isoferulic), 6.8 (1H, d, J = 8 Hz, H-5 aglycone), 6.74 (1H, d, J = 2 Hz, H-2 aglycone), 6.69 (1H, dd, J = 8, 2 Hz, H-6 aglycone), 6.38 (1H, d, J = 16 Hz, H-β isoferulic), 5.2 (1H, d, J = 1.5 Hz, H-1 rhamnosyl), 4.39 (1H, d, J = 8 Hz, H-1 inner glucosyl), 4.33 (1H, d, J = 8 Hz, H-1 outer glucosyl), 3.85 (3H, S, OCH_3), 3.81 (3H, S, OCH_3), 2.82 (2H, t, J = 7.5 Hz, H-β aglycone), 1.1 (3H, d, J = 6 Hz, Me-rhamnosyl). ^{13}C NMR (CD_3OD); aglycone moiety: δ 132.9 (C-1), 117.1 (C-2), 147.3 (C-3), 148.5 (C-4), 112.9 (C-5), 121.1 (C-6), 72.0 (C-α), 36.6 (C-β), 56.4 (OCH_3); isoferulic acid moiety: δ 127.0 (C-1), 112.8 (C-2), 147.2 (C-3), 149.8 (C-4), 114.2 (C-5), 124.5 (C-6), 168.2 (C-α), 114.6 (C-β), 148.0 (C-γ), 56.5 (OCH_3); inner glucose moiety: δ 104.1 (C-1), 76.0 (C-2), 81.3 (C-3), 70.4 (C-4), 74.7 (C-5), 69.4 (C-6); rhamnose moiety: δ 102.8 (C-1), 72.2 (C-2), 72.3 (C-3), 73.7 (C-4), 70.5 (C-5), 18.4 (C-6); outer glucose moiety: δ 104.4 (C-1), 75.2 (C-2), 77.9 (C-3), 71.2 (C-4), 78.0 (C-5), 62.3 (C-6). Acid hydrolysis of **4** gave isoferulic acid, glucose, and rhamnose by PC.



3 : R = xylosyl , R_1 = OH

4 : R = glucosyl , R_1 = OCH_3

RESULTS AND DISCUSSION

Reinvestigation of the air-dried aerial parts of *Verbascum sinaiticum* afforded the four compounds **1–4**. The mauve color of **3** and **4** under UV light changing to yellow with ammonia and a λ_{max} [$EtOH_{nm}$ (log ε): 295, 320] suggested isoferulic acid structures[8]. The ^{13}C NMR spectrum of **3** was similar to that of arenarioside except for the acid moiety, which exhibited signals at δ 55.8, 148.0 and 149.7, typical for isoferulic acid[9]. Acid hydrolysis of **3** afforded isoferulic acid. The ^1H NMR spectrum of **3** showed signals at δ 4.35, 4.27 and 5.04 in accord with the anomeric protons of glucosyl, xylosyl and rhamnosyl, respectively. Therefore, **3** is β-(3,4-dihydroxyphenyl)-ethyl-O-α-L-rhamnopyranosyl(1 → 3)-β-D[β-D-xylopyranosyl 1 → 6)]-(4-O-isoferulyl)-glucopyranoside. The ^{13}CNMR spectrum of **4** was identical with **7** isolated previously from *V. thapsus* except for the acid moiety signals, which showed signals at δ 147.2 and 149.8 identical to isoferulic acid[3]. The ^1H NMR spectrum showed three anomeric proton signals at δ 4.39, 4.33 and 5.20 identical to inner glucosyl, outer glucosyl and rhamnosyl respectively. Acid hydrolosis of compound **4** afforded isoferulic acid, glucose and rhamnose. Therefore, **4** is β-(3-hydroxy-4-methoxyphenyl)-ethyl-O-α-Lrhamnopyranosyl (1→3)-β-D[β-D-glucopyranosyl (1→6)]-(4-O-isoferulyl)-

glucopyranoside. The ^{1}H NMR, ^{13}C NMR, and acid hydrolysis data were in accord with those previously reported[10].

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