2,6-DIHYDROXY-4-METHOXYACETOPHENONE 2-O-β-D-GENTIOBIOSIDE FROM THE ROOTS OF Dorema aitchisonii

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From the residue formed on the dissolution of a concentrated alcoholic extract of the roots of Dorema aitchisonii Korov ex M. Pimen* in diethyl ether, by crystallization from alcohol and then from aqueous alcohol we have isolated colorless crystals of a phenolic glycoside $C_{21}H_{30}O_{14}$ with mp 167-169°C; $[\alpha]_D^{20}$ −54.4° (c 1.14; water). UV spectrum, $\lambda_{max}^{ethanol}$, nm): 225, 286, 325 (log ε 4.17, 4.26, 3.66).

IR spectrum ($\nu_{max}^{min.\ oil}$, cm^{-1}): 3500-3200 (—O—H of the carbohydrate residue), 1630 s (Ar—CO...H—O—), 1590 (Ar), 1510 w, 1435, 1420 w, 1400 w, 1340 w, 1300 s, 1270, 1225, 1205, 1175 (1140, 1115 s, 1085 s, 1060 sh., 1030) (—O—H of the carbohydrate residue), 955, 920, 895, 835 s, 760, 730, 700.

PMR spectrum (200.13 MHz, DMSO, ppm): aglycon moiety, 2.67 (3H, s, CH_3—CO—Ar), 3.82 (3H, s, CH_3—O—Ar), 6.12 and 6.33 (each 1H, d, J = 2.5 Hz, H-3 and H-5), 13.67 (s, H—O—Ar), carbohydrate moiety, 3.68 m, 3.98 (1H, d, J = 13.3 Hz), 4.18 (1H, d, J = 9.3 Hz), 4.47 (1H, t, J = 6.9 Hz), 4.81 (1H, d, J = 6.1 Hz), 4.91 (1H, d, J = 5 Hz), 4.96 (1H, d, J = 5.8 Hz), 5.04 (1H, d, J = 8.8 Hz), 5.18 (1H, d, J = 6.3 Hz), 5.25 (1H, d, J = 5 Hz), 5.44 (1H, d, J = 6.3 Hz).

^{13}C NMR spectrum (50.33 MHz, DMSO, ppm): aglycon moiety, 33.8 q (CH_3—CO—Ar), 56.5 q (CH_3—O—Ar), 94.5 d and 95.7 d (C-3 and C-5), 106.9 s (C-1), 161 s, 166.3 s and 166.5 s (C-2, C-6, and C-4), 204.6 s (C═O), carbohydrate moiety 61.8 t (C-6"), 69.8 t (C-6'), 70.3 d and 70.8 d (C-4' and C-4"), 73.8 d and 74.2 d (C-2' and C-2"), 76.2 d and 77.2 d (C-5' and C-5"), 77.2 d and 77.2 d (C-3' and C-3"), 100.9 d (C-1'), 104.2 d (C-1").

Acid hydrolysis led to an aglycon $C_9H_{10}O_4$, mp 137-139°C. IR spectrum $\nu_{max}^{min.\ oil}$, cm^{-1}): 3100, 1640 s, 1585 s, 1520, 1415 w, 1320 w, 1290, 1260 s, 1210, 1170, 1095, 1080, 1040 s, 1030 w, 985 sh., 970, 800 s, 760 w, 720 w.

PMR spectrum ($CDCl_3$, ppm): 2.6 (3H, s, CH_3—CO—Ar), 3.7 (3H, s, CH_3—O—Ar), 5.9 (2H, s, H-3 and H-5), 12.3 (2H, s, 2H—O—Ar).

^{13}C NMR spectrum ($CDCl_3$, ppm): 32.5 q (CH_3—CO—Ar), 55.4 q (CH_3—O—Ar), 93.2 d (C-3), 93.2 d (C-5), 105 s (C-1), 164.2 s (C-2), 164.2 s (C-6), 165.7 s (C-4), 203.1 s (C═O).

Judging from the IR spectra of the glycoside and the aglycon, each showing a very intense absorption band in the 1630-1640 cm^{-1} region, the substance contained a keto group conjugated with a benzene ring and participating in a hydrogen bond with a phenol group in the ortho position to a side chain. The phenol group itself absorbed at 3100 cm^{-1}, which, in its turn, indicated its participation in a strong hydrogen bond with the keto group. In the aromatic ring of the glycoside there were two unsubstituted protons (6.12 and 6.33 ppm) in the meta position to one another (J = 2.5 Hz in the PMR spectrum). The aglycon included a symmetrically substituted aromatic ring. In the PMR spectrum two aromatic protons resonated at 5.9 ppm. In the ^{13}C NMR spectrum of the aglycon the C-2 and C-6 nuclei absorbed at 164.2 ppm and the C-3 and C-5 similarly at 93.2 ppm; i.e., the phenolic moiety had the structure of 2,6-dihydroxy-4-methoxyacetophenone [1, 4].

The carbohydrate moiety consisted of a β-D-gentiobiose residue [2]. The chemical shifts of the ^{13}C nuclei of the analogous groups of the two carbohydrate units were close to one another and to literature figures for methyl O-β-D-glucopyranoside [3]. The positions of the carbon signals of the $-CH_2-O-R$ groups differed as the result of the presence of a

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*The plant material for the investigation was collected in Turkmenia (Badkhyz, Islim-Chashli).

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C_6-C_1 bond between the β-glucose residues. The C-6" atom of the free CH_2OH group resonated at 61.8 ppm (triplet). A second triplet appeared in a weaker field (69.8 ppm) and belonged to C-6' of the substituted CH_2OR group.

On the basis of the spectral characteristics and literature information it may be suggested that the glycoside isolated is 2,6-dihydroxy-4-methoxyacetophenone 2-O-β-gentiobioside. This glycoside is present in the roots of Dorema aitchisonii in considerable amount (about 0.5% on the weight of the dry roots).

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PHENYLPROPANOID GLYCOSIDES OF Pedicularis condensata, P. wilhelmsiana, AND P. sibthorpii

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In continuation of our investigations of glycosides of representatives of the family Scrophulariaceae growing in Armenia, we have subjected to analysis the epigeal parts of three species of pedicularis: Pedicularis condensata Bieb., P. wilhemsiana Fisch et Bieb., and P. sibthorpii Boiss., growing in the subalpine zone of the republic and not previously studied chemically.

The glycosides were isolated by the successive chromatography of the water-soluble fractions of methanolic extracts of the plants on columns of polyamide and silica gel by a method described previously [1].

Two phenylpropanoid glycosides (I and II) were isolated with yields of 0.33 and 0.03%, respectively, from P. condensata. On the basis of its UV, IR, ^1H and ^{13}C NMR, and mass spectra and also of a comparison with an authentic sample by TLC and HPLC, glycoside (I) was identified as verbascoside [1].

Glycoside (II), amorphous, $[\alpha]_D^{20}$ −117° (c 0.5; methanol) differed from verbacoside (according to its ^1H and ^{13}C NMR spectra) by the presence of an acetoxy group. Acetylation of glycoside (II) with pyridine–acetic anhydride (1:2) by the usual method led to verbascoside nonaacetate. The position of the acetoxy group at C-2' of the glucosyl moiety in glycoside (II) was established from the α- and β-effects of acylation observed in the ^{13}C NMR spectrum of glycoside (II) in comparison with that of verbascoside (C-1', $\Delta\delta$ = −3.0 ppm; C-2', $\Delta\delta$ = +3.5 ppm; C-3', $\Delta\delta$ = −5.7 ppm).

Thus, glycoside (II) was 2'-O-acetylverbascoside (2'-acetylacteoside), which has been detected previously in a number of plants of the family Orobanchaceae [2-4]. The ^1H and ^{13}C NMR spectra of glycoside (II) corresponded to those reported for 2'-acetylacteoside [2].

Only verbascoside was isolated from P. wilhelmsiana and P. sibthorpii, with yields of 0.2 and 1.5%, respectively. Phenylpropanoid glycosides have not previously been detected in plants of the genus Pedicularis.

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