NMR spectrum (CCl_4-CDCl_3 (4:1); 0 – TMS; δ, ppm, intensity, multiplicity, J, Hz): 6.16, 1H, d, 9.5 (3-H); 7.55, 1H, d, 9.5 (4-H); 7.28, 1H, d, 8.8 (5-H); 6.75, 1H, q, 8.8, 2.5 (6-H); 6.73, 1H, d, 2.5 (8-H); 4.57, 2H, d, 6.8 (1'-CH_2); 5.50, 1H, t, 6.8 (2'-CH); 1.79, 3H, s (3'-C–CH_3); 3.92, 1H, t, ΣJ = 14.0 (4'-H); 2.05-2.45, 4H, m (5'-CH_2, 8'-OH_2); 5.03, 1H, t, ΣJ = 16.0 (6'-CH); 1.60, 3H, s (7'-C–CH_3); 4.54, 1H, m (9'-CH); 2.67, 2H, s (4'-C–OH, 9'-C–OH); 5.36, 1H, d, 8.5 (10'-CH); 1.65, 6H, s [11'-$C(CH_3)_2$].

The acetylation of 70 mg of deacetyltadzhikorin with a mixture of acetic anhydride and pyridine under the conditions described below gave a diacetate (25.9 mg) identical with tadzhikorin acetate.

Acetylation of Tadzhikorin. Tadzhikorin (100 mg) was kept in 2 ml of a mixture of acetic anhydride and pyridine (1:1), and then the reaction mixture was worked up as described above for tadzhiferin; the residue after the evaporation of the ethereal extract was deposited on a column (85×7 mm) of silica gel L 40-100μ, and the substances were eluted with a mixture of petroleum ether and ethyl acetate (fractions 1-25 of 5 ml each), and then with chloroform (fractions 26-28 of 5 ml each). The last fractions gave in noncrystalline form 85.2 mg of tadzhikorin acetate (V), $C_{28}H_{34}O_7$, Rf 0.45.

NMR spectrum (CCl_4, 20°C, 0 – TMS; δ, ppm, intensity, multiplicity, J, Hz): 6.10, 1H, d, 9.5 (3-H); 7.49, 1H, d, 9.5 (4-H); 7.25, 1H, d, 8.8 (5-H); 6.71, 1H, q, 8.8, 2.5 (6-H); 6.73, 1H, d, 2.5 (8-H); 4.56, 2H, d, 6.5 (1'-CH_2); 5.64, 1H, t, 6.5 (2'-CH); 1.79, 3H, s (3'-C–CH_3); 4.94, 1H, t, ΣJ = 14.0 (4'-CH); 1.93, 3H, s and 1.96, 3H, s (4'-C–$OCOCH_3$, 9'-C–$OCOCH_3$); 2.05-2.50, 4H, m (5'-CH_2, 8'-CH_2); 4.94, 1H, t, ΣJ = 16.0 (6'-CH); 1.59, 3H, s (7'-C–CH_3), 5.60, 1H, m (9'-CH); 5.27, 1H, d, 9.0 (10'-CH); 1.72, 3H, s and 1.73; 3H, s [11'-$C(CH_3)_2$].

SUMMARY

Two new terpenoid coumarins – tadzhiferin (I) and tadzhikorin (II) – have been isolated from the fruit of Ferula tadshikorum M. Pimen.

On the basis of physicochemical and spectral investigations, the structure of 7-(9'-hydroxy-3',7',11'-trimethyldodeca-2',6',10'-trienyloxy)coumarin is proposed for (I) and that of 7-(4'-acetoxy-9'-hydroxy-3',7',11'-trimethyldodeca-2',6',10'-trienyloxy)coumarin for (II).

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AXILLAROSIDE – A NEW FLAVONOL GLYCOSIDE FROM Artemisia taurica

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UDC 574.918

There is information in the literature on the investigation of the flavonoids of some species of the genus Artemisia [1-5].

On separating the combined flavonoids from the influorescences of Artemisia taurica by column chromatography on polyamide sorbent, we isolated a substance with mp 253-255°C the physicochemical properties of which differed from previously known flavonoids.

Acid hydrolysis of the compound gave an aglycone and a carbohydrate component which we identified as D-glucose. The results of a spectrophotometric determination of the molecular weight of the glycoside and of the aglycone [6] and elementary analysis corresponded to the formulas $C_{23}H_{24}O_{13}$ and $C_{17}H_{14}O_8$, respectively.

Pyatigorsk Pharmaceutical Institute. All-Union Scientific-Research Institute of Medicinal Plants, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 599-601, September-October, 1976. Original article submitted September 26, 1975.

The NMR spectrum of the trimethylsilyl ether of the glycoside taken in CCl_4 contained the signals of the following protons: H-2' (multiplet with its center at 7.5 ppm, 2 H), H-5' (doublet at 6.83 ppm, J = 8.5 Hz, 1 H), two methoxy groups (singlets at 3.83 and 3.71 ppm with integral intensities of 3 H each), the proton of the anomeric center and the other glucose protons (doublet at 4.97 ppm, J = 6 Hz, 1 H, and multiplet in the 3.2-2.8 ppm region, 6 H). The value of the spin–spin coupling constant of the protons at C-1 and C-2 of the sugar corresponds to their mutual diaxial arrangement and, consequently, to the β-configuration of the glycosidic bond. A one-proton singlet at 6.56 ppm most probably relates to the H-8 proton of the flavonoid nucleus. Thus, the compound under investigation contained substituents in the 3,3',4',5,6, and 7 positions.

The positions of the main maxima of the absorption of the glycoside in the UV region, λ_{max}, 259, 272, 358 nm, permit its assignment to the group of flavonols with 3',4'-substitution in ring B. The UV spectra taken with the aid of ionizing and complex-forming additives show the presence in the glycoside and the aglycone of free hydroxy groups in the 3',4', and 5 positions. In the aglycone, the hydroxy group in position 7 was also found to be free, which is confirmed by the absorption spectra of the product of electrolytic reduction [7]. The value of the bathochromic shift of the maximum of the long-wave band by 14 nm in the presence of aluminum chloride and hydrochloric acid confirms that there is an oxygen-containing substituent in position 6 [8]. Thus, the methoxy groups can be present only in positions 3 and 6, and the aglycone is identical with axillarin (3',4',5,7-tetrahydroxy-3,6-dimethoxyflavone) [9], as is confirmed by the demethylation reaction [10], which led to the formation of quercetagetin.

In the glycoside under investigation, the carbohydrate component is attached at position 7 of the aglycone. The fact that acid hydrolysis of the compound takes place fairly slowly is in favor of the pyranose form of the oxide ring of the glucose.

The results obtained show that the flavonoid that we isolated has the structure of 3',4',5,7-tetrahydroxy-3,6-dimethoxyflavone 7-O-β-D-glucopyranoside. No compound of such structure has been described previously, and we propose for it the name axillaroside.

EXPERIMENTAL

The NMR spectrum was taken on a Varian HA-100 instrument (with HMDS as internal standard) and the UV spectra on a Hitachi EPS-3T spectrometer in methanol; the melting points were determined on a Kofler block.

The elementary analyses corresponded to the calculated figures.

Isolation of Axillaroside. The air-dry inflorescences of Artemisia taurica Willd., collected in August, 1972, in the environs of Georgievskaya (5 kg) were treated successively with petroleum ether and chloroform and were steeped with ethanol. The ethanolic extract was evaporated to dryness, and the residue was treated with water, chloroform, and ethyl acetate. The total flavonoids were precipitated from the combined ethyl acetate extracts by an eightfold volume of chloroform. This total material was deposited on a column of polyamide sorbent previously treated with hydrochloric acid. The column was eluted with water with gradually increasing concentrations of ethanol. The axillaroside was eluted with 20% ethanol, and after recrystallization from aqueous ethanol it was obtained in the form of light yellow acicular crystals with mp 253-255°C, R_f 0.20 (in 5% CH_3COOH), 0.76 (BAW, 4:1:5), 0.72 (BAW, 4:1:2). UV spectrum: λ_{max} 259, 272, 358 (in CH_3OH); 265, 368, 416 (+NaOAc); 270, 381 (+NaOAc + H_3BO_3); 271, 405 (+$ZrOCl_2$); 259, 272, 359 (+$ZrOCl_2$ + citric acid); 272, 278, 402 (+NaOMe).

Acid Hydrolysis. A mixture of 0.15 g of axillaroside and 3 ml of 30% hydrochloric acid was heated in the boiling water bath. The first crystals of the aglycone were observed after 1 h, and hydrolysis was complete after 3 h. The aglycone, $C_{17}H_{14}O_8$, formed small acicular crystals with mp 198-199°C (from ethanol). R_f 0.92 (BAW, 4:1:5), 0.59 (benzene–ethyl acetate–acetic acid, 70:30:2) on paper impregnated with a 20% ethanolic solution of formamide.

The hydrolyzate after the separation of the aglycone was shown by paper chromatography in various systems in the presence of markers to contain D-glucose.

Demethylation of the Aglycone. A solution of 0.04 g of the aglycone in 5 ml of acetic anhydride and 0.5 g of phenol was mixed with 9 ml of freshly distilled hydriodic acid. The mixture was heated in the water bath for 2 h and was then poured into 100 ml of water. The aglycone was extracted with ether, and the ethereal extract was washed with thiosulfate solution until the reaction for free iodine was negative. Evaporation of the ethereal extract yielded quercetagetin, $C_{15}H_{10}O_8$, with mp 324-325°C.

SUMMARY

From the influorescences of Artemisia taurica a new flavonoid, axillaroside, has been obtained; it has the structure of 3',4',5,7-tetrahydroxy-3,6-dimethoxyflavone 7-O-β-D-glucopyranoside.

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POLYPHENOLS AND ACIDS OF Ulugbekia tschimganica

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UDC 547.587.52:547.39

Investigating the herbage and roots of Ulugbekia tschimganica (B. Fedtsch.) Zak, family Boraginaceae, collected on Mount Bol'shoi Chimgan (Tashkent oblast), we detected in it five substances giving a reaction with ferric chloride and diazotized sulfamlic acid. Since the phenolcarboxylic acids of plants of this family are unstable compounds [1], they were studied in the form of their methyl derivatives. Chromatography on silica gel of extracts from the epigeal part of the plant yielded the methyl ester (I), having the composition $C_{19}H_{18}O_6$ (amorphous), of a new acid which we have called ulugbekic acid. The presence in the UV spectrum of the ester of maxima at (nm) 236 (shoulder), 250 (shoulder), 292, and 336 ($\log \varepsilon$ 4.07 and 4.10) showed the presence in its molecule of a 1-(3',4'-dihydroxyphenyl)but-1,3-dienyl chromophore. Bathochromic shifts of the long-wave maximum in the presence of alkali ($\Delta\lambda$ 30 nm) and of boric acid together with sodium acetate ($\Delta\lambda$ 22 nm) each showed the presence of a free ortho-dihydroxy grouping.

The alkaline fusion of (I) formed protocatechuic acid.

The IR spectrum of the substance (Fig. 1a) had absorption bands at (cm^{-1}) 3200-3500 (hydroxy groups), 1700-1740, 1150-1300, 1105 (ester of an unsaturated acid), 1620, 1540, 890, 880 (1,3,4-trisubstituted benzene ring), and 820 (trisubstituted ethylene group). On acetylation, the substance formed an amorphous tetraacetate in the IR spectrum of which the bands of the hydroxy groups had disappeared and an absorption band corresponding to the carbonyl of a phenol ester (1780 cm^{-1}) had appeared. Its NMR spectrum had two six-proton singlets at 2.10 and 2.12 ppm corresponding to the protons of four acetyl residues in an aromatic nucleus.

Thus, of the six oxygen atoms in the molecule of (I), four are in the form of phenolic hydroxyls and two in the form of an ester grouping of an unsaturated acid.

In view of the composition and the presence of four phenolic hydroxyls and six aromatic protons (see the NMR spectrum) it may be concluded that the molecule (I) includes two aromatic nuclei, each of which contains an ortho-dihydroxy grouping and which are linked with one another by a chain of five carbon atoms with a $COOCH_3$ group.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 601-607, September-October, 1976. Original article submitted January 20, 1976.