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 ε 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 (Δλ 30 nm) and of boric acid together with sodium acetate (Δλ 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.

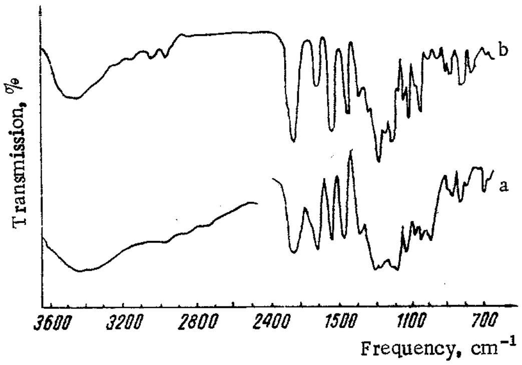


Fig. 1. IR spectra of the methyl derivatives of ulugbekic (a) and ulugbinic (b) acids.

In the NMR spectrum of (I) (Fig. 2a) there are the signals of six aromatic ortho- and meta-interacting protons in the 6.45-7.0 ppm region in the form of doublets with $J_1 = 8.5$ and $J_2 = 2$ Hz.

Doublets at 7.48 and 6.14 ppm, J = 17 Hz, are due to the olefinic protons of a $Ar-CH=CH-$fragment. The absence of secondary splitting in these signals shows that the fragment mentioned is connected with a tertiary carbon atom.

A two-proton doublet at 2.98 ppm, J = 7 Hz, corresponds to methylene protons at a benzene carbon atom located next to an ethylene bond, as is shown by the presence of the signal of an olefinic proton in the form of a triplet at 5.1 ppm with J = 7 Hz. The absence of appreciable secondary splitting of the latter signal shows that it is present in a $-C=CH-CH_2-Ar$ fragment.

The NMR spectrum of (I) also has a three-proton singlet at 3.59 ppm caused by a methyl ester grouping $COOCH_3$, which is attached to a tertiary carbon atom.

On the basis of the facts given, it may be concluded that the most probable structure for (I) is 1,5-bis(3',4'-dihydroxyphenyl)-3-methoxycarbonylpent-1,3-ene (Fig. 2a). This structure agrees well with the mass spectrum of the substance, which contains peaks with m/e 123, 135, 194, 283, and others.

Thus, ulugbekic acid is close in structure to lithospermic acid, which is found in a number of plants of this family [1-4]. Attempts to obtain the acid by saponifying the ester did not give satisfactory results but led to the formation of a mixture of substances and to resinification.

By the same method, we isolated from the herbage the methyl ester (II) with the composition $C_{20}H_{22}O_7$, mp 228°C, $[\alpha]_D^{20}$ +25° (c 0.6; acetone), of a second new acid which we called ulugbinic acid. Its UV spectrum had a maximum at 286 nm (log ε 3.90). In the presence of alkali there was a bathochromic shift in the spectrum by 4 nm, but with boric acid and sodium acetate the maximum did not change its position. The alkaline fusion of (II) formed resorcinol. Consequently, in the molecule of (II) there is no double bond conjugated with an aromatic nucleus and the hydroxy groups are present in the meta positions.

The IR spectrum of (II) (see Fig. 1b) contains a broad band in the 1740-cm^{-1} region and bands at 1200 and 1040 cm^{-1} (ester of an unsaturated acid), at 880 and 815 cm^{-1} (1,2,4-trisubstituted benzene nucleus), and at 3450-3500 cm^{-1} (hydroxy groups). The acetylation of (II) formed a diacetate with the composition $C_{24}H_{26}O_9$, mp 247°C, but on methylation with diazomethane another four methoxy groups appeared and a derivative $C_{24}H_{30}O_7$ was formed with mp 218-220°C, M^+ 430 in the IR spectrum of which the absorption bands of hydroxy groups had disappeared. It follows from this that four of the seven oxygen atoms in the molecule of (II) are present in the form of phenolic hydroxyls, two as an ester grouping, and one, apparently, in the form of an ether.

In the NMR spectrum of (II) (Fig. 2b) at 6.7-7 ppm there are the signals of six aromatic protons. A four-proton multiplet at 2.97 ppm shows the presence of two methylene protons at benzene carbon atoms, and a triplet at 5.0 ppm, J = 7 Hz, the presence of an olefinic proton adjacent to one of the groups mentioned. A three-proton singlet at 3.52 ppm is due to the methyl fragment of $COOCH_3$, and singlets at 5.70, 5.90 (1 H each), and at 6.14 ppm (2 H), which disappear on deuterium exchange and undergo displacement when the spectrum is taken in other solvents, are due to the protons of phenolic hydroxyls. A quartet at 4.0 ppm, $J_1 = 14$, $J_2 = 7$ Hz (appearing when the spectrum is recorded in acetone) is due to a gem-methoxyl proton in a $C=C-CHOCH_3$ grouping.

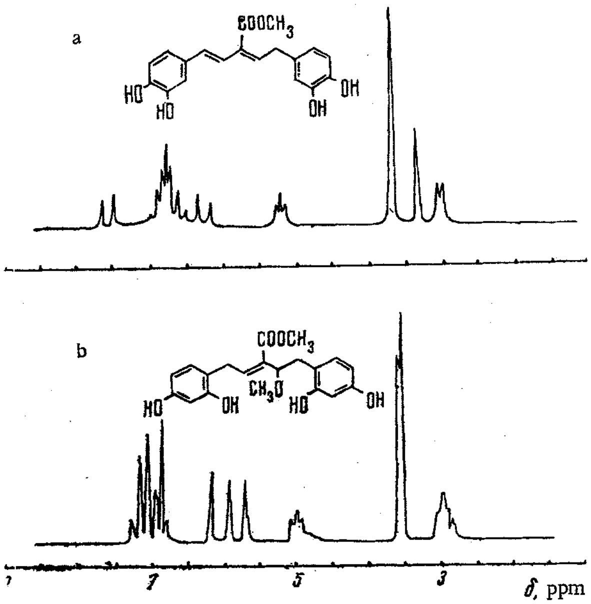


Fig. 2. NMR spectra of the methyl esters of: a) ulugbekic acid (in CD_3OD); b) ulugbinic acid (in pyridine).

These facts show that methyl ulugbinate has a structure close to that of methyl ulugbekate, containing two benzene nuclei connected by a hydrocarbon chain of five carbon atoms, a double bond in this chain not conjugated with an aromatic system, and a $COOCH_3$ fragment. In addition, there is a tertiary methoxy group in the chain.

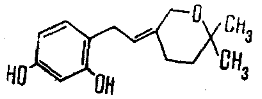
In view of the facts given, it may be concluded that substance (II) most probably has the structure of 1,5-bis(2',4'-dihydroxyphenyl)-3-methoxycarbonyl-4-methoxypent-2-ene (Fig. 2b). This agrees well with its mass spectrum, which has peaks with m/e 123, 136, 153, 161, and 301, and also with the corresponding spectra of its derivatives.

From the methylated acid fraction of an ethanolic extract of the herbage and roots we also isolated methyl 3,4-dihydroxycinnamate (caffeate) (III) and methyl fumarate (IV), which were identified by mixed melting points and IR spectra. By chromatography we showed the presence in the herbage and roots of the plant of free chlorogenic (V), caffeic (VI), and fumaric (VII) acids, and also of monomethyl fumarate (VIII).

Substance (IX) from the phenolic fraction of the extract forms colorless crystals readily soluble in acetone, DMSO, and caustic alkalis, less readily in methanol, and insoluble in chloroform, ether, pyridine, and dioxane. It is a new phenol which we have called ulugbin. The substance gives no reaction for carboxy or carbonyl groups or an oxide ring, and is not dehydrated by sulfuric acid. Its UV spectrum (λ_{max} 292 nm, log ε 3.56) shows the presence in the molecule of the same chromophore as in ulugbinic acid. A shift of the long-wave maximum in the presence of alkali shows the presence of free phenolic hydroxy groups. The alkaline fusion of (IX) gave resorcinol, and its mass spectrum in the region below 137 m/e was identical with that of ulugbinic acid. The IR spectrum contained absorption bands at 3200-3500 cm^{-1} (hydroxy groups), 1615, 1520, 1450, 870, and 815 cm^{-1} (1,2,4-trisubstituted benzene nucleus), 1030 and 1240 cm^{-1} (C−O−C bond), 900 cm^{-1} (gem-dimethyl group in a pyran ring), and 840 cm^{-1} (trisubstituted double bond).

The NMR spectrum of ulugbin (in CF_3COOH) contained following signals: doublets at 6.62 ppm, J = 2.5 Hz, and 6.59 ppm, J = 8 Hz, quartet at 6.30 ppm, J_1 = 8 Hz, J_2 = 2.5 Hz, and also a doublet at 3.0 ppm (J = 8 Hz, 2 H), and a triplet at 5.32 ppm, J = 8 Hz, corresponding to a 1-(2',4'-dihydroxyphenyl)-3-methylbut-2-enyl fragment. The presence of two phenolic hydroxyls was confirmed by a peak with m/e 123 in the mass spectrum. The third oxygen atom is most probably included in a heterocycle, as is indicated by the above-mentioned bands of a pyran ring in the IR spectrum and the absence from the mass spectrum of peaks corresponding to the elimination of water. In view of the composition of the substituent attached to the aromatic nucleus $-C_{10}H_{15}O-$ and the presence of one double bond and a C−C−C bond, this substituent must have a monocyclic structure. The NMR spectrum also contains the following signals: singlet at 0.97 ppm (6 H) of gem-dimethyl groups in a six-membered ring, multiplet at 2.07 ppm (2 H, methylene protons in a $C = C-CH_2$ fragment), doublets at 4.55and 3.30 ppm, J = 14 Hz, 1 H each (the methylene protons in a $C = C-CH_2-O$ fragment).

The facts obtained do not exclude the possibility that ulugbin has the structure



EXPERIMENTAL

The UV spectra were taken on a Hitachi spectrophotometer (in ethanol), the IR spectra on a UR-20 instrument (tables with KBr), the mass spectra on an MKh-1303 mass spectrometer, and the NMR spectra on a JNM-14 100/100 MHz instrument. The chemical shifts are given in the δ scale from the signal of HMDS taken as 0. The elementary analyses of the substances corresponded to the calculated figures.

The purity of the substances and the progress of the reactions were checked by thin-layer chromatography in Silufol in the toluene–ethyl acetate–ethanol (2 : 1 : 1) (1) and chloroform–methanol (9 : 1) (2) systems, and the chromogenic agents were a 1% ethanolic solution of ferric chloride and a solution of diazotized p-nitroaniline.

Isolation of the Acid Fraction. The dried and comminuted herbage (24 kg) was steeped with 150-liter portions of ethanol three times. The ethanolic extract was evaporated and the residue was acidified with 20% HCl and treated with ether (3 × 1 liter). The ethereal extract was evaporated and the residue (90 g, 0.38%) was treated successively with 2% sodium bicarbonate solution and 2% caustic soda solution. The sodium carbonate and caustic alkali extracts were acidified with 10% hydrochloric acid, and the acids and phenols were extracted with ether.

After the elimination of the solvents, two fractions were obtained: an acidic fraction A and a phenolic fraction B. Fraction A consisted of a brown resinous mass with R_f 0.40, 0.36, 0.23, 0.15 (yield 31.62 g; 0.13%). Fraction B consisted of a dark brown resinous mass with R_f 0.40, 0.36, 0.23, 0.15 (traces) and 0.17 (revealed only with vanillin/sulfuric acid); yield 6.4 g; 0.026%.

Preparation of the Methyl Esters of the Acids. A solution of 20 g of fraction A in 100 ml of methanol containing 5 ml of concentrated sulfuric acid was heated on the water bath for 1 h. After the end of the reaction, the solvent was distilled off, the residue was dissolved in ether, and the solution was washed with water. This gave a brown resin C (17 g) containing four substances, with R_f 0.51, 0.40, 0.30, and 0.26, insoluble in sodium carbonate solution and caustic alkalis.

Methyl Fumarate (IV). Resin C was transferred to a chromatographic column filled with KSK silica gel (70 × 16 cm), and the substance was eluted with cyclohexane. Elimination of the solvent gave 1.42 g (7.1%) of a crystalline substance with mp 102°C, M^+ 144, showing no depression of the melting point in admixture with an authentic sample.

Methyl Caffeate (III). When the column was eluted with chloroform, elimination of the solvent from the eluates gave 0.25 g (1.25%) of a crystalline substance with mp 157°C, M^+ 194, R_f 0.51 showing no depression of the melting point in admixture with an authentic sample.

Methyl Ulugbate (II). When the column was eluted with chloroform–ethyl acetate (9 : 1) and the solvents were distilled off, a crystalline substance was obtained with mp 228°C, R_f 0.36; yield 0.51 (2.54%).

Diacetate of (II). A solution of 0.1 g of the substance in 3 ml of pyridine was treated with 2 ml of acetic anhydride and the mixture was left for 12 h. After elimination of the solvent, the residue was recrystallized from acetone to form colorless crystals with mp 247°C, R_f 0.36.

Pentamethyl Derivative of (II). A solution of 0.1 g of the substance in 3 ml of acetone was treated with 6 ml of an ethereal solution of diazomethane. The solvent was evaporated off at room temperature under vacuum. This gave a colorless crystalline powder with mp 218-220°C, M^+ 430, R_f 0.94.

Isolation of Methyl Ulugbekate (I). Elution of the column with chloroform–ethyl acetate (4 : 1) gave 1.02 g of an amorphous substance (yield 6%) which could not be crystallized (it was purified by precipitation with chloroform from methanolic solutions); M^+ 342, R_f 0.26.

The tetraacetate of (I) was obtained by the method given for (II). Yellow amorphous substance with R_f 0.9.

Isolation of Ulugbin (IX). On standing, fraction B deposited a precipitate which, after recrystallization from hexane–methanol, consisted of colorless scale-like crystals with mp 215°C, R_f 0.17.

SUMMARY

From the herbage of Ulugbekia tschimganica (B. Fedtsch.) Zak two new phenolcarboxylic acids have been isolated in the form of their methyl derivatives: methyl ulugbekate $C_{19}H_{18}O_6$ (I) and methyl ulugbinate acid $C_{20}H_{22}O_7$ (II), mp 228°C.

It has been established that (I) most probably has the structure of 1,5-bis(3',4'-dihydroxyphenyl)-3-methoxycarbonylpent-1-ene and (II) that of 1,5-bis(2',4'-dihydroxyphenyl)-3-methoxycarbonylpent-1-ene and (II) that of 1,5-bis(2',4'-dihydroxyphenyl)-3-methoxycarbonyl-4-methoxypent-2-ene.

The presence of fumaric, caffeic, and chlorogenic acids, and also of mono and dimethyl fumarates has been established chromatographically.

The roots have yielded a new phenolic terpenoid, $C_{16}H_{20}O_4$, for which 3-(2,4-dihydroxyphenyl)-1-(5,5-dimethyltetrahydropyran-2-ylidene)propene has been suggested as one of the most likely structures.

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SOME PRODUCTS OF THE COUPLING OF GOSSYPOL WITH DIAZOTIZED AMINES

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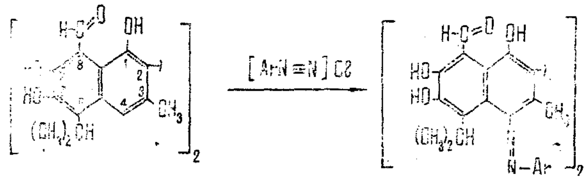
UDC 665.3/35:667.71

In order to find methods for the practical utilization of gossypol, we have obtained some products of the coupling of gossypol with diazotized amines which are capable of dyeing cotton fabrics.

Usually, in the reaction of diazonium salts with aromatic amines or phenols the azo group enters the para or ortho position to the amino or hydroxy group [1]. Markman and Zalesov have succeeded in introducing a diazo group into the gossypol molecule by coupling with diazonium salts [2].

Since the gossypol molecule contains two unsubstituted hydrogen atoms (4,4') present in the para position to the 1,1'-hydroxyls, the coupling reaction of gossypol with aromatic diazo compounds should take place with the formation of a symmetrical compound:



Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 607-609, September-October, 1976. Original article submitted February 11, 1976.