SUMMARY

It has been established that the oil of the ripe seeds of the cotton plant of variety 108-F contains 9,10-epoxyoctadec-cis-12-enoic (I) and 12,13-epoxyoctadec-cis-9-enoic (II) acids. In addition, 9-hydroxyoctadeca-cis,trans-10,12-dienoic (III) and 13-hydroxyoctadeca-cis,trans-9,11-dienoic (IV) acids, found previously in other oils, have been detected.

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NEW TERPENOID COUMARINS FROM Ferula tadshikorum

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Ferula tadshikorum M. Pimem. – a species separated [1] from the close species F. foetidissima – is one of the species of the genus Ferula L. that is widely distributed in Central Asia. Ferula tadshikorum is endemic to southern Tadzhikistan, southern Uzbekistan, and eastern Turkmenia. A qualitative comparison of extracts of the two species (TLC on Silufol) has shown [2] that they differ in chemical composition.

From an acetone extract of the fruit of F. tadshikorum we have isolated two new coumarin derivatives – $C_{24}H_{30}O_4$, mp 68-70°C, Rf 0.35 (I), and $C_{26}H_{32}O_6$, liquid, Rf 0.25 (II), which we have called, respectively, tadzhiferin and tadzhikorin. Both compounds are unbelliferone derivatives (characteristic UV spectra).

The IR spectrum of (I) (Fig. 1a) has two bands in the region of OH stretching vibrations – a narrow band at 3520 cm^{-1} and a broad band at 3300 cm^{-1}, and at the same time the carbonyl band is split into two components – 1730 and 1707 cm^{-1}. The spectrum of a solution of (I) in dioxane has only one hydroxy band (3500 cm^{-1}) and one carbonyl band (1746 cm^{-1}). Thus, the splitting of the bands in the IR spectrum taken in paraffin oil arises through the formation of a hydrogen bond between the OH and C = O groups in the crystalline state; in dioxane solution there is no such bond, and there is no splitting of the bands. Consequently, tadzhiferin is an ether of umbelliferone and a sequesterpene alcohol the residue of which contains a free hydroxyl.

The structure of the terpenoid residue is determined unambiguously from the NMR spectrum of (I) (Fig. 2a). In addition to the signals of a 7-monosubstituted coumarin nucleus, the spectrum contains the signals of four methyl groups on double bonds, three methylene groups with double bonds in the α position, a $-CH_2-O-Ar$ group, three vinyl protons, the proton of a hydroxy group, and one proton geminal to the hydroxyl. The assignment of the latter signal was confirmed by its downfield shift by 1.19 ppm on acetylation. It follows from the empirical formula of the terpenoid residue ($C_{15}H_{25}O-$) and the presence of three double bonds in it that it has a linear structure. The use of the double-resonance and INDOR methods enabled the positions of the individual structural elements in this chain to be determined unambiguously. The signals of all the methyl groups in the spectrum are broadened as the result of allyl interaction with vinyl protons. Under conditions of double resonance at an H_2 frequency corresponding successively to the resonance of the vinyl protons, a contraction of the signals of the methyl groups and an increase in their peak intensity was observed. At the same time, irradia-

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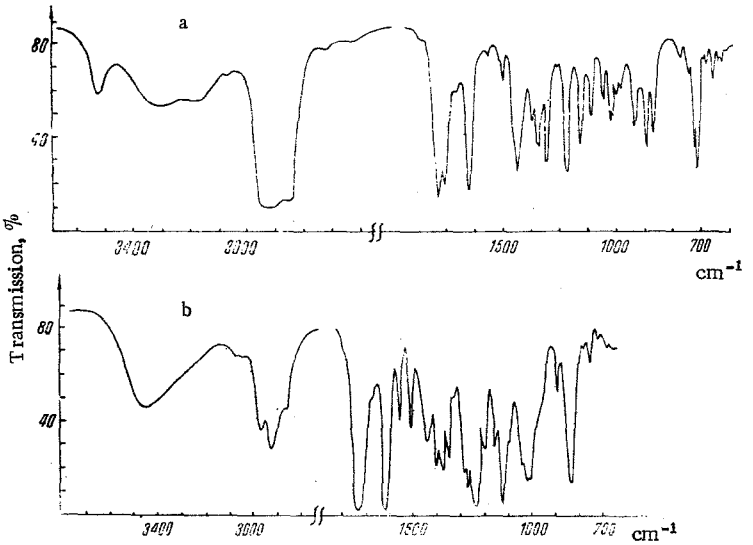
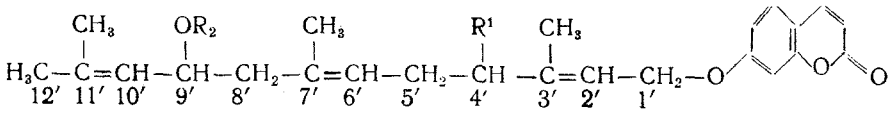


Fig. 1. IR spectra of tadzhiferin (a) (mull in paraffin oil) and tadzhikorin (b) (film of the substance).

tion of the doublet at 5.15 ppm led to an increase in the peak intensity of the signal of the two methyl groups (1.66 ppm) which shows the presence of a $(CH_3)_2C = CH-CH$ grouping. It was shown by the INDOR method that the proton geminal to the hydroxyl interacts, on the one hand, with the vinyl proton of the grouping mentioned above and, on the other hand, with the two protons of a methylene group. In tadzhiferin acetate (III), the latter give two quartets with J_{gem} = 14.0 Hz and J_{vic} = 6.0 and 8.0 Hz. It follows from these facts that there is a double bond adjacent to the methylene group and there is no vinyl proton in the α position. In this way, we may conclude that the molecule of (I) contains the following structural fragment:

$$(CH_3)_2C=CH-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-.$$

From the INDOR spectra on the components of the doublet from the $ArO-CH_2$ group (4.58 ppm) it follows that this group interacts with a vinyl proton (triplet at 5.51 ppm) which, in its turn, exhibits allyl interaction with one of the methyl groups (1.81 ppm). This shows the presence in (I) of another structural fragment $Ar-O-CH_2-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-$. The two remaining methylene groups can only join the two fragments, from which it follows that tadzhiferin has the structure of 7-(9'-hydroxy-3',7',11'-trimethyldodeca-2',6',10'-trienyloxy) coumarin (I).



I. $R^1 = R^2 = -H$

II. $R^1 = -OCOCH_3$; $R^2 = -H$

III. $R^1 = -H$; $R^2 = -CO-CH_3$

IV. $R^1 = -OH$; $R^2 = -H$

V. $R^1 = -OCOCH_3$; $R^2 = -CO-CH_3$

Tadzhikorin (II) also contains a free hydroxy group (band at 3460 cm^{-1} in the IR spectrum; Fig. 1, b); the NMR spectrum of (II) (Fig. 2b) is similar to that of tadzhiferin (I) with the only difference that in place of the signal of one CH_2 in (I) the spectrum of (II) has the signals of a $-CH-OCOCH_3$ grouping (one-proton triplet at 4.94 ppm, ΣJ = 14 Hz, and three-proton singlet at 1.95 ppm). The hydrolysis of (II) gave a diol (IV), and the acetylation of (II) led to an acetate (V). Analysis of the NMR spectra of (II), (IV), and (V) performed by double-

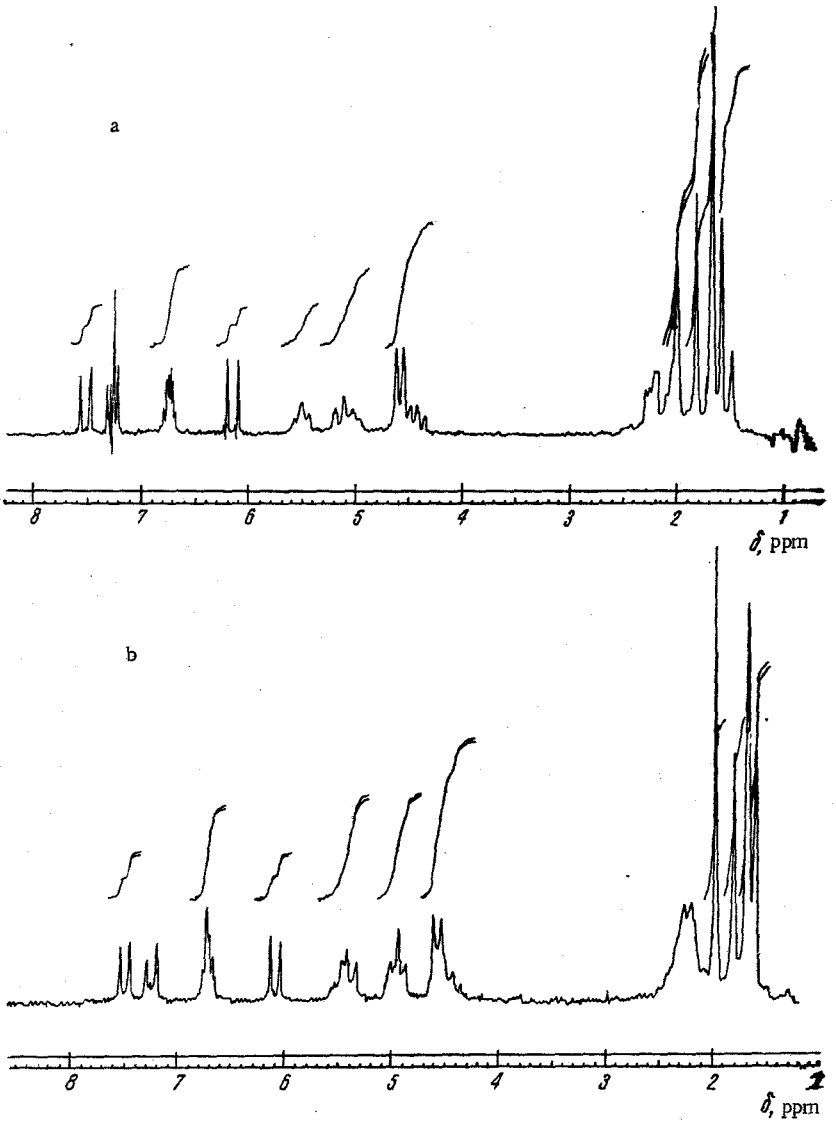


Fig. 2. NMR spectra of tadzhiferin (a) and tadzhikorin (b).

resonance methods (collapse, INDOR) enabled the structures of these substances to be determined. The presence of the fragments $Ar-O-CH_2-CH=C(CH_3)-$ and $(CH_3)_2C=CH-CH(OH)-CH_2-C(CH_3)=CH-$ in (IV) was shown by the same method as for (I). In the spectrum of (IV) there is a one-proton triplet at 3.92 ppm with $\Sigma J = 14$ Hz (CH−OH), shifting in (V) to 4.94 ppm ($CH-OCOCH_3$). The multiplicity of this signal shows that there is a methylene grouping adjacent to the −CH−OH− group; there are no other vicinal protons. The only possible position for the second hydroxy group in (IV) (acetoxy group in (II)) is the 4' position, and tadzhikorin has the structure of 7-(4'-acetoxy-1'-hydroxy-3',7',11'-trimethyldodeca-2',6',10'-trienyloxy)coumarin (II), and deacetyltadzhikorin and acetyltadzhikorin are represented by structures (IV) and (V), respectively.

Thus, the predominance in F. tadshikorum of tadzhikorin and tadzhiferin, in contrast to F. foetidissima which contains conferone and conferol, confirms the desirability of isolating F. tadzhikorum as an independent species.

EXPERIMENTAL

The UV spectra of solutions of the substances in ethanol were taken on a Hitachi EPS-3T spectrophotometer, the IR spectra on a UR-10 spectrometer, and the NMR spectra on a Varian HA-100D spectrometer. The thin-layer chromatography of the substances was performed on Silufol in the petroleum ether−ethyl acetate

(1 : 1) system. The elementary analyses of the substances corresponded to the calculated figures. The melting points of the substances were determined in capillaries on a BIT-1 block with an electric heater.

Isolation of Tadzhiferin and Tadzhikorin. The concentrated acetone extract obtained from 3 kg of the comminuted fruit of F. tadzhikorum collected in the environs of the village of Vaisun, Surkhandar'yaoblast (UzSSR) (49.5 g) was mixed with 100 g of neutral alumina (activity grade II) and transferred to a column containing 300 g of alumina (90 × 68 mm). Elution was performed with petroleum ether and mixtures of petroleum ether with increasing amounts of ethyl acetate, 300-ml fractions being collected. The residue after the evaporation of fractions 23-30 (1.95 g) (elution with a 1% solution of ethyl acetate in petroleum ether), in which a substance with Rf 0.35 predominated, was dissolved in methanol, the precipitate that deposited was filtered off, the filtrate was evaporated, and the evaporation residue was crystallized from a mixture of diethyl ether and petroleum ether. This gave 0.32 g of crystalline substance (I), $C_{24}H_{30}O_4$, mp 68-70°C, $[\alpha]_D^{23}$ +8° (c 0.94; $CHCl_3$), Rf 0.35 (tadzhiferin).

UV spectrum λ_{max} 243, 251, 295, 325 nm (log ε 3.65, 3.51, 3.92, 4.18, respectively), λ_{min} 260 (log ε 3.30).

NMR spectrum (CCl_4–$CDCl_3$ (10 : 1), 20°C, 0 – TMS; δ, ppm; intensity, multiplicity, J, Hz): 6.15, 1H, d, 9.5 (3–H); 7.53, 1H, d, 9.5 (4–H); 7.26, 1H, d, 8.8 (5–H); 6.74, 1H, q, 8.8, 2.5 (6–H); 6.74, 1H, d, 2.5 (8–H); 4.58, 2H, d, 6.8 (1'–CH_2); 5.51, 1H, t, 6.8 (2'–CH); 1.81, 3H, s (3'–C–CH_3); 1.96–2.20, 4H, m (4'–CH_2, 5'–CH_2); 5.04, 1H, t, 6.0 (6'–CH); 1.58, 3H, s (7'–C–CH_3); 2.00–2.30, 2H, m (8'–CH_2); 4.46, 1H, m (9'–CH); 1.48, 1H, s (0–H); 5.15, 1H, d, 9.0 (10'–CH); 1.66, 6H, s [11'–$C(CH_3)_2$].

The residue after the evaporation of fractions 39-51 (elution with a 2% solution of ethyl acetate in petroleum ether) (1.9 g), in which a substance with Rf 0.25 predominated, was treated with methanol, the precipitate that deposited was separated off, and the residue after evaporation of the filtrate (1.5 g) was mixed with 3.0 g of neutral alumina (activity grade II) and chromatographed on a column containing silica gel L 40-100 μ (180 × 15 mm), elution being performed with chloroform–petroleum ether (8 : 2) with the collection of 20-ml fractions. Fractions 8-11, after evaporation, yielded 0.53 g of the oily substance (II), $C_{26}H_{32}O_6$, $[\alpha]_D^{23}$ +15° (tadzhikorin).

UV spectrum: λ_{max} 243, 251, 325 nm (with log ε 3.65, 3.53, 4.19, respectively); λ_{min} 260 (log ε 3.59).

NMR spectrum (CCl_4, 20°C, 0 – TMS; δ, ppm; intensity, multiplicity, J, Hz): 6.09, 1H, d, 9.5 (3–H); 7.48, 1H, d, 9.5 (4-H); 7.24, 1H, d, 8.8 (5-H); 6.71, 2H, m (6-H, 8-H); 4.57, 2H, d, 6.5 (1'-CH_2); 5.67, 1H, t, 6.5 (2'-CH); 1.79, 3H, s (3'-C–CH_3); 4.94, 1H, t, ΣJ = 14.0 (4'-H); 1.95, 3H s ($OCOCH_3$); 2.05-2.45, 4H, m (5'-CH_2), (8'-CH_2); 4.94, 1H, t, ΣJ = 16.0 (6'-H); 1.59, 3H, s (7'-C–CH_3); 4.46, 1H, m (9'-CH); 5.37, 1H, d, 8.0 (10'-CH): 1.64, 3H, s [11'-$C(CH_3)_2$].

Acetylation of Tadzhiferin. Tadzhiferin (43 mg) was kept in 1 ml of a 1 : 1 mixture of acetic anhydride and pyridine at 20°C for 20 h, and then the reaction mixture was diluted with 10 ml of water and extracted with ether (5 × 2 ml), the ethereal solution was washed with 8% HCl (5 × 2 ml), and then with water (5 × 3 ml), dried with anhydrous sodium sulfate, and evaporated. This gave 35.1 mg of tadzhiferin acetate (III), $C_{26}H_{32}O_5$, mp 48-50°C, Rf 0.55.

NMR spectrum (CCl_4, 20°C, 0 – TMS; δ, ppm, intensity, multiplicity, J, Hz): 6.16, 1H, d, 9.5 (3-H); 7.54, 1H, d, 9.5 (4-H); 7.28, 1H, d, 8.8 (5-H); 6.74, 1H, q, 8.8, 2.5 (6-H); 6.73, 1H, d, 2.5 (8-H); 4.56, 2H, d, 6.8 (1'–CH_2) 5.47, 1H, t, 6.8 (2'-CH: 1.79, 3H, s (3'-C–CH_3); 1.95-2.10, 4H, m (4'-CH_2, 5'-CH_2); 5.05, 1H, m (6'-CH); 1.57, 3H, s (7'-C–CH_3); 2.20, 1H, q, 14.0, 6.0 and 2.40, 1H, q, 14.0, 8.0 (8'-CH_2); 5.65, 1H, m (9'-CH); 1.93, 3H, s ($OCOCH_3$); 5.08, 1H, d, 10.0 (10'-CH); 1.70, 3H, s and 1.71, 3H, s [11'-$C(CH_3)_2$].

Hydrolysis of Tadzhikorin. A solution of 1.6 g of tadzhikorin in 11 ml of a 5% methanolic solution of caustic potash was left at 20°C for 2 h, and then 20 ml of water was added and the mixture was acidified with hydrochloric acid and extracted with chloroform (3 × 25 ml). The chloroform solution was washed with 5% sodium carbonate solution (3 × 5 ml) and with water (4 × 5 ml), dried with anhydrous sodium sulfate, filtered, and evaporated in vacuum. The residue (300 mg) was chromatographed on a column (150 × 12 mm) with silica gel L 40-100 μ, and the substances were eluted with chloroform. The fractions containing, according to TLC, a substance with Rf 0.05 were combined and evaporated, and the residue was crystallized from a mixture of diethyl ether and petroleum ether (1 : 1). This gave 182 mg of deacetyltadzhikorin (IV), $C_{24}H_{30}O_5$, mp 65-66°C, Rf 0.05.

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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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.

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