CONCLUSION

The composition of the phenolic triglycerides isolated from ethanolic extracts of propolis, aspen buds, and wheat roots has been investigated.

Two new phenolic triglycerides have been identified: 2-acetyl-1,3-diferuloylglycerol and 2-acetyl-3-p-coumaroyl-1-feruloylglycerol.

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A STUDY OF THE COUMARINS OF *Haplophyllum obtusifolium*. THE STRUCTURE OF OBTUSIDIN AND OF OBTUSIPRENIN

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The epigeal part of *Haplophyllum obtusifolium* Ledeb has yielded scopoletin and the following new coumarins: obtusidin, $C_{15}H_{16}O_5$, mp 165-167°C, and obtusiprenin, $C_{15}H_{16}O_5$, mp 139-140°C. It has been established on the basis of chemical and spectral characteristics that obtusidin has the structure of 3-(1'-1'-dimethylallyl)-7,8-dihydroxy-6-methoxycoumarin, and obtusipernin that of 5-(3',3'-dimethylallyl)-7,8-dihydroxy-6-methoxycoumarin.

Previously, we [1, 2] and other [3] workers have isolated a number of coumarins from *Haplophyllum obtusifolium* Ledeb. Conttinuing work in this direction, we have studied the coumarins of the epigeal part of the plant collected on the Ustyurt plateau in the fruit-bearing period on August 16, 1981. The ground raw material was repeatedly extracted with ethanol. The concentrated ethanolic extract was chromatographed on a column of silica gel, as a result of which we isolated 7-(3',3'-dimethylallyloxy)-6-methoxycoumarin, obtusinin, obtusoside [1], fraxetin, capensin, obtusicin [2], and another three coumarins not previously detected.

Coumarin (I) with mp 201-203°C was identified by its spectral characteristics and by a direct comparison with an authentic sample as scopoletin.

Coumarins (II) with mp 165-167°C, and (III), with mp 139-142°C proved to be new, and we have called them obtusidin and obtusiprenin, respectively. The two substances have the same composition $C_{15}H_{16}O_5$, M^+ 276. According to their IR spectra and a positive reaction with a solution of $FeCl_3$, coumarins (II) and (III) contain phenolic hydroxy groups. The PMR spectrum of (II) contains the signals of protons due to the presence of CH_3O (3.72 ppm), H-5 (6.58 ppm, s), H-4 (7.50 ppm, s), and a 1',1'-dimethylallyl grouping [4-7]. The absence of substituent at C-5 was confirmed by the value of the chemical shift of H-4 [7, 8]. Consequently, obtusidin is a 3,6,7,8-tetrasubstituted coumarin and contains two phenolic hydroxy groups.

When it was treated with acetic anhydride in pyridine, obtusidin formed a diacetyl derivative (IX) (2.27 and 2.33 ppm, 3 H each, 2 Ar-OCOCH_3, in the PMR spectrum). The formation of a methylenedioxy derivative (V) as the result of the reaction of (II) with CH_2I_2

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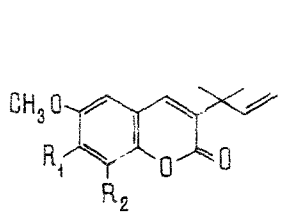
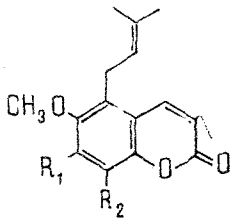
in the presence of K_2CO_3 showed the ortho arrangement of the phenolic hydroxyls.

Obtusidin gives a positive Gibbs reaction [9] and the hydroxy groups therefore occupy the C-7 and C-8 positions. The UV spectra of (II) and (III) are basically identical with the spectrum of fraxetin in both neutral and alkaline media. This shows the similar arrangement of the oxygen-containing substituents in the molecules of these coumarins. Consequently, the CH_3O group must occupy the C-6 position and the 1',1'-methylallyl group the C-3 position and, therefore, obtusidin has the structure of 3-(1',1'-dimethylallyl)-7,8-dihydroxy-6-methoxycoumarin (II). The proposed structure was confirmed by the performance of the passage from capensin to obtusidin as the result of a Claisen rearrangement [10, 11]. In this process fraxetinwas formed as well as obtusidin.





II. $R_1=R_2=OH$ III. $R_1=R_2=OH$

IV. $R_1=R_2=OCOCH_3$ VI. $R_1=R_2=OCOCH_3$

V. R_1, $R_2=CH_2O_2$ VII. $R_1=R_2=OCH_3$

VIII. R_1, $R_2=CH_2O_2$

Obtusiprenin is a 5,6,7,8-tetrasubstituted coumarin, since, with the exception of H-3 (6.18 ppm, d, 10 Hz), and H-4 (7.75 ppm, d, 10 Hz) no signals whatever of aromatic protons were detected in its NMR spectrum. The spectrum also shows the signals of the protons of a methoxy group and of a 3',3'-dimethylallyl group attached to an aromatic nucleus [7, 12]. The two remaining substituents are apparently hydroxy groups. In actual fact, the acetylation of (III) led to the diacetyl derivative (VI) (2.30 and 2.32 ppm, 3 H each, 2 Ar—$OCOCH_3$), and methylation with CH_3I in the presence of K_2CO_3 led to the dimethyl ether (VII).

The ortho arrangement of the hydroxy group was confirmed by the preparation of the methylenedioxy derivative (VIII). The chemical shift of the signal of the H-4 proton shows the absence of an oxygen-containing substituent at C-5 [7, 8]. Consequently, this position is occupied by the prenyl group.

On the basis of the facts given, the structure of 5-(3',3'-dimethylallyl)-7,8-dihydoxy-6-methoxycoumarin is proposed for obtusiprenin.

EXPERIMENTAL

The conditions of recording the spectra have been given previously [1]. The individuality of the substances was checked by thin-layer chromatography on Silufol UV-254 in the following systems: 1) chloroform—petroleum ether—ethanol (8:2:2), and 2) chloroform—petroleum ether (1:1).

Isolation of the Coumarins. The comminuted plant (3.4 kg) was extracted five times with ethanol and then five times with 45% ethanol. The extracts were concentrated in vacuum. This gave 320 g of ethanol-extracted and 340 g of aqueous-ethanol-extracted material. The ethanol-extracted material was chromatographed on a column of silica gel (1:15). The substances were extracted with petroleum ether and with petroleum ether—chloroform mixtures having increasing amounts of the latter. This yielded 7-(3',3'-dimethylallyloxy)-6-methoxycoumarin (0.19 g), capensin (5.77 g), obtusicin (8.76 g), scopoletin (0.15 g), obtusinin (6.64 g), fraxetin (4.92 g), and obtusoside. A solvent mixture with the 2:8 composition eluted a mixture of two coumarins which were separated by recrystallization from chloroform. This gave 0.45 g (0.012% on the weight of the plant) of obtusidin and 0.8 g (0.023%) of obtusiprenin.

Obtusidin, $C_{15}H_{16}O_5$, M^+ 276, mp 165-167°C (chloroform), E_f 0.74 (system 1). $\lambda_{max}^{C_2H_5OH}$: 230, 259, 345 nm (log ε 4.13, 3.67, 4.07). ν_{max}^{KBr}: 3255-3455 cm^{-1} (OH), 1684 cm^{-1} (C=O of an α-pyrone), 1622 and 1593 cm^{-1} (stretching vibrations of C=C bonds).

PMR Spectrum. (Py-d_5, δ scale, O — HMDS, ppm): 1.42 (6H, br.s, $-C(CH_3)_2$); 3.72 (3 H, s, $-OCH_3$)) 4.87 (d, 18 Hz) and 4.94 (d, 10.5 Hz, $-HC=CH_2$)) 6.15 (1 H, q, J_1 = 10.5 Hz, J_2 =

18 Hz, —CH=CH_2); 6.58 (1 H, s, H-5); 7.50 (1 H, s, H-4).

Obtusiprenin, $C_{15}H_{16}O_5$, M^+ 276, mp 139-140°C (chloroform) R_f 0.69 (system 1). $\lambda_{max}^{C_2H_5OH}$: 229, 262, 339 nm (log ε 4.16, 3.92, 4.07); ν_{max} 3395 cm^{-1} (OH), 1698 cm^{-1} (C=O of an α-pyrone), 1637, 1603, and 1580 cm^{-1} (stretching vibrations of a C=C bond). PMR spectrum (Py-d_5), δ, ppm: 1.53 and 1.65 (br. s, 3 H each, $=C(CH_3)_2$); 3.47 (2 H, d, 6.5 Hz, Ar—CH_2—CH); 3.81 (3 H, s, —OCH_3); 5.04 (1 H, m, —CH_2CH=), 6.18 (1 H, d, 10 Hz, H-3); 7.75 (1 H, d, 10 Hz, H-4).

Acetylation of (II). A solution of 37 mg of (II) in 1 ml of pyridine was treated with 1.5 ml of acetic anhydride. After 24 h, the acetyl derivative was isolated by the usual method. The diacetate (II) has mp 137-137°C. PMR spectrum ($CDCl_3$) δ, ppm: 1.41 (6 H, s, $-C(CH_3)_2$); 2.27 and 2.33 (3 H, s, each, 2 Ar—$OCOCH_3$); 3.73 (3 H, s, —OCH_3); 4.95 (d, 1.75 Hz); and 4.98 (d, 11 Hz, —CH=CH_2); 6.03 (1 H, q, J_1 = 11 Hz, J_2 = 17.5 Hz, —CH—CH_2); 6.73 (1 H, s, H-5); 7.40 (1 H, s, H-4).

The diacetate (III), mp 117-118°C. This was obtained by the method described above. PMR spectrum ($CDCl_3$), δ, ppm: 1.63 and 1.74 (3 H, br. s, each, $=C(CH_3)_2$); 2.30 and 2.32 (3 H, s, each, 2 Ar—$OCOCH_3$); 3.48 (2 H, d, 7 Hz, Ar—CH_2—CH); 4.95 (1 H, m =CH); 6.28 (1 H, d, 10 Hz, H-3); 7.71 (1 H, d, 10 Hz, H-4).

Methylenedioxy-(II). A mixture of 50 mg of (II), 0.5 ml of methylene iodide, and 200 mg of anhydrous potash in 20 ml of acetone was boiled for 6 h (by which time the reaction with $FeCl_3$ solution was negative). Then the reaction mixture was filtered, the filtrate was evaporated, the residue was diluted with water, and the reaction product was extracted with chloroform. The chloroform was distilled off and the residue was recrystallized from ethanol. mp 162-164°C, R_f 0.45 (system 2); M^+ 288.

Methylenedioxy-(III). This was obtained by the method described above. mp 75-76°C, R_f 0.49 (system 2); M^+ 288.

Methylation of (III). A mixture of 50 mg of (III), 150 mg of anhydrous potash, and 0.3 ml of methyl iodide in 15 ml of acetone was boiled for 8 h. Then the reaction mixture was filtered, the filtrate was evaporated, and the residue was dissolved in chloroform and passed through a column of alumina. The eluates were evaporated and an oily substance with R_f 0.49 (system 2) was obtained. The reaction with $FeCl_3$ solution was negative.

PMR spectrum ($CDCl_3$), δ, ppm: 1.64 and 1.76 (3 H, br. s, each, $=C(CH_3)_2$); 3.44 (2 H, d, 7 Hz, Ar—CH_2—CH=); 3.74 (3 H, s, —OCH_3); 3.95 (6 H, 2 —OCH_3); 5.14 (1 H, m, CH_2—CH=); 6.23 (1 H, d, 10 Hz, H-3); 7.67 (1 H, d, 10 Hz, H-4).

Claisen Rearrangement of Capensin. With heating, 0.25 g of capensin was dissolved in 2.5 ml of N,N-dimethylaniline, and the solution was boiled for 6 h. The cooled reaction mixture was diluted with 10% hydrochloric acid, and the reaction product was extracted with chloroform. The residue from the chloroform extract was chromatographed on a column of silica gel in the chloroform—petroleum ether (9:1) solvent system. This led to the isolation of 13 mg of obtusidin and 36 mg of fraxetin.

CONCLUSION

From the epigeal part of *Haplophyllum obtusifolium* have been isolated scopoletin and the new coumarins obtusidin and obtusiprenin. On the basis of chemical transformations and spectral characteristics, it has been shown that obtusidin has the structure of 3-(1',1'-dimethylallyl)-7,8-dihydroxy-6-methoxycoumarin, and obtusiprenin that of 5-(3',3'-dimethylallyl)-7,8-dihydroxy-6-methoxycoumarin.

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FLAVONOIDS OF *Datisca cannabina*.

V. DATISCANIN — A NEW GLYCOSIDE OF DATISCETIN

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The new flavonoid glycoside datiscanin has been isolated from the herbage of *Datisca cannabina* L., and the structure of 2',3,5,7-tetrahydroxyflavone 3-O-β-D-glucopyranoside has been established for it. After datiscin (datiscetin 3-rutinoside), this is the second datiscetin glycoside found in nature.

In the separation of the total flavonoids from the herbage of *Datisca cannabina* L. on polyamide columns [1], fractions of low-polarity glycosides were accumulated, and from these by rechromatography on silica gel a small amount of a new compound which we have called datiscanin (I) has been isolated. A comparison of the physicochemical characteristics of (I) with the properties of the glycoside datiscin (II) known for this plant showed that these compounds had identical UV spectra of PMR spectra differed only in the region of the resonance of the carbohydrate protons (Figs. 1 and 2). In the case of compound (I) in this region there are the signals only of a β-D-glucopyranose residue: δ 5.0 (J = 8 Hz), 3.1-3.8 (6 H). The signals of the aromatic protons were practically identical and were characteristic for the 2'-3,5,7-substitution of the flavone molecule.

The acid hydrolysis of (I) and (II) gave datiscetin (2',3,5,7-tetrahydroxyflavone), which was identified by its spectral characteristics and by comparison with an authentic sample. In contrast to the glycoside (I) and (II), having no long-wave maximum, there is such a maximum in the UV spectrum of the aglycone datiscetin (III) (Fig. 3). A hydrolysate of (I) was found chromatographically (PC, TLC) to contain glucose, while a hydrolysate of (II) contain glucose and rhamnose. Stepwise hydrolysis of (I) performed by Hörhammer's method [2] but at a lower temperature (complete hydrolysis took place at 105-107°C) enabled a product to be obtained which was identical with (I) for which the structure of datiscetin 3-O-β-D-glucopyranoside may be considered to have been demonstrated.

Up to the present time, the only natural glycoside of datiscentin was datiscin (datiscentin 3-rutinoside), which has been detected in *Datisca cannabina*. The new compound datiscanin that we have isolated and studied is the second datiscetin glucoside (datiscentin 3-glucoside).

Datiscanin is difficult to identify chromatographically in the mixture of flavonoids of *D. cannabina* because of the closeness of the R_f values. The presence of datiscanin in the total flavonoid fraction isolated from the herbage of *D. cannabina* was confirmed by high-performance liquid chromatography using an added "marker" (Fig. 4).

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