Acid Hydrolysis of (I). The hydrolysis of 30 mg of (I) was carried out with 5% sulfuric acid as described previously [2]. From the hydrolysis products scopoletin and also D-glucose and L-rhamnose were isolated and identified (PC, GLC).

Acetylation of (I). A mixture of 50 mg of (I), 0.5 ml of pyridine, 2 ml of acetic anhydride was kept at room temperature for 48 h. Then the acetyl derivative was isolated in the usual way. mp 83-84°C (ethanol); yield 42 mg. A mixture with the hexaacetate of (II) gave no depression of the melting point, and their IR spectra were identical.

Alkaline Hydrolysis of (I). A solution of 30 mg of (I) in 4 ml of 0.5% NaOH was left at room temperature for 30 min. Then it was neutralized with 5% hydrochloric acid and was extracted with diethyl ether. The solvent was distilled off and the residue was made alkaline with diethylamine. Diethylammonium acetate was detected by the PC method in the butanol—diethylamine—water (50:0.5:7.5) system. Haploperoside A was isolated from the evaporated aqueous solution after purification on a column of silica gel [2].

SUMMARY

It has been established that haploperoside B isolated from *Haplophyllum perforatum* has the structure of 7-[2-O-(4-acetyl-α-L-rhamnopyranosyl)-β-D-glucopyranosyloxyl]-6-methoxycoumarin.

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FLAVANONES OF *Tanacetum sibiricum*

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UDC 547.972

Six flavanones have been isolated for the first time from Siberian tansy, and two of them have proved to be new compounds.

We have already reported the isolation from Siberian tansy, *Tanacetum sibiricum*, of a flavone and of two flavonols (compounds I-III) [1]. From the same fraction we have now isolated six flavanones (compounds IV-IX), two of which have not been described in the literature.

All the substances isolated formed yellow crystals soluble in acetone and ethanol and gave a pink coloration with sodium tetrahydroborate.

In the IR spectra of the compounds the absorption band of a carbonyl group appears in the 1640-1635 cm^{-1} region, which is somewhat lower than in the corresponding flavones. The main UV absorption maximum of methanolic solutions of the flavanones isolated is at about 290 nm. In the PMR spectra (in CCl_4, $(CD_3)_2CO$, and C_5D_5N), there are the signals of a proton at C_2 and of two protons at C_3, H-2 appearing in the form of a quartet at 5.3-5.6 ppm,

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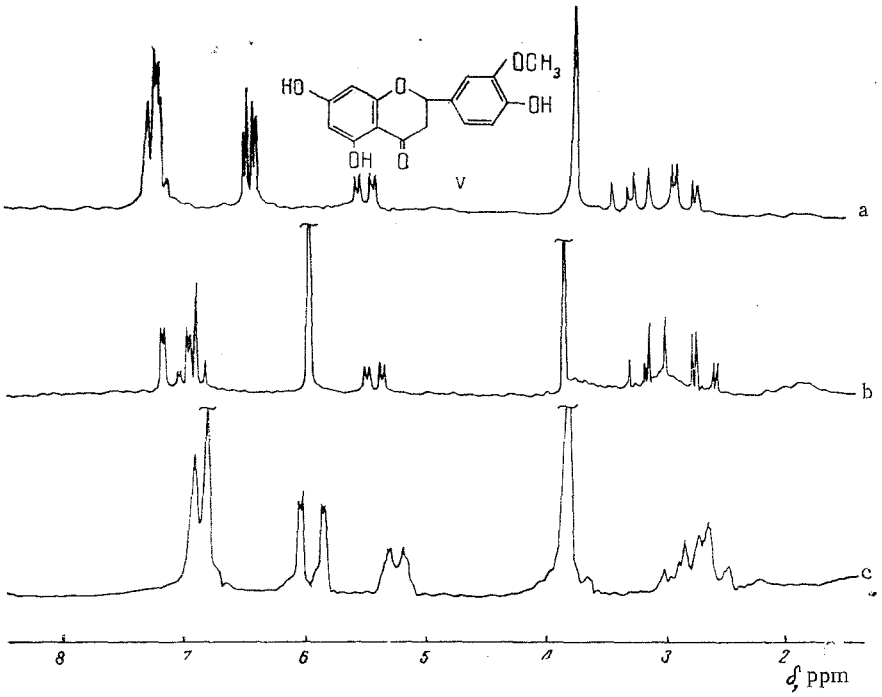


Fig. 1. PMR spectrum of compound (V): a) in C_5D_5N; b) in $(CD_3)_2CO$; c) in CCl_4.

with J_{trans} = 13.0 Hz, and J_{cis} = 3.5 Hz. A proton at C_3, present in the trans position with respect to the proton at C_2, resonates in the 3.1-3.4 ppm region in the form of a quartet with J_{gem} = 17.5 Hz and J_{trans} = 13.0 Hz. The signal of the second proton at C_3, present in the cis position with respect to H-2, has the form of a quartet with J_{cis} = 3.5 Hz and J_{gem} = 17.5 Hz at 2.6-3.0 ppm.

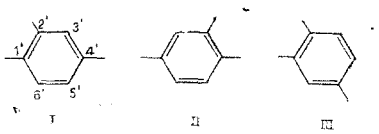
On the basis of the results of UV, PMR, and mass spectra, and also of a comparison with authentic samples, substance (IV) was identified as isosakuranetin and (VII) as naringenin [2].

The PMR spectrum of compound (VI) has two symmetrical doublets with J = 8.5 Hz and an integral intensity of 2 proton units in the weak-field region. This indicates the presence of a substituent in ring B at C_4'. The signal of a methoxy group appears at 3.8 ppm.

A singlet of 1 proton unit located at 6.2 ppm can be assigned either to H-6 or to H-8. Attempts to oxidize the flavanone to a flavone in order to determine the nature of the substitution in ring A led to the formation of a mixture of the starting material with an isomerization product. The Gibbs reaction with the formation of green coloration of the solution showed the presence of an unsubstituted proton at C_8 [3]. Consequently, substituents are present in ring A in the 5, 6, and 7 positions. The mass spectrum of substance (VI) revealed fragments of retrodiene decomposition D with m/z 209, A with m/z 182, and A − 15 with m/z 167, which corresponds to the presence of a methoxy group in ring A [4]. Bathochromic shifts in the UV spectrum of the compound on the addition of NaOAc by 35 nm and of $AlCl_3$ by 20 nm indicate the presence of hydroxy groups at C_5 and C_7 [5]. The substituent in position 6 is obviously a methoxy group. This conclusion is confirmed by the Overhauser effect [6].

Thus, compound (VI) has the structure of 4',5,7-trihydroxy-6-methoxyflavanone.

The structures of compounds (V), (VIII), and (IX) were established by studying the PMR spectra of the substances in various solvents. Analysis of the signals of the protons of the phenyl ring showed that three variants of the mutual positions of the substituents in ring B are possible



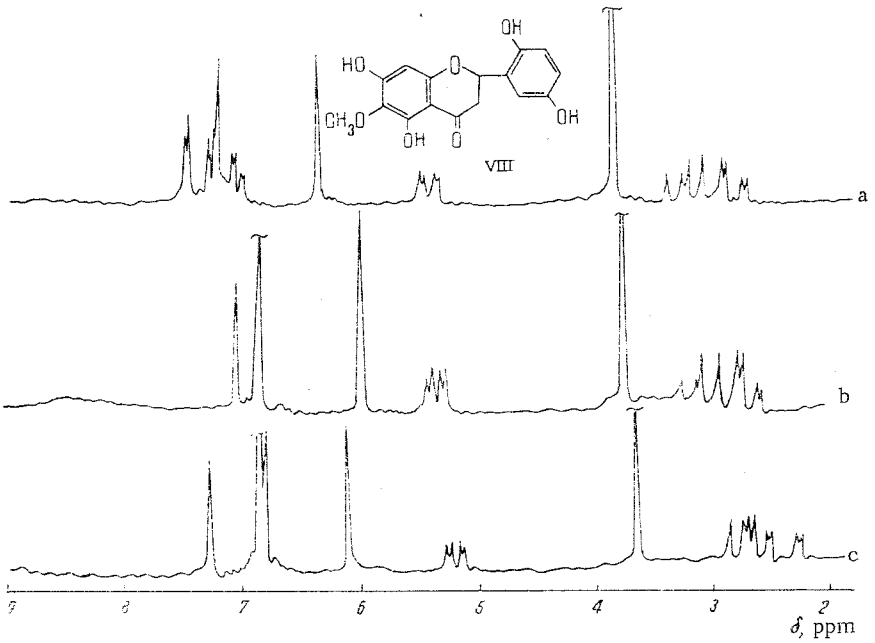
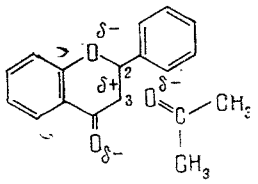


Fig. 2. PMR spectrum of compound (VIII): a) in C_5D_5N; b) in $(CD_3)_2CO$; c) in CCl_4.

The first variant can be excluded from consideration since in this case the doublet with J = 2.5 Hz relating to a proton in the ortho position with respect to which there is an OR substituent should be located in a considerably stronger field than the other signals from ring B (see the spectra of substances (VIII) and (IX) in D-pyridine and that of substance (V) in D-acetone) [7]. The choice between the two remaining variants was made by comparing the spectra in CCl_4 and in D-acetone, and also on the basis of the results of Overhauser effects and of double resonance. On comparing the spectra in CCl_4 and $(CD_3)_2CO$, we directed attention to the fact that in the case of compound (V) two signals are shifted downfield, and in the case of compound (VIII) and (IX) one. The same pattern is observed on passing from CCl_4 to dimethyl sulfoxide.

It is known that both solvents have a tendency to form associates with cations and with the parts of molecules upon which there is a positive charge [8]. For flavanones, such electron-deficient sections are the 2-3 positions



Association leads to the descreening of H-2' and H-6' but does not affect the positions of the other protons. Consequently, from a comparison of the spectra in CCl_4 and $(CD_3)_2CO$ (DMSO) it may be concluded that substituents are present at C_2' and C_6'.

In the PMR spectrum of substance (V) on passing from CCl_4 to $(CD_3)_2CO$ a downfield shift of the signal at 6.88 ppm by 0.25 ppm and of the signal at 6.78 ppm by 0.2 ppm are observed. In the cases of compounds (VIII) and (IX) however, only one signal in each case was shifted downfield, by 0.20-0.22 ppm.

Also in agreement with the results mentioned are those of double resonance, which indicate the existence of spin–spin coupling of the H-2 proton with H-2' and H-6' protons. The constants $J_{2,2'}$ and $J_{2,6'}$ are small (<1 Hz), as a result of which only a broadening of the signals takes place. Under double resonance conditions, the components of the multiplet contract and become higher.

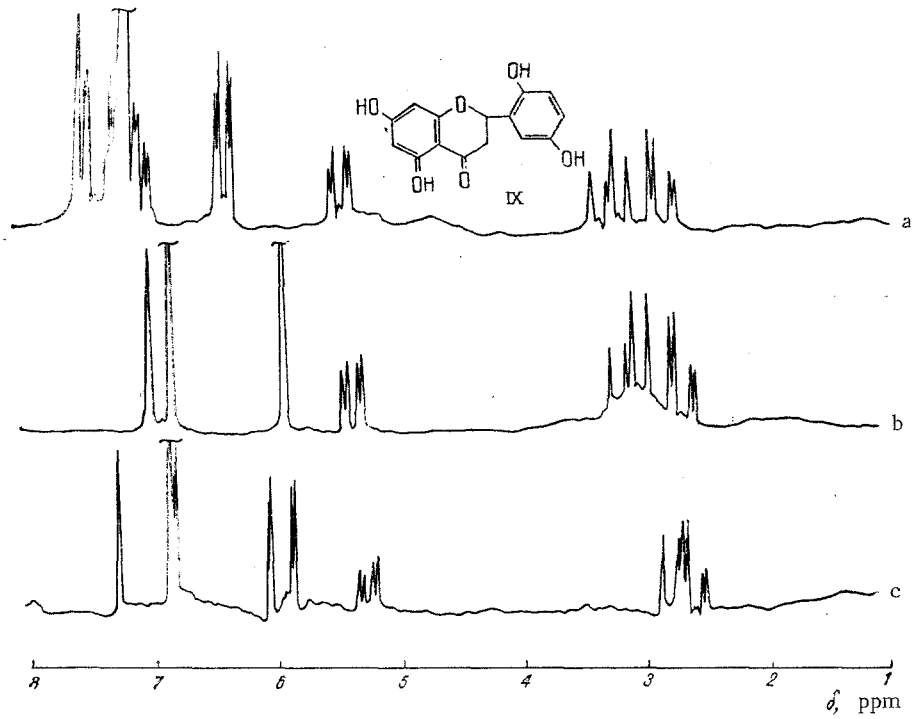


Fig. 3. PMR spectrum of compound (IX): a) in C_5D_5N; b) in $(CD_3)_2CO$; c) in CCl_4.

In compound (V), the form of the signal of the H-2 proton changes when both the H-2' and the H-6' protons are irradiated. In substances (VIII) and (IX), the components of the quartet contract and become higher only when one of the protons (H-6') is irradiated.

Thus, in compound (V) there are no substituents in the 2' and 6' positions (second variant, 3', 4'-substitution), and in compounds (VIII) and (IX) the third variant (2',5'-substitution) is realized.

In the PMR spectrum of substance (V) (D-pyridine) two doublets with J = 2.5 Hz are observed at 6.48 and 6.52 ppm, belonging to H-6 and H-8, and a singlet at 3.78 ppm corresponding to a methoxy group. According to UV and mass spectra, the methoxy group is present in ring B. Of the two possible positions of the methoxyl in the phenyl ring the C_3' position is more in keeping with the large value of the Overhauser effect (30%) for H-2' and its absence for the other protons when the protons of the methoxy group are irradiated with a second field.

Consequently, compound (V) is 4',5,7-trihydroxy-3'-methoxyflavanone (homoeriodictyol).

In the PMR spectrum of compound (VIII) (D-acetone), the singlet at 6.02 ppm can be assigned to H-6 or H-8. The comparatively small difference in the chemical shifts of the protons at C_6 and C_8 in the flavanones does not permit an assignment of the signals to be made. However, the positive Gibbs reaction indicates that the proton at C_8 is not substituted and that the substituent is present at C_6. A singlet at 3.8 ppm belongs to a methoxy group. The positive gossypetone reaction can be explained only by the presence of p-dihydroxy substitution in ring B, and therefore the methoxy group is located in ring A [9]. This is in harmony with the mass spectrum. A bathochromic shift in the UV spectrum on the addition of NaOAc by 38 nm shows the presence of a hydroxy group in position 7, and a shift in the longwave direction by 24 nm on the addition of $AlCl_3$ indicates an unsubstituted hydroxyl at C_5. Consequently, the methoxy group is present at C_6. This conclusion is confirmed by the absence of an Overhauser effect on irradiation of the methoxy group with a second field.

Thus, compound (VIII) has the structure of 2',5,5',7-tetrahydroxy-6-methoxyflavanone.

In compound (IX), the substituents are hydroxy groups located at C_5, C_7, C_2', and C_5'. On the basis of the results of PMR, UV, and mass spectroscopy and the gossypetone reaction, and also of a comparison of physicochemical constants of the substance that we isolated with

those described in the literature, compound (IX) was identified as 2',5,5',7-tetrahydroxyflavanone [10].

EXPERIMENTAL

PMR spectra were taken on a Varian HA-100D instrument at 100 MHz (with tetramethylsilane as internal standard), IR spectra on a UR-20 instrument (paraffin oil), UV spectra on a Hitachi EPS-3T instrument and mass spectra on a Varian CH-8 instrument at 70 eV. Melting points were determined on a Kofler block, and angles of rotation on a Polamat A polarimeter at 546 and 578 nm with recalculation to λ 589 nm. Chromatographic monitoring was carried out by thin-layer chromatography on Silufol in the chloroform–methanol (9:1) system and by paper chromatography on FN-16 paper (15% CH_3COOH and 30% CH_3COOH).

Isolation. The air-dry flowers (500 g) were extracted with low-boiling petroleum ether in a Soxhlet until the coloration of the plant extract has disappeared. After being dried, the meal was re-extracted with methanol. The methanolic extract was left for a day, the amorphous deposit that had formed was filtered off, and the filtrate was evaporated to a viscous extract. The extract was deposited on silica gel L 100/250 μ and was fractionated in a column (18 × 8 cm) successively with petroleum ether, petroleum ether–chloroform, chloroform, and ethanol. The chloroform fraction was evaporated and was deposited for separation on a column of silica gel with elution by chloroform and by mixtures of chloroform and ethanol with increasing concentrations of the latter. The chloroform eluted from the column fractions containing substances (IV) and (I) (fraction 3 and 4), which were subjected to rechromatography and to recrystallization. Chloroform fractions 5-6 and 7-11 gave, by recrystallization, substances (V) and (VI), respectively. Fractions 14-25 yielded substance (II). A mixture of 4% of methanol with chloroform eluted the substances (VII) (fractions 26-27), (III) and (VIII) (fraction 29), and (IX) (fraction 32). The substances were purified by rechromatography and recrystallization from aqueous ethanol.

Substance (IV) had the composition $C_{16}H_{14}O_5$, M^+ 286 and formed white crystals with mp (decomp.) 195°C; $[\alpha]_D^{20}$ − 15.7° (C 0.3; acetone).

UV spectrum, λ_{max} (nm): MeOH 226, 290; + MeONa 250 sh, 325; + $AlCl_3$ 223, 312; + $AlCl_3$+ HCl 223, 311; NaOAc 250 sh, 330; NaOAc+H_3BO_3 292, 325 sh, 325; sh.

PMR spectrum (ppm) in $(CD_3)_2CO$: 7.5 (d, 8.5 Hz, 2 H) — H-2', H-6'; 7.0 (d, 8.5 Hz, 2H) — H-3', H-5'; 5.95 (s, 2H) — H-8, H-6; 5.5 (q, J_{cis} = 3.5 Hz, J_{trans} = 13.0 Hz, 1H) — H-2; 3.85 (s, 3H) — OCH_3; 3.25 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.75 (q, J_{cis} 3.5 Hz; J_{gem} = 17.5 Hz, 1H) — H-3-cis; in C_5D_5N: 7.54 (d, 8.5 Hz, 2H) — H-2', H-6'; 7.0 (d, 8.5 Hz, 2H) — H-3', H-5'; 6.45 (d, 2.5 Hz, 1H) — H-8; 6.35 (d, 2.5 Hz, 1H) — H-6; 5.4 (q, J_{cis} = 3.5 Hz, J_{trans} = 13.0 Hz, 1H) — H-2; 3.68 (s, 3H) — OCH_3; 3.25 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.85 (q, J_{cis} = 3.5 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-cis.

Mass spectrum (m/z): 286, 172, 152, 134.

Substance (V) with the composition $C_{16}H_{14}O_6$, M^+ 302, was a crystalline pale yellow substance with mp 226-227°C (decomp.) $[\alpha]_D^{20}$ − 1.3° (c 0.3; acetone).

UV spectrum (nm), λ_{max}: 229, 288; MeONa 248, 323; $AlCl_3$ 223, 312; $AlCl_3$+HCl 223, 310; NaOAc 288 sh, 303; NaOAc+H_3BO_3 288, 305 sh.

PMR spectrum (ppm) in C_5D_5N: 6.35 (d, 2.5 Hz, 1H) — H-2'; 6.2-6.3 (m, 2H) — H-6', H-5'; 6.52 (d, 2.5 Hz, 1H) — H-8; 6.48 (d, 2.5 Hz, 1H) — H-6; 5.5 (q, J_{cis} = 3.5 Hz, J_{trans} = 13.0 Hz, 1H) — H-2; 3.78 (s, 3H) — OCH_3; 3.25 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.85 (q, J_{cis} = 3.5 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-cis; in DMSO: 7.15 (d, 2.5 Hz, 1H) — H-2'; 6.98 (q, 2.5 Hz, 8.5 Hz, 1H) — H-6'; 6.85 (d, 8.5 Hz, 1H) — H-5'; 5.95 (s, 2H) — H-8, H-6; 5.45 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.86 (s, 3H) — OCH_3; in $(CD_3)_2CO$: 7.13 (d, 2.5 Hz, 1H) — H-2'; 6.98 (q, 2.5 Hz, 8.5 Hz, 1H) — H-6'; 6.79 (d, 8.5 Hz, 1H) — H-5'; 5.92 (s, 2H) — H-8, H-6; 5.4 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.85 (s, 3H) — OCH_3; 3.15 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.65 (q, J_{cis} = 3.5 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-cis; in CCl_4 (TMS ether): 6.88 (br.s, 1H) — H-2'; 6.78 (br.s, 2H) — H-6' and H-5'; 6.04 (d, 2.5 Hz, 1H) — H-8; 5.82 (d, 2.5 Hz, 1H) — H-6; 5.25 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.82 (s, 3H) — OCH_3; 2.7 (m, 2H) — H-3-cis and H-3-trans.

Mass spectrum (m/z): 302, 179, 152, 150.

Substance (VI), with the composition $C_{16}H_{14}O_6$, M^+ 302, formed light yellow crystals with mp 282-286°C $[\alpha]_D^{20}$+2.2° (c 0.8; acetone).

UV spectrum (nm), λ_{max}: MeOH 224, 292, 340 sh., MeONa 246, 327, $AlCl_3$ 224, 316; $AlCl_3$+HCl 224, 314; NaOAc 253 sh., 327; NaOAc+H_3BO_3 294, 330.

PMR spectrum (ppm) in $(CD_3)_2CO$: 7.4 (d, 8.5 Hz, 2H) — H-2', H-6'; 6.9 (d, 8.5 Hz, 2H) — H-3', H-5'; 6.21 (s, 1H) — H-8; 5.42 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.8 (s, 3H) — OCH_3; 3.2 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.75 (q, J_{gem} = 17.5 Hz, J_{cis} = 3.5 Hz, 1H) — H-3-cis.

Mass spectrum (m/z): 302, 209, 182, 120.

Dehydrogenation. A solution of 90 mg of substance (VI) in 3 ml of ethanol was treated with 3 ml of a 10% solution of Na_2SO_3 and 5 ml of a 10% solution of $NaHSO_3$ and the mixture was heated in the water bath at 100°C for 8 h. The course of the reaction was monitored by TLC in system 1 and by PC in system 2. The precipitate formed (22 mg) was filtered off.

PMR spectrum of the reaction product in $(CD_3)_2CO$ (ppm): 7.42 (d, 8.5 Hz) and 7.38 (d, 8.5 Hz) — 2H; 6.9 (d, 8.5 Hz) and 6.86 (d, 8.5 Hz) — 2H; 6.0 and 6.02 s — 1H; 5.55 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz) and 5.45 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz) — 1H; 3.75 s and 3.68 s — 3H; 3.25 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz) and 3.1 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz) — 1H; 2.8 (q, J_{gem} = 17.5 Hz, J_{cis} = 3.5 Hz) and 2.6 (q, J_{gem} = 17.5 Hz, J_{cis} = 3.5 Hz) — 1H.

Substance (VII), with the composition $C_{15}H_{12}O_5$, M^+ 272, formed white crystals with mp 248-252°C.

PMR spectrum in $(CD_3)_2CO$ (ppm): 7.26 (d, 8.5 Hz, 2H) — H-2' and H-6'; 6.9 (d, 8.5 Hz, 2H) — H-3' and H-5'; 5.95 (s, 2H) — H-6 and H-8; 5.42 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.55 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.66 (q, J_{gem} = 17.5 Hz, J_{cis} = 3.5 Hz, 1H) — H-3-cis.

Mass spectrum (m/z): 272, 179, 153, 152, 120.

Substance (VII), with the composition $C_{16}H_{14}O_7$, M^+ 318, formed light yellow crystals with mp 197-203°C (decomp.) $[\alpha]_D^{20}$ (c 0,2; acetone).

UV spectrum (nm), λ_{max}: MeOH 230 sh., 290: MeONa 246, 327; $AlCl_3$ 225 sh., 314, 395; $AlCl_3$ +HCl 223, 313, 395; NaOAc 250 sh., 328 NaOAc+H_3BO_3 292, 327 sh.

PMR spectrum in $(CD_3)_2CO$ (ppm): 7.05 (br.s, 1H) — H-6'; 6.88 (br.s, 2H) — H-3' and H-4'; 6.02 (s, 1H) — H-8; 5.4 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.8 (s, 3H) — OCH_3; 3.1 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.7 (q, J_{gem} = 17.5 Hz, J_{cis} = 3.5 Hz, 1H) — H-3-cis; in C_5D_5N: 7.48 (d, 2.5 Hz, 1H) — H-6'; 7.25 (d, 8.5 Hz, 1H) — H-3'; 7.1 (q, 8.5 Hz and 2.5 Hz, 1H) — H-4'; 6.35 (s, 1H) — H-8; 5.5 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.82 (s, 3H) — OCH_3; 3.2 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.85 (q, J_{gem} = 17.5 Hz, J_{cis} = 3.5 Hz, 1H) — H-3-cis; in CCl_4: (TMS ether): 7.26 (br.s, 1H) — H-6'; 6.85 (br.s, 2H) — H-3' and H-4'; 6.1 (s, 1H) — H-8; 5.2 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.65 (s, 3H) — CH_3; 2.9-2.4 (m, 2H) — H-3-trans and H-3-cis.

Mass spectrum (m/z): 318, 209, 182, 136, 135, 121.

Substance (IX) with the composition $C_{15}H_{14}O_7$, M^+ 288, formed pale yellow crystals with mp 201-203°C (decomp.) $[\alpha]^{20}$ — 1.0° (c 0.1; acetone).

UV spectrum (nm), λ_{max}: MeOH 228 sh., 288, 330 sh.; MeONa 246, 325; $AlCl_3$ 222, 312, 380 $AlCl_3$+HCl 222, 310, 380; NaOAc 290 sh., 325; NaOAc+H_3BO_3 292, 327 sh.

PMR spectrum in $(CD_3)_2CO$ (ppm): 7.05 (br.s, 1H) — H-6'; 6.85 (br.s, 2H) — H-4', H-3' 5.95 (s, 2H) — H-6, H-8; 5.4 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.15 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.7 (q, J_{gem} = 17.5 Hz, J_{cis} = 3.5 Hz, 1H) — H-3-cis; in C_5D_5N: 7.5 (d, 2.5 Hz, 1H) — H-6'; 7.32 (d, 8.5 Hz, 1H) — H-3'; 7.1 (q, 8.5 and 2.5 Hz, 1H) — H-4'; 6.45 (d, 2.5 Hz, 1H) — H-8; 6.35 (d, 2.5 Hz, 1H — H-6; 5.5 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 3.3 (q, J_{trans} = 13.0 Hz, J_{gem} = 17.5 Hz, 1H) — H-3-trans; 2.85 (q, J_{gem} = 17.5 Hz, J_{cis} = 3.5 Hz, 1H) — H-3-cis; in CCl_4 (TMS ether): 6.82 (br.s,

3H) — H-6', H-4', H-3'; 6.0 (d, 2.5 Hz, 1H) — H-8; 5.81 (d, 2.5 Hz, 1H) — H-6; 5.2 (q, J_{trans} = 13.0 Hz, J_{cis} = 3.5 Hz, 1H) — H-2; 2.7 (m, J_{gem} = 17.5 Hz, J_{cis} = 3.5 Hz, J_{trans} = 13.0 Hz, 2H) — H-3-trans, H-3-cis.

Mass spectrum (m/z): 288, 179, 152, 136, 135.

SUMMARY

Six flavanones have been isolated from Siberian tansy for the first time: isosakuranetin, naringenin, homoeriodictyol, 2',5,5',7-tetrahydroxyflavanone, 2',5,5',7-tetrahydroxy-6-methoxyflavanone, and 4',5,7-trihydroxy-6-methoxyflavanone. The last two are new compounds.

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SYNTHESIS AND STRUCTURE OF AMINO ESTERS OF MENTHOL

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The conditions for the acylation of (—)-menthol with monochloroacetyl chloride have been studied. Amino esters of (—)-menthol have been obtained by the nucleophilic replacement of the chlorine in (—)-menthol monochloroacetate by residues of secondary amines. Their properties and their mass, IR, and ^{13}C NMR spectra are described.

Analysis of literature information has shown that of amines of the terpene series particular interest is presented by derivatives of menthol, many of which are biologically active substances with diuretic, antimicrobial, antiviral, and ganglion-blocking properties [1-3].

In the present paper we describe the synthesis and spatial structures of new amino esters of menthol.

The amino esters of menthol were obtained from menthol monochloroacetate and secondary amines in accordance with the following scheme (see next page).

The acylation of (—)-menthol (I) was effected with monochloroacetyl chloride, which is more reactive than the acid and reacts with the alcohol faster.

The reaction gave a 78-80% yield of (—)-menthol monochloroacetate (II) (MMCA). It must be mentioned that the yield of menthol monochloroacetate depends strongly on the solvent used and the temperature conditions. As solvents we used CCl_4, tetrahydrofuran, and benzene.

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