acids were isolated from the combined phospholipids and the individual fractions by cold saponification with a 1 N methanolic solution of caustic potash [3]. The fatty-acid composition was determined by gas chromatography on a UKh-2 chromatograph at 197°C with a column 2.5 m long; the stationary phase was PEGS.

The peaks of the fatty acid methyl esters on GLC were identified by their relative retention times using the linear dependence of the logarithms of these magnitudes on the number of carbon atoms [8, 9].

SUMMARY

The fractional and fatty-acid compositions of the phospholipids of Psoralea seeds have been studied for the first time. It has been established that the total phospholipids consist of phosphatidylcholines, phosphatidylethanolamines, phosphatidylinositols, N-acyl-PEs, N-acyllyso-PEs, lysophosphatidylcholines, and, possibly, phosphatidylglycerols, and also of two unidentified phospholipids.

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COUMARINS OF *Haplophyllum ramosissimum*

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In a study of an alcoholic extract from the epigeal part of *Haplophyllum ramosissimum* collected in the Chardzhou region in the flowering period, we isolated in the individual state three substances (I-III) possessing properties characteristic for coumarin derivatives.

Compound (I) corresponds in its composition, $C_{15}H_{16}O_4$, its mp of 81-82°C, and its IR and PMR spectra to a known coumarin – 7-(3',3'-dimethylalloyloxy)-6-methoxycoumarin [1].

Substances (II) and (III) are new and have not been described in the literature. We have called them ramosin and ramosinin, respectively. Ramosin has the composition $C_{19}H_{22}O_3$ (II), mp 68-69°C, M^+ 298 and gives an IR spectrum typical for 7,8-disubstituted coumarins in which absorption bands are observed at 1730 cm^{-1} (α-pyrone C = O) and 1610, 1570, and 1500 cm^{-1} (–CH = CH– bond in an aromatic ring).

The presence in the PMR spectrum of (II) of four one-proton doublets at 6.16 and 7.54 ppm (J = 10 Hz, H-3 and H-4), and 7.24 and 6.80 ppm (J = 8.5 Hz, H-5 and H-6) confirms the assignment of (II) to the group of 7,8-disubstituted coumarins. The spectrum also contains the signals of the protons of four methyl groups at double bonds (singlets at 1.64, 1.70, 1.74, and 1.80 ppm, 3 H each); of two methylene groups, one of them being attached to oxygen (doublet at 4.60 ppm, J = 7 Hz) and the other being bound directly with an aromatic ring (doublet at 3.50 ppm, J = 7 Hz); and of two olefinic protons (triplets at 5.24 and 5.48 ppm, J = 7 Hz).

On the basis of the facts given, the structure of (II) is determined unambiguously at 8-(3',3'-dimethylallyl)-7-(3',3'-dimethylallyloxy)coumarin, which agrees well with its chemical properties.

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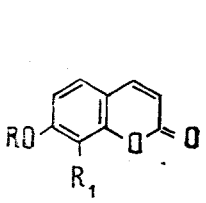


II. R=R$_1$=CH$_2$–CH=C(CH$_3$)(CH$_3$)

IV. R=H; R$_1$=CH$_2$–CH=C(CH$_3$)(CH$_3$)

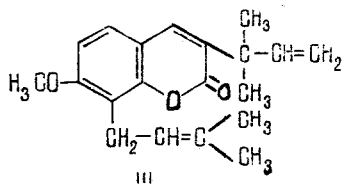
V. R=CH$_3$; R$_1$=CH$_2$–CH=C(CH$_3$)(CH$_3$)

Compound (II) readily underwent acid hydrolysis, forming a substance (IV) with the composition $C_{14}H_{14}O_3$, mp 123-124°C which was shown to be identical with the known coumarin osthenol [2]. The production of osthole (V), $C_{15}H_{16}O_3$, mp 84-85°C, when (IV) was methylated with methyl iodide is a weighty piece of evidence in favor of the structure (II) proposed for ramosin.

Ramosinin (III) has the composition $C_{20}H_{24}O_3$, mp 85-86°C, M^+ 312, and gives an IR spectra in which there are absorption bands at 1710 cm^{-1} (α-pyrone C = O) and 1620, 1570, and 1510 cm^{-1} (vibrations of an aromatic ring). The PMR spectrum of (III) differs sharply from the spectra of (I) and (II). Above all, it lacks the doublets characteristic for the H-3 and H-4 protons, and in place of them in the weak field of the spectrum there are a singlet at 7.50 ppm (1 H) and two doublets at 7.24 and 6.80 ppm (J = 8.5 Hz, 1 H each), which relate to protons in positions 4, 5, and 6, respectively, of the coumarin ring. Consequently, (III) is a trisubstituted coumarin, one of the substituents occupying position 3 in the α-pyrone ring and the other two positions 7 and 8.

The spectrum of (III) also shows the signals of the protons of a methylene group on a double bond in the form of two quartets at 5.10 and 5.19 ppm, J_1 = 18 Hz, J_2 = 2 Hz, of an olefinic proton at 6.20 ppm (quartet, J_1 = 18 Hz, J_2 = 10.5 Hz), and of two methyl groups on a quaternary carbon atom (singlet at 1.46 ppm, 6 H). These facts indicate that one of the substituents is a –C(CH$_3$)(CH$_3$)–CH=CH$_2$ fragment. The presence in the spectrum of two three-proton singlets at 1.66 and 1.82 ppm, of a two-proton doublet at 3.50 ppm, J = 7 Hz, and of a one-proton triplet at 5.20 ppm, J = 7 Hz, shows the presence in the molecule of (III) of a Ar–CH$_2$–CH=C(CH$_3$)(CH$_3$) fragment, as well. A three-proton singlet at 3.86 ppm is assigned to the protons of a methoxy group attached to the aromatic ring in position 7.

Thus, on the basis of what has been said above and taking into account the chemical shifts of the protons of the methyl and methylene groups, we propose as the most probable structure for ramosinin 3-(1',1'-dimethylallyl)-8-(3',3'-dimethylallyl)-7-methoxycoumarin (III). When a 1',1'-dimethylallyl fragment is present in the aromatic ring, the signals of the protons of the methyl groups appear in a weaker field [3, 4] than in the case of (III).



III

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer (in paraffin oil), the PMR spectra on a Varian HA-100 spectrometer (in $CDCl_3$, 0 – HMDS), and the mass spectra on a Hewlett-Packard chromato-mass spectrometer. The melting points were determined on a Kofler block. The elementary analyses of all the compounds corresponded to the calculated figures.

Isolation of the Coumarins. The comminuted epigeal part of the plant under investigation (3 kg) was extracted with ethanol. The extract was concentrated in vacuum and the residue obtained (56 g) was chromatographed on a column of alumina (1700 g, activity grade II). Elution was performed with petroleum ether (frac-

tions 1-12), with mixtures of petroleum ether and chloroform in ratios of 3 : 1 (fractions 13-33), 2 : 1 (fractions 34-42), and 1 : 1 (fractions 43-56), and with chloroform (fractions 57-74). The volume of each fraction was 250 ml.

After evaporation of the solvent and rechromatography, fractions 26-33 yielded a substance with the composition $C_{15}H_{16}O_4$ (I), mp 81-82°C, which was identified as 7-(3',3'-dimethylallyloxy)-6-methoxycoumarin from the similarity of the IR and PMR spectra. Yield 2.1% on the resin.

Fractions 34-46 contained a mixture of two substances (II) and (III), which, after the solvent had been distilled off, were reseparated on a column of alumina (500 g, activity grade III) under the conditions described above. This yielded compound (II), $C_{19}H_{22}O_3$, mp 68-69°C (yield 1.5% on the resin), M^+ 298, and compound (III), $C_{20}H_{24}O_3$ (yield 0.8% on the resin), mp 85-86°C, M^+ 312.

Acid Hydrolysis of (II). A solution of 0.5 g of (II) in 12 ml of glacial acetic acid was treated with 0.2 ml of concentrated sulfuric acid and the mixture was heated on the water bath at 80°C with a reflux condenser for 20 min. After the usual working up, 0.26 g of substance (IV) with the composition $C_{14}H_{14}O_3$, mp 123-124°C, identical with osthenol, was obtained.

Methylation of (IV). To 0.1 g of (IV) in 5 ml of ethanol were added 0.1 g of potassium carbonate and 0.3 ml of methyl iodide, and the mixture was heated on the water bath for three hours. Then it was diluted and was extracted with chloroform. After drying and evaporation of the solvent, substance (V) with the composition $C_{15}H_{16}O_3$, mp 84-85°C, identical with osthole was obtained.

SUMMARY

7-(3',3'-Dimethylallyloxy)-6-methoxycoumarin and two new coumarins – ramosin and ramosinin – have been isolated from the epigeal part of Haplophyllum ramosissimum.

On the basis of IR, PMR, and mass spectroscopy and chemical reactions, the structure of 8-(3',3'-dimethylallyl)-7-(3',3'-dimethylallyloxy)coumarin (II) has been proposed for ramosin and that of 3-(1',1'-dimethylallyl)-8-(3',3'-dimethylallyl)-7-methoxycoumarin (III) for ramosinin.

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