The PMR spectra of laricyl coumarate and laricyl ferulate were taken by G. A. Kalabin.

LITERATURE CITED

1. W. J. Taylor and A. R. Battersby, Oxidation Coupling of Phenols, N. J. (1976), p. 276.
2. S. A. Medvedeva, L. D. Modonova, V. G. Leont'eva, V. N. Glazkova, and N. A. Tyukavkina, Khim. Prirodn. Soedin., 113 (1971).
3. V. G. Leont'eva, L. D. Modonova, and N. A. Tyukavkina, Khim. Prirodn. Soedin., 268 (1973).
4. F. Sundom, Acta Chem. Scand., 22, 854 (1973).
5. L. D. Modonova, V. K. Voronov, V. G. Leont'eva and N. A. Tyukavkina, Khim. Prirodn. Soedin., 165 (1972).
6. V. G. Leont'eva, L. D. Modonova, and N. A. Tyukavkina, Izv. Sibirskogo Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 4, 159 (1974).
7. N. S. Vul'fson, Preparative Organic Chemistry [in Russian], Moscow—Leningrad (1964), p. 621.

FUROCOUMARINS OF *Komarovia anisospermum*

A. I. Sokolova, Yu. E. Sklyar,
M. E. Perel'son, and M. G. Pimenov

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The monotypic genus *Komarovia* Korov. is considered close systematically to the genus *Ferula* L. [1], but this contradicts a number of morphological facts and, in particular, the carpological features of *Komarovia anisospermum* Korov. (heteromericarpia). A study of the chemical composition of the plant may assist in answering the question of the taxonomic propinquity of these two genera.

The thin-layer chromatography of a petroleum ether extract of the roots of *Komarovia anisospermum* showed that the predominating substances in it had R_f 0.64, 0.56, and 0.48. By column chromatography on silica gel we isolated all three substances: R_f 0.64, $C_{16}H_{14}O_4$, mp 106-108°C (I); R_f 0.56, $C_{22}H_{24}O_5$, mp 53-54°C (II); and R_f 0.48, $C_{17}H_{16}O_5$, mp 100-101°C (III).

Substance (I) was identical with isoimperatorin in its melting point, a mixed melting point, and its IR and NMR spectra.

According to its UV and IR spectra, substance (II) is a linear furocoumarin with O-alkyl substituents at C_5 and C_8 [2, 3]. It also follows from the NMR spectrum of substance (II) (Fig. 1) that it is based on the psoralen nucleus substituted in positions 5 and 8: doublets at 7.85 and 5.99 ppm, J = 9.5 Hz, are due to the H_4 and H_3 protons, and doublets at 7.48 and 6.88 ppm, J = 2 Hz, to the $H_{5'}$ and $H_{4'}$ protons, respectively. One of the O-alkyl substituents is a methoxy group, which appears in the spectrum in the form of a three-proton singlet at 4.08 ppm, and the other is a geranyloxy group (3,7-dimethylocta-2,6-dienyloxy group): one-proton triplet at 5.46 ppm, J = 7 Hz, and two-proton doublet at 4.69 ppm, J = 7 Hz, due to the methine and methylene protons in the $Ar{-}O{-}CH_2{-}CH{=}C$ grouping; two-proton singlets at 1.89 and 1.93 ppm, and a broadened one-proton singlet at 4.90 ppm, $W_{1/2}$ = 6 Hz, due to the methylene and methine protons of the $={C}{-}CH_2{-}CH_2{-}CH{=}C{-}$ fragment; and three three-proton singlets at 1.60, 1.55, and 1.47 ppm due to the protons of the three methyl groups located at C_7 and C_3 of the geranyl residue. The facts given correspond to two variants of the structure of the substance: 8-geranyloxy-5-methoxypsoralen and 5-geranyloxy-8-methoxypsoralen.

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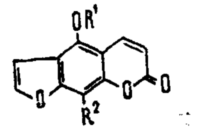

I. $R^1 = -CH_2-CH=C(CH_3)_2$, $R^2 = H$
II. $R^1 = -CH_3$,
$R^2 = -O-CH_2-CH=C(CH_3)-$
$-CH_2-CH_2-CH=C(CH_3)_2$
III. $R^1 = -CH_3$, $R^2 = -O-CH_2-CH=C(CH_3)_2$
IV. $R^1 = -CH_3$, $R^2 = -OH$
V. $R^1 = -CH_3$, $R^2 = -OCOCH_3$

Substance (II) differs in its physicochemical constants from 5-geranyloxy-8-methoxypsoralen (mp 74.5-75.5°C) isolated previously from *Citrus aurantifolia* (Rutaceae) [4]. By the partial dealkylation of (II) the geranyl residue was eliminated, giving the hydroxycoumarin (IV), $C_{12}H_8O_5$, mp 218-221°C, the acetylation of which led to the corresponding acetate (V), $C_{14}H_{10}O_6$, mp 177-180°C. These substances had constants differing from those of 5-hydroxy-8-methoxypsoralen (mp 270°C) and its acetate (mp 207-209.5°C) [4], and corresponded in their melting points and IR spectra to 8-hydroxy-5-methoxypsoralen (IV) and 8-acetoxy-5-methoxypsoralen (V) [4, 6]. The structure of the product of partial dealkylation and its acetate shows that the geranyl residue in (II) is present in position 8. The results of a measurement of the intramolecular nuclear Overhauser effect (NOE) in the spectrum of (II) lead to the same conclusion. If the methoxy group were at C_5, an NOE could be expected between the protons of the methyl group and H_4 and $H_{4'}$; if, however, the methoxy group were present at C_8, no NOE can be present. When the sample was irradiated with a supplementary frequency corresponding to the resonance of the methoxy group (4.08 ppm), the integral intensity of the $H_{4'}$ signal increased by 17% and that of the H_4 signal by 8%, which unambiguously indicates the location of the methoxy group at C_5.

Thus, substance (II) is 8-geranyloxy-5-methoxypsoralen. This substance has not previously been isolated in the individual state. A mixture of (II) with phellopterin has been isolated from *Casimiroa edulis* Llave et Lex (Rutaceae) by Dreyer [5], and this was considered to be a crystalline complex, since it was not separated by chromatography on alumina. When geranyl bromide was condensed with 8-hydroxy-5-methoxypsoralen, it gave a noncrystalline product, a mixture of which with phellopterin gave an NMR spectrum similar to that of the mixture isolated.

According to its NMR spectrum, substance (III) is a 5,8-disubstituted furocoumarin [δ, ppm: 6.05, d, 1 (H, J = 9.5 Hz (H_3); 7.85, d, 1 H, J = 9.5 Hz (H_4); 6.87, d, 1 H, J = 2 Hz ($H_{4'}$); 7.49, d, 1 H, J = 2 Hz ($H_{5'}$)], containing a methoxy group (4.09, s, 3 H), and an isopentenyloxy group) 1.66, s, 6 H [$C=C(CH_3)_2$]; 4.69, d, 2 H, J = 7 Hz ($O-\underline{CH_2}-CH=$); 5.48, t, 1 H,

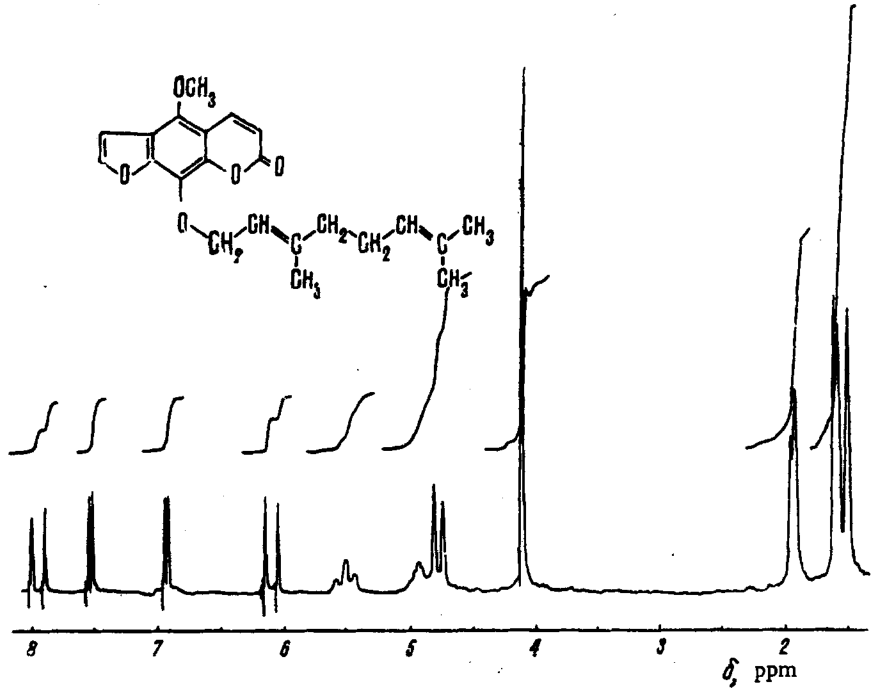

Fig. 1. NMR spectrum of 8-geranyloxy-5-methoxypsoralen (II).

J = 7 Hz ($O-CH_2-CH=$)). The acid hydrolysis of (III) gave 8-hydroxy-5-methoxypsoralen with mp 218-221°C, and the acetylation of the latter gave 8-acetoxy-5-methoxypsoralen with mp 177-180°C [4-6]. Consequently, substance (III) is 8-isopentenyloxy-5-methoxypsoralen (phellopterin) [4, 5].

Thus, judging from its chemical composition, the genus *Komarovia* is taxonomically remote from the genus *Ferula*, for which the presence of sesquiterpene lactones, alcohols, and their ethers, especially umbelliferone derivatives, is characteristic.

EXPERIMENTAL METHOD

For chromatographic separation we used silica gel L 40/100 μ. Thin-layer chromatography was performed on Silufol in the petroleum ether—ethyl acetate (1:1) system. The melting points of the substances were determined in capillaries in a block with a BIT-2 electric heater. The elementary analyses of the substances corresponded to the calculated figures. The IR spectra of the substances in paraffin oil were taken on a UR-10 spectrometer, the UV spectra of solutions in ethanol on a Hitachi EPS-3T spectrophotometer, and the NMR spectra of solutions in CCl_4 at 20°C (0 — HMDS) on a Varian HA-100D spectrometer.

Isolation and Separation of the Combined Coumarins. The comminuted dried roots of *Komarovia anisospermum* collected in Uzbekistan (Urgut, Zeravshanskii range) (2.28 kg) were extracted with petroleum ether in portions of 7.8, 4.1, and 4.9 liters, and the combined extracts were evaporated. This gave 75.7 g of a syrupy residue which was distributed between petroleum ether and methanol (1:1; 3 × 0.5 liter). Evaporation of the petroleum ether layer yielded 51.4 g of an oily residue containing traces of coumarins, and the methanolic layer yielded 22 g of a syrupy residue giving, in TLC on Silufol, three spots with R_f 0.64, 0.56, and 0.48. The last of them was adsorbed on 100 g of silica gel and deposited on a column (65 × 250 mm) containing 312 g of silica gel. Elution was performed with carbon tetrachloride (fractions I and II) and then with mixtures of carbon tetrachloride and increasing concentrations of ethyl acetate: 1% — fractions 12-28; 2% — fractions 29-51; 3% — fractions 52-59; and 4% — fractions 60-80, 500-ml fractions of the eluate being collected.

Isoimperatorin (I). Fractions 30-33 yielded 520 mg of colorless crystals with the composition $C_{16}H_{14}O_4$, mp 106-108°C (from methanol), R_f 0.64.

The IR spectrum was identical with that of isoimperatorin. NMR spectrum, δ, ppm: 6.05, d, 1 H, J = 9.5 Hz (H_3); 7.93, d, 1 H, J = 9.5 Hz (H_4); 6.83, d, 1 H, J = 2 Hz ($H_{4'}$); 7.46, d, 1 H, J = 2 Hz ($H_{5'}$); 5.44, t, 1 H, J = 7 Hz ($=C\underline{H}-CH_2-O$); 4.82, d, 2 H, J = 7 Hz ($O-C\underline{H}_2-CH$); 1.77, s, 3 H, and 1.65, s, 3 H [$C=C(CH_3)_2$].

8-Geranyloxy-5-methoxypsoralen (II). Fractions 37-43 yielded 3.86 g of a substance with the composition $C_{22}H_{24}O_5$ in the form of yellow crystals with mp 53-54°C (from ethyl acetate), R_f 0.56. λ_{max}^{EtOH}, nm: 223, 242, 249, 269, 274 infl., 315; log ε: 4.44, 4.17, 4.16, 4.27, 4.26, and 4.09, respectively. ν , cm^{-1}: 3152, 3125 (C-H of a furan nucleus), 1718 (C=O of an α-pyrone ring), 1608, 1590 (C=C).

Phellopterin (III). From fraction 55 was isolated 256 mg of a substance with the composition $C_{17}H_{16}O_5$ in the form of yellowish crystals with mp 100-101°C (from ethyl acetate), R_f 0.48.

Hydrolysis of 8-Geranyloxy-5-methoxypsoralen. A solution of 108 mg of (II) in 5 ml of glacial acetic acid was treated with 0.04 ml of concentrated sulfuric acid. The crystalline precipitate that deposited was separated off and washed with 1 ml of ether. This gave 28 mg of a substance $C_{12}H_8O_5$, mp 218-221°C, identical according to its IR spectrum and melting point with 8-hydroxy-5-methoxypsoralen (IV). Its acetate (V), obtained by a known method, had mp 177-180°C (literature data: 177-179°C [4], 180-181°C [6]).

Hydrolysis of Phellopterin. Phellopterin (104 mg) was hydrolyzed by the method described above. This gave 22 mg of a substance $C_{12}H_8O_5$, mp 218-221°C. A mixture with a sample of the (IV) obtained in the preceding experiment gave no depression of the melting point, and the IR spectra of these samples were identical. Acetate, mp 177-180°C, identical with (V) according to its IR spectrum and a mixed melting point.

SUMMARY

Three furocoumarins have been isolated from the roots of *Komarovia anisospermum* Korov.: isoimperatorin, phellopterin, and 8-geranyloxy-5-methoxypsoralen. This is the first time that the last-mentioned of these substances has been isolated in the pure state.

LITERATURE CITED

1. Flora of the USSR, Vol. XVII [in Russian] (1951), p. 149; E. P. Korovin, "Komarovia Eug. Kor. — A new Asiatic genus of the family Umbelliferae," in: To the President of the Academy of Sciences of the USSR Academician Vladimir Leont'evich Komarov for His 70th Birthday and the 45th Year of His Scientific Activity [in Russian], Akad. Nauk SSSR, Moscow–Leningrad (1939), pp. 427-438.
2. T. V. Bukreeva, Zh. Prikl. Khim., 39, No. 7, 1653 (1966).
3. T. V. Bukreeva, Zh. Prikl. Khim., 39, No. 7, 1541 (1966).
4. W. L. Stanley and S. H. Vannier, Phytochem., 6, No. 4, 585 (1967).
5. D. L. Dreyer, J. Org. Chem., 33, No. 9, 3577 (1968).
6. L. H. Briggs and R. C. Cambie, Tetrahedron, 2, 256 (1958).

STRUCTURE OF THE SESQUITERPENE LACTONE TANACIN

A. I. Yunusov, N. D. Abdullaev, Sh. Z. Kasymov,
G. P. Sidyakin, and M. R. Yagudaev

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In preceding papers, we have reported the isolation of lactones from *Tanacetum pseudoachillea* C. Winkl. and on the beginning of a study of the structure of tanacin [1].

Tanacin has the composition $C_{20}H_{26}O_5$, mp 128-129°C (ethanol), $[\alpha]_D^{21}$ $-74°$ (c 1.0; methanol), and it is readily soluble in benzene, chloroform, methanol, and pyridine, less readily soluble in petroleum ether, and insoluble in water. The IR spectrum of tanacin (I) (Fig. 1) shows absorption bands at 1760 cm^{-1} (carbonyl of a γ-lactone), 1710 and 1258 cm^{-1} (α,β-unsaturated ester group), and 1655 cm^{-1} (double bond).

The hydrogenation of (I) gave a tetrahydro derivative (II) with the composition $C_{20}H_{30}O_5$, mp 141-143°C, mol. wt. 350 (mass spectrometrically), in the IR spectrum of which the absorption band of the carbonyl groups had shifted in the high-frequency direction as compared with the bands of (I) by 15 and 20 cm^{-1}. This fact shows that the two double bonds are located in the α positions to the carbonyls of the ester and lactone groups.

The assignment of the signals in the proton magnetic resonance (PMR) spectrum of (I) (deuteropyridine, 0 — HMDS) was done by the method of multifrequency resonance. The results of the assignment and the spectral characteristics found on their basis are summarized in Fig. 2 and Table 1.

In the PMR spectrum of (I) in the region characteristic for vinylmethyl groups there is a broadened singlet (3 H) at 1.88 ppm and, overlapping with it, a doublet (3 H) at 1.91 ppm with weak secondary splitting. In addition, at 5.92 ppm there is a quartet, one of the broadened components of which is masked by the neighboring multiplet corresponding to one proton unit. These signals are characteristic for the protons of the angelic acid radical [3], and, consequently, their presence shows the existence in the molecule of (I) of a hydroxy group esterified with a residue of this acid.

There is another three-proton signal at 1.75 ppm belonging to a methyl group on a double bond. It has weak splitting with $^3J = 1.3$ Hz, and is converted into a narrow singlet if the

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