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QUINONES OF *Salvia sclarea*

A. S. Romanova, A. V. Patudin,
L. N. Pervykh, and L. P. Zobenko

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We have previously made a qualitative estimate of the presence of quinones in the roots of all species of sage growing in the Soviet Union, finding a definite connection between the presence of quinones of the type of royleanone or tanshinone in the plants and the systematic positions of the corresponding species [1-3]. On comparing the tanshinone-containing species with the aid of thin-layer chromatography it was found that many species differ in the set of substances they obtain.

The comminuted roots of *Salvia sclarea* L. were covered with petroleum ether (1:6), stirred for 15 min and steeped for 12 h. The extract was evaporated in vacuum and a resinous residue was obtained. This operation was repeated three times.

To isolate individual substances, approximately 10 mg of the resinous residue from the petroleum ether fraction was dissolved in 0.5 ml of chloroform and was deposited on a silica gel plate in the form of a number of spots. After chromatography in chloroform, the corresponding bands were removed, the substances were eluted with chloroform, and, after the solvent had been distilled off in vacuum, reddish or orange residues were obtained which were crystallized from chloroform or benzene. The operation was repeated several times. The following substances were isolated from the roots of wild clary sage and were identified:

Isotanshinone (I), $C_{18}H_{12}O_3$ — orange-red crystals, mp 217-219°C, melting point of a mixture with an authentic sample 218-219°C; R_f 0.72 (chloroform, pinkish-orange spot). IR spectrum (paraffin oil, cm^{-1}): 3150, 1660, 1585; UV spectrum (ethanol, nm): 234, 293, 346, 450.

Tanshinone (II), $C_{19}H_{18}O_3$ — red crystals, mp 198-200°C; melting point of a mixture with an authentic sample 198-200°C. R_f 0.53 (chloroform, pink spot). IR spectrum (paraffin oil, cm^{-1}): 3150, 1690, 1670, 1580: UV spectrum (ethanol, nm): 224, 252, 269, 350, 460.

Methyl tanshinonate, $C_{20}H_{18}O_5$ — red crystals with mp 174-176°C, melting point of a mixture with an authentic sample 175-178°C R_f 0.32 (chloroform, pink spot). IR spectrum (paraffin oil, cm^{-1}): 3150, 1725, 1690, 1580; UV spectrum (ethanol, nm): 223, 252, 269, 352, 465.

Hydroxytanshinone, $C_{19}H_{18}O_4$ — red crystals, mp 185-187°C; melting point of a mixture with an authentic sample 185-187°C; R_f 0.13 (chloroform, cherry-red spot); IR spectrum (paraffin oil, cm^{-1}): 3525, 3150, 1685, 1670, 1580; UV spectrum (ethanol, nm): 222, 252, 273, 348, 462.

All these substances have been obtained earlier by Japanese workers from the roots of *Salvia milthiorhiza* Bunge [4].

In addition we isolated another substance consisting, after crystallization from ethanol, of orange-red crystals, $C_{19}H_{18}O_4$, R_f 0.8 (chloroform, pink spot). IR spectrum (paraffin oil, cm^{-1}): 3345, 3070, 1645, 1570; UV spectrum (ethanol, nm): 203, 252 infl., 258.5, 283, 293 infl., 360. Molecular weight 310. The facts given permit the assumption that the substance is new and of the isotanshinone type. We have obtained this substance previously from the roots of Drobov's sage.

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NEW TERPENOID COUMARINS OF *Ferula kopetdaghensis*

A. A. Nabiev, T. Kh. Khasanov,
and V. M. Malikov

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By the chromatographic separation on a column of silica gel of a methanolic extract of the roots of *Ferula kopetdaghensis* Eug. Kor. we have isolated two new coumarins: $C_{26}H_{32}O_5$, M^+ 424. n_D^{20} 1.5607. $[\alpha]_D^{18}$ + 29.8° (c 0.67; $CHCl_3$), R_f 0.85 (I) (0.0083% of the weight of the dry plant) and $C_{24}H_{28}O_4$, M^+ 380, n_D^{20} 1.5837, $[\alpha]_D^{20}$ + 47° (c 0.84; $CHCl_3$), R_f 0.73 (II) (0.0061%) in the chloroform–ethyl acetate (3:1) system on Silufol, which we have called, respectively, fekolin and fekolone. Both compounds are umbelliferone derivatives (characteristic UV spectra). The IR spectrum of (I) shows absorption bands at 1738 cm^{-1} (C=O of an α-pyrone), 1730 cm^{-1} (C=O of an ester group), and 1617 and 1560 cm^{-1} (aromatic ring).

The PMR spectrum of fekolin (JNM-4H-100/100 MHz, $CDCl_3$, 0 — HMDS), δ, ppm: 0.84, s (2 CH_3–C–); 1.67 and 1.73, singlets (2CH_3–C=CH); 1.99, s (CH_3–COO^-); 4.56, d, J = 6.0 Hz (Ar–O–CH_2–CH); 4.61, m, ΣJ = 15 Hz (H–C–OAc); 5.19, m, $W_{1/2}$ = 10 Hz and 5.41, t, J = 6.0 Hz (2H–C=C–CH_3); 6.18, d, J = 9.5 Hz (C_3–H); 6.79, m (C_6–H , C_8–H); 7.35, d, J = 9.0 Hz (C_5–H); 7.60 d, J = 9.5 Hz (C_4–H).

The results obtained enabled us to assign fekolin to the acylated terpenoid coumarins. In fact, the alkaline hydrolysis of (I) gave a substance $C_{24}H_{30}O_4$, M^+ 382, mp 124-125°C, $[\alpha]_D^{20}$ +31° (c 1.0; $CHCl_3$) which was identified as kopetdaghin [1]. Consequently, fekolin is the natural acetate of kopetdaghin.

In the IR spectrum of fekolone (II), in addition to other absorption bands there is a band at 1710 cm^{-1} (ketone C=O). The presence of a carbonyl group was established by the preparation of a 2,4-dinitrophenylhydrazine with mp 89-90°C.

From the composition of fekolone and its spectral characteristics, it may be assumed that the terpenoid part of (II) has a monocyclic nature. This was confirmed by the preparation of 1,2,3,4-tetramethylbenzene on the dehydrogenation of fekolone with selenium.

The PMR spectrum of fekolone resembled the spectrum of farnesiferol B [2] but differed by the absence of the signal of the hemihydroxylic proton and by a shift of the signals of the methyl groups, on the basis of which it may be considered that (II) is the ketone of farnesiferol B. This was confirmed by the preparation of farnesiferol B by the reduction of fekolone with sodium tetrahydroborate. Furthermore, a mixture of the 2,4-dinitrophenylhydrazone of (II) and of the ketone of farnesiferol B gave no depression of the melting point.

Thus, fekolone is the natural ketone corresponding to farnesiferol B.

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