POLYPHENOLS FROM THE LEAVES OF Hippophae rhamnoides

T. K. Chumbalov, M. M. Mukhamed'yarova, and V. V. Polyakov

UDC 547.972

In the leaves of Hippophae rhamnoides collected in the environs of Alma-Ata we have shown by paper chromatography the presence of phenolic acids, flavonol aglycones and glycosides, hydrolyzable tannin substances, and coumarins.

For their isolation, the leaves were extracted with methanol and the concentrated extracts were diluted with water and extracted successively with benzene, ether, ethyl acetate, and butanol.

Two-dimensional paper chromatography in 15% acetic acid and in the BAW (4 : 1 : 5) system of the ethereal fraction showed the presence of seven substances of polyphenolic nature, five of which were isolated by partition column chromatography on polyamide and silica gel and by preparative paper chromatography.

On the basis of qualitative reactions, UV spectroscopy with ionizing and complex-forming reagents, reaction products, Rf values in various solvent systems, and comparison with authentic samples, these substances were identified as quercetin $C_{15}H_{10}O_7$, mp 309-311°C; kaempferol, $C_{15}H_{10}O_6$, mp 273-275°C; isorhamnetin $C_{16}H_{12}O_7$, mp 303-305°C, myricetin, $C_{15}H_{11}O_8$, mp 356-360°C; and gallic acid $C_7H_6O_5$, mp 224-226°C.

S. M. Kirov Kazakh State University, Alma-Ata.

Original article submitted May 12, 1976.

MONOTERPENE COMPOUNDS OF THE ESSENTIAL OILS OF PLANTS OF THE GENUS Santolina

V. A. Ushakov, D. A. Murav'eva, and L. A. Bakina

UDC 547.913+582.998

We have studied the composition of the monoterpene compounds of the essential oils from the epigeal parts of Santolina virens Willd. (green lavender cotton) and S. chamaecyparissus L. (Cyprus lavender cotton), family Compositae, which are widely cultivated in the southern regions of our country and are used in folk medicines. The essential oils were obtained by treating the epigeal mass of each species of lavender cotton with steam. The yields of essential oils were 1.9% (for the green lavender cotton) and 0.8% (for the Cyprus lavender cotton) of the weight of the air-dry plant. The physicochemical constants of the essential oils of the Cyprus lavender cotton were: n_D^{20} 1.4822, d_{20}^{20} 0.8950, α_D^{20} −3.22; acid No. 2.32; ester No. 14.25; ester No. after acetylation 70.59; free alcohols 3.17%; and from green lavender cotton: d_{20}^{20} 0.8900, n_D^{20} 1.4860, α_D^{20} −4.00; acid No. 3.29; ester No. 29.10; ester number after acetylation 99.21; free alcohols 2.97%.

The monoterpene fractions of the essential oils were obtained by fractional distillation of the oils in vacuum (bp 66-70°C/5 mm); they amounted to 68 and 71%, respectively. To isolate fractions of monoterpene hydrocarbons and monoterpene oxygen compounds we used the chromatographic separation of the monoterpene fractions of the essential oils on column of Al_2O_3 (activity grade II). Petroleum ether was used as the eluent. The separation was monitored by IR spectroscopy.

Pyatigorsk Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 5, p. 663-664, September-October, 1976. Original article submitted November 26, 1975.

The composition of the fractions of monoterpene hydrocarbons were studied by the GLC method on a Pye-104 chromatograph. β,β'-Oxydipropionitrile (12%) at 70°C and PEGA (10%) at 100°C were used as stationary phases. To identify the monoterpene hydrocarbons we used the values of the relative retention volumes given in the literature and, in addition, the presence of the majority of them was confirmed with the aid of markers.

By means of GLC analysis we identified the following hydrocarbons in the monoterpene fractions of the essential oils of the Cyprus and the green lavender cottons: α-* and β-pinenes, α-fenchene, sabinene, myrcene,* α- and β-phellandrenes, limonene,* γ-terpinene,* and p-cymene.*

When the fraction of monoterpene oxygen compounds from the essential oil of the Cyprus lavender cotton was rechromatographed on a column of Al_2O_3 (activity grade II), we isolated a substance $C_{10}H_{16}O_3$ with mol. wt. 152 (mass spectrum). Its properties (n_D^{20} 1.4708, d_4^{25} 0.8750, bp 64.5°C/9 mm Hg; semicarbazone with mp 96.4-96.8°C) and its spectral characteristics (IR, UV, and NMR spectra) permitted this substance to be identified as artemisia ketone. In addition, we obtained a 2,4-dinitrophenylhydrazone with mp 78.5-79°C.

From the fraction of monoterpene oxygen compounds from the Cyprus lavender cotton (after the isolation of the artemesia ketone) and also from all the fractions of monoterpene oxygen compounds from the essential oil of the green lavender cotton by our own modification of the method of L. Francesconi and N. Granata [1, 2] we isolated a hydroxylamine oxime with mp 190-190.5°C, the hydrolysis of which gave a very volatile liquid substance. Its physicochemical constants (n_D^{20} 1.4687, d_4^{20} 0.8886, semicarbazone with 220°C coincided with literature information for the monoterpene ketone α-santolinenone [1-3].

*These substances were identified with the aid of markers.

LITERATURE CITED

1. L. Francesconi and N. Granata, Gazz. Chim. Ital., 150 (1914).
2. L. Francesconi, N. Granata, and A. Sanna, Gazz. Chim. Ital., 354 (1914).
3. L. Francesconi and N. Granata, Gazz. Chim. Ital., 167 (1915).

ESTERS OF THE ROOTS OF Ferula dshizakensis

V. N. Borisov, A. I. Ban'kovskii, V. I. Sheichenko, V. S. Kabanov, and M. G. Pimenov

UDC 547.26[1].11:638.88

Continuing a study of esters of plants of the genus Ferula, from a methanolic extract of the roots of Ferula dshizakensis Korov, collected in May, 1973, in the budding phase (Uzbek SSR, R. Sanzar) we have isolated a mixture of two diastereomeric compounds with the composition $C_{17}H_{22}O_3$ (M^+ 274). Alkaline hydrolysis and reduction with $LiAlH_4$ gave p-hydroxybenzoic acid, $C_7H_6O_3$, mp 207-209°C (comparison of physicochemical properties and mixed melting point) and two epimeric hydroxyterpenes with the composition $C_{10}H_{18}O$ (M^+ 154), mp 207°C. In the PMR spectrum (CCl_4, 0 – HMDS, 20°C) of the hydroxyterpenes an axially-oriented proton geminal to an exo-OH group appears in the form of a triplet at 3.47 ppm (1H; $W_{1/2}$ = 10 Hz) and an equatorial methine proton at an endo-OH group in the form of a multiplet at 3.86 ppm (1H; $W_{1/2}$ = 11 Hz) [1, 2].

The ratio of the integral intensities of the geminal and hydroxy-group protons and a calculation of the ratio of the relative intensities of the dehydration and molecular peaks for the terpenols corresponded to a quantitative ratio of the diastereomers in the natural mixture of 1 : 1 [3].

Oxidation of the terpenoid alcohols with chromium trioxide in 60% acetic acid gave a common ketone $C_{10}H_{16}O$, mp 177°C, identified as camphor.

All-Union Scientific-Research Institute of Medicinal Plants, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 5, p. 665, September-October, 1976. Original article submitted March 1, 1976.