PHENOLIC COMPONENTS OF *Ferula juniperina*

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Continuing a study of the phenolic compounds of plants of the genus *Ferula* [1-4], from the roots of *Ferula juniperina* Eug. Kor. collected in the Kuraminskii range in the south of Almalyk, chromatographing a methanolic extract on a column of type KSK silica gel with elution by hexane—ether (4:1) we have isolated three substances which we have called juferin, juniferin, and juniferinin.

Juferin has the composition $C_{22}H_{30}O_4$, mp 89-90°C, $[\alpha]_D^{20}$ + 120.4° (c 0.77; ethanol), R_f 0.5 (system 1: hexane—ethyl acetate (3:1); Silufol; stained with a 1% solution of vanillin in sulfuric acid). It was not saponified by the action of caustic soda. The UV spectrum of juferin has maxima at 213.5 nm (log ε 4.3) and 255.5 nm (log ε 4.5), which shows the presence of a double bond and an aromatic nucleus, and in the IR spectra there are absorption bands at 1600, 1610, and 1520 cm^{-1} (aromatic nucleus), 1680 cm^{-1} (double bond), 3050 cm^{-1} (exocyclic methylene), and 3430 cm^{-1} (hydroxy group).

Juniferin is a colorless crystalline substance with the composition $C_{23}H_{32}O_5$, mp 85-86°C, $[\alpha]_D^{20}$ − 1.6° (c 5.8; ethanol), R_f 0.21 (system 1).

Juniferinin is a substance with the composition $C_{24}H_{32}O_5$, mp 164-165°C, $[\alpha]_D^{20}$ + 33.4° (c 1.8; ethanol), R_f 0.35 (system 1).

In the UV spectra of juferin and juferinin absorption maxima are observed at 211 nm (log ε 4.0) and 260 nm (log ε 4.3) which shows the presence of a double bond and an aromatic nucleus. The presence of phenolic hydroxyls in the para positions is confirmed by a bathochromic shift of the long-wave maximum with an increase in the value of log ε. The IR spectra of the two substances have identical absorption bands at 3200-3600 cm^{-1} (hydroxy group), 1680, 1250 cm^{-1} (ester group), and 1600-1620, 1520, and 1450 cm^{-1} (aromatic nucleus), which confirms their common structure.

On being heated with 5% KOH, juniferin and juniferinin formed the same sesquiterpene diol with the composition $C_{15}H_{26}O_2$, mp 135-136°C, $[\alpha]_D^{20}$ − 85.4° (c 2; ethanol), R_f 0.05 (system 1), which we have called juniferol. Its UV spectrum has an absorption maximum at 211 nm (log ε 3.2) (double bond), and the IR spectrum absorption bands at 3400 cm^{-1} (hydroxy group), at 1380-1460 cm^{-1} (gem-dimethyl group), and 1665 cm^{-1} (double bond). The secondary nature of the hydroxy groups was confirmed by the preparation of a diacetate in the form of a liquid with $[\alpha]_D^{20}$ − 70.37° (c 2.6; methanol), n_D^{20} 1.4915. In its IR spectrum, the absorption band at 3400 cm^{-1} had disappeared and the band of an ester group has appeared at 1750 cm^{-1}.

Summarizing these facts, it may be concluded that juniferin and juniferinin are esters of a sesquiterpene diol, juniferol, juniferinin being a diester, since on its hydrolysis two acids are formed: acetic and p-hydroxybenzoic, while the hydrolysis of juniferin forms only a vanillic acid.

Investigations to establish the structures of the substances isolated are continuing.

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STRUCTURES OF ASHURBIN AND ARABSIN

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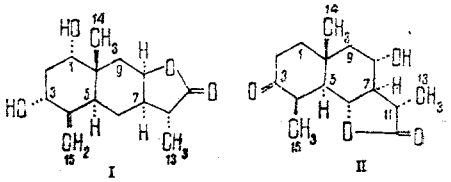
We have previously reported the isolation of the sesquiterpene lactones hanphyllin and granilin [1] from *Artemisia ashurbajevii* C. Winkl. Continuing the separation of the combined lactones, by means of a mixture of benzene and acetone (97:3) we have isolated a new sesquiterpene lactone with the composition $C_{15}H_{22}O_4$, mp 175-176°C, $[\alpha]_D^{18}$ +12.7° (c 1.1; methanol), which we have called ashurbin. Ashurbin is readily soluble in acetone and pyridine and sparingly soluble in ether, benzene, chloroform, and water. Its IR spectrum had absorption bands at 3450-3150 cm^{-1} (OH group), 1780 cm^{-1} (γ-lactone carbonyl), and 1658 cm^{-1} (C=C). In the mass spectrum there are the peaks of ions with m/e 266 (M^+), M − 15, M − 15 − 18, M − 18 − 18, and M − 15 − 18 − 18, which shows the presence of two hydroxy groups in ashurbin. The NMR spectrum of ashurbin (deuteropyridine, δ scale) has the signals of tertiary and secondary methyls (singlet at 0.70 ppm and doublet at 1.05 ppm, J = 8 Hz). Signals at 3.39 and 4.43 ppm relate to hemihydroxyl protons. Consequently, both hydroxyls are secondary. The signal of the lactone proton is superposed on the signal of the hemihydroxyl proton at 4.43 ppm. Singlets at 4.56 and 4.91 ppm correspond to the protons of an exomethylene group, and the signals at 5.73 and 6.98 ppm to a hydroxylic proton. A comparison of the composition of granilin and ashurbin, and also a study of spectral characteristics, shows that ashurbin differs from granilin [2, 3] by the presence of a methyl group in place of an exomethylene group in the lactone ring. This group has the α orientation, since the signals of the proton at C_7 in granilin and ashurbin are in the form of multiplets in the 2.7 ppm-region and the sums of the spin–spin coupling constants differ by 3 Hz. Furthermore, the hydrogenation of granilin in the presence of 5% Pd/C gave dihydrogranilin with mp 174-175°C which was shown by its IR spectrum and by a mixed melting point to be identical with ashurbin. Consequently, ashurbin has the structure of 1,3α-dihydroxy-5,7,8α(H),11β(H)-eudesm-4(15)-en-8,12-olide (I). Continuing a study of the lactones of the epigeal part of *Artemisia absinthium* L. [4], by the chromatographic separation of the combined lactones on silica gel (elution by benzene–acetone (9:1)) we isolated a mixture of two substances. By repeated recrystallization from benzene it was possible to separate them into two individual compounds. The first lactone was identified from its IR spectrum and melting point as absinthin [5], and the second ($C_{15}H_{22}O_4$, mp 193-194°C), as arabsin [4]. When artemisin was subjected to catalytic hydrogenation over 5% Pd/C, tetrahydroartemisin was obtained [6, 7], with mp 192-193°C, and according to its IR spectrum and a mixed melting point, this was identical with arabsin.

Thus, the structure and configuration of arabsin has been established as 8α-hydroxy-3-oxo-4,5,7α(H),6,11β(H)-eudesman-6,12-olide (II):



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