THE STRUCTURES OF JUFERIN AND JUNIFERIDIN

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Juferin, with the composition $C_{22}H_{30}O_4$, mp 90-91°C (from hexane–ethyl acetate), $[\alpha]_D^{20}$ +120.4° (c 0.77; ethanol), R_f 0.5 [system 1: hexa –ethyl acetate (3:1)] has been isolated from the roots of *Ferula juniperina* [1].

UV spectrum: λ_{max} 213.5 nm (log ε 4.3); 255.5 nm (log ε 4.5). IR spectrum, ν_{max}, cm^{-1}: 980 (trans-disubstituted olefinic protons), 1380, 1360 (gem-dimethyl group), 1520, 1595, 1690 (aromatic nucleus), 3080 (exomethylene group), 3200-3600 (hydroxy group) [2].

In the region of olefinic protons in the PMR spectrum of juferin there are two doublet signals at 5.38 ppm (J = 16 Hz) and 5.86 ppm (J = 16 Hz), and also a triplet signal at 5.21 ppm ($J_1 = J_2 = 7.5$ Hz). A multiplet at 4.52 ppm ($^1/_2\Sigma$ =10 Hz) is due to a hemihydroxylic proton. Two doublet signals appear in the weak-field region at 6.81 ppm (J = 10 Hz) and 7.82 ppm (J = 9 Hz), corresponding to two pairs of ortho-interacting protons of an aromatic nucleus, and also a broadened singlet at 8.0 ppm due to the presence of a phenolic hydroxyl. The signals of terminal methyl groups appear in the strong field at 1.07 and 0.98 ppm (singlets, 3 H each), and of a methyl group on a double bond at 1.37 ppm (singlet, 3 H).

On the whole, the PMR spectrum of juferin is similar to that of ferocin with the exception of the CSs of the signals of the hemihydroxylic proton, the methyl at a double bond, and the triplet signal of an olefinic proton, the differences in which are 28, 18, and 11 Hz, respectively.

The hydrolysis of juferin with 15% caustic potash solution gave p-hydroxybenzoic acid ($C_7H_6O_3$, mp 210-212°C) and a sesquiterpene alcohol ($C_{15}H_{26}O$, mp 51-53°C). IR spectrum, λ_{max}, cm^{-1}: 3200-3600 (OH), 3080, 1645, 900 (>C=CH_2), 1600, 975 (–C(H)=C–), 1360, 1380 (gem-dimethyl grouping), 885 cm^{-1} (–CH–C<) [2]), which has been called juferol. In the PMR spectrum of juferol, which differs only slightly from that of fecerol [3], the signal of the hemihydroxylic proton appears in the form of a multiplet at 3.25 ppm ($^1/_2\Sigma$ = 9 Hz), while in fecerol it appears at 3.48 ppm (m, $^1/_2\Sigma$ = 18 Hz). This difference in the CSs and SSCCs can be explained by a difference in the orientation of the hemihydroxylic proton in these alcohols and permits the orientation in fecerol to be determined as axial and in juferol as equatorial. The above-mentioned difference in the PMR spectra of ferocin and juferin is also apparently explained by the assumption that differently oriented hemiacyl protons have different effects on the closest protons. Thus, juferol is a stereoisomer of fecerol with respect to the orientation of the hydroxy groups, and juferin is p-hydroxybenzoyljuferol.

Continuing the separation of the combined esters, we have isolated another ester, with the composition $C_{34}H_{32}O_5$, mp 162-163°C (hexane–ethyl acetate, yield 0.02%), $[\alpha]_D^{24}$ +2.1° (c 0.65; MeOH), R_f 0.27 (system 1), which has been called juniferidin [1]. The alkaline hydrolysis of (I) with 5% aqueous ethanolic alkali gave a diol with the composition $C_{15}H_{26}O_2$ (II), mp 121-122°C (petroleum ether): $[\alpha]_D^{24}$ –62.5° (c 1.73; ethanol), and p-hydroxybenzoic acid, $C_7H_6O_3$, mp 210-212°, while acetic acid was detected chromatographically in the hydrolysis products.

The acetylation of (I) with acetic anhydride in pyridine led to the monoacetate (III) of (I) with the composition $C_{26}H_{34}O_6$, colorless oil, $[\alpha]_D^{24}$ +10.1° (c 1.75; methanol). A comparison of the spectral characteristics (IR, PMR, and mass spectra) of juniferidin (I), the diol (II), and the acetate (III) with the corresponding derivative of juniferinin [4] showed that juniferinin and juniferidin are isomeric compounds. This was confirmed by the

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different R_f values of compounds (I) and juniferinin, by a depression of the melting point of a mixture of juniferidin with juniferinin (Δ mp 60°C), and by their different specific rotations.

On the basis of the facts given above, for juniferidin we propose the structure of 2-acetoxy-5-p-benzoyljuniferol. The study of the stereochemistry of juniferinin and juniferidin is continuing.

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A SESQUITERPENE LACTONE FROM THE SEEDS OF *Ferula malacophylla*

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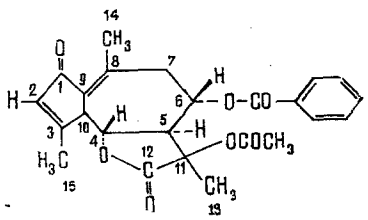
From the combined extractive substances of the seeds of *Ferula malacophylla* [1] by adsorption chromatography on neutral alumina (activity grade IV) we have isolated a previously undescribed sesquiterpene compound with the composition $C_{24}H_{24}O_7$ (I), M^+ with m/e 424, mp 208-209°C (ethanol), R_f 0.17, which we have called malaphyllinin. The IR spectrum of (I) has adsorption bands at (cm^{-1}): 1790 (CO of a γ-lactone), 1740 (CO of an acetyl group), 1702 (CO of an ester group), 1690 (CO of an α,β-unsaturated cyclopentanone), and 1640, 1620, 1600, 1590, and 1515 (double bonds in conjugation). It follows from the NMR spectrum of malaphyllinin that it has the same carbon skeleton and the same arrangement of the lactone ring and the substituents as malaphyllin [1] (s — singlet; d — doublet; q — quartet; m — multiplet; sx — sextet):

Proton	ppm, J, Hz, multiplicity
H-2	6,21; m, 1/2 W=4,0
H-1	4,72; q, $J_{4,5}$=10,0; $J_{4,10}$=11,0
H-5	3,67; q, $J_{5,6}$=10,3; $J_{4,5}$=10,0
H-6	5,73; sx, $J_{6,7e}$=3,9; $J_{6,7a}$=10,3
H-7a	2,58; q, $J_{7a,7e}$=18,1; $J_{7a,6}$=10,3
H-7e	3,04; q, $J_{7e,7a}$=18,1; $J_{7e,6}$=3,9
H-10	3,63; d, $J_{10,4}$=11,0
CH_3-13	1,61; s
CH_3-14	2,26; s
CH_3-15	2,26; s

The NMR spectrum of malaphyllinin also has the signals of the protons of an acetyl group (2.12 ppm, 3 H) and of a benzoic acid residue (7.30-8.10 ppm, 5 H). These compounds differ only by the fact that in malaphyllinin there is a benzoic acid residue in the C_6 position, while in malaphyllin there is a veratric acid residue. In the products of the saponification of malaphyllinin acetic and benzoic acids were detected by gas chromatography with markers.

On the basis of the facts given above, for malaphyllinin we suggest the structure of 11-acetoxy-6-benzoyloxy-1-oxoguaia-2,8-dien-4,5-olide:



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