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LACTONES OF *Ferula gigantea*

A. A. Savina, D. A. Fesenko,
L. I. Dukhovlinova, Yu. E. Sklyar,
M. G. Pimenov, and Yu. V. Baranova

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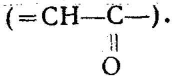
The following substances have been isolated from an acetone extract of *Ferula gigantea* B. Fedtsch.: a coumarin — umbelliferone, $C_9H_6O_2$, mp 230-233°C; and sesquiterpene lactones — talassin A, $C_{25}H_{30}O_7$, mp 188-191°C; malaphyllinin, $C_{24}H_{24}O_7$, mp 231-235°C; malaphyll, $C_{29}H_{32}O_9$, mp 212-213°C; and malaphyllin, $C_{26}H_{28}O_9$, mp 216-218°C. Structures have been proposed for three new sesquiterpene lactones on the basis of an analysis of their spectral characteristics.

Species of *Ferula* belonging to the section Palaeonartex Korov. contain various sequiterpenes. In view of this, it appears of interest to study *F. gigantea* B. Fedtch. [1] (subsection Tumidae M. Pimen. et J. Baranova); *F. inflata* Korov. and *F. latifolia* Korov. are assigned to this species according to the literature [2]. The material for investigation was collected close to the settlement of Shurobad, Kulyab oblast, Tadzhikistan at the type site of *F. inflata*.

Chromatography on silica gel of an acetone extract of the roots of the *Ferula* yielded eight compounds: I) $C_{25}H_{30}O_7$, mp 188-191°C; II) $C_{27}H_{28}O_7$, mp 263-266°C; III) $C_{24}H_{24}O_7$, mp 231-235°C; IV) $C_{28}H_{30}O_8$, mp 232-234°C; V) $C_9H_6O_3$, mp 230-233°C; VI) $C_{25}H_{26}O_8$, mp 192-193°C; VII) $C_{29}H_{32}O_9$, mp 212-213°C; VIII) $C_{26}H_{28}O_9$, mp 216-218°C.

On the basis of the identity of its IR spectrum and PMR spectrum with corresponding spectra of an authentic sample, compound (V) was identified as umbelliferone. The remaining substances were, according to their spectral characteristics, sesquiterpene lactones.

An analysis of spectral characteristics (Table 1) enabled the main structural elements of the molecules of these compounds to be determined. Strong absorption bands at 1789-1795 cm^{-1} in the IR spectra of these compounds show the presence of a γ-lactone grouping. A guaiadienone grouping is responsible for the presence in the UV spectra of these substances of absorption maxima in the 251-264 nm region (log ε 4.25-4.53) and for absorption bands in the IR spectra at 1689-1697 cm^{-1} (C=O of an α,β-unsaturated cyclopentanone), 1640-1645 and 1620-1625 cm^{-1} (—C=C—), and in the PMR spectra of six-proton singlets with 2.20-2.28 ppm (2 CH_3—C=) and a broadened singlet at 6.22-6.28 ppm, $W_{1/2}$ = 4.0 Hz  $(=CH-\underset{\overset{\|}{O}}{C}-)$. In addition to the C=O groups of a cyclopentanone and a γ-lactone, the molecules of the sesquiterpene lactones contain two other carbonyls, of ester groups, as follows both from the IR spectra (two absorption bands in the 1745-1710 cm^{-1} interval, sometimes overlapping one another) and also from the presence in the ^{13}C NMR spectra of four singlet signals of carbonyl carbons in the 165-174 ppm region.

The closeness of the characteristics of the PMR spectra of the lactones described to one another and to the spectra of talassin A [3], olgin, and olgoferin [4], isolated pre-

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All-Union Scientific-Research Institute of Medicinal Plants, Moscow. M. V. Lomonosov Moscow State University, Botanical Garden, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 490-495, July-August, 1979. Original article submitted March 5, 1979.

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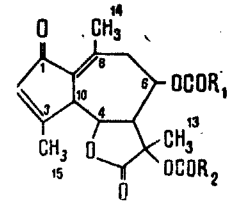
TABLE 1. Characteristics of the PMR Spectra of the Sesquiterpene Lactones (Chemical Shifts, ppm; Multiplicities, Hz*)

	H-2	H-4	H-5	H-6	H-7a	H-7e	H-10	CH_3-13	CH_3-14,15	Protons of the acyl residues							
										aliphatic acyl		aromatic acyl					
										CH_3–	CH=	H-2	H-6	H-3	H-5	H-4	OCH_3
I. $R_1=R_2=-C(CH_3)=CH-CH_3$	6,22 us $W_{\frac{1}{2}}$ =4,0	4,73 q $J_{4,5}$= =10,0 $J_{4,10}$= =10,2	3,65 q $J_{4,5}$= =10,0 $J_{5,6}$= =11,0	5,66 sx $J_{6,7e}$= =3,5 $J_{5,6}$= $J_{6,7a}$= =11,0	2,48 q $J_{7a,7e}$= =19,5 $J_{7a,6}$= =11,0	2,91 q $J_{7e,7a}$= =19,5 q $J_{7e,6}$= =3,5	3,60 d $J_{10,4}$= =10,2	1,63 s	2,24 s	1,99 d 1,86 s	6,22 m						
II. $R_1=-C_6H_5$, $R_2=-CH=C(CH_3)_2$	6,27 us	4,80 q	3,78 q	5,80 sx	2,60 q	3,08 q	3,69 d	1,62 s	2,28 s	1,97 s 1,20 s	5,78 us	8,09 m		8,57 q		7,4 t	
III. $R_1=-C_6H_5$, $R_2=-CH_3$	6,22 us	4,73 q	3,72 q	5,76 sx	2,59 q	3,04 q	3,65 d	1,62 s	2,25 s	2,15 s		8,05 m		7,48 t		7,60 t	
IV. $R_1=-4-(CH_3O)C_6H_4-$ $R_2=-CH=C(CH_3)_2$	6,28 us	4,81 q	3,77 q	5,81 sx	2,61 q	3,14 q	3,70 d	1,62 s	2,26	2,00 s 2,20 s	5,81 us	8,04 m		6,99 m			3,91 s
VI. $R_1=4-(CH_3O)C_6H_4-$, $R_2=-CH_3$	6,22 us	4,72 q	3,68 q	5,72 sx	2,56 q	3,04 q	3,61 d	1,58 s	2,25 s	2,14 s		7,99 m		6,96 m			3,88 s
VII. R_1=3,4-di-$(CH_3O)C_6H_3-$, $R_2=-CH=C(CH_3)_2$	6,24 us	4,78 q	3,72 q	5,79 sx	2,56 q	3,04 q	3,65 d	1,56 s	2,20 s	1,90 s 2,12 s	5,75 us	7,54 d J=2,5	7,72 q J=8,0 J=2,5		6,92 d J=8,0		3,87 s 3,92 s
VIII. R_1=3,4-di-$(CH_3O)C_6H_3-$, $R_2=-CH_3$	6,22 us	4,71 q	3,67 q	5,73 sx	2,56 q	3,02 q	3,62 d	1,58 s	2,23 s	2,11 s		7,53 d J=2,5	7,65 q J=8,0; J=2,5		6,90 d J=8,0		3,90 s 3,92 s

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*Abbreviations adopted: s) singlet; d) doublet; t) triplet; q) quartet; m) multiplet; us) unresolved signal appearing in the form of a singlet; sx) dextet. The spin-spin coupling constants are given only for the protons of compound (I); in the other compounds the coupling constants are the same as in compound (I).

viously, shows that they are all diacyl derivatives of a guaianolide. The considerable magnitude of the chemical shift of the proton at C-6 (5.66-5.81 ppm) shows the presence of one of the acyloxy groups in this position. The absence of splitting of the signal of the CH_3 group of the lactone ring shows that the second ester group is present at C-11. The assignment of the signals of all the protons of the five- and seven-membered rings was confirmed by double-resonance experiments. The SSCC values for the three vicinal methine protons ($J_{6,7}$, $J_{5,6}$, $J_{4,5}$, $J_{4,10}$) show the trans linkage of the lactone and seven-membered rings.

On the basis of the identity of the PMR spectra and the closeness of the other physicochemical constants, lactone (I) was identified as talassin A [3, 4], (III) as malaphyllinin [5], (VII) as malaphyll, and (VIII) as malaphyllin [6]. The other three compounds are new and have been called giferolide (II), ferugolide (IV), and gigantolide (VI).

The PMR spectra (Table 1) showed that the acid residues in the giferolide (II) molecule are benzoyl and senecioyl, in ferugolide they are anisoyl and senecioyl, and in gigantolide anisoyl and acetyl. The mutual arrangement of the acyl residues in each of the lactones was determined by the value of the chemical shift of the proton at C-6. As follows from the literature, the position of the signal of this proton is determined by the nature of the acid residue. In the case of saturated aliphatic acids the proton in a hemiacyl position to the ester group gives a signal in the 4.68-4.84 ppm region [4, 7]. On passing to α,β-unsaturated or aromatic acids, the H-signal undergoes a considerable downfield shift to 5.49-5.65 and 5.73 ppm, respectively [4, 6].

Among the diacyloxyguanolides that we are considering it is possible to isolate three combinations of aromatic and saturated acids and three combinations of aromatic and unsaturated acids. However, in all cases the chemical shift of the C-6 proton is practically the same. Consequently, it is determined by a factor common to all the compounds, i.e., there is an aromatic acid at C-6.

Thus, giferolide, ferugolide, and gigantolide have the structures (II), (IV), and (VI), respectively.

The mass spectra of substances (II-IV) and (VI-VIII) contain molecular peaks of considerable intensity. The main directions of fragmentation of the molecular ions are connected with the splitting out of acyl fragments with localization of the charges on them. The formation of ions corresponding to the ejection of neutral molecules of acids is also observed, and in the case of the substituted benzoates the charge may be localized on the aromatic acid molecule being eliminated, because of which the spectrum contains not only the peak $M - R_1COOH]^{\cdot +}$ but also an intense peak of $R_1COOH]^{\cdot +}$.

A characteristic ion in the mass spectra of compounds (II-IV) and (VI-VIII) is an ion with m/e 242. The formation of this ion is connected with the splitting out of an acyloxy group, accompanied by rearrangement processes. In the region of mass numbers less than 242, the spectra of the lactones studied contain ions with m/e 227, 224, 213, 214, 199, 186, and 171, arising in the decomposition of the ion with m/e 242.

Thus, the skeleton of compounds (II-IV) and (VI-VIII) begins to break down in the later stages of the decomposition of the molecular ion after the splitting out of the acyl residues.

The results of the investigation performed show that in its chemical composition *F. gigantea* is extremely close to other species of the subsection Tumidae M. Pimen. et J. Baranova of the section Paleonartex Korov., namely *F. malacophylla* and *F. diversittata*. For all these species, in contrast to the other taxons within the section, the presence of a series of sesquiterpene lactones is characteristic.

EXPERIMENTAL

The compounds obtained were dried in vacuum over P_2O_5. The melting points were determined on a Kofler block. The IR spectra were taken on UR-20 spectrometer (mulls in paraffin oil). The UV spectra were obtained on a Hitachi EPS-3T spectrophotometer (solutions of the substances in 96% ethanol). The PMR spectra were measured on a Varian HA-100D spectrometer with $CDCl_3$ as solvent and TMS as standard. The ^{13}C NMR spectra were obtained on a Varian CFT-20 instrument and the mass spectra on a Varian CH-8 instrument. The elementary analyses corresponded to the calculated figures.

Isolation of the Combined Lactones. The comminuted roots of *Ferula gigantea* (1.442 kg) were extracted twice with acetone in portions of three liters and 1.6 liters for 17 h each. After the elimination of the solvent in the vacuum, 146.4 g of a viscous resinous residue was obtained.

Separation of the Lactones. A portion of the extract (50.0 g) was chromatographed on a column containing 1 kg of silica gel L 40/100 μ. Mixtures of petroleum ether and ethyl acetate with increasing concentrations of the latter were used as eluents. Fractions with a volume of 300 ml were collected.

Isolation of Talassin A (I). Fractions 115-118 (eluent a 25% solution of ethyl acetate and petroleum ether) furnished 0.064 g of a crystalline substance, $C_{25}H_{30}O_7$, mp 188-191°C (from a mixture of ethyl acetate and petroleum ether), $[\alpha]_D^{21}$ −2.3° (c 0.278; chloroform); UV spectrum, λ_{max}, nm (log ε): 202, 224, 252 (4.15, 4.34, 4.25). IR spectrum, cm^{-1}: 1795, 1710, 1692, 1640, 1620. Mass spectrum: M^+ 442, m/e 83, 105, 342, 364, 382.

Isolation of Giferolide (II). Fractions 129-135 (27% solution of ethyl acetate in petroleum ether) yielded 0.186 g of a crystalline substance with the composition $C_{27}H_{28}O_7$, mp 263-266°C, decomp. (ethyl acetate—petroleum ether), $[\alpha]_D^{21}$ −5.9° (c 0.689;chloroform). UV spectrum, λ_{max}, nm (log ε): 202, 231, 254 (inflection) (4.43, 4.49, 4.30). IR spectrum, cm^{-1}: 1790, 1710, 1691, 1642, 1621, 1605. Mass spectrum: M^+ 464, m/e 83, 105, 242, 260, 342, 364, 382.

Isolation of Malaphyllinin (III). Fractions 142-147 (35% solution of ethyl acetate) gave 1.236 g of a yellowish powder with the composition $C_{24}H_{24}O_7$, mp 231-235°C (ethanol), $[\alpha]_D^{21}$ +19° (c, 1.156; chloroform). UV spectrum, λ_{max}, nm (log ε): 202, 238, 251 (infl.) (4.35, 4.33, 4.30). IR spectrum: 1795, 1745, 1715, 1695, 1645, 1625, 1610. Mass spectrum: M^+ 424, m/e 43, 105, 242, 260, 302, 364, 382.

Isolation of Ferugolide (IV). Fractions 149 (36% solution of ethyl acetate) provided 18 mg of a crystalline substance, $C_{28}H_{30}O_8$, mp 232-234°C (ethyl acetate—petroleum ether). UV spectrum, λ_{max}, nm (log ε): 203, 210-214, 216, 232 (infl.), 260, 323 (4.39, 4.38, 4.38, 4.33, 4.50, 2.29). IR spectrum, cm^{-1}: 1791, 1720, 1697, 1645, 1625, 1610. Mass spectrum: M^+ 494, m/e 83, 135, 152, 242, 260, 342, 394, 412.

Isolation of Umbelliferone (V). Fractions 152-155 (37-40% solution of ethyl acetate furnished 0.201 g of a microcrystalline substance, $C_9H_6O_2$, mp 230-233°C (ethanol). UV spectrum, λ_{max}, nm (log ε): 217, 245, 255, 329 (4.06, 3.52, 3.40, 4.12). PMR spectrum: 7.84, 1 H, d, J = 10.0 Hz (H-4); 7.46, 1 H, d, J = 8.5 Hz (H-5); 6.79, 1 H, q, J_1 = 8.5 Hz, J_2 = 2.5 Hz (H-6); 6.73, 1 H, d, J = 2.5 Hz (H-8); 6.18, 1 H, d, J = 10.0 Hz (H-3).

Isolation of Gigantolide (VI). Fractions 157-160 (40% solution of ethyl acetate) yielded 0.335 g of a crystalline substance, $C_{25}H_{26}O_8$, mp 192-193°C (ethyl acetate—petroleum ether), $[\alpha]_D^{21}$ +2.1° (c 0.804; chloroform). UV spectrum, λ_{max}, nm (log ε): 202, 211, 261 (4.37, 4.23, 4.53). IR spectrum, cm^{-1}: 1789, 1745, 1708, 1689, 1640, 1620, 1610. Mass spectrum: M^+ 454, m/e 43, 135, 152, 242, 260, 302, 394, 412.

Isolation of Malaphyll (VII). Fractions 168-172 (45-50% solution of ethyl acetate) gave 0.802 g of a crystalline substance, $C_{29}H_{32}O_9$, mp 212-213°C (ethyl acetate—petroleum ether), $[\alpha]_D^{21}$ −5.6° (c 0.958; chloroform). UV spectrum, λ_{max}, nm (log ε): 205, 223, 262, 295 (4.57, 4.70, 4.43, 3.93). IR spectrum, cm^{-1}: 1789, 1720, 1710, 1690, 1640, 1620, 1604. Mass spectrum: M^+ 524, m/e 83, 165, 182, 242, 260, 342, 424, 442.

Isolation of Malaphyllin (VIII). Fractions 176-183 (50-60% solution of ethyl acetate) provided 1.65 g of a crystalline substance, $C_{26}H_{28}O_9$, mp 216-218°C, $[\alpha]_D^{21}$ +3.1° (c 0.855; chloroform). UV spectrum, λ_{max}, nm (log ε): 203, 223, 264, 296 (4.29, 4.35, 4.37, 3.85). IR spectrum, cm^{-1}: 1790, 1745, 1710, 1692, 1641, 1621, 1605. Mass spectrum: M^+ 484, m/e 43, 165, 182, 242, 260, 302, 424, 442.

SUMMARY

From the roots of *Ferula gigantea* B. Fedtch. we have isolated umbelliferone, talassin A, malaphyll, malaphyllinin, and malaphyllin and three new sesquiterpene lactones (giferolide, ferugolide, and gigantolide), the structures of which have been established on the basis of spectral characteristics.

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ANABSIN — A NEW DIGUAIANOLIDE FROM *Artemisia absinthium**

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

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The new diguaianolide anabsin, $C_{30}H_{40}O_7$, mp 276°C (decomp.), $[\alpha]^{25}$ +110° (c 1.7; acetone) has been isolated from *Artemisia absinthium* L. Anabsin acetate, dehydroanabsin, and dehydroanabsin acetate have been obtained. A comparative study of the ^1H and ^{13}C NMR spectra of anabsin, absinthin, and anabsinthin has been made. The structure of anabsin has been established and structures have been suggested for absinthin and anabsinthin. The most probable biogenesis of anabsin in plants has been put forward.

Continuing a study of the sequiterpene lactones of *Artemisia absinthium* L., family Compositae, in addition to the known lactones artabsin and absinthin [1, 2], we have isolated a new compound anabsin (I), $C_{30}H_{40}O_7$, mp 276°C (decomp.), $[\alpha]_D^{25}$ +110° (c 1.7; acetone).

Anabsin dissolves on heating in dilute solutions of alkalis, and on acidification is liberated in unchanged form, which is characteristic for compounds containing a lactone ring.

The IR spectrum of (I) (Fig. 1) has absorption bands at 3385 and 1760-1780 cm^{-1}, which are characteristic for a hydroxy group and the carbonyl of a γ-lactone ring. The signals of the carbon atoms of the carbonyls of the ester groups in the ^{13}C NMR spectrum appear in the form of singlets at 178.4 and 178.9 ppm. Consequently, in the anabsin molecule four oxygen atoms participate in the formation of two γ-lactone rings.

The PMR spectrum of (I) (Fig. 2) shows the three-portion signals of six methyl groups: doublets at 0.97 and 1.09 ppm with ^3J = 6.7 Hz, 2 ($CH—CH_3$); singlets at 1.22, 1.31, and 1.57 ppm, 3 ($—C—CH_3$); broadened singlet at 1.90 ppm ($—CH=C—CH_3$). The signals of protons geminal to lactone oxygen atoms (lactone protons) appear in the form of one-proton doublets at 4.18 and 4.74 ppm with ^3J = 9.7 and 9.0 Hz, respectively, the components of the second doublet being considerably broadened. The nature of the splitting of these signals shows that each of the lactone protons interacts with only one vicinal proton. A broadened one-proton singlet at 4.07 ppm with $J \lesssim 1$ Hz belongs to a proton in the geminal position to a secondary hydroxy group (hemihydroxylic proton) of the molecule of (I), since it is just the signal that is shifted downfield and is present at 5.07 ppm in the spectrum of the acetyl derivative of anabsin (II). Anabsin acetate was obtained by the acetylation of (I) with acetic anhydride in pyridine. The signals of three methine protons had the form of broadened doublets at 2.81 and 3.77 ppm with ^3J = ^3J = 9.9 Hz and a singlet at 2.69 ppm, and the

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