Hydroxylactone (VI). A solution of 200 mg of the lactone (I) in 8 ml of 4% KOH (ethanolic) was heated at 50-60°C in the water bath for 2 h. The mixture was cooled, diluted with water and acidified with 5% H_2SO_4 to pH 1. The reaction product was extracted with ethyl acetate and chromatographed on silica gel. This gave 45 mg of a crystalline substance with the composition $C_{15}H_{19}O_5Cl$, mp 191-193.5°C, M^+ 314. IR spectrum, cm^{-1}: 3430 (OH); 1750 (γ-lactone); 1660, 1635 (C=C); 740 (C—Cl).

SUMMARY

From the epigeal part of *Saussurea elegans* Ledeb. have been isolated the lactones chlorohyssopifolin B and elegin, $C_{19}H_{23}O_6Cl$. On the basis of spectral characteristics and chemical transformations it has been established that elegin has the structure of 15-chloro-3,4-dihydroxy-8-methacryloyloxyguaia-10(14),11(13)-dien-6,12-olide.

LITERATURE CITED

1. I. D. Sham'yanov, A. Mallabaev, U. Rakhmankulov, and G. P. Sidyakin, Khim. Prirodn. Soedin., 819 (1976).
2. R. Adams (editor), Organic Reactions, Vol. 2, Wiley (1942-1949).
3. A. G. Gonzalez, J. Bermejo, et al., Tetrahedron Lett., 20, 2017 (1972); Phytochemistry, 13, No. 7, 1193 (1974); J. Chem. Soc., 15, 1163 (1976).
4. A. G. Gonzalez, J. Bermejo, et al., Can. J. Chem., 56, No. 4, 491 (1978).

THE LACTONES OF *Ferula malacophylla*

V. Yu. Bagirov, V. I. Sheichenko,
R. Yu. Gasanova, and M. G. Pimenov

UDC 547.615.256.54.011.5

As a result of the chromatographic separation of the total extractive substances of the roots of *Ferula malacophylla* [1], we have isolated sesquiterpene lactones corresponding to the compositions $C_{25}H_{30}O_7$ (I), M^+ m/e 442, mp 191-192°C (ethanol); $C_{29}H_{32}O_9$ (II), M^+ with m/e 524, mp 204-205°C (ethanol); and $C_{26}H_{28}O_9$ (III), M^+ with m/e 484, mp 216-217°C (ethanol).

The UV spectrum of compound (I) shows absorption maxima at 224 and 250 nm (log ε 4.56 and 4.49), and its IR spectrum contains absorption bands at (cm^{-1}) 1795 (CO of a γ-lactone), 1710 (CO of an ester group), 1690 (CO of an α,β-unsaturated cyclopentanone), and 1640 and 1618 cm^{-1} (double bonds in conjugation).

On the basis of the identity of their UV, IR, NMR, and mass spectra and also of the absence of a depression in a mixed-melting point with an authentic sample of the substance, compound (I) was identified as talassin A [2, 3]. So far as concerns compounds (II) and (III), they are new, not previously described in the literature, and we have called them malaphyll and malaphyllin, respectively.

The UV spectrum of malaphyll contains absorption maxima at 221, 260, and 292 nm (log ε 4.61, 4.46, and 3.95), and the UV spectrum of this molecule has absorption bands at (cm^{-1}) 1795 (CO of a γ-lactone), 1720, 1710 (CO of an ester); 1692 (CO of an α,β-unsaturated cyclopentanone); and 1640, 1620, 1615, and 1505 (double bonds in conjugation). The NMR spectra of malaphyll and malaphyllin (see Table 1 and Fig. 1) are extremely similar to the spectra of talassins A and B [3] and of olgin and olgoferin [4]. This indicates the identity of the skeleton and lactone rings, and the positions of the substituents in these molecules.

Consequently, malaphyll and malaphyllin also belong to the group of guaiadienolides acylated at C_6 and C_{11} and differ from the lactones mentioned only by the corresponding acyl residues. The presence in the PMR spectra of malaphyll and malaphyllin of the signals of the protons of two methoxy groups (3.92 and 3.94 ppm) and of the protons of an aromatic ring (6.92 ppm, 1 H, doublet, J_{ortho} = 8.2 Hz; 7.53 ppm, 1 H, doublet, J_{meta} = 2 H; and 7.65 ppm,

---

V. L. Komarov Institute of Botany, Academy of Sciences of the Azerbaidzhan SSR, Baku. All-Union Scientific-Research Institute of Medicinal Plants, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 445-449, July-August, 1978. Original article submitted May 10, 1978.

0009-3130/78/1404-0377$07.50 © 1979 Plenum Publishing Corporation

TABLE 1

Proton	δ, ppm; J, Hz; multiplicity	
	Talassin A	malaphyll and malaphyllin
H-2	6,20; m 1/2 $W=4{,}0$	6,21; m, 1/2 $W=4{,}0$
H-4	4,73; q, $J_{4,5}=10{,}0$ $J_{4,10}=11{,}0$	4,72; q, $J_{4,5}=10{,}0$ $J_{4,10}=11{,}0$
H-5	3,64; q, $J_{5,6}=10{,}3$ $J_{4,5}=10{,}0$	3,67; q, $J_{5,6}=10{,}3$ $J_{4,5}=10{,}0$
H-6	5,65; q, $J_{6,7e}=3{,}9$ $J_{6,7a}=10{,}3$	5,73; q, $J_{6,7e}=3{,}9$ $J_{6,7a}=10{,}3$
H-7a	2,49; q, $J_{7a,7e}=18{,}1$ $J_{6,7a}=10{,}3$	2,58; q, $J_{7a,7e}=18{,}1$ $J_{7a,6}=10{,}3$
H-7e	2,93; q, $J_{7e,7a}=18{,}1$ $J_{7e,6}=3{,}9$	3,04; q, $J_{7e,7a}=18{,}1$ $J_{7e,6}=3{,}9$
H-10	3,62; d, $J_{10,4}=11{,}0$	3,63; d, $J_{10,4}=11{,}0$
CH_3-13	1,62; s	1,61; s
CH_3-14	2,24; s	2,26; s
CH_3-15	2,24; s	2,26; s

Note. s) singlet; d) doublet; q) quartet; m) multiplet.

1 H, quartet, J_{ortho} = 8.2 Hz and J_{meta} = 2 Hz) shows that one of the acyls in compounds (II) and (III) is a 3,4-dimethoxybenzoic acid residue. The saponification of malaphyll and malaphyllin formed an aromatic acid with the composition $C_9H_{10}O_4$, M^+ with m/e 182, mp 182-183°C (ethanol), which we have identified as veratric acid [5]. The second acyl group in malaphyll is a 2,2-dimethylacrylic, i.e., senecioic, acid residue. This is shown both by the presence in the NMR spectrum of malaphyll of two singlet signals of the protons of vinylmethyl groups (1.97 and 2.20 ppm, 3 H each) and of the signal of an olefinic proton (6.22 ppm, 1 H), and also by gas chromatography with markers [6].

The positions of the acyl residues in the malaphyll and malaphyllin molecules follow from a consideration of the signals of the H-6 proton and of the proton of the methylene group (H-7e and H-7a). In a comparative study of the NMR spectra of these molecules with talassin A, a downfield shift of the signals of the H-6, H-7e, and H-7a protons of from 0.08 to 0.13 ppm is observed. An evaluation of the contribution of the currents to the chemical shifts of the H-7e and H-7a protons [7] for a molecule in which the H-6 proton, the oxygen atom of the ester carbonyl group, and the benzene ring are present in the same plane gives a value of the paramagnetic shift of $\sim$0.1 ppm for these protons, i.e., close to the observed value. Also in favor of the location of the aromatic methyl group at C_6 is the comparatively large value of the chemical shift of the H-6 proton (5.73 ppm) in malaphyll and malaphyllin relative to the position of the same signal in the spectra of talassins A and B and olgin and olgoferin [4].

Thus, on the basis of the facts presented for malaphyll we suggest the structure of 1-hydroxy-11-senecioyloxy-6-veratroyloxyguaia-2,8-dien-4,5-olide.

The third compound — malaphyllin — has in its UV spectrum absorption maxima at 223, 262, and 293 nm (log ε 4.39, 4.41, 3.93). The IR spectrum of this molecule shows absorption bands at (cm^{-1}) 1792 (CO of a γ-lactone); 1740 (CO of an acetyl group); 1703 (CO of an ester group); 1690 (CO of an α,β-unsaturated cyclopentanone); and 1640, 1620, 1600, 1590, and 1515 (double bonds in conjugation).

A comparative study of the features of the NMR spectra (see Fig. 1 and Table 1) of malaphyll and malaphyllin shows that these compounds differ only by the acyl substituent at C_{11}. In the malaphyllin molecule, the acyl in the C_{11} position is an acetic acid residue. This is confirmed both by the presence in the NMR spectrum of malaphyllin of the signal of the protons of an acetyl group (2.15 ppm, 3 H) and also by gas chromatography with markers [6].

The facts given above permit the suggestion for malaphyllin of the structure of 11-acetoxy-1-oxo-6-veratroyloxyguaia-2,8-dien-4,5-olide.

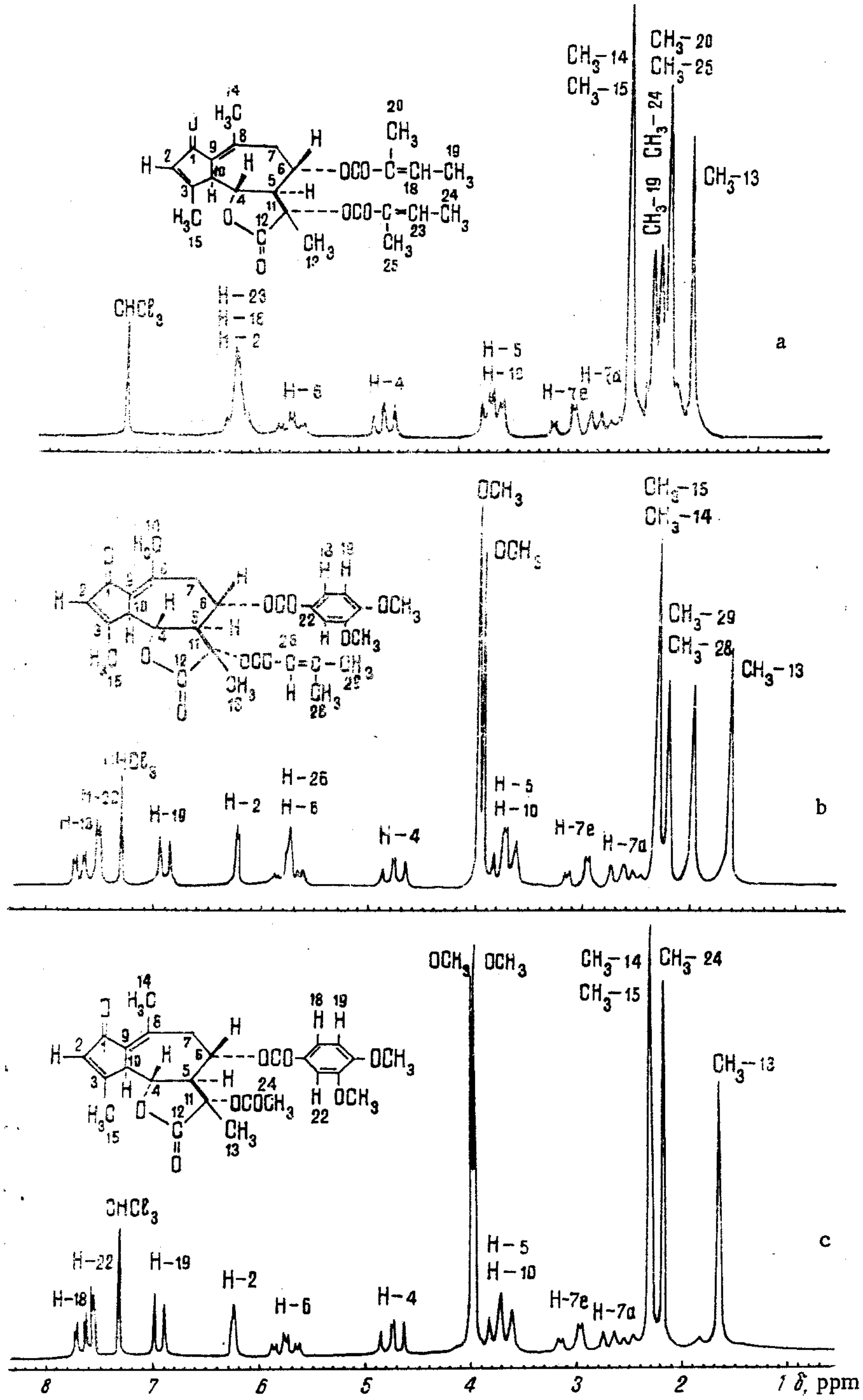

Fig. 1. NMR spectra of talassin A (a), malaphyll (b), and malaphyllin (c).

EXPERIMENTAL

The UV spectra were recorded in 96% ethanol on an EPS-3T spectrophotometer (Hitachi), the IR spectra (mulls in paraffin oil) on a UR-20 spectrophotometer, the NMR spectra (in $CDCl_3$, 0 — TMS, δ scale) on a JNM-4H-100 MHz spectrometer (Varian), and the mass spectra on a CH-8 spectrometer (Varian). The R_f values were obtained on "Silufol UV-254" plates in the chloroform system, and the melting points of the substances were determined on a Kofler block.

Isolation of Talassin A (I), Malaphyll (II), and Malaphyllin (III). A solution in 5 ml of chloroform of 1 g of the viscous resin obtained by the acetone extraction of the roots of

F. malacophylla was deposited on a column of neutral alumina (activity grade IV, 250 g). Elution was carried out with hexane—chloroform (1:2), 5-ml fractions being collected. The individuality of the fraction was checked on Silufol plates. Fractions 6-8 yielded compound (I) with the composition $C_{25}H_{30}O_7$, M^+ with m/e 442; mp 191-192°C (ethanol), R_f 0.28. When the column was then eluted with hexane—chloroform (1:3), fractions 24-26 yielded a compound with the composition $C_{29}H_{32}O_9$, M^+ with m/e 524, mp 204-205°C (ethanol), R_f 0.17, and fractio 27-29 yielded a compound with the composition $C_{26}H_{28}O_9$, M^+ with m/e 484, mp 216-217°C (ethanol), R_f 0.14.

Saponification of Malaphyll (II). A solution of 0.5 g of malaphyll in 100 ml of 2% ethanolic KOH was heated in a boiling-water bath for 1 h. Then the ethanol was evaporated off in vacuum and the residue was diluted with water and was repeatedly treated with chloroform. The alkaline solution was acidified with 5% H_2SO_4 and was extracted with diethyl ether. The extract was washed with water and dried over sodium sulfate. The solvent was distilled off, and the residue was dissolved in ethanol. On standing, crystals of veratric acid deposited with the composition $C_9H_{10}O_4$, M^+ with m/e 182, mp 182-183°C (ethanol). UV spectrum: λ_{max} 254 and 290 nm (log ε 3.97 and 3.64). IR spectrum, ν_{max}: 3040 (OH of a carboxyl); 1685 (CO of a carboxyl); 1602, 1590, and 1527 (benzene ring).

We detected senecioic and acetic acids, respectively, in the hydrolysis products of malaphyll and malaphyllin by gas chromatography with markers [6].

SUMMARY

1. From the roots of *Ferula malacophylla* three sesquiterpene lactones have been isolated: talassin A and the two new ones — malaphyll and malaphyllin.

2. On the basis of spectral and chemical characteristics, for malaphyll is proposed the structure of 1-oxo-11-seneciocyloxy-6-veratroyloxyguaia-2,8-dien-4,5-olide, and for malaphyllin 11-acetoxy-1-oxo-6-veratroyloxyguaia-2,8-dien-4,5-olide.

LITERATURE CITED

1. M. G. Pimenov and Yu. V. Baranova, Byull, Glav. Bot. Sada, No. 106, 43 (1977).
2. E. Ya. Kiseleva, O. A. Konovalova, and K. S. Rybalko, Khim. Prirodn. Soedin., 668 (1971)
3. O. A. Konovalova, K. S. Rybalko, and M. G. Pimenov, Khim. Prirodn. Soedin., 122 (1973).
4. O. A. Konovalova, K. S. Rybalko, and V. I. Sheichenko, Khim. Prirodn. Soedin., 590 (1975)
5. M. Goryaev and I. Pliva, Methods of Investigating Essential Oils [in Russian], Alma-Ata (1962), p. 588.
6. V. S. Kabanov and V. V. Vandyshev, Khim. Prirodn. Soedin., 711 (1974).
7. C. E. Johnson and F. A. Bovey, J. Chem. Phys., 29, 1012 (1958).