SESQUITERPENE LACTONES OF *Ferula olgae*

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The presence in the roots of *Ferula olgae* Regel et Schmalh, of two new sesquiterpene lactones, olgoferin and olgin, has been reported previously. On the basis of UV, IR, NMR, and mass spectra we have suggested structures (I) and (IIIa) for them [1].

The present paper gives the results of the isolation from this type of raw material of another four sesquiterpene lactones and of chemical transformations of olgoferin, olgin, and 4-acetoxypruteninone, on the basis of which the structures of olgin, 4-acetoxypruteninone, and talassin B have been reconsidered. Tables 1 and 2 give the constants of the substances

TABLE 1

Lactone and its composition	mp, °C	$[\alpha]_D^{20}$, deg	IR characteristics, ν_{max}	UV characteristics, λ_{max}
Olgoferin (I) $C_{23}H_{26}O_7$	240–244 (from ethanol)	+46,9 (*c* 5,1; chlf.)	1790 (γ-lactone) 1710 (OCO–C=C), 1690 (CO–C=C), 1640 and 1620 cm^{-1} (C=C)	253,5 nm, ε 22 011
Oferin (II) $C_{23}H_{28}O_7$	214–216 (Kofler) from a mixture of benzene and petroleum ether	±0 (*c* 2,62; chlf.)	1790 (γ-lactone) 1735 (OCO), 1710 (OCO–C=C), 1690 (CO–C=C), 1640 and 1620 cm^{-1} (C=C in conjugation)	254 nm, ε 16 045
Olgin (III) $C_{21}H_{24}O_7$	176–178 (from ethanol)	+25 (*c* 4,0; chlf.)	1795 (γ-lactone) 1745 (OCO), 1712 (OCO–C=C), 1688 (CO–C=C), 1638 and 1616 cm^{-1} (C=C in conjugation)	254 nm, ε 12 672
Talassin A (IV) $C_{25}H_{30}O_7$	188–191 (from a mixture of petroleum ether and diethyl ether)	–29,6 (*c* 2,0; chlf.)	1790 (γ-lactone) 1717 (OCO), 1690 (C=C–C=O), 1645 and 1620 (C=C in conjugation) cm^{-1}	248 nm, ε 24 000
Talassin B (V) $C_{24}H_{30}O_7$	205–208 (from a mixture of petroleum ether and diethyl ether)	–72,1 (*c* 4,16; chlf.)	1800 (γ-lactone) 1750 (OCO), 1720 (OCO–C=C), 1700 (C=C–C=O), 1650 and 1623 cm^{-1} (C=C in conjugation)	251 nm, ε 26 000
Laferin (4-acetoxyprut-eninone) (VI) $C_{25}H_{32}O_7$	142–144 (Kofler) from a mixture of petroleum ether and diethyl ether	–3,1 (*c* 2,97; chlf.)	1800 (γ-lactone) 1745 ($OCOCH_3$), 1710 (OCO–C=C), 1690 (CO–C=C), 1640 and 1620 cm^{-1} (C=C in conjugation)	253,5 nm, ε 16 500

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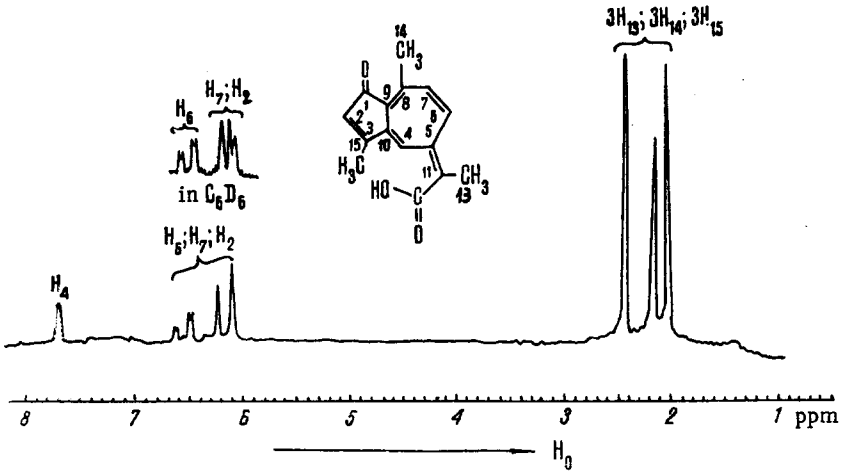


Fig. 1. NMR spectrum of (VIII).

isolated and their UV, IR, and NMR spectra. It can be seen from the tables that all the sesquiterpene lactones isolated contain a guaiadienone grouping (λ_{max} 248-254 nm; λ_{max} 1690, 1640, 1620 cm^{-1}; two singlets of 3 H each at 2.0-2.20 ppm). The fact that these lactones belong to the guaianolide group was confirmed by the production of chamazulene on their dehydrogenation.

The lactones isolated differ in the structure of their molecule only by the nature of the acyl groups, the positions of which are the same in all of them: one of them is located at C_{11}, as is shown by a 3 H singlet at 1.3-1.6 ppm and ν_{max} 1790-1800 cm^{-1}1 and the second acyl group is located at C_6, as is shown by a sextet at 5.20-5.55 ppm. The correctness of these conclusions has been shown by chemical transformations. All the lactones, on hydrolysis in 4% ethanolic KOH, gave an acid (VIII) with the composition $C_{15}H_{14}O_3$ in the form of red crystals (for its NMR spectrum, see Fig. 1). The formation of this acid is possible only through the intermediate product (VII). The ease of splitting off the hydroxy groups present in the β position to the guaiadienone group has already been mentioned in a study of the structure of austricin and grossmisin [2, 3], and, as is well known, tertiary hydroxyls are also readily split off.

The hydrogenation of the lactone (I) formed the octahydro and hexahydro derivatives (IX) and (X). The hydrolysis of (X) in the presence of K_2CO_3 also led to the splitting off of hydroxyls with the formation of a yellow crystalline substance with the composition $C_{15}H_{16}O_3$ (XII). It follows from UV and NMR spectra (Fig. 2) that secondary and tertiary hydroxyls were split off and a chromophoric grouping was formed.

The hydrolysis of olgoferin in 4% KOH at room temperature took place partially. The tertiary hydroxy group arising reacted with the double bond at C_8-C_9, which led to the appearance of the oxide (XIII), in the NMR spectrum of which an upfield shift of the protons of the two methyls was observed (see Table 2), while the IR spectrum lacked the absorption band of a hydroxyl. Thus, the chemical transformations confirmed that the lactones isolated belong to the group of guaiadienolides acylated at C_6 and C_{11}.

On comparing the results obtained with literature data it can be seen that the lactones (IV) and (V) are identical with talassins A and B, respectively [4], lactone (VI), with 4-acetoxypruteninone (6-acetoxypruteninone in our numbering) [5], and lactones (I) (II), and (III) which we have named, respectively, olgoferin, oferin, and olgin, are new, not having been described previously in the literature.

In olgoferin, both acyl groups consist of methacrylic acid residues: in the NMR spectra there are the signals of the protons of two methyls — singlet at 1.90 ppm — and of 4 vinyl protons — broadened signals in the 5.60–and 6.15–ppm regions (Fig. 3); in the hexahydro and octahydro derivatives of olgoferin (X) and (IX) these signals disappear, and new signals of the protons of the methyls of isobutyric acid appear.

In olgin, the acyl groups are different; one of them is an acetoxy group and the other

TABLE 2

Compound	Proton at					
	C_3	C_4	C_6	C_{13}	C_{14}	C_{15}
I	s. 6,12	q . 4,70 $J_{4,5}$ = 10; $J_{4,10}$ = 11,8	sex 5,55 $J_{6',7}$ = 2,0; $J_{6,7}$ = 11; $J_{6,5}$ = 11	s. 1,61	s. 2,20	s. 2,20
II	s. 6,10	q . 4,61 $J_{4,5}$ = 10; $J_{4,10}$ = 11,8	sex 5,50 $J_{6',7}$ = 2,0; $J_{6,7}$ = 11; $J_{6,5}$ = 11	s. 1,52	s. 2,20	s. 2,20
III	s. 6,12	q . 4,61 $J_{4,5}$ = 10: $J_{4,10}$ = 11,8	sex 5,49 $J_{6',7}$ = 2,0; $J_{6,7}$ = 11; $J_{6,5}$ = 11	s. 1,52	s. 2,19	s. 2,19
IV	s. 5,85	q . 3,90 $J_{4,5}$ = 10; $J_{4,10}$ = 11,8	sex 5,20 $J_{6',7}$ = 2,0; $J_{6,7}$ = 11; $J_{6,5}$ = 11	s. 1,32	br.s 2,0	br. s 2,0
V	br.s 5,85	q . 3,90 $J_{4,5}$ = 10; $J_{4,10}$ = 11,8	sex 5,20 $J_{6',7}$ = 2,0 $J_{6,7}$ = 11; $J_{6,5}$ = 11	s. 1,35	br. s 2,0	br. s 2,0
VI	br.s 6,12	q . 4,60 $J_{4,5}$ = 10; $J_{4,10}$ = 11,8	sex 5,52 $J_{6',7}$ = 2,0 $J_{6,7}$ = 11; $J_{6,5}$ = 11	s . 1,53	br. s 2,20	br. s 2,20
VIII	s. 6,11	br.s 7,72	q 6,52 $J_{6,7}$ = 13	s. 2,45	br. s 2,15	br. s 2,05
IX	—	q . 4,70	m 4,90	s. 1,42	1,10—1,20	1,10—1,20
XV	—	q . 4,70	m. 5,20	s. 1,42	br. s 2,12	d in the range 1.0-1.2
XII	—	d. 4,98	—	d. 2,45 J = 3,0	s. 1,95	d 1,10
XIII	s. 6,10	t. 4,60	sex 5,50	s. 1,20	s. 1,20	s 2,20
XVIII	—	t . 4,60	m . 5,0	s. 1,20	d in the rangel.0-1.2	d in the range 1.0-1.2
XX	s. 6,12	t . 3,88	sex 4,75	d . 1,15	s. 2,28	s 2,50
XXI	s. 6,15	t . 3,72	sex 4,84	d. 1,30	s. 2,28	s 2,45

At other atoms

I s 1.90 (6 H), methyl; br. sig 5.60 and 6.15 (4 H), vinyl protons of methacryloyl

II two d at 1.2 (6 H), methyls of isobutyric acid; br. sig. at 5.60 and 6.12, vinyl protons, and s 1.81 — methacryloyl methyl

III s 1.95, acetyl methyl; s 1.85, methyl; and sig. 6.10 and 5.60, vinyl protons of methacryloyl

IV br. s 1.75 and 1.85 (12 H) m (2H), 5.56, signals of angeloyl protons

V two d at 0.98 and 1.05 (6 H), methyls of isobutyric acid; br. s 1.75 (6 H), methyls; and br. s 5.55, the vinyl proton of angeloyl

VI br. d 1.84 and 1.94 (6 H); br. s 6.16, angeloyl protons; s 2.03 (6 H), acetyl protons

VIII d 6.19. H_7

IX in the 1.0-1.2 region (12 H), protons of reduced acyls

XV s 2.0 (3 H), acetyl methyls; d in the range 1.0-2.0 (6 H), methyls of the second acyl group

XII two d 6.10 and 6.50, H_6 and H_7

XIII s 2.20, methyl; br. s 6.10 and 5.60, vinyl protons of methacryloyl

XVIII t 0.90 and d in the range 1.0-1.2, methyls of α-methylbutyric acid

XX s 2.12, protons of acetyl methyl

XXI s 2.10, protons of acetyl methyl

Notes. The figures are given in ppm relative to HMDS; s) singlet; d) doublet;50 triplet; q) quartet; sex) sextet; m) multiplet; br. sig.) broadened signal. The spectra of the substances were taken in $CDCl_3$ solution, J, Hz; except for (IV) and (V), taken in C_6D_6 solution.

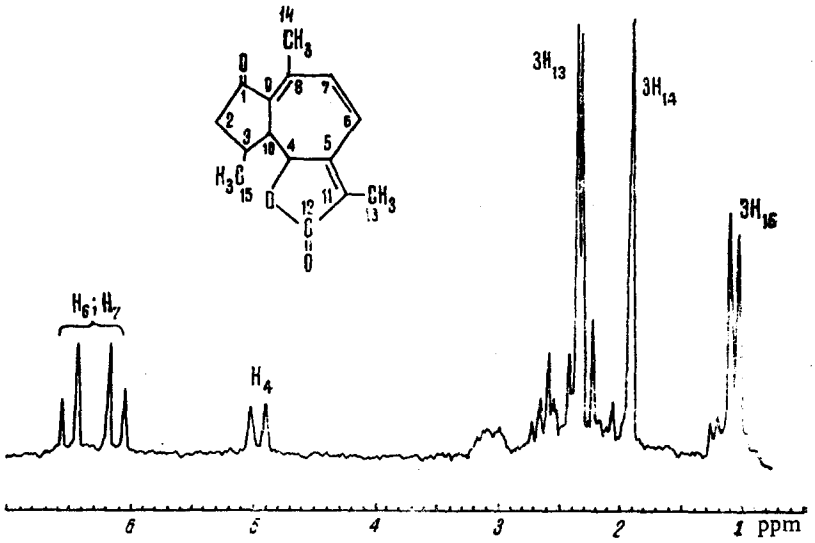


Fig. 2. NMR spectrum of (XII).

a methacryloyloxy group (see Table 2). Their positions in the olgin molecule were determined in the following way. The hydrogenation of olgin formed the hexahydro and tetrahydroderivatives (XIV) and (XV). The hydrolysis of (XV) gave a yellow crystalline substance identical with substance (XII). The hydrolysis of (XIV) gave substance (XVI), the IR spectrum of which showed the absorption bands of a hydroxy and a carbonyl of an ester group, while the NMR spectrum lacked the signal of acetyl protons while containing the signals of a hemiacyl proton (m 5.25 ppm) and the protons of the methyls of isobutyric acid (two d in the 1.05-1.15-ppm region). Consequently, the acetoxy group in olgin is located at C_{11}, and the methacryloyloxy group at C_6, and not conversely, as stated previously [1].

As mentioned above, one of the lactones isolated was identical in its composition and IR and NMR spectra with 4-acetoxypruteninone, first isolated from *Laserpitium prutenicum* L. [5]. Its structure was suggested on the basis of its IR, UV, mass, and NMR spectra without the production of derivatives.

When 4-acetoxypruteninone was hydrogenated, we obtained the hexahydro derivative (XVII), the hydrolysis of which in K_2CO_3 gave substance (XVIII). In its NMR spectrum there were no signals of acetyl protons, while the presence of signals of a hemiacyl proton and of the protons of the methyls of α-methylbutyric acid were present, i.e., the acetoxy group is located not at C_6, as believed previously, but at C_{11}. Consequently, this lactone must be named differently. We have proposed to call it laferin.

I. $R_1=R_2=CO-C(CH_3)=CH_2$

II. $R_1=CO-C(CH_3)=CH_2$; $R_2=CO-CH(CH_3)_2$

III. $R_1=CO-C(CH_3)=CH_2$; $R_2=COCH_3$

IIIa. $R_1=COCH_3$; $R_2=CO-C(CH_3)=CH_2$

IV. $R_1=R_2=CO-C(CH_3)=CHCH_3$

V. $R_1=CO-C(CH_3)=CHCH_3$; $R_2=CO-CH(CH_3)_2$

Va. $R_1=CO-CH(CH_3)_2$; $R_2=CO-C(CH_3)=CHCH_3$

VI. $R_1=CO-C(CH_3)=CHCH_3$; $R_2=COCH_3$

IX. $R_3=R_4=CO-CH(CH_3)_2$

X. $R_5=R_6=CO-CH(CH_3)-CH_3$

XI. $R_3=R_4=H$

XIV. $R_3=CO-CH(CH_3)_2$; $R_4=COCH_3$

XV. $R_5=CO-CH(CH_3)_2$; $R_6=COCH_3$

XVI. $R_3=CO-CH(CH_3)_2$; $R_4=H$

XVII. $R_3=CO-CH(CH_3)-CH_2CH_3$; $R_4=COCH_3$

XVIII. $R_3=CO-CH(CH_3)-CH_2CH_3$; $R_4=H$

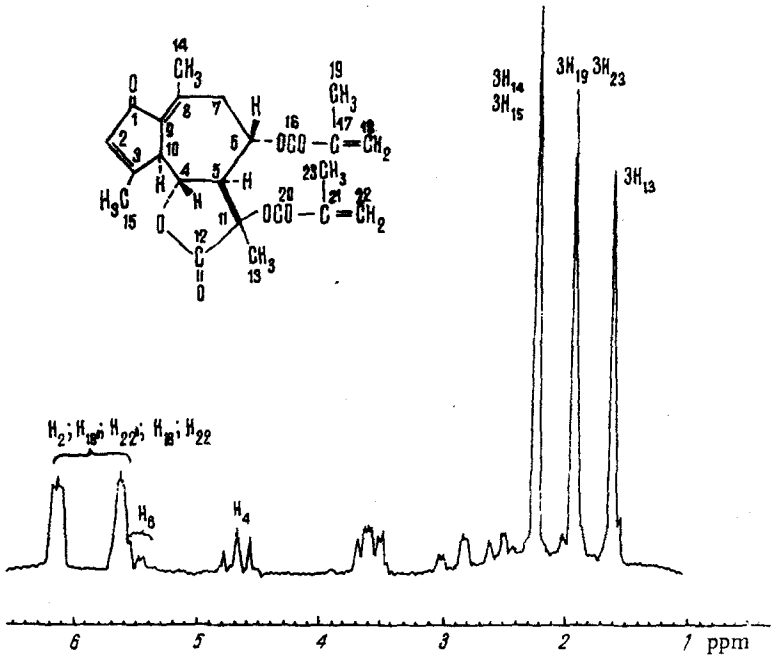
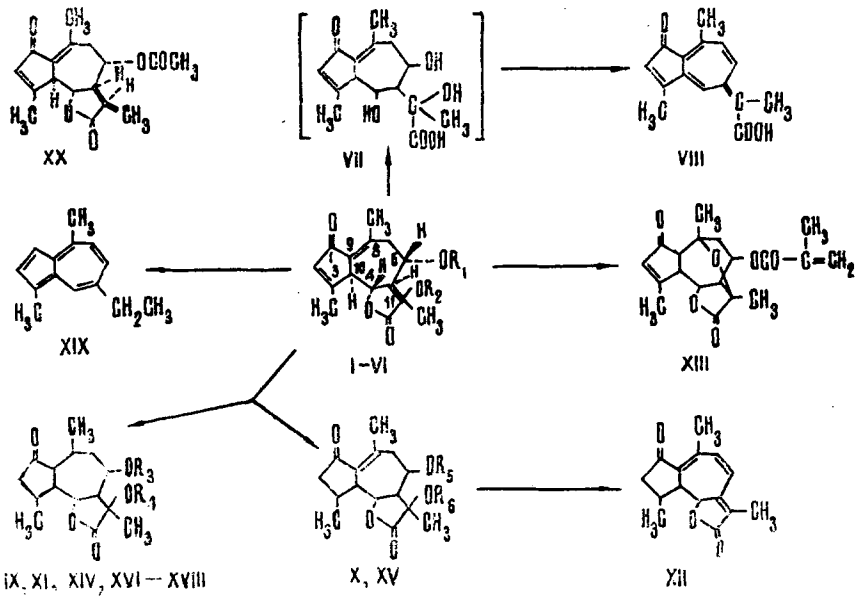


Fig. 3. NMR spectrum of olgoferin (I).

The new sesquiterpene lactone oferin has a molecular weight differing from that of olgoferin by two hydrogen atoms. The results of NMR spectroscopy have shown that one acyl group in its molecule is reduced as compared with olgoferin, i.e., it is an isobutyric acid residue, and the second — just as in olgoferin — is a methacryloyl residue.

In considering the values of the chemical shifts of the hemiacyl proton in the NMR spectra of (I-XXI), we directed our attention to the fact that on reduction of an α-β-unsaturated acyl group the signal of the hemiacyl proton shifts upfield (see Table 2). In the guaiadienones with an acetoxy group at C_6, the signal of the hemiacyl proton is in the region of stronger fields; for example, in acetylgrossmisin (XX) it is at 4.75 ppm and in its

C_{11}-stereoisomer — acetylaustricin (XXI) it is at 4.84 ppm, while in the guaiadienones with α,β-unsaturated acyls at C_6 the signal of the hemiacylproton is present in a weaker field;



for example in olgoferin (I) at 5.55 ppm, in olgin (III), at 5.49 ppm, and so on, i.e., the position of the hemiacyl proton is affected by the nature of the acyl group: in the presence of an α,β-unsaturated acyl the signal is present in a weaker field. This enables us to conclude that in oferin and talassin B the α,β-unsaturated acyls are located at C_6 and not at C_{11} (Va) as has been shown for talassin B [4]. Consequently, oferin is represented by structure (II) and talassin B by (V).

In the NMR spectra of the lactones isolated, the coupling constants $J_{4,5}$, $J_{4,10}$, and $J_{6,5}$ for all the lactones are the same and have a value greater than 10 Hz, which shows the trans arrangement of the protons at C_4–C_5, C_4–C_{10}, and C_5–C_6.

EXPERIMENTAL

Chromatography was performed in a thin layer (TLC) on neutral alumina (activity grade IV) in the benzene–methanol (9:1) system.

The substances obtained were dried in a vacuum pistol over P_2O_5 with heating by ethanol vapor: crystalline substances were dried for 2 h and noncrystalline substances for 6 h.

The IR spectra (mulls in paraffin oil) were taken on a UR-10 spectrometer, the UV spectra (solutions in 96% ethanol) on a Hitachi EPS-3T spectrophotometer, the NMR spectrometer on a Varian JNM-4H-100 MHz spectrometer in $CDCl_3$ solution, and the mass spectra on a Varian CH-8 spectrometer. The analyses of all the compounds corresponded to the calculated figures.

Isolation of the Combined Lactones. The coarsely comminuted roots of *Ferula olgae* Regel et Schmalh. collected in August, 1970, in Kirghizia in the valley of the R. Kokomerena (2 kg) were steeped with acetone in a ratio of 1:5 at room temperature for 24 hours three times. The solvent was distilled off under vacuum. This yielded 195 g of crude resin giving a single spot on TLC in various absorbents with various systems. The resin was chromatographed on neutral alumina (activity grade IV) in a ratio of 1:30. A mixture of petroleum ether and benzene (1:1) eluted cream-colored crystals with mp 205-215°C (14.3 g) and with mp 160-180°C (10.2 g); and benzene eluted almost colorless crystals with mp 160-170°C (13.1 g).

Isolation of Olgoferin (I) and Oferin (II). The crystals with mp 205-215°C were washed repeatedly with ether and were recrystallized from ethanol. This gave substance (I) with the composition $C_{23}H_{26}O_7$, mp 240-244°C (from ethanol), mol. wt. 414.

The mother solutions after the isolation of the olgoferin were rechromatographed on neutral alumina (activity grade IV) in a ratio of 1:100. The eluates obtained on elution with a mixture of petroleum ether and diethyl ether (8:2) yielded substance (II), $C_{23}H_{28}O_7$,

mp 214-216°C (from a mixture of benzene and petroleum ether), mol. wt. 416.

Isolation of Olgin (III). The crystals with mp 160-170°C were recrystallized three times from ethanol. This gave substance (III) with the composition $C_{21}H_{24}O_7$, mp 176-178°C, mol. wt. 388.

Isolation of Talassins A (IV) and B (V) and of Laferin (VI). The crystals with mp 160-180°C were rechromatographed on neutral alumina (activity grade IV) with elution by ether. Three fractions were obtained: 1st with mp 160-190°C, 2nd with mp 145-150°C, and 3rd with mp 160-170°C. Fraction 1 was rechromatographed on silica gel with elution by petroleum ether–diethyl ether (7:3). This yielded two substances with the composition $C_{25}H_{30}O_7$, one with mp 188-191°C (from a mixture of petroleum ether and diethyl ether), $[\alpha]_D^{20} - 29.6°$ (c 2.0 ; chloroform), mol. wt. 442 (mass spectrometrically), and the other with the composition $C_{24}H_{30}O_7$, mp. 205-208°C (from a mixture of petroleum ether and diethyl ether), $[\alpha]_D^{20} - 72.1°$ (c 4.16; chloroform), mol. wt. 430 (mass spectrometrically). From their compositions and constants, and also their Ir, UV, and NMR spectra the substances were identical with talassins A and B, isolated previously from *Talassia transiliensis* (Herd.) Korov. [4].

Fraction 2 with mp 145-150°C was rechromatographed again on neutral alumina (activity grade IV). Elution was performed with petroleum ether–diethyl ether (7:3). A substance was isolated which, after recrystallization from petroleum ether–diethyl ether, had mp 142-144°C (Kofler), $[\alpha]_D^{20} - 3.1°$ (c 2.97; chloroform), composition $C_{22}H_{26}O_7$, mol. wt. 402 (mass spectrometrically).

The constants and IR, UV, and NMR spectra of the substance were identical with those of 4-acetoxypruteninone [5]. As mentioned above, the acetoxy group in the molecule of this substance is located at C_{11}, in view of which it must be given a different name. We proposed to call it laferin.

According to mass spectra, olgoferin is accompanied by oferin and a substance with mol. wt. 428 which are extremely difficult to separate; and oferin is accompanied by a substance with mol. wt. 418. However, we were unable to isolate the substances with mol. wts. 428 and 418 because of their small amount.

Hydrolysis of Olgoferin (I). A. Preparation of (VIII). A mixture of 0.5 g of olgoferin and 100 ml of a 2% ethanolic solution of KOH was shaken at room temperature for 5 min. The resulting dark brown solution was diluted with water, acidified with 5% H_2SO_4, and extracted with chloroform. The chloroform extract was washed with 5% $NaHCO_3$ solution and with water. After the solvent had been driven off, 0.05 g of a resin was obtained. The sodium carbonate extract was acidified with 5% H_2SO_4 and extracted five times with chloroform, and the chloroform extract was washed with water to neutrality. After the solvent had been driven off, a red crystallizing mass was obtained which was chromatographed on silica gel and eluted with ether. This gave 0.13 g of red crystals of (VIII), which were recrystallized from benzene giving a product with mp 171-173°C (from benzene), composition $C_{15}H_{14}O_3$; molecular weight determined mass spectrometrically; IR spectrum: ν_{max} 1700 cm^{-1} (C=O), 1670 cm^{-1} (C=O), and 1635 and 1620 cm^{-1}(C=C). UV spectrum: (I) λ_{max} 266 nm (ε 17,625); (II) λ_{max} 392 nm (ε 11,305).

Compound (VIII) was obtained in high yield by heating 0.21 g of olgoferin in 30 ml of ethanol with 0.5 g of K_2CO_3 in 5 ml of water, and also by the hydrolysis of oligin, 11-acetoxypruteninone, and talassins A and B under the same conditions.

B. Preparation of (XIII). A mixture of 0.3 g of olgoferin with 100 ml of 4% aqueous KOH was left at room temperature with periodic shaking for ten days and was then diluted with water and was extracted four times with chloroform. The chloroform extract was washed with water, and elimination of the solvent gave 0.18 g of the initial compound (identified by its melting point and IR and NMR spectra).

The mother solution was acidified and the reaction product was extracted four times with chloroform, the chloroform extract being washed with sodium bicarbonate solution and then with water. This gave 0.05 g of a vitreous product (XIII) with the composition $C_{19}H_{22}O_6$.

IR spectrum: ν_{max} 1800 cm^{-1} (γ-lactone), 1720 and 1700 cm^{-1}(OCO and C=O), and 1650 and 1625 cm^{-1} (C=C).

After acidification of the sodium carbonate extract, about 0.01 g of a resinous product was isolated.

Hydrogenation of Olgoferin (I). Preparation of the Octahydro and Hexahydro Derivatives (IX) and (X). In the presence of 0.2 g of PtO_2 (Adams), 4 g of olgoferin in 300 ml of ethanol was hydrogenated until the absorption of hydrogen ceased; 3.5 moles was absorbed. After the removal of the catalyst and the ethanol, a vitreous product was obtained which on TLC gave two spots with R_f 0.46 and 0.22. When the hydrogenation product was allowed to stand, crystals appeared, and they were washed with ether and recrystallized from a mixture of petroleum ether and diethyl ether mp 180-182°C; composition $C_{23}H_{34}O_7$ (IX); on TLC R_f 0.22.

IR spectrum: λ_{max} 1790 cm^{-1} (γ-lactone), and 1750 and 1740 cm^{-1} (C=O and OCO).

The second hydrogenation product (X) formed a vitreous mass with the composition $C_{23}H_{32}O_7$, giving on TLC a single spot with R_f 0.46.

UV spectrum: λ_{max} 248 nm (ε 13,937). IR spectrum: λ_{max} 1800 cm^{-1} (γ-lactone), 1750-1735 cm^{-1} (C=O and OCO), and 1640 cm^{-1} (C=C).

Hydrolysis of the Hydrogenation Products of Olgoferin. A. Preparation of (XII). A mixture of 0.3 g of hexahydroolgoferin (X) in 20 ml of ethanol and 0.5 g of K_2CO_3 in 10 ml of water was shaken for 20 min. Then it was left at room temperature for three days and was diluted with water and extracted four times with chloroform. After the solvent had been driven off, a yellow crystallizing mass was obtained which on TLC gave a single spot with R_f 0.42. On recrystallization from ether, yellow crystals deposited with mp 213-215°C of substance (XII) with the composition $C_{15}H_{16}O_3$.

IR spectrum: ν_{max} 1750 and 1720 cm^{-1} (C=O), 1650 and 1610 cm^{-1} (C=C).

UV spectrum: I, λ_{max} 242 nm (ε 22,997); II, λ_{max} 349 (ε 13,652).

B. A mixture of 0.5 g of (IX) in 30 ml of ethanol and 0.5 g of K_2CO_3 in 10 ml of water was shaken and was then left at room temperature for three days. The reaction product was worked up in a similar manner to the preceding experiment. The residue consisted of the starting material

C. Preparation of (XI). A mixture of 0.5 g of (IX) and 100 ml of a 4% solution of KOH was heated in the boiling water bath for 20 min with periodic shaking and was then diluted with water and was extracted four times with chloroform. The chloroform extract was washed with water. After the solvent had been driven off, 0.005 g of the starting material was obtained. The mother liquor was acidified with a solution of H_2SO_4 to pH 1 and extracted with chloroform three times, and the extract was washed three times with $NaHCO_3$ solution and with water. After elimination of the solvent, 0.15 g of a vitreous product (XI) with the composition $C_{15}H_{22}O_5$ was isolated.

IR spectrum: λ_{max} 3400-3350 cm^{-1} (OH), 1780 cm^{-1} (γ-lactone), 1740 cm^{-1} (C=C).

The sodium carbonate extract was acidified with H_2SO_4 solution and extracted with chloroform, and the extract was washed with water. The solvent was driven off, giving about 0.2 g of a dark resinous residue.

Hydrogenation of Olgin. Preparation of (XIV) and (XV). In the presence of 0.2 g of PtO_2 (Adams), 2.75 g of (III) in 200 ml of ethanol was hydrogenated until the absorption of hydrogen ceased, 2.5 moles being absorbed. After the elimination of the catalyst and the ethanol, a crystallizing product was obtained giving, on TLC, two spots with R_f 0.24 and 0.45. The crystals were washed with ether and recrystallized from a mixture of diethyl ether and petroleum ether; on TLC they gave a single spot with R_f 0.24, mp 208-210°C; composition $C_{21}H_{30}O_7$ (XIV).

IR spectrum: λ_{max} 1800 cm^{-1} (γ-lactone), 1750 and 1720 cm^{-1} (OCO and C=O). The mother solution after the isolation of the crystals was chromatographed on neutral alumina (activity grade IV), being eluted with ether. This gave a vitreous product showing on TLC a single spot with R_f 0.45; composition $C_{21}H_{28}O_7$ (XV).

IR spectrum: ν_{max} 1800 cm^{-1} (γ-lactone), 1750, 1718, and 1630 cm^{-1} (C=C).

UV spectrum: λ_{max} 248.5 nm (ε 16,411).

Hydrolysis of Hydrogenated Olgin. A. Preparation of (XII). A mixture of 0.5 g of (XV) in 20 ml of ethanol and 0.5 g of K_2CO_3 in 10 ml of water was shaken and was left at room temperature for a day. Then the solution was concentrated under vacuum, diluted with water, and extracted four times with chloroform. The chloroform extract was washed with

water, and after the solvent had been driven off a crystalline product deposited; it was washed with ether, mp 211-212°C; from its NMR and mass spectra, this substance was identical with (XII).

B. Preparation of (XVI). Compound (XIV) (0.5 g) was hydrogenated under the conditions described for the hydrogenation of (XV). After the solvent had been eliminated, a vitreous product with the composition $C_{19}H_{28}O_6$ (XVI) was obtained.

IR spectrum: λ_{max} 3400-3500 cm^{-1} (OH), 1780 cm^{-1} (γ-lactone), and 1750 and 1720 cm^{-1}.

Hydrogenation of Laferin (VI). Preparation of (XVII). In the presence of 0.3 g of PtO_2, 5.25 g of laferin in 200 ml of ethanol was hydrogenated until the absorption of hydrogen ceased, 3 moles being absorbed. The residue consisted of a vitreous product with the composition $C_{22}H_{32}O_7$ (XVII).

IR spectrum: ν_{max} 1800 cm^{-1} (γ-lactone), 1750 cm^{-1} (OCO), and 1730 cm^{-1} (C=O).

Hydrolysis of (XVII). Preparation of (XVIII). A mixture of 1.5 g of (XVII) in 20 ml of ethanol and 1.5 g of K_2CO_3 in 10 ml of water was shaken and was left at room temperature for 5 days. The ethanol was partially evaporated under vacuum and was diluted with water, and the reaction product was extracted with chloroform, after which the extract was washed with water. Elimination of the solvent yielded 0.1 g of a vitreous product.

The mother liquors were acidified with 5% H_2SO_4 solution and extracted with ethyl acetate, and the extract was washed with 5% $NaHCO_3$ solution and with water. After the elimination of the solvent, (XVIII) was isolated (0.8 g of a vitreous product), giving on TLC a single spot with R_f 0.94 (ether system); composition $C_{20}H_{30}O_6$.

IR spectrum: ν_{max} 3450 cm^{-1} (OH), 1780 cm^{-1} (γ-lactone), 1750 cm^{-1} (C=O), 1720 cm^{-1} (OCO).

Dehydrogenation of Olgoferin. Preparation of (XIX). A mixture of 2 g of olgoferin and 2 g of selenium was heated at 280-350°C for 3 h. The reaction product was chromatographed on neutral alimina (activity grade I), being eluted with petroleum ether. This gave 0.03 g of a blue-violet liquid showing on TLC in the petroleum ether system a single spot with R_f identical with that of the spot of chamazulene taken as marker.

SUMMARY

1. Six sesquiterpene lactones have been isolated from *Ferula olgae* Regel et Schmalh. Three of them have been identified with talassins A and B and 4-acetoxypruteninone, which have been described previously.

2. The structure of olgoferin has been confirmed by chemical reactions, and the structures previously proposed for olgin, 4-acetoxypruteninone, and talassin B have been reconsidered.

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