in a sealed tube in the water bath for 2 h. After cooling and dilution with water, the reaction product was extracted with ether and was purified by PTLC. In its R*f* value, melting point, and absorption and mass spectra, the substance coincided completely with the natural sample given above.

Pigment Y — Anydroethylidene-6,6'-bis(2,3,7-trihydroxynaphthazarin). R*f* 0.30; sparingly soluble in all the solvents tested, mp > 310°C. Absorption spectrum: $\lambda_{max}^{CH_3OH}$ 212, 269, 320, 469, 490, 525 nm. Mass spectrum: m/e 484 (M$^+$). ^{1}H NMR spectrum (DMSO-d$_6$, δ, ppm): 1.6 (doublet, J = 6.8 Hz, 3 H, CH$_3$); 4.35 (q, J = 6.8 Hz, 1 H, CH).

Pigment X (10 mg) was heated in 5 ml of concentrated sulfuric acid for 10 min in a boiling-water bath. The mixture was poured onto ice, and the reaction product was extracted with ether and purified by PTLC. Yield 5 mg. The natural and synthetic samples were identical in their R*f* value, melting point, and absorption and mass spectra.

SUMMARY

From a mixture of the pigments of the sea urchin *Strongylocentrotus dröebachiensis*, in additionto the known spinochromes A, C, D, and E, we have isolated a binaphthoquinone and its anhydro derivative. On the basis of ^{13}C NMR spectra the position of the ethylidene bridge symmetrically binding the two naphthazarin fragments of the binaphthoquinone has been definnitely established, and the structure of this compound has been determined as ethylidene-6,6'-bis(2,3,7-trihydroxynaphthazarin).

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STRUCTURE OF THE SESQUITERPENE LACTONE ELEGIN

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We have previously reported the isolation from *Saussurea elegans* Ledeb. of a new sesquiterpene lactone elegin (I) with the composition $C_{19}H_{23}O_6Cl$, mp 158-159°C, $[\alpha]_D^{24}$ + 82.5° (c 2.125; ethanol), M$^+$ 382 [1]. In the present paper we give proof of its structure.

The PMR spectrum of elegin contains the following characteristic signals: singlet at 1.90 ppm — protons of a methyl group on a double bond; doublets at 5.47 ppm (J = 2.5 Hz) and 6.08 ppm (J = 3.5 Hz) — protons of an exocyclic methylene of a γ-lactone ring; singlet at 4.88 ppm — protons of an exocyclic methylene at C-10; singlets at 5.51 and 6.12 ppm — protons of a vinylmethylene at C-17; doublets with their centers at 4.26 and 4.68 ppm (J_1 = J_2 = 11 Hz; Cl—CH$_2$—C—OH); doublet at 7.25 ppm (J = 5 Hz; OH at C-3); and singlets at 6.70 ppm (OH at C-4). Analysis of the PMR spectrum and the formation of chamazulene when elegin was dehydrogenated over selenium (200-220°C, 10-12 min) showed that it belonged to the sesquiterpene lactones of the guaiane series.

The acetylation of (I) with acetic anhydride in pyridine yielded a monoacetate with the composition $C_{21}H_{25}O_7Cl$ (II), mp 168-170°C, M$^+$ 424. The acetylation of (I) with acetyl chlo-

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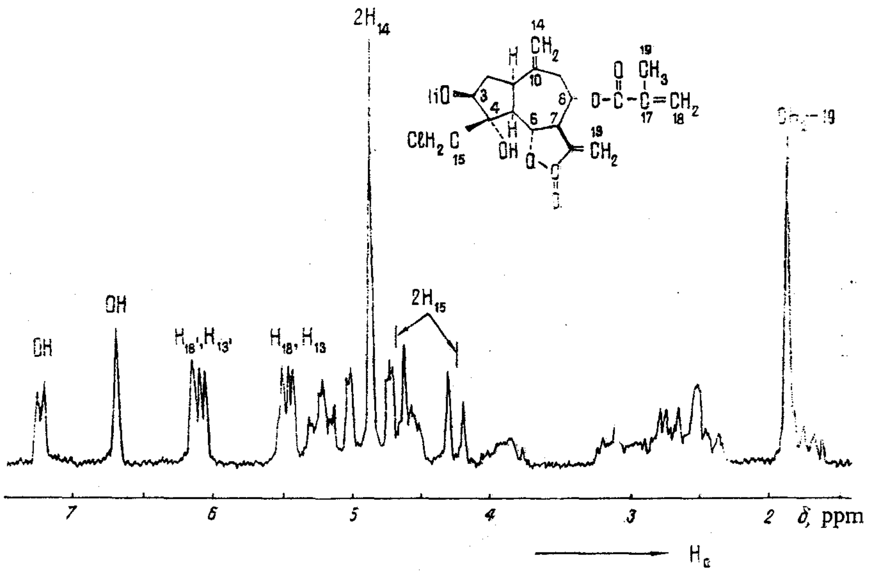
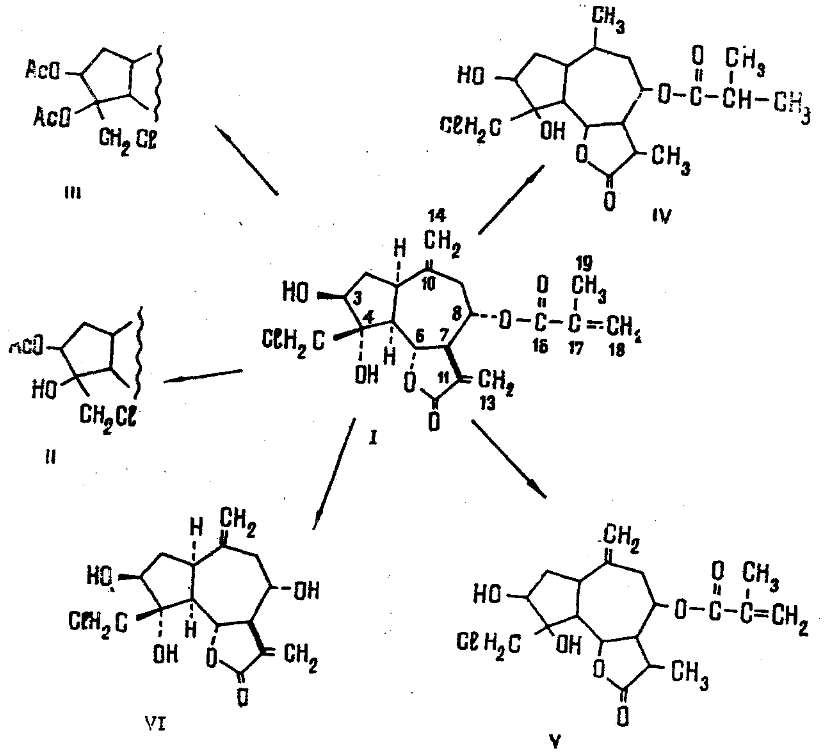


Fig. 1. PMR spectrum of elegin.

ride let to a diacetyl derivative with the composition $C_{23}H_{27}O_8Cl$ (III), mp 194-195°C, M^+ 466, which shows the tertiary nature of the second hydroxy group. The PMR spectrum of (III) had the characteristic signals of acetyl groups in the form of two three-proton singlets at 1.91 and 1.96 ppm.



Elegin was oxidized by periodic acid, but slowly, and did not form an acetonide, which is characteristic for the trans isomers of α-diols [2]. The exhaustive hydrogenation of (I) in the presence of a Pt catalyst in ethanol led to a hexahydro derivative of the composition $C_{19}H_{29}O_6Cl$ (IV), mp 229-230°C, M^+ 388. The absence of signals of exomethylene groups and of a vinylmethylene in the PMR spectrum of (IV) and also the appearance of two three-proton doublets at 0.78 and 1.28 ppm (CH_3 at C-10 and C-11) and of a six-proton doublet at 1.09 ppm [$-O-CO-CH(CH_3)_2$] confirm that the double bonds in elegin are due to the presence of two exomethylene groups at C-10 and C-11 and of a vinylmethylene at C-17.

The signal of a lactone proton in the form of a triplet at 4.88 ppm (J = 10 Hz) in the PMR spectrum of (IV) shows the position of the lactone ring at C-6—C-7 and, consequently, the acyl residue must be present at C-8, as is confirmed by the multiplet nature of the signal of hemiacyl proton at 5.12 ppm. The reduction of elegin with sodium tetrahydroborate gave dihydroelegin (V) with the composition $C_{19}H_{25}O_6Cl$, mp 180-181°C, $[\alpha]_D^{24}$ +39.1° (c 0.92; chloroform), M^+ 384, which corresponds to the product of the reduction of the known lactone chlorohyssopifolin A [3].

Continuing the separation of the combined lactones of *Saussurea elegans* by chromatography on silica gel [eluent: benzene—ether (7:3)], we isolated a guaianolide with the composition $C_{15}H_{19}O_5Cl$, mp 193-194°C, $[\alpha]_D^{25}$ + 74° (c 0.27; ethanol); M^+ 314.

By a comparison of IR spectra and a mixed-melting point, this guaianolide was found to be identical with the known lactone chlorohyssopifolin B [3], kindly supplied to us by Dr. J. Bermejo (Spain).

We obtained the same hydroxylactone (VI) by the alkaline hydrolysis of elegin. It was identified by a comparison of IR spectra and a mixed-melting point. The nature of the products of hydrogenation and of alkaline hydrolysis shows that the acyl group in the elegin molecule consists of a methacrylic acid residue. This is also confirmed by the fragments of the mass-spectrometric decomposition of the lactone itself and of its derivatives.

Mass spectrum of elegin: m/e 296 (M^+ —86); of dihydroelegin: m/e 298 (M^+ —86); of hexahydroelegin: m/e 300 (M^+ —88); with strong ions having m/e 69 and 41 in (I) and (V) and with m/e 71 and 43 in (IV).

Thus, on the basis of chemical transformations and spectral characteristics it is possible to conclude that elegin has the structure of 15-chloro-3,4-dihydroxy-8-methacryloyloxyguaia-10(14),11(13)-dien-6,12-olide.

From the plant *Centaurea linifolia* Vahl., A. G. Gonzalez and J. Bermejo have isolated a number of substances, including the lactone linichlorin A for which they proposed the structure which we have now established for elegin [4].

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument (tablets with KBr), the mass spectra on an MKh-1303 instrument, and the PMR spectra on a JNM-4H-100 spectrometer in deuterochloroform, 0 — HMDS.

Monoacetylelegin (II). To a solution of 100 mg of (I) in 1.5 ml of pyridine was added 1.5 ml of acetic anhydride, and then the mixture was kept at room temperature for 6 h, after which the solvent was evaporated off. Chromatography of the residue on silica gel (KSK, 200 μ) gave 70 mg of (II) with the composition $C_{21}H_{23}O_7Cl$, mp 168-170°C (benzene), M^+ 424. IR spectrum, cm^{-1}: 3525 (OH), 1770 (CO of a γ-lactone), 1740 (CO of an acetyl group), 1715 (α,β-unsaturated ester), 1660, 1635 (C=C), 740 (C—Cl).

Diacetylelegin (III). A mixture of 100 mg of elegin and 5 ml of acetyl chloride was kept at room temperature for 24 h. This gave 60 mg of (III) with the composition $C_{23}H_{27}O_8Cl$, mp 194-195°C (from ethanol). IR spectrum, cm^{-1}: broad band at 1775-1750 (CO of a γ-lactone and of acetyl groups), 1710 (α,β-unsaturated ester), 1665 and 1635 (C=C).

Hexahydroelegin (IV). The hydrogenation of 100 mg of (I) in 10 ml of ethanol was carried out in the presence of 18 mg of PtO_2 until the absorption of hydrogen ceased. Yield 60 mg, $C_{19}H_{29}O_6Cl$, mp 229-230°C (ethanol); M^+ 388. IR spectrum, cm^{-1}: 3440, 3380 (OH), broadened band; 1745 (CO of a γ-lactone and of an ester); 735 (C—Cl).

Dihydroelegin (V). A solution of 100 mg of (I) in 10 ml of methanol was treated with 50 mg of sodium tetrahydroborate. The reaction mixture was kept at 0°C for 10 min. The excess of sodium tetrahydroborate was decomposed with water, followed by acidification with 5% HCl. The reaction product was extracted with ethyl acetate and was purified on a column of silica gel. The crystals that deposited had mp 166-167°C. After two recrystallizations from a mixture of acetone and hexane, the substance melted at 180-181°C. The yield of (V) was 70 mg; composition $C_{19}H_{25}O_6Cl$; $[\alpha]_D^{24}$ +39.1° (c 0.92; chloroform); M^+ 384. IR spectrum, cm^{-1}: 3420 (OH), 1750 (γ-lactone), 1715 (ester), 1640 (C=C); 740 (C—Cl).

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.

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THE LACTONES OF *Ferula malacophylla*

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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,

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