structure – the fact that the compound was dimeric. Further electron-density (ED) syntheses constructed for the whole mass of reflections revealed the lacking basis atoms and confirmed the bislactone structure of the compound under investigation. The structure was refined first by successive approximations (R = 0.156) and subsequently in the anisotropic approximation (R = 0.100). At this stage, a difference ED synthesis was carried out and the positions of 30 of the H atoms out of 40 were found. The final value of the divergence factor after several MLS iterations taking the coordinates of the H atoms into account was 0.087. The coordinates of the basis atoms are given in Table 3.

## SUMMARY

The structure of a dimeric lactone of a new type from Artemesia leucodes artelein, has been established unambiguously on the basis of an analysis of its IR, high-resolution mass, PMR, and $^{13}C$ NMR spectra and an x-ray structural investigation of its acetyl derivative.

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# STRUCTURE AND STEREOCHEMISTRY OF PALLININ

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UDC 547.992:547.37

The roots of Ferula pallida Korov. have yielded pallinin, $C_{25}H_{38}O_5$, mp 79-80°C, $[\alpha]_D^{20}$ −148.5° (c 0.1; $CHCl_3$) – an ester of the new carotane alcohol pallinol and angelic acid. A structure and absolute configuration have been proposed for it on the basis of chemical transformations and spectral characteristics.

Continuing a study of the esters of Ferula pallida Korov. [1, 2], from the neutral fraction of the ethanolic extract of the roots collected in the Chimkent province, Kazakh SSR, we have isolated by column chromatography a new ester with the composition $C_{25}H_{38}O_5$ ($M^+$ 418), mp 79-80°C, $[\alpha]_D^{20}$ −148.5° (c 0.1; $CHCl_3$), which has been called pallinin (I).

The IR spectrum of pallinin was characteristic for esters of sesquiterpene alcohols and it showed the absorption bands of the carbonyl group of an ester of an unsaturated acid (1700 $cm^{-1}$), of a secondary-tertiary double bond (1650, 960 $cm^{-1}$), and of a hydroxy group (3400-3620 $cm^{-1}$).

The PMR spectrum of the substance contained the signals of the protons of an isopropyl group (d, 0.83, 0.90 ppm, J = 7.5 Hz, 6 H), of an angular methyl group (s, 1.15 ppm, 3 H), of a methyl group at a double bond (br.s, 1.76 ppm, 3 H), of two gem-acyl protons (d, 4.83

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ppm, J = 7.5 Hz, 1 H, sx, 5.20 ppm, $J_1 = J_2 = 10.5$ Hz, $J_3 = 2.5$ Hz, 1 H) and of an olefinic proton (br.d, 5.58 ppm, J = 7.5 Hz). In addition, in the 1.8-1.9 ppm there were signals characteristic of the methyl groups of an angelic acid residue, as was confirmed by a two-proton quartet (J = 7.5 Hz) at 6.01 ppm due to the olefinic protons of angeloyl groups [3].

The mass spectrum of pallinin was typical for esters of sesquiterpene alcohols [4, 5], having the peaks of ions with m/z 418 ($M^+$), 318 $(M - C_5H_8O_2)^+$, 218 $(M - 2C_5H_8O_2)^+$, 200 $(M - 2C_5H_8O_2 - H_2O)^+$, and 175 $(M - 2C_5H_8O_2 - C_3H_7)^+$.

Analysis of literature information and the IR, PMR, and mass spectra of pallinin showed that it was a diester of a carotane triol. In actual fact, the dehydrogenation of pallinin in the presence of palladium gave daucalene, $C_{15}H_{18}$ (IV).

The alkaline hydrolysis of pallinin gave a new sesquiterpene alcohol, pallinol, $C_{15}H_{26}O_3$ (III), and angelic acid $C_5H_8O_2$. Consequently, pallinin is an ester of a new carotane alcohol — pallinol — with angelic acid.

The PMR spectrum of pallinol showed the signals of an isopropyl group (d, 0.90 ppm, J = 7.5 Hz, 6 H), of an angular methyl group (s, 0.99 ppm, 3 H), of a methyl group at a double bond (br.s, 1.73 ppm, 3 H), and of two gem-hydroxylic protons (d, 3.69 ppm, J = 7.5 Hz, 1 H, sx, and 3.85 ppm, $J_1 = 10.5$, $J_2 = 10.5$, $J_3 = 2.5$ Hz) and one olefinic proton (d, 5.58 ppm, J = 7.5 Hz, 1 H).

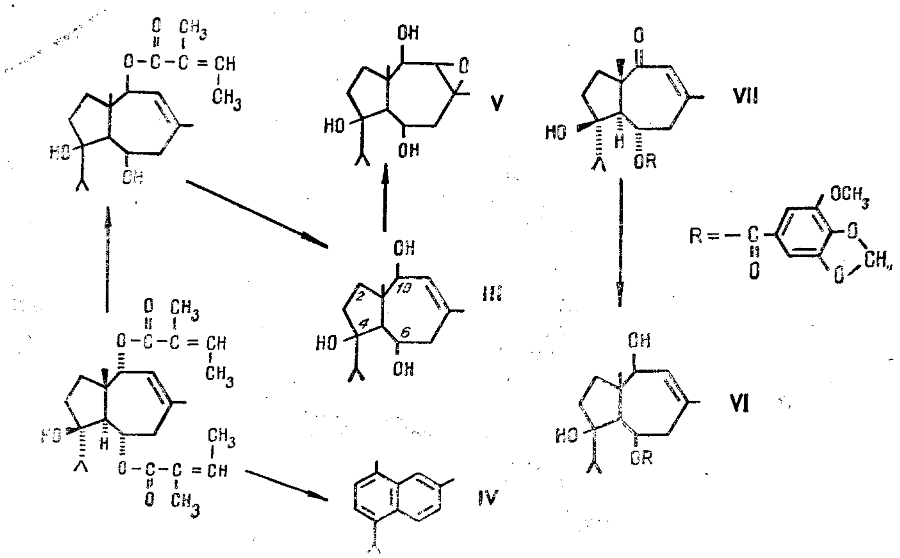
These facts, together with the elementary composition and the result of dehydrogenation, indicated that pallinol was a bicyclic carotane alcohol containing two secondary and one tertiary hydroxy group and a double bond. The positions of the hydroxy groups and of the double bond in pallinol were determined in the following way.

The multiplicity (sx, 3.85 ppm) of the signal of one of the gem-hydroxylic protons in the spectrum of pallinol showed that one hydroxy group was located at $C_6$, as in the other known carotane alcohols ferutinol [6], akichenol [7], lapidol [8], and laserol [9].* The same facts indicated that $C_5$ and $C_7$ were free from substituents and the tertiary hydroxy group was located at $C_4$ of the carotane nucleus.

As mentioned above, in the PMR spectrum of pallinol there were the signals of a methyl group at a double bond and of an olefinic proton. In view of the sextet nature of $C_6$—H signal, it may be considered that the double bond is located at $C_8$—$C_9$.

The signal of the gem-hydroxylic proton at the second secondary hydroxy group appeared in the form of a doublet at 3.69 ppm with a coupling constant (J = 7.5 Hz) equal to the SSCC of the signal of the olefinic proton at 5.58 ppm (J = 7.5 Hz). Consequently, the hydroxy group is located at $C_{10}$.

Thus, pallinol has the structure of 4,6,10-trihydroxycarot-8-ene.



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*As in Russian text. No reference [9] is given in Russian Literature Cited list, however — Editor.

We confirmed the proposed structure and determined the absolute configuration of pallinol, as shown above.

The configuration of the sesquiterpene alcohol lapidol (IV) had been established previously by correlation with ferutinol (jaschkeanadiol [4]). From the same plant, we had isolated palliferin and palliferinin, esters of lapidol with aromatic acids [1]. A comparison of the proposed structures of lapidol and pallinol showed that the latter was a dihydro derivative of lapidol. To make the transition between lapidol and pallinol, we reduced palliferinin with $NaBH_4$. In this process, in addition to the reduction of the carbonyl group of the lapidol, the ester group underwent hydrolysis with the formation of dihydrolapidol A, $C_{15}H_{26}O_3$, mp 125-126°C, $[\alpha]_D^{20}$ + 37.1° and dihydrolapidol B, $C_{15}H_{26}O_3$, mp 182-183°C, $[\alpha]_D^{20}$ +43.7°. Dihydrolapidol A proved to be identical with pallinol according to its IR and PMR spectra and a mixed melting point.

Since the absolute configuration of lapidol, with the trans linkage of the cyclopentane and cycloheptane rings, the β orientation of the $C_4$—OH and the α orientation of the $C_6$—OH had been established, these configurations of the asymmetric centers were adopted for pallinol. The orientation of the $C_{10}$ hydroxy group followed from the SSCC value of the $C_{10}$—H signal (d, 7.5 Hz); it has the α-pseudoaxial configuration.

In the PMR spectra of pallinin the signals of the two gem-acyl protons appeared in a weaker field than in the spectrum of pallinol. Consequently, the angeloyl residues in it are located at $C_6$ and $C_{10}$, and pallinin has the absolute configuration (I).

## EXPERIMENTAL

Thin-layer chromatography (TLC) was performed on Silufol-R plates in the solvent systems: 1) chloroform—ethyl acetate (7:3), and 2) hexane—ethyl acetate (2:1). Silica gel 100/160 μm (Chemapol) and KSK silica gel were used for column chromatography, and melting points were determined on an instrument with a small heated stage of the Boëtius type with a RNMK 05 observing device. Optical rotations were determined on a Zeiss polarimeter. UV spectra were taken on EPS-3T spectrophotometer (Hitachi) in ethanol, IR spectra on a UR-20 instrument (tablets with KBr), mass spectra on a MKh-1310 instrument, and PMR spectra on a JNM-4H 100 MHz spectrometer in $CDCl_3$. Chemical shifts are given in the δ scale (HMDS — 0).

Isolation of the Total Esters. The dried and comminuted roots (2 kg) of *Ferula pallida* were extracted with ethanol (5 × 6 liters), and the solvent was distilled off. The concentrated extract was diluted with water (1:2) and extracted with ether to complete exhaustion (3 × 500 ml). The ethereal extract was treated successively with 5% sodium carbonate solution (3 × 0.3 liter) and a 1% caustic potash solution (3 × 0.3 liter). The sodium carbonate and caustic potash solutions, separately, were acidified and extracted with ether, and the new ethereal extracts were washed with water and dried. This gave 2.8 g of acidic fraction and 10 g of phenolic fraction. The mother liquor from the original ethereal extract was washed with water to neutrality. The solvent was driven off to give 162 g of combined neutral substances.

Separation of the Combined Neutral Substances. The combined esters from the neutral fractions, in an amount of 50 g, were transferred to a column filled with silica gel (125 × 6 cm) and were eluted by the petroleum ether—ethyl acetate system with increasing concentrations of the latter, 400-ml fractions being collected. From fractions XXVII-XXX was isolated 0.8 g of a substance with the composition $C_{25}H_{38}O_5$ (I), mp 79-80°C (from a mixture of petroleum ether and ethyl acetate), $[\alpha]_D^{20}$ −148.5° (c 0.1; $CHCl_3$); $\nu_{max}^{KBr}$: 3400-3620, 1700, 1650 $cm^{-1}$. PMR spectrum ($CDCl_3$), δ, ppm: 0.83, 0.90 (6 H, d, J = 7.5 Hz); 1.15 (3 H, C-1, s); 1.76 (3 H, br.s); 4.83 (1 H, d, J = 7.5 Hz); 5.20 (1 H, sx, $J_1 = J_2 = 10.5$, $J_3 = 2.5$ Hz); 5.68 (1 H, d, J = 7.5 Hz); 6.01 (2 H, q, J = 7.5 Hz).

Hydrolysis of Pallinin. a) In a 250-$cm^3$ round-bottomed flask, 993 mg of the substance was dissolved in 10 ml of methanol, and then 30 ml of a 5% aqueous solution of caustic potash was added and the mixture was heated on the water bath under reflux for 45 min. The solvent was distilled off in vacuum, the residue was diluted with water, and the reaction product was isolated with diethyl ether. The ethereal extract was washed with water and dried, and the ether was distilled off. This gave compound (II), $C_{20}H_{30}O_3$. Yield 690 mg. mp 108-110°C (from a 1:1 mixture of hexane and ethyl acetate). PMR spectrum ($CDCl_3$), δ, ppm: 0.85, 0.92 (6 H, d, J = 7.5 Hz); 1.09 (3 H, s); 1.75 (3 H, br.s); 3.97 (1 H, sx, $J_1 = J_2 = 10.5$, $J_3 = 2.5$ Hz); 4.85 (1 H, d, J = 7.5 Hz); 5.95 (1 H, q, J = 6 Hz). Mass spectrum: m/z 318 ($M^+$), 275, 218, 175.

b) The substance (500 mg) was hydrolyzed with 10% aqueous ethanolic caustic potash with heating on the water bath for 7 h. Then the reaction mixture was worked up by the method described above. This gave 353 mg of pallinol, $C_{15}H_{26}O_3$, $[\alpha]_D^{20}$ +37.3° (c 0.1; $CHCl_3$). PMR spectrum ($CDCl_3$, δ, ppm): 0.90 (6 H, d, J = 7.5 Hz); 0.99 (3 H, s); 1.73 (3 H, br.s); 3.69 (1 H, d, J = 7.5 Hz); 3.85 (1 H, sx, $J_1 = J_2 = 10.5$, $J_3 = 2.5$ Hz); 5.58 (1 H, m).

Dehydrogenation of Pallinin. A mixture of 400 mg of the substance with 400 mg of 10% Pd/$CaCO_3$ was heated at 240-250°C for 3 h. After cooling, the reaction mixture was extracted with petroleum ether, the extract was washed with phosphoric acid and with water and was dried and evaporated, and the oily residue was chromatographed on alumina with elution by hexane. This gave 70 mg of daucalene with a characteristic naphthalene-like odor, mp 60-62°C.

Epoxypallinol. With stirring at room temperature, 25 ml of an ethereal solution of perphthalic acid was added dropwise to a solution of 500 mg of (III) in 20 ml of absolute diethyl ether. The course of the reaction was monitored with the aid of TLC in system 2. After the end of the reaction, the mixture was diluted with water, and the ethereal layer was separated off and was washed with a saturated solution of $(NH_4)_2SO_3$. This gave 300 mg of compound (V), $C_{15}H_{26}O_4$, mp 161-162°C.

PMR spectrum ($CDCl_3$, δ, ppm): 0.88 (6 H, d, J = 7.5 Hz); 1.19 (3 H, s); 1.40 (3 H, s); 3.88 (1 H, m); 3.99 (1 H, m); and 4.95 (1 H, m).

Reduction of Palliferinin. With cooling and stirring, 2 g of sodium tetrahydroborate was added in portions to a solution of 1.91 g of (VII) in 100 ml of methanol. After the end of the reaction, the mixture was worked up in the usual way. The residue after the elimination of the solvent was chromatographed on a column of silica gel (2 × 90 cm), the substance being eluted with the hexane—ethyl acetate (10:1) system. This gave compounds A – $C_{15}H_{26}O_3$, mp 125-126°C, $[\alpha]_D^{20}$ +37.1°) and B – $C_{15}H_{26}O_3$, mp 182-183°C, $[\alpha]_D^{20}$ +43.7°. A mixture of dihydrolapidol A and pallinol gave no depression of the melting point.

PMR spectrum of dihydrolapidol B ($CDCl_3$, δ, ppm): 0.88 (s, 3 H); 0.88, 1.01 (6 H, d, J = 7 Hz); 1.7 (3 H, br.s); 3.89 (1 H, m); 4.08 (1 H, d, J = 4 Hz); and 5.27 (1 H, m).

## SUMMARY

An ester of the carotane alcohol pallinol and angelic acid has been isolated from the roots of Ferula pallida Korov. A structure and absolute configuration have been proposed for this ester, pallinin, on the basis of chemical transformations and spectral characteristics.

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