account. Numerous attempts to determine the structure by the direct method using the MULTAN program were unsuccessful. A Debye correction was introduced for the known geometry of the molecule [3]. To evaluate the significance of the variants of the phases of the reflection we used the NQEST criterion [4] (94 quartets with $E_{main} = 1.6$, $E_{cross} = 0.56$, and $B_{min} = 0.5$). Among the 64 variants of the phases that were calculated for 204 $E > 1.4$, the best had NQEST = −0.03 and did not lead to resolution. Then we calculated 128 variants of the phases, among which there was one correct variant with NQEST = −0.13. The use of magic numbers by the methods of Lessinger and Margulis [5] enabled us to find the correct variant from only 60 calculated varients. The refinement of the structure found was carried out in the isotropic and anisotropic full-matrix approximations to $R = 0.087$ and $R_w = 0.072$, where $w = 1/\sigma(F)^2$. The coordinates of the atoms are given in Table 1.

SUMMARY

The crystal and molecular structure of a ketone (9α-hydroxymurola-4-one) synthesized from δ-cadinol has been investigated. Under the conditions of its production and isolation, the ketone retains the configurations of the asymmetric centers.

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STRUCTURE OF FERTENIN

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Continuing a study of the phenolic components of *Ferula tenuisecta* Eug. Kor. [1-5] we have isolated a new substance with the composition $C_{22}H_{30}O_5$, mp 209-211°C (decomp.), $[\alpha]_D^{22}$ +125° (c 0.8; ethanol), which we have called fertenin (I).

UV spectrum: λ_{max} 260 nm (log ε 3.80). This maximum underwent a bathochromic shift when the spectrum was taken with the addition of alkali, which is due to the presence of a phenolic hydroxy group.

IR spectrum, ν_{max}, cm^{-1}: 3200-3600 (hydroxy group); 1685 (ester carbonyl conjugated with an aromatic nucleus); 1610, 1590, 1520 (aromatic nucleus); 1290, 1070, 856 (oxide ring) [6].

The mass spectrum of fertenin was characteristic for the spectra of esters of sesquiterpene alcohols [4, 7] and had the peaks of ions with m/e 331 $(M - C_3H_7)^+$, 236 $(M - C_7H_6O_3)^+$, 218 $(M - C_7H_6O_3 - H_2O)^+$, 203 $(M - C_7H_6O_3 - H_2O - CH_3)^+$, 193 $(M - C_7H_6O_3 - C_3H_7)^+$, 175 $(M - C_7H_6O_3 - C_3H_7 - H_2O)^+$, and 138 $(C_7H_6O_3)^+$.

The PMR spectrum of fertenin shows the signals of methyl groups in the form of two three-proton doublets at 0.81 and 0.89 ppm with J = 5 Hz; of methyls on carbon atoms bearing oxygen at 1.24 (s, 3 H), and 1.31 ppm (s, 3 H) [6]; of an epoxide proton at 2.91 ppm (d, J = 10 Hz, 1 H); and of olefinic protons at 5.39 and 5.61 ppm (d, J = 10 Hz, 1 H each). On the signal

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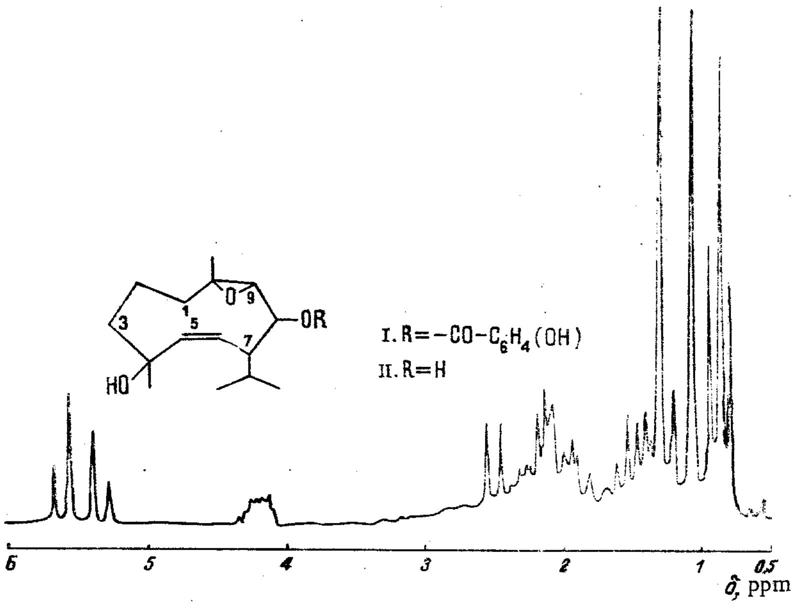

Fig. 1. PMR spectrum of fertenol.

of an olefinic proton at 5.61 ppm is superposed the multiplet of a gem-acyl proton with its center at 5.66 ppm. Two-proton doublets at 7.82 (J = 10 Hz) and 6.83 ppm (J = 10 Hz) are due to the presence of four ortho-interacting protons of an aromatic nucleus.

The acetylation of ferinin with acetic anhydride in pyridine yielded an acetate having the composition $C_{24}H_{32}O_6$, mp 122-123°C, the IR spectrum of which still contained the absorption band of a hydroxy group (3200-3600 cm^{-1}); the fertenin molecule therefore contains a tertiary hydroxy group. When the substance was hydrolyzed with 5% aqueous alcoholic alkali, the neutral part of the hydrolyzate yielded a sesquiterpene diol with the composition $C_{15}H_{26}O_3$, mp 126-127°C, $[\alpha]_D^{22}$ +128° (c 0.5; ethanol), which we have called fertenol (II), and the acidic fraction yielded p-hydroxybenzoic acid [3].

IR spectrum of the alcohol, ν_{max}, cm^{-1}: 3200-3600 (hydroxy group), 880, 1040, 1290 (oxide ring). There were no absorption bands of a carbonyl group of an aromatic nucleus.

In the PMR spectrum of the diol, the signals of the methyl groups were present in the form of two doublets (3 H each) at 0.82 ppm (J = 5 Hz) and 0.91 ppm (J = 5 Hz) and of two singlets (3 H each) at 1.06 and 1.31 ppm, which is characteristic for methyls having a heteroatom — oxygen — in the geminal position [6]. A one-proton doublet at 2.49 ppm (J = 10 Hz) must be assigned to an epoxide proton, and two doublets (1 H each) at 5.32 and 5.61 ppm, respectively, with equal SSCCs (J = 10 Hz), to cis-olefinic protons interacting with one another.

A multiplet at 4.15 ppm is due to a gem-hydroxylic proton forming a multispin system with neighboring protons, as is confirmed by its paramagnetic shift in the spectrum of the substance itself (Δδ = 1.51 ppm).

On the basis of the composition of fertenol, the nature of the methyl groups (PMR and mass spectra), and the presence of an epoxide ring at one double bond, it may be assumed that (II) has the skeleton of the monocyclic sesquiterpene germacrane. As mentioned above, in the PMR spectra of (I) and (II) the epoxide proton is represented by doublets at 2.91 ppm (J = 10 Hz) and 2.49 ppm (J = 10 Hz), respectively. This permits the assumption that there is only one proton in a vicinal position to the epoxide proton and, probably, this is a gem-acyl proton in (I) and a gem-hydroxyl proton in (II). To confirm this, we oxidized fertenol and obtained a ketone with the composition $C_{15}H_{24}O_3$ (III), the IR spectrum of which contained, in addition to the absorption band of a carbonyl group (1680 cm^{-1}) the absorption band of a hydroxy group (3200-3600 cm^{-1}). The latter also confirmed the deduction that in fertenol the hydroxy groups are secondary and tertiary, and is in harmony with the PMR spectrum.

In the PMR spectrum of the ketone, the methyl groups of the isopropyl residue were represented in the form of a six-proton doublet at 0.85 ppm (J = 8 Hz), methyl groups attached to carbon bearing oxygen by signals at 1.17 and 1.32 ppm (3 H each), and the proton of a tertiary hydroxy group by a signal at 4.86 ppm (1 H). The signals of cis-olefinic protons were observed in the form of two one-proton doublets at 5.47 and 5.80 ppm (J = 10 Hz), and the epoxide proton was revealed in the form of a one-proton singlet at 2.64 ppm, i.e., the oxidation of the hydroxy group changed the multiplicity of the signal of the epoxide proton. Thus, the assumption that the epoxide proton occupies the geminal position to the gem-hydroxyl proton was confirmed.

The constancy of the multiplicity of the signals of the olefinic protons in the spectra of (II) and (III) shows the absence of an interaction of the olefinic and gem-hydroxylic protons in fertenol. In addition to this, in the UV spectrum of (III) there is no absorption band of an α,β-unsaturated ketone and therefore the hydroxy group in fertenol is not an allylic one.

The double bond in fertenol and fertenin is disubstituted and from the PMR spectra the olefinic protons interact only with one another. It has been shown previously that in substances with a gemacrane skeleton and a cis double bond at C_5–C_6 the vicinal SSCC between the H-6 and H-7 protons is less than 1 Hz, i.e., the dihedral angles between them are close to 90°, and this is shown in a broadening of the signal of the olefinic proton, while allylic coupling with the methyl group at C_4 is also observed [7]. Such a pattern was observed in the spectra of fertenin and fertenol.

The facts given above enable the one-proton singlet at 3.58 ppm in the PMR spectrum of the ketone to be assigned to a methine proton present between the double bond and the ketone carbonyl [8, 9].

Thus, the double bond and the epoxide ring are present at C_5–C_6 and C_9–C_{10}, respectively, and the hydroxy groups at C_4 and C_8, and fertenol has the structure of 9-epoxygermacr-5-ene-4,8-diol (II). The value of the CS of the signal of the gem-acyl proton in the spectrum of fertenin shows that in (I) the p-hydroxybenzoic acid is present at C_8, and fertenin has the structure (I).

EXPERIMENTAL

The UV spectra were recorded on a Hitachi EPS-3T spectrophotometer (in ethanol), the IR spectra on UR-10 instrument (tablets with KBr), the mass spectra on a MKh-1303 mass spectrometer, and the PMR spectra on a JNM-4H-100 MHz spectrometer in $CDCl_3$ solution.

Separation and isolation were performed by the method described previously [5]. From 20 g of resin containing the phenolic components of *Ferula tenuisecta* we obtained 0.3 g of gertenin.

Fertenin was hydrolyzed with 5% aqueous ethanolic alkali; 0.2 g of the initial substance yielded 0.14 g of fertenol and 0.06 g of p-hydroxybenzoic acid.

Acetylation of Fertenin. A solution of 50 mg of fertenin in 2 ml of pyridine was treated with 2 ml of acetic anhydride. The reaction mixture was worked up in the usual way, and the acetyl derivative $C_{24}H_{32}O_6$, mp 122-123°C was crystallized from ether.

Oxidation of Fertenol. A pyridine solution of 0.1 g of chromium trioxide was added dropwise to a solution of 0.14 g of fertenol in anhydrous pyridine, and the mixture was stirred with a magnetic stirrer at room temperature for 4 h. Then it was diluted with water, and the keto derivative that had been formed was extracted with ether. The ethereal solution was washed with dilute acid and with water and was dried with anhydrous sodium carbonate. This gave 0.1 g of the ketone $C_{15}H_{24}O_3$, mp 86-88°C. IR spectrum: ν_{max} 1680, 3200-3600 cm^{-1}.

SUMMARY

The roots of *Ferula tenuisecta* have yielded a new ester $C_{22}H_{30}O_5$, mp 209-211°C, $[\alpha]_D^{22}$ +125° (c 0.8; ethanol), which has been called fertenin. On the basis of chemical transformations and spectral characteristics, a structure has been proposed for it as the 8-p-hydroxybenzoate of fertenol — 9-epoxygermacr-5-ene-4,8-diol.

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STRUCTURE OF GLEHNOL — A SESQUITERPENE ALCOHOL, $C_{15}H_{26}O$, WITH A NEW TYPE OF CARBON SKELETON

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In a study of the chemical composition of the oleoresin of *Picea glehnii* Mast. (sakhalin spruce), we have previously isolated four sesquiterpene alcohols, three of which have been identified as (+)-epicubenol, (+)-cubebol, and epicubebol [1]. The spectral characteristics of the fourth compound did not agree with those of known sesquiterpene alcohols. In the present work we give the results of a study of the structure of this alcohol, which has a new type of carbon skeleton, and which we have called glehnol.

Glehnol consists of a colorless viscous liquid with $[\alpha]_D^{20}$ —10° and its p-nitrobenzoate melts at 85°C. The IR spectrum of glehnol has the absorption bands of a trisubstituted double bond (847, 1660, 3042 cm^{-1}) and of a hydroxy group (3630 cm^{-1}). The ^1H and ^{13}C NMR spectra confirm the presence of a trisubstituted double bond in the structure (broadened singlet at 5.06 ppm, 1 H; a singlet at 142.03 and doublet at 125.84 ppm), a methyl group on a double bond (singlet at 1.76 ppm, 3 H), a secondary hydroxy group ($-\underset{|}{\mathrm{C}}\mathrm{HO\underline{H}}$, singlet at 3.64 ppm, 1 H, width of the signal at half-height 3.5 Hz; doublet at 75.65 ppm).

TABLE 1. Bond Lengths (Å) and Valence Angles (°) of the Molecule

Parameter	Value	Parameter	Value
C (1)—C (2)	1.54 (2)	C (6) — C (7)	1,55 (2)
C (1)—C (5)	1,52 (2)	C (6) — O (1)	1.43 (2)
C (1)—O (2)	1.48 (2)	C (7) — C (8)	1,53 (2)
C (2)—C (3)	1.54 (2)	C (7) — C (11)	1,56 (2)
C (2)—C (15)	1.49 (2)	C (8) — C (9)	1,53 (2)
C (2)—O (2)	1.48 (1)	C (9) — C (10)	1,52 (2)
C (3)—C (4)	1,57 (2)	C (10) — C (14)	1,59 (2)
C (4)—C (5)	1,59 (2)	C (11) — C (12)	1.61 (3)
C (5)—C (6)	1,51 (2)	C (11) — C (13)	1,57 (2)
C (5)—C (10)	1.51 (2)		
C (5) C (1) C (2)	110 (1)	C (1) C (5) C (10)	112 (1)
C (5) C (1) O (2)	111 (1)	C (6) C (5) C (10)	111 (1)
C (2) C (1) O (2)	58 (1)	C (5) C (6) C (7)	112 (1)
C (1) C (2) C (3)	109 (1)	C (5) C (6) O (1)	111 (1)
C (1) C (2) O (2)	59 (1)	C (7) C (6) O (1)	107 (1)
C (1) C (2) C (15)	125 (1)	C (6) C (7) C (8)	111 (1)
O (2) C (2) C (3)	1.0 (1)	C (6) C (7) C (11)	110 (1)
O (2) C (2) C (15)	117 (1)	C (8) C (7) C (11)	111 (1)
C (3) C (2) C (15)	121 (1)	C (7) C (8) C (9)	109 (1)
C (2) C (3) C (4)	104 (1)	C (8) C (9) C (10)	116 (1)
C (3) C (4) C (5)	108 (1)	C (9) C (10) C (5)	110 (1)
C (4) C (5) C (1)	104 (1)	C (9) C (10) C (14)	112 (1)
C (4) C (5) C (6)	108 (1)	C (5) C (10) C (14)	114 (1)
C (4) C (5) C (10)	111 (1)	C (7) C (11) C (12)	108 (1)
C (1) C (5) C (6)	110 (1)	C (7) C (11) C (13)	111 (2)
C (1) O (2) C (2)	63 (1)	C (12) C (11) C (13)	103 (2)

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