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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 ($-\underset{|}{C}HO\underline{H}$, 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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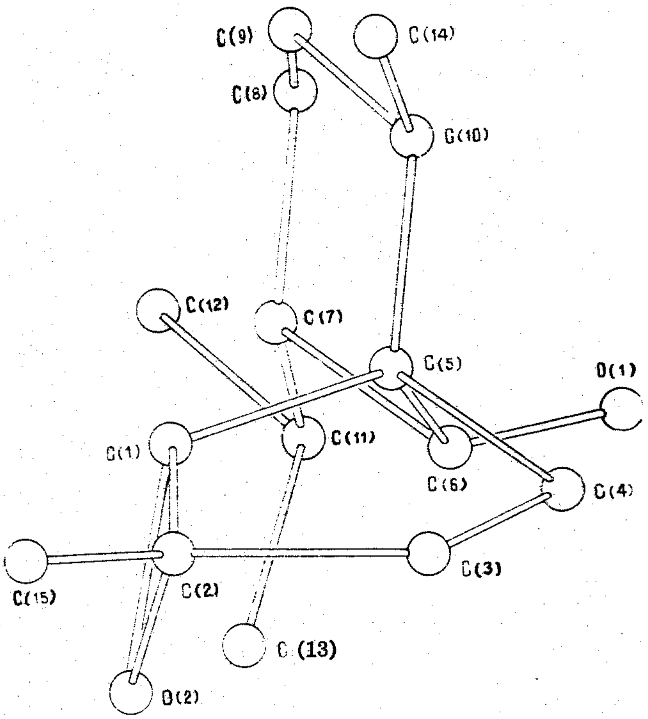


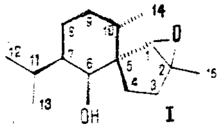
Fig. 1. Crystal structure and relative configuration of glehnol epoxide.

The epoxidation of glehnol with monoperphthalic acid gave a crystalline epoxide with mp 83-84°C and $[\alpha]_D^{20}$ +14°. The PMR spectrum of this compound had, in addition to the signal of a $-\mathrm{CH}=\underset{|}{\mathrm{C}}-\mathrm{CH_3}$ group, the signals of a $\underset{\diagdown\mathrm{O}}{-\mathrm{CH}-\overset{|}{\mathrm{C}}-\mathrm{CH_3}}$ group (2.87 ppm, singlet, 1 H; 1.37 ppm, singlet, 3 H). The spectrum also contained the signals of three secondary methyl groups at (ppm) 0.85 (3 H, doublet, J = 6.5 Hz), 0.93 (3 H, doublet, J = 6 Hz), and 0.99 (3 H, doublet, J = 6 Hz). The signal of the carbonyl proton was present in a field weaker than that for glehnol (singlet at 3.78 ppm; the width of the signal at half-height was 4 Hz).

Of the two crystalline derivatives of glehnol, only in the case of the epoxide (I) were single crystals suitable for x-ray structural analysis obtained.

The structure and relative configuration of the glehnol epoxide molecule are shown in Figure 1, and the bond lengths, valence angles, and torsional angles are given in Table 1.

The six-membered ring of the molecule has the chair conformation with an axial hydroxy group. The isopropyl group is oriented in such a way that the hydrogen atoms at C(7) and C(11) are in the anti relationship. The five-membered ring of the molecule is nonplanar. The C(1), C(2), C(3), and C(5) atoms are in one plane and the C(4) atom deviates from it by 0.37 Å in the direction of the O(2) oxygen atom. The corresponding dihedral angle is 157°. The O(1)···O'(2) intermolecular distance is 2.81 Å.



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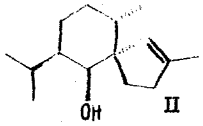

II

It follows from the facts given above that glehnol has the structure (II) and is the first representative of sesquiterpenoids of a new structural type. In contrast to the sesquiterpene of the spirane type with five- and six-membered rings, the isopropyl group in glehnol is present in the six-membered and not in the five-membered ring. The absolute configuration of glehnol requires further study.

TABLE 2. Coordinates (10^3) and Temperature Factors (Å^{-2}) of the Atoms

Atom	x/a	y/b	z/c	B_{iso}	Atom	x/a	y/b	z/c	B_{iso}
C (1)	293 (2)	186 (1)	099 (1)	4,6	C (2)	444 (2)	190 (2)	236 (1)	5,4
C (3)	484 (2)	336 (2)	279 (1)	5,9	C (4)	391 (2)	418 (2)	148 (1)	6,2
C (5)	233 (1)	327 (2)	052 (1)	4,2	C (6)	243 (2)	347 (2)	−090 (1)	5,3
C (7)	095 (2)	260 (2)	−191 (1)	5,2	C (8)	−105 (2)	292 (2)	−185 (1)	5,8
C (9)	−112 (2)	282 (2)	−039 (2)	6,0	C (10)	039 (2)	360 (2)	065 (1)	5,9
C (11)	113 (2)	279 (2)	−337 (1)	8,3	C (12)	315 (3)	220 (3)	−341 (2)	9,2
C (13)	−032 (3)	188 (4)	−440 (2)	12,9	C (14)	016 (2)	342 (2)	212 (1)	7.1
C (15)	480 (2)	081 (2)	337 (1)	6,4	O (1)	205 (1)	483 (1)	−132 (1)	6,5
O (2)	496 (1)	164 (0)	110 (1)	5,3					

EXPERIMENTAL

Glehnol, isolated by the method described previously [1], had $[\alpha]_D^{20}$ +10° (c 5.0; $CHCl_3$). IR spectrum, cm^{-1}: 847, 940, 1050, 1130, 1380, 1470, 1660, 3042, 3630.

Glehnol p-Nitrobenzoate. A solution of 50 mg of glehnol in 5 ml of anhydrous pyridine was treated with 100 mg of p-nitrobenzoyl chloride and the mixture was heated on the water bath under reflux at 70°C for 3 h. After cooling to room temperature, the reaction products were chromatographed on SiO_2 (10 g). This yielded 20 mg of glehnol p-nitrobenzoate in the form of long needles with mp 85°C (ethanol, CCl_4, hexane), and 20 mg of glehnol was recovered.

Glehnol Epoxide. A mixture of 50 mg of glehnol and 70 mg of monoperphthalic acid in 2 ml of $CHCl_3$ was kept at 0°C for 15 h. The reaction products were chromatographed on SiO_2 (20 g). A mixture of diethyl ether and hexane (3:7) eluted 30 mg of glehnol epoxide with mp 83-84°C (hexane) and $[\alpha]_D^{20}$ +14 (c 1.5; CCl_4).

IR spectrum, cm^{-1}: 560, 605, 655, 685, 760, 835, 908, 916, 935, 970, 992, 1000, 1030, 1058, 1072, 1097, 1130, 1140, 1182, 1200, 1230, 1303, 1324, 1370, 1380, 1420, 1465.

The x-ray structural experiment was carried out on a "Sinteks $P2_1$" diffractometer in Mo radiation with a graphic monochromator. The crystals belonged to the monoclinic system, with a = 7.361(3), b = 10.025(5), c = 10.355(5) Å, β = 106.15(3)°, z = 2, space group $P2_1$. The $2\theta/\omega$ scanning method was used in the range $2\theta < 40°$. A correction linear with time was introduced for the fall (approximately 15%) in the intensity of control reflections. Absorption was not taken into account. We made use of 611 reflections with $I > 3\sigma$. The structure was found by the direct method using the MULTAN program and was refined in the anisotropic approximation to R = 0.090. The coordinates of the atoms are given in Table 2.

SUMMARY

1. The sesquiterpene alcohol glehnol with a new type of carbon skeleton has been isolated from the oleoresin of the sakhalin spruce.

2. The structure of glehnol epoxide has been studied by x-ray structural analysis.

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