tation, the side chain is nevertheless forced to exist in certain preferred conformations. As can be seen for the case of the aldehyde (V), when a chromophore is also present in the side chain, the situation becomes still more complicated and can be clarified only by considering the ORD curves of similar compounds.

EXPERIMENTAL

The ORD curves were recorded at room temperature on a Spectropol I instrument in quartz cells with a layer thickness of the solution of the substance of 1 cm.

SUMMARY

Labd-8(17)-ene diterpenoids with a 13Z double bond or voluminous substituents in the side chain do not obey Carman's additive scheme, and when there are no asymmetric centers in the side chain they have more negative values of the molecular optical rotation than is predicted by this scheme.

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STEREOSELECTIVITY OF THE EXHAUSTIVE EPOXIDATION OF CEMBRENE BY PERACETIC ACID.

CRYSTALLINE AND MOLECULAR STRUCTURE OF TRIEPOXYCEMBRENE

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The epoxidation of the diterpene hydrocarbon cembrene with peracetic acid in methylene chloride in the presence of sodium bicarbonate forms a single triepoxide — 4,5:7,8:11,12-triepoxycembrene with the 4S,5R,7S,8S,11S,12S configuration of the asymmetric centers. The structure and stereochemistry of triepoxycembrene have been determined with the aid of x-ray structural analysis.

It has been established previously [1], that the epoxidation of cembrene (I) with peracetic and perbenzoic acid takes place stereospecifically at each of the trisubstituted double bonds, and on further epoxidation the 7S,8S- and 11S,12S-epoxycembrenes give one and the same 7S,8S:11S,12S-diepoxycembrene. The stereochemistry of the epoxidation of 4S,5R-epoxycembrene has not been studied because of the instability of this epoxide with respect to adsorbents.

We have found that when cembrene is treated with an excess of peracetic acid in methylene chloride in the presence of sodium bicarbonate, according to TLC all the mono- and

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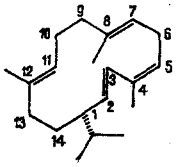
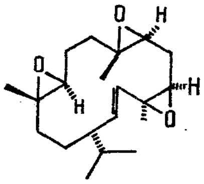
diepoxides of cembrene are converted into the same compound which is now stable to the action of peracetic acid. Crystallization of the product from ethanol gave colorless crystals with mp 122-123°C and $[\alpha]_D^{25}$ +18.3° (c 4.37), the elementary analysis of which corresponded to the empirical formula $C_{29}H_{32}O_3$ (triepoxycembrene). According to its IR spectrum, this compound retained the trans-disubstituted double bond present in cembrene (980 cm^{-1}) but contained no hydroxy or keto groups, while the UV spectrum lacked absorption maxima in the 210-400 region. The results obtained indicate that the product was 4,5:7,8:11,12-triepoxycembrene (II). In order to confirm this assumption, it was studied by x-ray structural analysis using a single crystal formed when a solution of the substance in carbon tetrachloride was allowed to stand. It was established that it was in fact the triepoxide (II) (Fig. 1) and, taking into account the known S configuration of cembrene at C_1, it possesses the 4S,5R,7S,8S,11S,12S configuration. The geometry of the oxide rings corresponds to literature information [2]. The length of the other bonds also have the usual values within the limits of error. The oxygen atoms in the triepoxide (II) are remote from one another, forming a triangle with sides of 4.66, 5.65, and 7.34 Å.



I



II

Thus, in the epoxidation of the intermediate mono- and diepoxycembrenes, the initial orientations of all the trisubstituted double bonds of cembrene relative to the ring are preserved unchanged, ensuring, in the final account, the formation of a single triepoxide. The conformation of the triepoxide (II) differs sharply from that of cembrene itself [3]. The values of the torsional angles in the ring for these molecules are given in Table 1. The values of the torsional angles around the C_3—C_4, C_6—C_7, C_{10}—C_{11}, C_{12}—C_{13}, and C_{13}—C_{14} bonds differ substantially. This difference is apparently caused by a disturbance of the conjugated diene system of cembrene on its epoxidation. The features of the conformation of the triepoxide (II) also appear in its NMR spectrum. Thus, while in 4S,5R-epxoycembrene the H_2 and H_3 protons are magnetically nonequivalent and give separate signals [1], in the triepoxide (II) they form the spin-coupled AB part of a ABX system and appear in the form of a narrow multiplet in the 5.68-5.90 ppm region. On the other hand, while the C_4 methyl group in 4S,5R-epoxycembrene and in 4,5:11,12-diepoxycembrene gives a signal at 1.32 and 1.30 ppm, respectively [1], in the triepoxide (II) a signal (singlet) with an unusually low-field shift (1.50 ppm) is observed for it. In the triepoxide (II), this methyl group is strongly descreened, apparently, by the neighboring disubstituted double bond or one of the epoxy rings.

The other two methyl groups of the triepoxide (II) give singlets at 1.18 and 1.22 ppm, and the epoxide proton at C_5, as in 4S,5R-epoxycembrene, gives a signal in a lower field (doublet of doublets at 3.18 ppm, J = 10.0 and 4.5 Hz) than the epoxide proton H_7 and H_{11}. In the NMR spectrum of the triepoxide (II), the latter give practically coincident signals and appear in the form of a single doublet of doublets at 2.68 ppm with J = 7 and 3 Hz.

EXPERIMENTAL

The NMR spectrum of the triepoxide (II) was recorded on a Varian A56/60A instrument for solutions in carbon tetrachloride with hexamethyldisiloxane as standard, δ scale. The IR spectrum was obtained on a UR-20 instrument, and melting points were determined on a Kofler block.

The Triepoxide (II). A solution of cembrene (0.34 g, 1.25 mmole) in 15 ml of methylene chloride was treated with 3 g of sodium bicarbonate and, with vigorous stirring at room temperature a freshly-prepared solution of 6 mmole of peracetic acid, obtained by Greenspan's method [4], in 1 ml of methylene chloride was added dropwise at room temperature. After the reaction mixture had been stirred for 2 h, another 10 ml of peracetic acid solution containing 4 mmole of the peracid was added and it was left overnight. After the usual working up, 0.32 g was obtained of a product consisting, according to TLC, of the triepoxide with traces of diepoxide and more polar compounds. Crystallization of this product from ethanol yielded 0.20 g of the triepoxide (II) with mp 122-123°C and $[\alpha]_D^{25}$ +18.3° (c 4.37; chloroform).

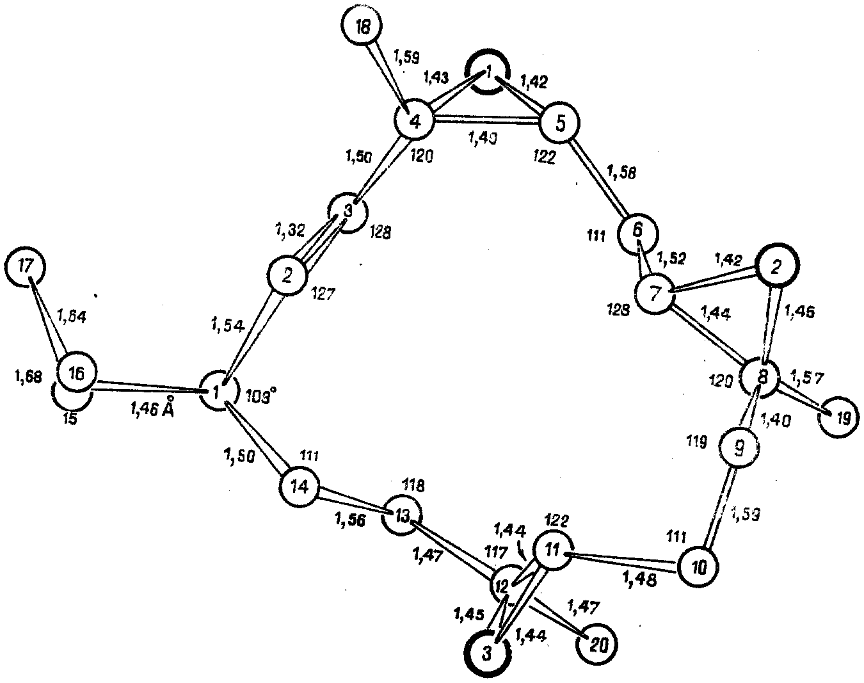


Fig. 1. Crystal structure of triepoxycembrene (II).

TABLE 1. Comparison of the Torsional Angles in the Molecules of Triepoxycembrene (II) and of Cembrene (I)

Angle	Magnitude of the angle, deg	
	in triepoxycembrene	in cembrene
C (14) C (1) C (2) C (3)	108.9	121.4
C (1) C (2) C (3) C (4)	−176.6	−177.2
C (2) C (3) C (4) C (5)	106.5	178.1
C (3) C (4) C (5) C (6)	−6.9	−2.1
C (4) C (5) C (6) C (7)	−91.4	−67.2
C (5) C (6) C (7) C (8)	−159.8	130.9
C (6) C (7) C (8) C (9)	−157.5	−175.7
C (7) C (8) C (9) C (10)	91.0	116.3
C (8) C (9) C (10) C (11)	−56.7	−60.9
C (9) C (10) C (11) C (12)	111.9	−161.3
C (10) C (11) C (12) C (13)	−154.4	178.8
C (11) C (12) C (13) C (14)	−41.6	121.3
C (12) C (13) C (14) C (1)	156.6	−54.9
C (13) C (14) C (1) C (2)	−78.6	−64.4

Found, %: C 74.63; H 9.71. $C_{20}H_{32}O_3$. Calculated %: C 74.76; H 9.55.

The x-ray structural experiment was performed on a Syntex $P2_1$ diffractometer using Mo radiation with a graphite monochromator. The crystal selected for the experiment, with dimensions of $0.4 \times 0.5 \times 0.8$ nm^3, was a chip from a large one and had no clear faces. Triepoxycembrene (II) crystals belong to the rhombic system, $a = 9.765(9)$, $b = 10.084(7)$, $c = 19.958(11)$ Å; space group $P2_12_12_1$; $Z = 4$: $d_{calc} = 1.08$ g/cm^3. The intensities of 2010 independant reflections were measured by the $2\theta/\omega$ method, and 692 of them had $I > 3\sigma$ and were included in the calculations. The temperature factor calculated from a Wilson plot proved to be fairly high at 6.3 Å^2, which is possibly connected with the low quality of the crystal selected.

The structure was interpreted with the aid of the MULTAN-XTL programme, and the correct phase variant was that which was best according to a RESID evaluation and third with respect to NQEST = −0.093. The structure was refined in the full-matrix anisotropic approximation to R = 0.111, using the weighting scheme $W^{-1} = \sigma_F^2 + (0.02\ F_E)^2$. The coordinates of

TABLE 2. Coordinates (× 10^3) of the Atoms and Isotropic Temperature Factors (× 10) of the Atoms of the Triepoxycembrene (II) Molecule

Atom	x/a	y/b	z/c	B
C (1)	246 (3)	165 (3)	854 (2)	76
C (2)	105 (4)	204 (3)	826 (2)	81
C (3)	013 (4)	123 (3)	799 (2)	65
C (4)	—122 (3)	160 (3)	768 (2)	83
C (5)	—137 (3)	154 (3)	698 (2)	46
C (6)	—011 (4)	126 (3)	650 (1)	70
C (7)	056 (3)	254 (4)	627 (1)	81
C (8)	144 (3)	276 (3)	570 (2)	65
C (9)	234 (4)	383 (3)	569 (2)	70
C (10)	386 (3)	363 (3)	597 (2)	75
C (11)	383 (2)	315 (3)	667 (1)	77
C (12)	428 (2)	183 (3)	684 (1)	62
C (13)	369 (3)	124 (3)	745 (2)	79
C (14)	354 (2)	216 (3)	808 (2)	71
C (15)	249 (5)	209 (9)	924 (3)	172
C (16)	124 (6)	154 (6)	975 (2)	122
C (17)	251 (10)	316 (11)	940 (4)	191
C (18)	—224 (3)	249 (3)	810 (2)	90
C (19)	175 (3)	155 (4)	523 (1)	104
C (20)	479 (3)	076 (3)	640 (1)	79
O (1)	—181 (2)	045 (2)	737 (1)	86
O (2)	—001 (2)	312 (2)	569 (1)	104
O (3)	518 (2)	296 (2)	695 (1)	96

the atoms are given in Table 2. The standard deviations for the bond lengths are approximately 0.05 A and for the angles about 3°.

SUMMARY

The epoxidation of cembrene with an excess of peracetic acid in methylene chloride forms 4S,5R:7S,8S:11S,12S-triepoxycembrene, the structure and stereochemistry of which have been established with the aid of x-ray structural analysis.

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