SUMMARY

1. It has been established from CD-spectroscopic characteristics that in trans-carotane derivatives a positive Cotton effect in the 260-249 nm region corresponds to an ester group at C_6.

2. A link has been established between the position of the carbonyl groups and the sign of the Cotton effect in the 340-nm region.

3. It has been established that the hydrolysis of an ester group at C_6 takes place more readily in an alkaline medium than in an acid medium, and that in carbonyl-containing carotanes dehydration takes place as well as hydrolysis.

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PHOTOSENSITIZED OXIDATION OF ISOCEMBROL.

VII. PRODUCTS OF REACTION AT THE C_{11} DOUBLE BOND

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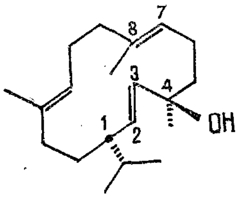
It has been established that in the photooxidation of isocembrol, in addition to other compounds, five products of oxidation at the C_{11} double bond are formed, and their structures and stereochemistry have been established by chemical transformations and physicochemical methods. In the stereochemical respect, the photooxidation of isocembrol at the C_{11} double bond is similar to its epoxidation at the same bond.

Continuing a study of the oxidation of cembrane diterpenoids by singlet oxygen [1], we have investigated the products of the photosensitized oxidation of isocembrol (I) — a component of the oleoresin of coniferous plants [2], tobacco [3], and soft corals [4]. The structure [2] and stereochemistry [5] of this alcohol have been established previously with the aid of chemical and spectral methods.



I

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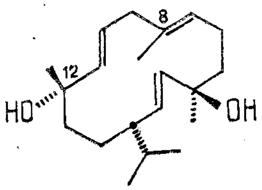
The conditions for performing the reaction and for the treatment of the reaction mixture were the same as were used in the photooxidation of cembrene [1]. With a reaction time of 3 h, the degree of conversion amounted to 70.7%. According to TLC, the products consisted of two groups of compounds differing in polarity. The first group, as was found, consisted of products of the reaction at the C_{11} double bond of isocembrol and it is this group which is described in the present paper. The second group included compounds formed by reactions at two double bonds of the isocembrol and the products of reaction at the C_7 double bond.

Using adsorption chromatography on silica gel, the first group of compounds was separated into five crystalline components. One of the least polar compounds had the empirical formula $C_{20}H_{34}O_2$ (high-resolution mass spectrometry), mp 120-121°C, yield 12.8% (here and below, on the isocembrol that reacted). The absence from its PMR spectrum of the signal of a carbinol proton and the presence of the singlets of two tertiary methyl groups adjacent to hydroxy groups, coinciding with one another (1.28 ppm, 6 H), showed that the substance under investigation was a ditertiary diol. In its spectrum it was possible to observe a high intensity band of a tertiary hydroxy group (3610 cm^{-1}) and the band of a trans-disubstituted double bond (980 cm^{-1}) having approximately twice the integral intensity of that for isocembrol. The latter fact showed that the molecule of the compound under investigation contained two trans-disubstituted double bonds and was an analog of the cembra-2E,4Z,7E,10E-tetraen-12-ol obtained previously by the photooxidation of the cembrene [1]



II

Since it appeared difficult to establish the position of the second hydroxy group (at C_8 or C_{12}) and its configuration reliably with the aid of chemical and spectral methods, we carried out an X-ray structural analysis of this substance. It was established that the compound under investigation was a diol with the formula (II). The structure of its molecule is shown in Fig. 1. The bond lengths in the ring are the usual ones. The valence angles in the ring are appreciably increased, for example, the C_4—C_5—C_6 angle is 107.8(6)° and the mean value of C—C_{sp^3}—C angle is 114.4°. The conformation of the molecule differs from that for cembrene [6] and triepoxycembrene [7]. In the crystal, the molecules of the diol (II) are linked by hydrogen bonds into layers lying in the xy plane. The hydrogen bonds have the following characteristics: a) O1—H(O1)...O2' (1/2 − x, y − 1/2, 1/2 − z), O1...O2 distance 2.815 Å, H(O1)...O2' distance 1.86 Å, the angle O1—H(O1)...O2' is 169.9°; b) O2—H(O2)...O1' (x − 1/2, 1/2 + y, z), O2...O1' distance 2.755 Å, H(O2)...O1 distance 1.70 Å, the O2—H(O2)...O1' angle is 154.2°. It is interesting to note that four molecules of the diol (II) form eight-membered "H-rings" around the second-order axes of rotation. The layers are connected by van der Waals interactions, of which 1H14...H(O1)' is slightly shortened — 2.26 Å (1/2 − x, 1/2 + y, 1/2 − z).

A second product of the photooxidation of isocembrol was obtained with a yield of 20%, mp 75-77°C. According to its PMR spectrum, it contained a secondary hydroxy group (the signal of a carbinol proton was observed at 3.94 ppm as a doublet of doublets with J = 4.6 and 7.0 Hz), and an exomethylene group (two identical narrow multiplets at 4.96 and 5.05 ppm, 1 H each). The presence of the latter was confirmed by the IR spectrum (bands at 907, 1650, and 3080 cm^{-1}).

It is known that on dehydration with phosphorus oxychloride in pyridine isocembrol gives a mixture of cembrene and isocembrene [9]. We used this to determine the structure and stereochemistry of the compound under investigation. Its acetylation with acetic anhydride in pyridine gave a monoacetate the dehydration of which with phosphorus oxychloride in pyridine led to a mixture of two compounds incapable of separation by chromatography (1:3; PMR spectrum). It was possible to separate them by thin-layer chromatography after the acetyl protection had been removed with lithium tetrahydroaluminate in diethyl ether. The component present in smaller amount was identified as the alcohol (III), obtained previously by the photooxidation of cembrene [1]. The second component was, according to its IR and PMR spectrum, the corresponding $\Delta^{4(18)}$ isomer. Consequently, the initial diol had the structure (IV).

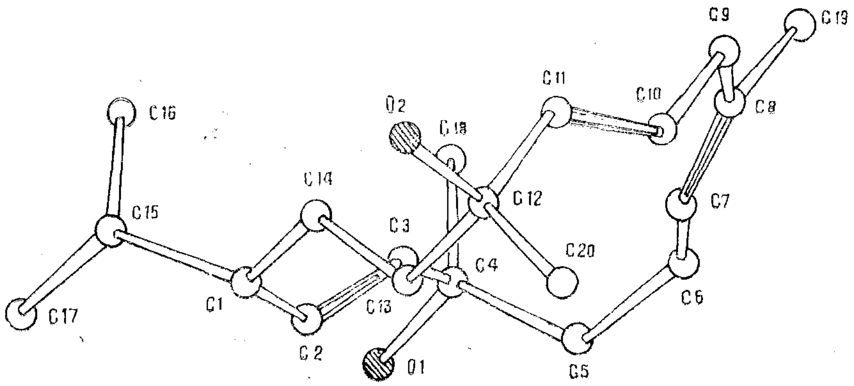


Fig. 1. Crystal structure of the diol.

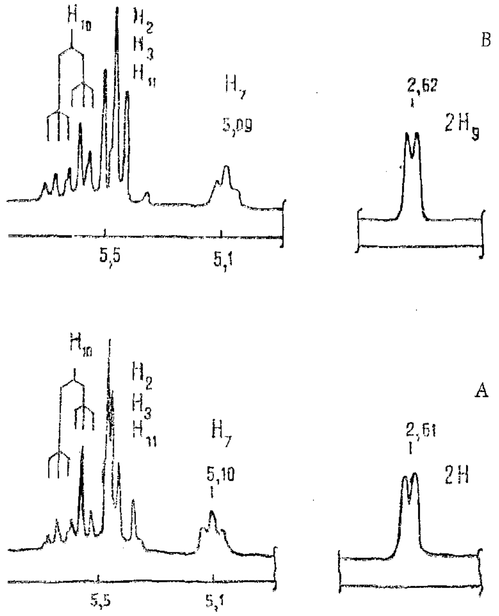
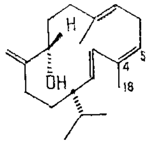
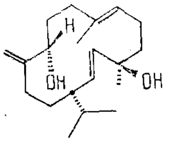


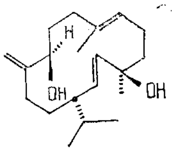
Fig. 2. Fragments of the PMR spectra of the diols (II) (A) and (VI) (B).



III



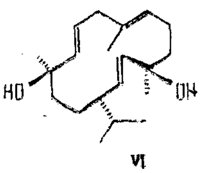
IV



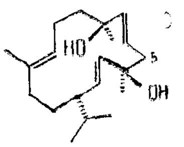
V

The third product of the photooxidation of isocembrol with mp 87-88°C, yield 2.2%, had a PMR spectrum similar to that of the diol (IV). It was the C_{11}-epimer (V) of the diol (IV), as was shown in the following way. Oxidation of the diol (IV) with chromium trioxide in pyridine gave the corresponding C_{11} ketone [ν_{max} 1680 cm^{-1}, λ_{max} 223 nm (ε 10,300)], and the reduction of this with lithium tetrahydroaluminate in diethyl ether formed a mixture of the diols (IV) and (V) (1:2, determined from the relative integral intensities of the H_3 signals in the PMR spectrum). By chromatographing this mixture it was possible to obtain the diol (V), identical with a sample obtained by the photooxidation of isocembrol.

The fourth product of the photooxidation of isocembrol, with mp 101-102°C, yield 2.5%, had the empirical formula $C_{20}H_{34}O_2$ (high-resolution mass spectometry). Its IR spectrum almost coincided with that of the diol (II). It was acetylated by acetic anhydride in pyridine, and its PMR spectrum did not contain the signal of a carbinol proton. Consequently, it was a ditertiary diol, like the diol (II). Two structures are possible for it — the C_{12}-epimer (VI) of the diol (II), and the C_8-epimer of the known diol (VII), which has been isolated from tobacco leaves [10].



VI



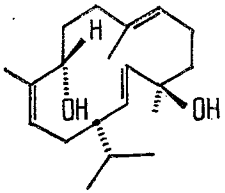
VII

A comparison of the PMR spectra of the compound obtained and of the diol (II) showed that this compound had the structure (VI). In actual fact, the protons of the methylene group adjacent to the trans-disubstituted double bond are magnetically equivalent for the compound under investigation and the diol (II), giving identical doublets with almost coincident chemical shifts (Fig. 2). In the structure of (VII), this group (at C_5) is adjacent to the asymmetric center (C_4), and its protons will be magnetically nonequivalent, as is actually observed in the spectrum of the diol (VII) (doublets of doublets at 2.47 and 2.18 ppm).

An additional confirmation of the correctness of structure (VI) was obtained by comparing the mass spectra of this compound and of the diols (II) and (VII). The mass spectrum of the substance under investigation was close to that of the diol (II), the main ions in both spectra being those with m/z 81 and 92. The nature of the fragmentation of the diols (VII) has different features; in particular, the main ion in its mass spectrum is that with m/z 83, and the peaks of the ions with m/z 81 and 93 amount to only 30 and 15% of the main peak. For compound (VII), the peak of the ion with m/z 83 has the form of an isolated singlet, and for the diol (II) and the compound under investigation it is split into two peaks, which shows the formation of two ions with the same mass numbers but different elementary compositions.

The differences in the fragmentation of the diols (II) and (VII) are due to the fact that these substances are structural isomers, and the similarity of the mass spectra of the diol (II) and the substance under investigation shows that they are stereoisomers. Thus, the diol isolated is an epimer not of the diol (VII) but of the diol (II) and has the structure (VI).

The fifth product of the photooxidation of isocembrol, with mp 174-175°C, yield 2.5%, was an isomer of the diols described above ($C_{20}H_{34}O_2$, high-resolution mass spectometry). In the qualitative respect, its PMR spectrum differs from that of isocembrol only by the appearance of the signal of a carbinol proton at 3.77 ppm (doublet of doublets). Consequently, the double bond present in the vicinity of the hydroxy group that has been introduced into the molecule is trisubstituted. Since there are no signals in the PMR spectrum of the protons of a $=C-CH_2-C=$ grouping (2.4-3.5 ppm) [11], the compound under investigation can be ascribed structure (VIII) as the only possible one; it corresponds to an attack of the singlet oxygen on the C_{11} double bond of isocembrol with the migration of the latter to the C_{12}—C_{13} position.



VIII

The correctness of structure (VIII) and also of its configuration at C_{11}, was established by the conversion of 11S,12S-epoxyisocembrol [12] into the diol (VIII) under the action of antimony trichloride in absolute diethyl ether. This reagent has been used by Dhillon et al. [13] to isomerize a sesquiterpene epoxide into the corresponding allyl alcohol. Thus, diol (VII) has the 11S configuration.

For the point of view of known features of the photooxidation of olefins [14], the C_{11} double bond of isocembrol exhibits normal behavior — the neighboring allyl hydrogen atoms are eliminated mainly from the more substituted side of the double bond (methyl group at C_{12}, methylene group at C_{10}). In the stereochemical respect, however, the photooxidation of isocembrol at the C_{11} double bond is analogous to the epoxidation of the same compound [12] and to the photooxidation of cembrene [1] — in all these cases alcohols with S configuration of the asymmetric center arising are formed predominantly or exclusively.

TABLE 1. Chemical Shifts (ppm) and Spin–Spin Coupling Constants (Hz, shown in parentheses) for Some Signals in the PMR Spectra of the Products of the Photooxidation of Isocembrol*

Compound	H_2	H_3	H_7	H_{11}	Me_4	Me_8	Me_{12}	$-CH(C\underline{H}_3)_2$
II†	—	—	5,10 tm	—	1,27 s	1,61 s	1,27 s	0,78 d; 0,84 d (6,0; 6,0)
IV	5,39 dd (16,0; 8,0)	5,84 d (16,0)	5,10 tm	3,95 dd (7,5; 5,0)	1,29 s	1,57 s	—	0,82 d; 0,83 d (6,5; 6,5)
V	5,27 dd (16,0; 8,8)	5,50 d (16,0)	5,10 m	4,03 tm (6,0)	1,31 s	1,57 s	—	0,82 d; 0,79 d (6,5; 6,5)
VI†	—	—	5,09 tm	—	1,26 s or 1,27	1,63 s	1,27 s or 1,26	0,77 d; 0,83 d (6,0; 6,0)
VIII‡	5,17 dd (16,0; 8,5)	5,50 d (16,0)	5,18 m	3,77 dd (10,0; 3,0)	1,31 s	1,50 s or 1,52	1,52 s or 1,50	0,80 d; 0,85 d (6,7; 6,7)

*Arbitrary symbols: d — doublet; t — triplet; m — multiplet; dd — doublet of doublets; tm — triplet of multiplets.

†The signals of the H_{10} proton appeared in the form of a doublet of triplets (Fig. 2) at 5.58 ppm (diol (II)) and 5.62 ppm (diol (VI)), $J_{10,9}$ and $J_{10,11}$ being 6.5 and 16.0 Hz, respectively, in both cases.

‡The signal of the H_{13} proton practically coincided with the signal of the H_7 proton.

TABLE 2. Coordinates of the Atoms ($\times 10^4$ and $\times 10^3$ for H, z coordinates of the atoms multiplied by -1) of the Diol (II) Molecule

Atom	x	y	z	Atom	x	y	z
C_1	2987 (7)	2728 (5)	2390 (4)	O_1	3737 (5)	0280 (3)	3103 (2)
C_2	3238 (7)	1921 (5)	2719 (4)	O_2	1300 (4)	4955 (3)	3130 (2)
C_3	2560 (7)	1580 (5)	3155 (3)	H_1	382 (7)	309 (3)	237 (3)
C_4	2764 (9)	0740 (5)	3419 (3)	H_2	399 (6)	156 (3)	253 (3)
C_5	3286 (7)	0784 (5)	4064 (3)	H_3	189 (5)	184 (4)	334 (3)
C_6	2348 (9)	1017 (5)	4562 (3)	$1H_5$	357 (6)	012 (4)	416 (2)
C_7	1803 (8)	1855 (4)	4530 (3)	$2H_5$	409 (6)	114 (4)	410 (3)
C_8	0687 (8)	2101 (5)	4736 (3)	$1H_6$	282 (5)	086 (4)	496 (3)
C_9	0197 (7)	2978 (5)	4696 (3)	$2H_6$	172 (6)	053 (4)	457 (3)
C_{10}	1073 (7)	3587 (4)	4405 (3)	H_7	237 (6)	226 (4)	436 (3)
C_{11}	0940 (7)	3889 (4)	3874 (3)	$1H_9$	—003 (5)	315 (3)	510 (3)
C_{12}	1912 (8)	4416 (5)	3552 (3)	$2H_9$	—065 (6)	292 (3)	442 (3)
C_{13}	2784 (7)	3835 (4)	3191 (4)	H_{10}	167 (5)	376 (2)	462 (3)
C_{14}	2134 (7)	3835 (4)	2706 (4)	H_{11}	015 (6)	370 (4)	363 (3)
C_{15}	2495 (9)	2542 (5)	1754 (4)	$1H_{13}$	342 (6)	415 (4)	304 (3)
C_{16}	1281 (8)	2058 (5)	1749 (3)	$2H_{13}$	319 (6)	346 (4)	350 (3)
C_{17}	3447 (9)	2291 (7)	1354 (4)	$1H_{14}$	169 (6)	374 (3)	241 (3)
C_{18}	1528 (8)	0257 (4)	3317 (4)	$2H_{14}$	140 (6)	299 (4)	289 (3)
C_{19}	—0227 (7)	1510 (5)	5026 (4)	H_{15}	240 (6)	326 (4)	149 (3)
C_{20}	2702 (7)	4940 (5)	3961 (3)	$H(O_1)$	365 (6)	012 (4)	269 (3)
				$H(O_2)$	034 (6)	525 (3)	316 (2)

TABLE 3. Some Bond Lengths (Å) of the Diol (II) Molecule

Parameter	Value	Parameter	Value	Parameter	Value
C_1-C_2	1,519 (12)	C_4-O_1	1,452 (09)	$C_{10}-C_{11}$	1,295 (11)
C_1-C_{14}	1,501 (11)	C_5-C_6	1,539 (1)	$C_{11}-C_{12}$	1,516 (11)
C_1-C_{15}	1,547 (12)	C_6-C_7	1,469 (10)	$C_{12}-C_{13}$	1,542 (11)
C_2-C_3	1,329 (11)	C_7-C_8	1,327 (12)	$C_{12}-C_{20}$	1,500 (11)
C_3-C_4	1,493 (11)	C_8-C_9	1,507 (11)	$C_{12}-O_2$	1,438 (09)
C_4-C_5	1,551 (11)	C_8-C_{19}	1,502 (11)	$C_{13}-C_{14}$	1,523 (11)
C_4-C_{18}	1,522 (12)	C_9-C_{10}	1,498 (10)	$C_{15}-C_{16}$	1,501 (12)
				$C_{15}-C_{17}$	1,410 (13)

EXPERIMENTAL

PMR spectra were obtained from a Bruker WP-200 instrument ($CDCl_3$, internal standard chloroform, the signal of which was taken as 7.24 ppm, δ scale). High-resolution mass spectra were recorded on an MS-902 instrument (direct introduction, 120°C, energy of the ionizing electrons 70 ev). IR spectra were obtained on a UR-20 instrument in $CHCl_3$ solution, and angles of optical rotation were measured for solutions in chloroform on a Zeiss polarimeter.

Column chromatography was performed on air-dry type KSK silica gel with grain dimensions of 0.140-0.315 mm at a ratio of substance to sorbent of $\sim$1:20, the eluent in all cases being petroleum ether with increasing concentrations (from 0 to 90%) of diethyl ether.

The IR spectra of the diols obtained contained in identical positions the bands of a trans-disubstituted double bond (980 cm^{-1}) and of free hydroxy groups (3610-3620 cm^{-1}), and, for the diols (IV) and (V), in addition, the bands of an exomethylene group were observed (907, 1650, and 3080 cm^{-1}).

Photooxidation of Isocembrol. A solution of 3.65 g of isocembrol and 0.42 g of Rose Bengal in 130 ml of methanol was irradiated at 22°C in a quartz cell with the light of a high-pressure mercury lamp (DRSh-1000) while air was bubbled through the solution for 3 h. The reaction mixture obtained was evaporated at 20°C in a rotary evaporator to 1/3 of its initial volume and it was then cooled to 0°C and, with stirring, 0.6 g of sodium tetrahydroborate was added. After the mixture had stood for an hour, the resulting solution was evaporated to dryness, and the residue was treated with a saturated aqueous solution of sodium chloride and extracted with diethyl ether. The extract was dried with sodium sulfate, the solvent was driven off, and the residual product was chromatographed on silica gel. This gave, successively, 1.07 g of unchanged isocembrol (29.3% of that taken for the reaction), 0.35 g of the diol (II) with mp 120-121°C (from acetonitrile) and $[\alpha]_D^{20}$ +56.9° (c 4.39), 0.65 g of a mixture of the diols (IV) and (VIII), 0.06 g of the diol (V) with mp 101-102°C (from a mixture of hexane and diethyl ether), and 0.07 g of the diol (VI) with mp 87-88°C (from acetonitrile).

Rechromatography of the mixture of diols (IV) and (VIII) on silica gel with 5% of silver nitrate yielded 0.55 g of the diol (IV) with mp 75-77°C (from a mixture of hexane and diethyl ether), $[\alpha]_D^{22}$ −12° (c 5.50), and 0.07 g of the diol (VIII) with mp 174-175°C (from a mixture of hexane and diethyl ether), $[\alpha]_D^{20}$ −93° (c 1.08). Details of the PMR spectra of products (II), (IV), (V), (VI), and (VIII) are given in Table 1.

X-Ray Structural Analysis of the Diol (II). The x-ray structural experiment was performed on a Syntex $P2_1$ diffractometer using Mo radiation with a graphite monochromator and a crystal with dimensions of 0.3 × 0.7 × 0.8 mm^3. Crystallographic results: a = 10.553(2), b = 16.112(4), c = 22.435(5), z = 8, space group C 222_1, d_{calc} = 1.065 g/cm^3. A total of 1036 independent reflections with $2\theta < 40°$ was measured by the $2\theta/\theta$ scanning method, and 843 reflections with $I > 2\sigma$ were used in the calculations. The structure was interpreted by the direct method using the "MULTAN-XTL" program. It is interesting to note that the correct variant had ABSFOM = 1.67, while many incorrect variants had anomalously high values of ABSFOM of $\sim$2.4. The coordinates of the hydrogen atoms were calculated geometrically. The structure was refined by the method of least squares in the full-matrix anisotropic approximation (the hydrogen atoms were taken into account separately in the isotropic approximation with fixed B = 6.0 Å) to R = 0.053 and R_w = 0.043, where $w^{-1} = \sigma_F^2 + (0.008F)^2$. High temperature factors were obtained for the C_{17} atom (B_{11} = 8.3, B_{22} = 18.6, B_{33} = 5.8, B_{12} = −1.4, B_{13} = 1.9, B_{23} = −1.7 $Å^2$), which apparently affected the value of the length of the C_{15}-C_{17} bond that was found.

Preparation of the Alcohol (III) from the Diol (IV). A solution of 0.20 g of the diol (IV) in 5 ml of pyridine was treated with 2 ml of acetic anhydride, and the mixture was left at room temperature for 12 h. After the usual working up, 0.18 g of product [the 11-O-acetate of the diol (IV), oil, IR spectrum: 1740 cm^{-1} (C=O), 3610 cm^{-1} (OH)] was obtained, and to a solution of this in 5 ml of pyridine cooled to 0°C was added 0.2 ml of phosphorus oxychloride. After the mixture had been left at 0°C for 10 h and had then been worked up in the usual way, a product (0.10 g) was obtained which was treated with an excess of lithium tetrahydroaluminate in diethyl ether. The usual working up and chromatography led to 0.02 g of the alcohol (III), the IR and PMR spectra of which coincided with those of an authentic sample [1], and 0.06 g of its isocembrene analog (1S, 11S-cembra-2E,7E,4(18),12(20)-tetraen-11-ol); IR spectrum (cm^{-1}): 890, 907, 1650, 3080 (two exomethylene groups), 980 (trans-disubstituted double bond), 3020 (OH).

Conversion of the Diol (IV) into the Diol (V). A reagent obtained by mixing 0.3 g of chromium trioxide with 5 ml of pyridine at room temperature was added to a solution of 0.30 g of the diol (IV) in 5 ml of pyridine. The reaction mixture was kept at 80°C for 20 min and then by the usual working up procedure and chromatography 0.15 g of the C_{11} ketone (1S-cembra-2E,7E,12(20)-trien-11-one) was obtained with mp 70-71°C (from acetonitrile) $\lambda_{max}^{C_2H_5OH}$ 223 nm (ε 10,300). IR spectrum (cm^{-1}): 1680 (conjugated carbonyl), 3610 (OH). Its reduction by lithium tetrahydroaluminate in absolute diethyl ether (20°C, 1 h) gave 0.14 g of a mixture of the diols (IV) and (V), the chromatography of which on silica gel yielded 0.07 g of the diol (V) with mp 87-88°C (from acetonitrile), this being identified by comparison with an authentic sample by TLC and PMR spectroscopy.

Synthesis of the Diol (VIII) from 11S,12S-Epoxyisocembrol. To a solution of 0.48 g of 11S,12S-epoxycembrol in 10 ml of absolute diethyl ether cooled to 0°C were added 0.05 ml of pyridine and a solution of 0.2 g of antimony trichloride in 5 ml of absolute diethyl ether. After the reaction mixture had been left to stand at 0-5°C for 1 h, it was diluted with diethyl ether and treated with a saturated aqueous solution of sodium bicarbonate. The ethereal solution was filtered off, dried with sodium sulfate, and evaporated to dryness. Chromatography of the product on silica gel yielded 0.26 g of the initial substance and 0.11 g of the diol (VIII) with mp 174-175°C (from diethyl ether), the PMR spectrum of which coincided with that of the diol (VIII) obtained by the photooxidation of isocembrol.

SUMMARY

1. The photooxidation of isocembrol forms five products of reaction at the C_{11} double bond — two pairs of alcohols epimeric at C_{11} and C_{12} and the product of the migration of C_{11} double bond into the C_{12}—C_{13} position.

2. The photooxidation of isocembrol at the C_{11} double bond takes place steroselectively — the main products have the S configuration of the asymmetric center formed and correspond to an attack by singlet oxygen on the C_{11} double bond from the same side as in the case of cembrene.

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DETERMINATION OF STICHOPOSIDES IN THE BODY OF THE HOLOTHURIAN *Stichopus japonicus*

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A method has been developed for the quantitative determination of triterpene glycosides — stichoposides — in the tissues of the Far Eastern holothurian *Stichopus japonicus* Selenka. The quantitative determination of the combined triterpene glycosides was based on the isolation of a glycosidic fraction from an ethanolic extract on a column of Polikhrom-1 with subsequent spectrophotometry at 268 nm of the product formed as the result of the reaction of the glycosides with 1 N NaOH. The quantitative determination of the individual glycosides is based on the densitometry of slides or thin-layer chromatography in silica gel with the aid of a Lyuman-IUF-1 luminescence microscope.

The structures of the triterpene glycosides of marine Echinodermata have been studied fairly fully [1, 2]. However, the absence of specific methods for their quantitative determination and the difficulties in obtaining derivatives for gas—liquid chromatography and in separating homologs with the aid of liquid chromatography — all this is interfering with the solution of the main problem of understanding the physiological role of the triterpene glycoside in the producing organisms. In the present paper we discuss a new methodological approach to the quantitative estimation of the individual stichoposides in the tissues of a Far Eastern holothurian.

The tissues of the holothurian *Stichopus japonicus* Selenka contain three triterpene glycosides: stichoposides A, B, and C, which differ from one another by their carbohydrate moieties. It is impossible to separate stichoposide A from stichoposide C by thin-layer chromatography [2], stichoposide C (holotoxin C) being present in trace amounts. In early

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