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 C₆.

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 C₆ 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.

LITERATURE CITED


PHOTOSENSITIZED OXIDATION OF ISOCEMBROL.

VII. PRODUCTS OF REACTION AT THE C₁₁ 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 C₁₁ 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 C₁₁ 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.


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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 C7 double bond of isocembre 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 isocembre and the products of reaction at the C7 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 C22H36O2 (high-resolution mass spectrometry), mp 120–121°C, yield 12.8% (here and below, on the isocembre 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 isocembre. 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].

Since it appeared difficult to establish the position of the second hydroxy group (at C8 or C12) 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 C₄–C₅–C₆ angle is 107.8(6)° and the mean value of C–C–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 isocembre 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 isocembre 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 monoaacetate 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 the cembrene [1]. The second component was, according to its IR and PMR spectrum, the corresponding Δ⁴(18) isomer. Consequently, the initial diol had the structure (IV).