Fraction D consisted of a mixture of related compounds. By crystallizing it was possible to isolate only one compound in the individual state — a saturated tricyclic tertiary alcohol with mp 64-65°C and $[\alpha]_D^{20}$ +70.4° (CHCl$_3$). In its physicochemical constants and spectral characteristics, this alcohol proved to be identical with cubebol and differed from it only in the sign of the optical rotation. The residue after crystallization consisted of a mixture of cubebol and an oily alcohol in a ratio of 1:1. It may be assumed that the second alcohol of fraction D is epicubebol, since cubebol is found in natural raw material together with its epimer. This also agrees with the PMR spectrum of fraction D. To confirm the structure of both alcohols we performed the dehydration of the mixture of compounds of fraction D (POCl$_3$, pyridine, 0°C), which led to a mixture of hydrocarbons the main one of which was (—)-δ-cadinene. This result agrees well with the result of the acid isomerization of α-cubebene into δ-cadinene [5].

Thus, in the oleoresin of the Sakhalin spruce eleven monoterpene hydrocarbons, two monoterpene alcohols, 15 sesquiterpene hydrocarbons, and three sesquiterpene alcohols have been identified. This is the first time that eremophilene, cubenol, and cubebol have been isolated from oleoresins of the family *Pinaceae*.

LITERATURE CITED

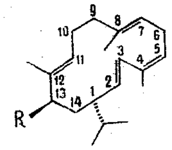
1. É. N. Shmidt, Zh. V. Dubovenko, M. A. Chirkova, Yu. G. Tagil'tsev, and V. A. Pentegova, Izv. Sibirskogo Otd. Akad. Nauk SSR, Ser. Khim. Nauk, series No. 1, No. 2, 11 (1978).
2. V. A. Khan, Zh. V. Dubovenko, and V. A. Pentegova, Khim. Prirodn. Soedin., 111 (1976).
3. Y. Ohta and Y. Hirose, Tetrahedron Lett., 2073 (1967).
4. F. Šorm, J. Vonasek, and V. Herout, Collec. Czech. Chem. Commun., 25, 919 (1960).
5. Y. Ohta and Y. Hirose, Tetrahedron Lett., 4181 (1968).

REGIOSELECTIVE AND STEREOSELECTIVE OXIDATION OF CEMBRENE BY SELENIUM DIOXIDE

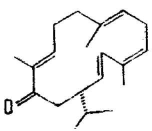
V. A. Raldugin, L. Ya. Korotkikh,
N. I. Yaroshenko, and V. A. Pentegova

UDC 547.595.9+547.366

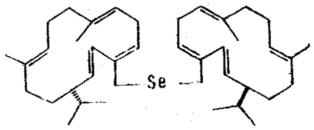
According to the mechanism of the allyl oxidations of olefins by selenium dioxide [1] and the characteristics of this reaction that have been found [2], the diterpene hydrocarbon cembrene (I) [3] should be oxidized primarily at the two methylene groups present in similar environments at C$_9$ and C$_{13}$. In fact, it was found that cembrene is oxidized predominantly at the C$_{13}$ methylene group, forming the alcohol (II) [n_D^{22} 1.5180, $[\alpha]_D^{24}$ +188.5° (chloroform)] and its acetate (III) [n_D^{22} 1.5188, $[\alpha]_D^{20}$ +183° (chloroform)] with total yield of 55% on the cembrene that reacted. The oxidation was carried out by stirring for two hours at 60-70°C a mixture of 4 g of cembrene, 0.59 g of selenium dioxide, 5 ml of acetic anhydride, and 50 ml of acetic acid, followed by pouring onto ice and extraction of the total reaction products with petroleum ether.



I. R = H
II. R = OH
III. R = OCOCH$_3$



IV



V

Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 410-411, May-June, 1978. Original article submitted January 10, 1978.

0009-3130/78/1403-0348$07.50

The structure of the alcohol (II) was shown by its reduction according to Corey [4] to cembrene and its oxidation with chromium trioxide in pyridine to the ketone (IV) (IR spectrum: 1680 cm^{-1}), in which the position of the β-enone system was established with the aid of NMR using double resonance. This alcohol has the R configuration, since the circular curve of its O-nitrobenzoate shows a negative Cotton effect at 330 nm [5]. Acetylation of the alcohol (II) gave the acetate (III).

The preferential nature of the oxidation of cembrene at the C_{13} methylene group can be explained by the smaller steric hindrance of the approach of the reagent in the first stage of the reaction [1] to the C_{11}–C_{12} double bond as compared with the C_7–C_8 double bond. The epoxidation of cembrene with peroxy acids is less selective, but in this case, also, the attack of the reagent on the C_{11}–C_{12} double bond is preferred [6].

Highly oxidized cembrane diterpenoids with an oxygen-containing functional group at C_{13} have been found in nature [7], and the compounds that we have described can be used for the synthesis of their analogs.

By chromatographing the reaction mixture on SiO_2, in addition to the alcohol (II) and its acetate, we isolated another oily product (yield ~20%), the IR spectrum of which had no absorption bands of oxygen-containing functional groups, which agrees with its high chromatographic mobility in TLC on SiO_2. The UV spectrum of this compound [$\lambda_{max}^{C_2H_5OH}$ 244 nm (log ε 4.22)] is similar to that of cembrene [3] but the NMR spectrum differs from that of cembrene [8] by the absence of the signal of the C_4 methyl group, a downfield shift of the H_5 signal (δ 5.59 ppm), and the appearance of a new signal (2H, singlet) at 3.21 ppm. The mass spectrum of this substance contains the peak of the molecular ion with m/e 622, the distribution of the isotopic peaks in which shows the presence of a selenium atom in it. In view of the mass of this ion and the spectral characteristics, the structure of dicembrenyl selenide (V) may be proposed for the compound isolated. The formation of such selenides has been observed by Olson [9] and by Hand [10] in the oxidation of ethylene and of imidazolopyridines.

LITERATURE CITED

1. E. N. Trachtenburg, C. H. Nelson, and J. R. Carver, J. Org. Chem., 35, 1653 (1970).
2. A. Gillemonat, Ann. Chim. Paris, 11, 143 (1939).
3. W. G. Dauben, W. F. Thiessen, and P. R. Resnick, J. Org. Chem., 30, 1693 (1965).
4. E. J. Corey and K. Achiwa, J. Org. Chem., 34, 3667 (1969).
5. U. Nagai and H. Iga, Tetrahedron, 26, 725 (1970).
6. V. A. Raldugin, L. Ya. Korotkikh, A. I. Rezvukhin, and V. A. Pentegova, Khim. Prirodn. Soedin., 525 (1976).
7. D. Van der Helm, E. L. Enwall, A. J. Weinheimer, T. K. Karns, and L. S. Ciereszko, Acta Crystallogr., B32, 1558 (1976).
8. V. A. Raldugin, A. I. Rezvukhin, and V. A. Pentegova, Khim. Prirodn. Soedin., 598 (1971).
9. D. H. Olsen, Tetrahedron Lett., 2053 (1966).
10. E. S. Hand and W. W. Paudler, J. Org. Chem., 40, 2916 (1975).