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Structural formulas I and II

Figure 1: Structural formulas I and II

Abstract

Full Text

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ON THE ISOLATION OF (+)-δ-CADINOL FROM THE OLEORESIN OF *PINUS SIBIRICA* R. MAYR AND ITS IDENTITY WITH TORREOL AND SESQUIGEOOL

(Presented by Academician B. A. Kazanskii, 29 XII 1960)

In the analysis of heavy cedar oil obtained in the industrial processing of Siberian cedar oleoresin (*Pinus sibirica* Rup. Mayr), a sesquiterpene alcohol of composition $C_{15}H_{26}O$, m.p. 137°, $[\alpha]_D^{20} + 111.94°$, readily subliming in vacuo, was isolated (^{1}).

In the present work this alcohol was isolated by adsorption chromatography on alumina from the neutral fraction of cedar oleoresin; after recrystallization and sublimation it had the following constants: m.p. 141°, $[\alpha]_D^{20} + 118.4°$.

On saturation of the sesquiterpene alcohol with gaseous hydrogen chloride in moist ether, (+)-cadinene hydrochloride was obtained, m.p. 118°, $[\alpha]_D^{20} + 38.6°$. On oxidation with osmium tetroxide, a crystalline triol of m.p. 157° was isolated.

The infrared spectrum of the alcohol proved to be identical with the spectrum of (−)-δ-cadinol (^{2}), previously isolated from the essential oil of juniper (*Juniperus communis* L.), for which structure I was proposed (^{3}). On the basis of these data, the alcohol from Siberian cedar oleoresin can unambiguously be assigned the structure of δ-cadinol, while its optical properties and the properties of the dihydrochloride indicate that it is the optical antipode of (−)-δ-cadinol. Thus, its configuration may be expressed by formula II.

I II

In the literature (^{4}), a so-called torreol (from *Torreya nucifera*) is described with m.p. 139-140° and $[\alpha]_D^{20} + 107.1°$. Japanese authors report that torreol gives cadinene hydrochloride, but, in contradiction to this, state that acetone was obtained on ozonization of torreol. Comparing these facts with our data, we consider that torreol is identical with the (+)-δ-cadinol isolated by us, and its structure may therefore be expressed by formula II.

The so-called sesquigeool, obtained by Sebe (^{5}), and *Pinus pentaphylla* have constants very close to those of (+)-δ-cadinol (m.p. 135.5°; $[\alpha]_D^{20} + 99.5^\circ$). Sebe isolated (+)-$\delta$-cadinene hydrochloride from sesquigeool. This provides grounds for considering that sesquigeool is also identical with (+)-δ-cadinol.

Experimental Part

Isolation of δ-cadinol. 120 g of Siberian cedar resin were treated at room temperature with a 1% aqueous solution of sodium hydroxide. Extraction with ether gave 30 g of neutral substances, which were chromatographed on neutral alumina (1.5 kg). Elution was carried out with petroleum ether, followed by the addition of 15 and 50% benzene, benzene, and alcohol. On elution with benzene, a crystalline fraction was obtained (450 mg). The isolated crystals were recrystallized from petroleum ether and sublimed under vacuum, m.p. 141° and $[\alpha]_D^{20} + 118.4^\circ$ ($C = 2.87$, alcohol).

(+)-Cadiene dihydrochloride. Gaseous hydrogen chloride was passed through a solution of δ-cadinol (300 mg) in moist ether (5 ml) for 4 h. The crystals obtained, after three recrystallizations from ethyl acetate, had m.p. 118° and $[\alpha]_D^{20} + 38.6^\circ$ ($C = 3.68$, chloroform).

Cadinane-1,4,10-triol. To 50 mg of δ-cadinene in dry ether (4 ml) was added a solution of OsO_4 (62 mg) in dry ether (4 ml) and pyridine (0.3 ml). After 48 h, crystals separated, which were treated according to the method of [6]. The isolated triol had m.p. 157° (petroleum ether and benzene 3 : 1).

$C_{15}H_{28}O_3$ (256.4).	Found, %:	C 70.17;	H 10.74
	Calculated, %:	C 70.27;	H 11.01

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CITED LITERATURE

1. V. A. Penterova, M. A. Chirkova, *Tr. Khim.-metallurgich. inst. SO AN SSSR*, no. 13, 47 (1959).

2. J. Plíva, M. Horák et al., *Die Terpene, Sammlung der Spektren und physikalischen Konstanten*, vol. I, Sesquiterpene, Berlin, 1960.

3. O. Motl, V. Sýkora et al., *Coll.*, **23**, 1287 (1958); *Chem. listy*, **52**, 316 (1958).

4. K. Nisida, H. Uota, *J. Soc. Chem. Ind. Japan, Suppl.*, **43**, 64 (1940); *Chem. Abstr.*, **34**, 6936 (1940); *J. Soc. Chem. Ind. Japan, Suppl.*, **44**, 119 (1941); *Chem. Abstr.*, **38**, 4262 (1944).

5. Y. Sebe, *J. Chem. Soc. Japan*, **61**, 1269 (1940); *Chem. Abstr.*, **37**, 4064 (1943).

6. R. Criegee, B. Marchand, H. Wannowius, *Ann.*, **550**, 99 (1942).

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