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Figure 1: Structural formulas I-VII of resin acids

Abstract

Full Text

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ISODEXTROPIMARIC ACID–A COMPONENT OF THE RESIN ACIDS OF THE OLEORESIN OF SIBERIAN STONE PINE–PINUS SIBIRICA (RUPR.) MAYR.

(Presented by Academician B. A. Arbuzov, 30 XII 1957)

Systematic work on the study of the resin acids of the oleoresin of conifers was carried out by V. V. Shkatelov [1] and B. A. Arbuzov [2].

In the composition of the oleoresin of various native conifers the following resin acids were found: levopimaric (I) [3,4], abietic (II) [5,6], neoabietic (III) [7], palustric (IV) [8,9], dehydroabietic (V) [9], dextropimaric (VI) [3,4]. α- and β-sapinic acids, which were formerly considered the principal components of the acid fraction of the oleoresin of Scots pine [3] and Norway spruce [4,10], proved not to be individual substances, but to be mixtures of such acids as levopimaric, abietic, neoabietic, palustric, and dextropimaric acids [8].

Isodextropimaric acid (VII), differing from dextropimaric acid (VI) only in the different spatial position of the substituents at C_7, was first isolated from the oleoresin of the American longleaf pine *Pinus palustris* [11], but in the balsams of native conifers it had not yet been found.

The present investigation showed that isodextropimaric acid, along with abietic acid [12], is a component of the acid fraction of the oleoresin of Siberian stone pine.

Experimental part

The oleoresin was collected from a stand of Siberian stone pine in the Gorno-Altai Autonomous Oblast. The trees were tapped by the descending-bark method. The time during which the oleoresin remained in the receiver was 4-7 days. The oleoresin contained 18% turpentine. The resin acids of the oleoresin were converted

Fig. 1. Absorption ultraviolet spectra: 1—initial resin acids, 2—resin acids after treatment with maleic anhydride, 3—isodextropimaric acid

Figure 2: Fig. 1. Absorption ultraviolet spectra: 1—initial resin acids, 2—resin acids after treatment with maleic anhydride, 3—isodextropimaric acid

Fig. 2. Crystals of isodextropimaric acid obtained by recrystallization of the acid from ethyl acetate

Figure 3: Fig. 2. Crystals of isodextropimaric acid obtained by recrystallization of the acid from ethyl acetate

into sodium salts. Neutral substances were removed from the solution of the salts by repeated extraction with sulfuric ether. The salts were decomposed with a 0.5% aqueous solution of acetic acid and, after the usual treatment, a mixture of resin acids was obtained (Fig. 1, 1) with m.p. 66-70° and $[\alpha]_D = 26.5^\circ$ (the specific rotation was always determined for 1% solutions in ethanol).

The resin acids (106 g) were dissolved in kerosene (b.p. 160-180°) and treated with maleic anhydride at 145-150° for 20 hours. The reaction product was dissolved in a 2% aqueous solution of caustic soda; the neutral substances were extracted with sulfuric ether, and the salts were acidified to pH 6.2 by adding crystalline boric acid to the solution. This gave 20 g of resin acids (Fig. 1, 2) with m.p. 65-73°, $[\alpha]_D = +24.1^\circ$. The acids obtained were converted in the usual way into bornylamine salts, which after two recrystallizations from alcohol melted at 178-180° and had $[\alpha]_D = 0.0^\circ$. The bornylamine salts were decomposed with boric acid. From the resin acids obtained in this way (m.p. 152-156°), after three recrystallizations from acetic acid, isodextropimaric acid was isolated with m.p. 162-164°. The elemental analysis, neutralization number, and ultraviolet absorption spectrum (Fig. 1, 3) of the isolated acid fully correspond to isodextropimaric acid. The methyl ester of isodextropimaric acid, obtained by treating it with diazomethane, had its characteristic m.p. 61-62°.

Fig. 1. Absorption ultraviolet spectra: 1—initial resin acids, 2—resin acids after treatment with maleic anhydride, 3—isodextropimaric acid.

Fig. 2. Crystals of isodextropimaric acid obtained by recrystallization of the acid from ethyl acetate.

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Note: Figure translations are in progress. See original paper for figures.