DEHYDROABIETIC AND PALUSTRIC ACIDS–CONSTITUENTS OF THE OLEORESIN OF NORWAY SPRUCE (*PICEA EXCELSA* LINK.)

1957

SovietRxiv

Abstract

Full Text

CHEMISTRY

I. I. Bardyshev and Kh. A. Cherches

DEHYDROABIETIC AND PALUSTRIC ACIDS –CONSTITUENTS OF THE OLEORESIN OF NORWAY SPRUCE (*PICEA EXCELSA* LINK.)

(Presented by Academician B. A. Arbuzov, June 7, 1957)

Levopimaric, dextropimaric, and α-sapinic acids were found in the acidic fraction of the oleoresin of Norway spruce (^{1}), and comparatively recently the presence of abietic acid was demonstrated (^{2}).

The present study has shown that dehydroabietic and palustric acids are also constituents of spruce oleoresin. Earlier (^{3}), the presence of dehydroabietic acid in the oleoresin of *Pinus palustris* was shown spectrophotometrically. Palustric acid was found in the oleoresin of *Pinus palustris* (^{4}) and *Pinus silvestris* L. (^{5}).

Experimental Part

The oleoresin was obtained by tapping spruce plantations growing on the territory of Belorussia. Resin acids were isolated from the fresh oleoresin by crystallization from alcohol.

Isolation of dehydroabietic acid. 105 g of resin acids were neutralized with warm (50°) 2% sodium hydroxide solution. After 24 hours a gelatinous precipitate of salts separated from the solution; it was removed, and resin acids (40 g) were regenerated from the mother liquor with boric acid. These acids were treated with maleic anhydride at 130-150°. The resin acids that did not react with maleic anhydride, m.p. 150° (Fig. 1, curve 1), were converted into ethanolamine salts, which after two recrystallizations from a mixture of ethyl acetate with alcohol had m.p. 160.5-162° and $[\alpha]_D = +47.9°$*. From the salts (2.2 g) dehydroabietic acid was regenerated; after five recrystallizations from alcohol it had m.p. 171-171.5°; $[\alpha]_D = +61.5°$. The specific absorption coefficient of dehydroabietic acid was 2.4 at 268 mμ and 2.2 at 275 mμ (Fig. 1, curve 2).

$$C_{20}H_{28}O_2. \quad \text{Found, \%: C 80.28; 80.3; H 9.01; 9.3}$$
$$\text{Calculated, \%: C 79.95; H 9.39}$$

For the neutralization of 1 g of acid, 187.1 mg of KOH was consumed.

Fig. 1. Ultraviolet absorption spectra: 1—resin acids that did not react with maleic anhydride at 150°; 2—dehydroabietic acid. Fig. 2. Ultraviolet absorption spectra: 1—resin acids that did not react with maleic anhydride at room temperature; 2—bornylamine salt of palustric acid after the third recrystallization; 3—palustric acid.

Figure 1: Fig. 1. Ultraviolet absorption spectra: 1—resin acids that did not react with maleic anhydride at 150°; 2—dehydroabietic acid. Fig. 2. Ultraviolet absorption spectra: 1—resin acids that did not react with maleic anhydride at room temperature; 2—bornylamine salt of palustric acid after the third recrystallization; 3—palustric acid.

$C_{20}H_{28}O_2$. Calculated 186.7 mg KOH.

Isolation of palustric acid. By washing the ethereal solution of oleoresin with 1% sodium hydroxide solution and decomposing the salts obtained with boric acid, unchanged resin acids were isolated (170 g). The thoroughly dried acids, in order to remove levopimaric acid, were treated at room temperature with maleic anhydride distilled twice in a solution of dry acetone. 58 g of acids that had not reacted with maleic anhydride and had $[\alpha]_D = +60°$ (Fig. 2, curve 1), were converted into ethanolamine salts, and the latter were recrystallized from alcohol. The first four fractions of the salts precipitated from solution were recrystallized twice more from alcohol. The ethanolamine salts (4.9 g) were washed with ether and then converted into bornylamine salts, which were subjected to fivefold recrystallization from alcohol (Fig. 2, curve 2). After fourfold recrystallization from alcohol, the palustric acid isolated from the bornylamine salt had m.p. 163-164°, $[\alpha]_D = +70.6°$, and a specific absorption coefficient of 29.3 at 266 mμ (Fig. 2, curve 3).

* The specific rotation was determined for 1% alcoholic solutions of the acids. The absorption spectra were likewise studied in alcoholic solutions.

Fig. 1. Ultraviolet absorption spectra: 1—resin acids that did not react with maleic anhydride at 150°; 2—dehydroabietic acid.

Fig. 2. Ultraviolet absorption spectra: 1—resin acids that did not react with maleic anhydride at room temperature; 2—bornylamine salt of palustric acid after the third recrystallization; 3—palustric acid.

$C_{20}H_{30}O_2$.

Found, %: C 79.28; 79.30; H 9.72; 9.70
Calculated, %: C 79.42; H 10.00

Institute of Chemistry
Academy of Sciences of the BSSR

Received
2 VI 1957

CITED LITERATURE

1. S. S. Malevskaya, S. D. Kharad, ZhPKh, **23**, 2 (1950).
2. I. I. Bardyshev, Kh. A. Cherches, ZhPKh, **29**, 1888 (1956).
3. G. C. Harris, *J. Am. Chem. Soc.*, **70**, 3671 (1948).
4. V. M. Loeblich, D. E. Baldwin, R. W. Lawrence, *J. Am. Chem. Soc.*, **77**, 2823 (1955).
5. I. I. Bardyshev, L. I. Ukhova et al., Abstracts of Reports at the All-Union Conference on the Chemistry of Plant Substances, Tashkent, 1956.

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