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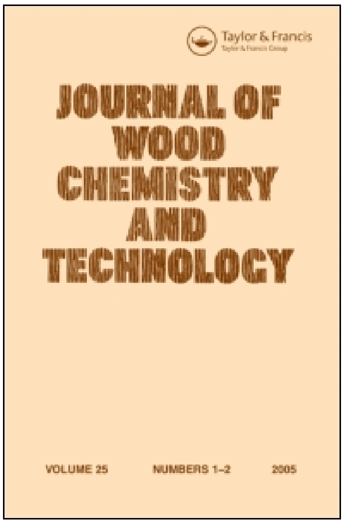

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ON THE PALLADIUM-ON-CHARCOAL DISPROPORTIONATION OF ROSIN

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ABSTRACT

Changes in the composition of gum rosin during disproportionation in the presence of 5% palladium-on-charcoal have been determined by gas chromatography. The principal reaction product was dehydroabietic acid. The exocyclic vinyl group of the pimaric/isopimaric-type resin acids was hydrogenated completely. Only a small amount of dihydroabietic acids was formed. Eight dihydro resin acids were identified. No tetrahydro resin acids were observed.

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INTRODUCTION

Disproportionated rosins are used industrially as emulsifiers in the production of synthetic rubber, as compounding ingredients for rubber, and as raw materials for manufacture of synthetic resins. The advantage they offer is connected with increased resistance to autoxidation. Dehydroabietic acid, the main constituent of the disproportionated rosin, is also of potential value in the pharmaceutical industry.[1-3] For example, a transformation of dehydroabietonitrile into C-aryl-18-norsteroid in 12% overall yield has recently been reported.[4]

Disproportionation of rosin is generally understood as an exchange of hydrogen between molecules of resin acids, whereby some resin acids are dehydrogenated and the others hydrogenated. At temperatures between 250° and 275°C the reaction takes place slowly; addition of a catalyst[5] like strong mineral acids, iodine, sulfur, sulfur dioxide, selenium, Raney nickel or noble metals on charcoal or even pure charcoal increases the reaction rate.

Several investigations have been made of the transformations of individual component resin acids during rosin disproportionation.[6-11] Fleck and Palkin[6,7] reported that disproportionation of abietic acid with Pd-C at 225°C resulted in the formation of dehydroabietic and dihydroabietic acids and small amounts of tetrahydroabietic acid; at 275°C the principal reaction product was dehydroabietic acid. Later, Loeblich and Lawrence reported[11] that Pd-C disproportionation of gum rosin at 210°C gave 65% of dehydroabietic acid, 20.4% of a mixture of dihydroresin acids, 5.0% of tetrahydroresin acids and 7.6% of unidentified acids. The only information in the literature on the composition of the dihydro- and tetrahydro resin acids of disproportionated rosin was a short statement (no experimental details given) by Enos et al.[12] They stated that disproportionation of rosin at 270°C results in formation of dehydroabietic acid as the main product with the removed hydrogen partly used in hydrogenation of the exocyclic vinyl group of the pimaric/isopimaric-type acids; dihydroabietic acids amounted to only 2-3% and no tetrahydroabietic acids were found.

The purpose of our work was to obtain more detailed information on the rate of disproportionation of rosin with Pd-C and the changes that occur in resin acid composition.

EXPERIMENTAL

In a typical disproportionation experiment 50 g of gum rosin was heated under nitrogen (electrical heating mantel) in a 100 ml three neck round bottom flask equipped with mechanical stirrer, thermometer, and automatic temperature controller. The 5% Pd-C catalyst was added when temperature reached 230°C (after about 5 minutes). The reaction time was calculated from this point. After less than an additional 5 minutes, the temperature reached 270°C. The mixture was heated at that temperature for a total of 3 hours.

The resin acids were separated from neutrals by the DEAE-sephadex method.[13,14] The acid fraction was methylated with diazomethane and analyzed by glass capillary gas chromatography using BDS and DB-1 (a bonded methyl silicone) liquid phases at 190°C.[15] The peaks were identified by comparing relative retention times with those of authentic materials.

RESULTS AND DISCUSSION

DEAE-Sephadex analysis showed that only 5% of the gum rosin was converted to neutral materials during the disproportionation with Pd-C catalyst. The change that occurred in the resin acid composition is summarized in Table 1. The starting gum rosin consisted of about 65% abietic-type acids (abietic, palustric, and neoabietic acid) and about 22% pimaric/isopimaric-type acids (pimaric, isopimaric, and sandaracopimaric acid). On completion of

TABLE 1. Composition of Resin Acids in Gum Rosin and the Corresponding Disproportionated Rosin[a]

Rosin	Abietic-type acids[b] (%)	Pimaric/ isopamaric-type acids[c] (%)	Dehydroabietic acids (%)	Dihydroabietic-type acids (%)	Dihydro-(pimaric/ isopimaric-type) acids (%)
Original Gum Rosin[d]	64.4	21.9	6.3	0	0
Disproportionated Gum Rosin	0	0	68.0	2.2	20.1

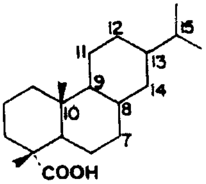
[a] Three hours at 270°C, 0.1% of 5% Pd-C, N_2 atmosphere. The original gum rosin contained 8.8% neutrals which increased to 13.9% upon disproportionation.

[b] Abietic, palustric, and neoabietic acids.

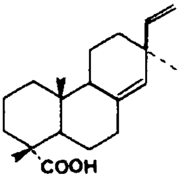
[c] Pimaric, isopimaric, and sandaracopimaric acids.

[d] Contained also 2.7% communic acid.

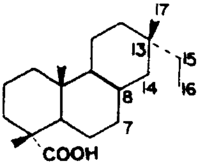
the reaction, most of the abietic-type acids were dehydrogenated to dehydroabietic acid. All pimaric/isopimaric-type resin acids were completely hydrogenated to dihydro- (pimaric/isopimaric) acids. Only a small amount of dihydroabietic acids was formed. The dihydroabietic acids in disproportionated gum rosin consisted of 13β-abiet-8-enoic acid, 13β-abiet-8(14)-enoic acid and 8-abietenoic acid; the dihydro-(pimaric/isopimaric) acids were composed of 8-isopimarenoic acid, 8-pimarenoic acid, 8(14)-pimarenoic acid, 8(14)-isopimarenoic acid and 7-isopimarenoic acid.



ABIETIC-TYPE
RESIN ACIDS



PIMARIC ACID



ISOPIMARIC-TYPE
RESIN ACIDS

Abietic acid [7,13 diene]
Palustric acid [8,13 diene]
Neoabietic acid [8(14),13(15) diene]
Dehydroabietic acid [8,11,13 triene]

Isopimaric acid [7,15 diene]
Sandaracopimaric acid -
[8(14),15 diene]

Argentation resin chromatography[16] of methylated disproportionated gum rosin was used to separate methyl esters of tetrahydro resin, if present, from methyl esters of dihydro resin acids and dehydroabietic acid. No tetrahydro resin methyl esters could be identified, however.

Figure 1 summarizes the changes in resin acid composition of gum rosin that occurred during the course of the disproportionation. Most of the dehydroabietic acid formed within 20 minutes (reaction half time of about 5 minutes) with a corresponding decrease in the amount of abietic acids. The increase in dihydro resin acids (half time ca. 35 minutes) was appreciably slower, however. Be-

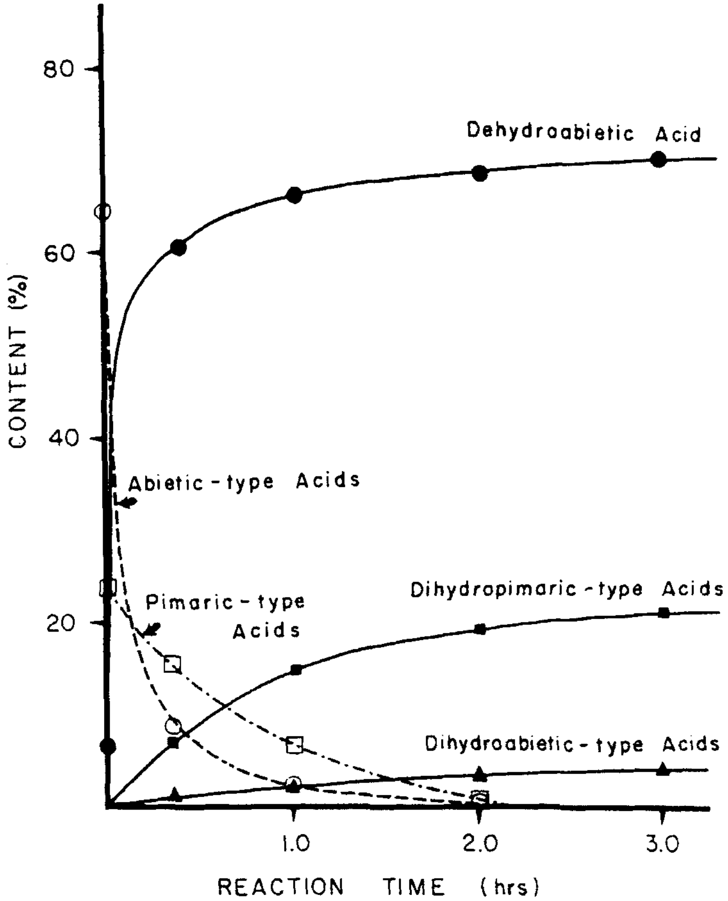


Figure 1. Change in resin acid composition during Pd-C disproportionation of gum rosin. Pimaric acid and isopimaric-type acids are plotted together as pimaric-type acids.

cause the rate of dehydrogenation of the abietic-type acids was so rapid in comparison to hydrogenation, only relatively small amounts of dihydroabietic acids were formed. However, the nonconjugated, less sterically-hindered exocyclic vinyl groups of the pimaric/isopimaric-type resin acids were readily hydrogenated. The preferential hydrogenation of the exocyclic double bonds in terpenoids is well known and is both kinetically and thermodynamically favored.[17-20]

GLC data showed that the 7 and 8(14) double bonds of both dihydroabietic and dihydro-(pimaric/isopimaric) acids were isomerized to the 8(9) position by either the catalyst and/or the acidity of the system at the high temperature.

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