[CONTRIBUTION FROM SOUTHERN PINE CHEMICAL COMPANY]

Resin Acids from Pine Tar

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Pine tar is obtained by destructive distillation of the resinous wood of several species of Southern pine, largely *Pinus palustris* Miller (longleaf pine) and *Pinus caribaea* Morelet (slash pine). The mixture of resin acids extracted from pine tar has now been found to be similar to the "pyroabietic" acid obtained by heating abietic acid or rosin at 275–350° and which has been shown[1] to consist in large part of a mixture of dehydro- and dihydroabietic acids formed by disproportionation of the original acids.

Various samples of recrystallized acids from tars produced by commercial batch distillation of resinous wood had melting points ranging from 153 to 165° and rotations α_D +36° to +47°. Similar recrystallized samples from tars produced in the Cline[2] continuous retort had melting points from 158 to 168° and rotations α_D +16° to +30°.

Resin acids from both sources contained substantial quantities of dehydro- and dihydroabietic acids. The batch tar contained less total resin acids than the continuous tar but contained a higher proportion of dehydroabietic acid as would be expected since the resin acids are exposed to more vigorous and longer thermal treatment in the batch distillation process.

Experimental

After removal of most of the hydrocarbons and phenols by distilling the tars until the temperature of the still pot was 210–215° at 10 mm., the still residue was dissolved in four or five volumes of ether and extracted several times with excess 1% sodium hydroxide. The black alkaline extract was acidified and the precipitated resinous product treated with eight to ten volumes of pentane or hexane which dissolved the resin acids but not the black acidic pitch. After filtration, the hydrocarbon solution of the acids was extracted with excess 1% alkali and discarded. On acidification of the alkaline extract, the crude resin acids were precipitated. Various batch produced tars yielded 15 to 21% and continuous tars 20 to 26% crude resin acids. These acids were readily recrystallized from aqueous methanol.

Thirty-four grams of recrystallized acids, m. p. 162–166°, α_D +40° (2% in ethanol), from a batch distilled tar was powdered and added in small portions with stirring to 210 cc. of concd. sulfuric acid at 15–20°. The mixture was stirred for thirty minutes and poured into 2 liters of ice and water mixture. The precipitated sulfonation product was digested with 2 liters boiling water and filtered. The clear aqueous filtrate was acidified with 100 cc. of concd. hydrochloric acid and allowed to cool overnight. Twenty-three and five-tenths grams of the crude precipitated sulfonated acid was obtained (54%). After recrystallization from acetic acid the product melted at 235° (cor.); α_D + 72.6°. For further identification as sulfodehydroabietic acid, the product was converted to the dimethyl ester; m. p. 175–6°, α_D +76.2°; and also hydrolyzed to dehydroabietic acid; m. p. 171–172°, α_D + 61°.

The water insoluble resin from the sulfonation was dissolved in ether and extracted with 1% sodium hydroxide. On evaporation of the ether 1.35 g. (4%) of neutral product was obtained which melted after recrystallization from methanol at 130.5–131.5°, α_D −5°. For further identification as the lactone of dihydroabietic acid it was saponified to yield hydroxytetrahydroabietic acid; m. p. 164–165°, dec.

A sample of 52 g. of resin acids from tar produced by the Cline retort, m. p. 160–163°, α_D +26°, yielded on similar treatment 26.5 g. (40%) sulfodehydroabietic acid and 2.5 g. (4.8%) lactone.

Summary

The resin acids of pine tar consist largely of dehydroabietic and dihydroabietic acids. The relative proportions of these acids depend upon the method used in distilling the resinous wood.

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(1) Fieser and Campbell, THIS JOURNAL, **60**, 159 (1938); Fleck and Palkin, *ibid.*, **60**, 921 (1938).

(2) Jacobs, *Ind. Eng. Chem.*, **32**, 214 (1940).