Chromatographic Investigation of Disproportionated Rosin

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FOR MANY YEARS rosin and rosin derivatives have been used industrially in paper-sizing, in soap manufacture, in various coating compositions, and in making synthetic resins. The main disadvantage of rosin in many of its industrial applications is the ease with which the abietic-type acids are oxidized. This disadvantage can readily be overcome by converting the abietic-type acids into the much more stable mixture of dehydroabietic acid and dehydroresin acids. This conversion product is referred to as disproportionated or dehydrogenated rosin. In this paper disproportionated and dehydrogenated rosin will be considered as disproportionated rosin since, even when dehydrogenation catalysts were used, the products contained appreciable amounts of dihydroresin acids. This disproportionated rosin has proved to be quite superior to rosin in many applications, especially as an emulsifying agent in the polymerization step of preparing G.R.S. rubber. At present there are several commercially prepared disproportionated rosins on the market. These products are all prepared by heating rosin at 180°–300°C. with a suitable catalyst (7, 8, 9, 10, 11, 13, 14).

Although more than 50% of the acidic portion of disproportionated rosin is dehydroabietic acid, the variations in the processes cause a considerable variation in the composition of the remaining acids. This variation in the composition of the acids other than dehydroabietic acid is important since incomplete disproportionation of the oxygen-sensitive, conjugated-diene acids, such as l-abietic, neoabietic, and palustric (15) acids, will decrease the over-all stability and usefulness of the product.

In the past there has been a considerable amount of time devoted to studies on the composition of disproportionated rosin, previously termed "pyroabietic" acid. It was found that "pyroabietic" acid was a mixture of dehydro-, dihydro-, and tetrahydroabietic acids (1, 2, 3, 4, 12). The separation of this mixture of resin acids is difficult. A separation can be obtained in one of two ways: fractional recrystallization of the methyl ester of "pyroabietic" acid from methanol and water (3) or sulfonation of the disproportionated product to give sulfodehydroabietic acid, the lactone of the dihydroresin acids, and tetrahydroresin acids (5). Ultraviolet absorption analysis of a disproportionated rosin is considerably more difficult if there is as much as 1 or 2% l-abietic or neoabietic acid present. The specific extinction coefficients of these conjugated-diene acids are so high (77 at 241 mμ and 80 at 251 mμ, respectively) that the comparatively weak absorption of dehydroabietic acid (2.56 at 276 mμ and 2.12 at 268 mμ) is easily masked in their presence. Also a small amount of retene which may be formed at the high temperatures used in the disproportionation processes will greatly interfere with ultraviolet absorption analysis.

An excellent method for separating acids of similar chemical structure is the technique of partition chromatography. Some natural and synthetic resins have been separated by reversed-phase partition chromatography (16). More recently, the technique of Ramsey and Patterson (17) for the separation of saturated, straight-chain fatty acids has been adapted to the separation of the resin acids in pine oleoresin and rosin (15). This paper shows that essentially the same method is applicable to the separation of the components of disproportionated rosin.

Experimental and Discussion

Disproportionation of Rosin. For detailed chromatographic analysis a sample of rosin was disproportionated in the laboratory. Five hundred grams of WW gum rosin and 10 g. of 5% palladium on carbon catalyst (Baker and Company) were heated at 210°C. for three and one-half hours with stirring and a stream of nitrogen blowing over the sample. The mixture was then dissolved in 1.5 liters of isooctane and filtered with vacuum to remove the catalyst. The excess solvent was distilled off at atmospheric pressure. The last traces of solvent were removed by steam distillation. The product had an $[\alpha]_D = +46.5°$ (2% soln. in 95% EtOH) acid no. = 155.9, grade = M.

Chromatographic Separation of the Disproportionated Rosin. In general, the procedure for the chromatographic separation of the fatty acids described by Ramsey and Patterson (17) was used. The modifications made in adapting this technique to the analysis of oleoresin and rosin are described by Loeblich, Baldwin, and Lawrence (15). More recent work showed that decreasing the inside diameter of the chromatographic column from 18 mm. to 10 mm., thereby tripling the height of the silicic acid bed, gave a more effective separation of the acidic components of rosin. The analyses described in this paper were carried out using a 10-mm. I.D. column.

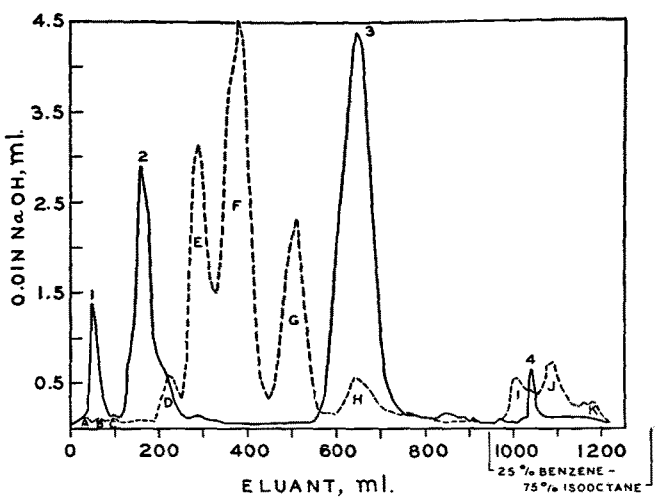

FIG. 1. Curve 1; ----; *Chromatogram of WW Gum Rosin:* Peaks A, B, C, D, unidentified acids; Peak E, palustric acid, dextropimaric acid, iso-dextropimaric acid; Peak F, l-abietic acid, dextropimaric acid, iso-dextropimaric acid; Peak G, neoabietic acid; Peak H, dehydroabietic acid; Peaks I, J, K, unidentified acids.

Curve 2; ———; chromatogram of laboratory disproportionated gum rosin.

Isooctane was used to elute all the acids through dehydroabietic acid, and the eluting solvent was then changed to 25% benzene–75% isooctane. For the purpose of analysis 0.5–0.6 meq. of disproportionated gum rosin were chromatographed, using 19 g. of silicic acid (silicic acid, Mallinckrodt, 100-mesh, suitable for chromatographic analysis by the method of Ramsey and Patterson), 1 g. of Celite, and the required amount of 2-aminopyridine-furfuryl alcohol mixture (15). The chromatographic curves for WW gum rosin, the starting material, and for the laboratory disproportionated gum rosin are shown in Figure 1. The peak effluent volumes (p.e.v.) of the four peaks obtained in the chromatogram of disproportionated rosin and the percentage of the total acidic portion of the original material that they represent are: peak 1, p.e.v. = 50, 5%; peak 2, p.e.v. = 160, 26%; peak 3, p.e.v. = 650, 65%; peak 4, p.e.v. = 1040, 2%.

The change that occurs during the disproportionation process is illustrated by the chromatograms of the original rosin and the disproportionated product. The acids in gum rosin represented by peaks E, F, and G, namely, palustric, l-abietic, neoabietic, dextropimaric, and iso-dextropimaric acids, have been completely converted to dehydroabietic acid (peak 3), dihydro- and tetrahydroresin acids (peak 2), and other unidentified acids (peaks 1 and 4).

Isolation and Characterization of Peaks 1, 2, 3, and 4. For isolation of these various components two large columns 31 mm. I.D. x 120 cm. in length were used. Each column contained 200 g. of silicic acid. Two solutions containing 8.5 g. of disproportionated rosin in 50 ml. of isooctane were prepared. Forty ml. of each solution were placed on each column, and 5 ml. of the remaining solution were titrated to determine the meq. of acid being chromatographed. The effluent was collected in 100-ml. fractions, and the meq. of acid present in each fraction was determined by titrating a 2-ml. aliquot. Again, four peaks were obtained at peak effluent volumes of 500, 1,600, 6,500, and 10,400, representing 5%, 26%, 65%, and 2%, respectively, of the total acidic portion of the disproportionated rosin.

Peak 1; p.e.v. = 50. Fractions 3–8 from the large chromatograms were combined. After removal of the solvent the material was dissolved in ether and extracted with 2% aqueous NaOH to separate any neutral materials present. The alkali extract was then acidified with 3N acetic acid and extracted with ether. The ether extract was washed neutral, dried over Na_2SO_4, evaporated to dryness, and dried at 60°C. in an Abderhalden drier. The resulting material was a very pale yellow, viscous resin which could not be crystallized. This material had a neutral eq. = 354; $[\alpha]_D = +29.4$ (2% soln. in 95% EtOH), and showed no characteristic absorption in the ultraviolet region.

This acid did not form an insoluble cyclohexylamine salt in isooctane. On that basis it was concentrated from disproportionated rosin by precipitating the cyclohexylamine salt of the resin acids. The salt was removed by filtration; the isooctane mother liquor was washed with dilute acid and then extracted with 2% aqueous NaOH to separate the acidic portion from the neutral materials. Acidification of the NaOH extract with 3N acetic acid, followed by extraction with ether, yielded a mixture of acids which contained 70% of the acid with a p.e.v. = 50. This concentrate was then chromatographed to obtain the pure acid.

This acid is formed during the disproportionation of gum rosin. It is present only as a trace in the original rosin (Figure 1, curve 1). Examination of the chromatograms of commercially disproportionated rosins (Figure 2) shows that it is present in quantities not greater than 1% compared with the 5% found in gum rosin disproportionated with 5% palladium on carbon catalyst.

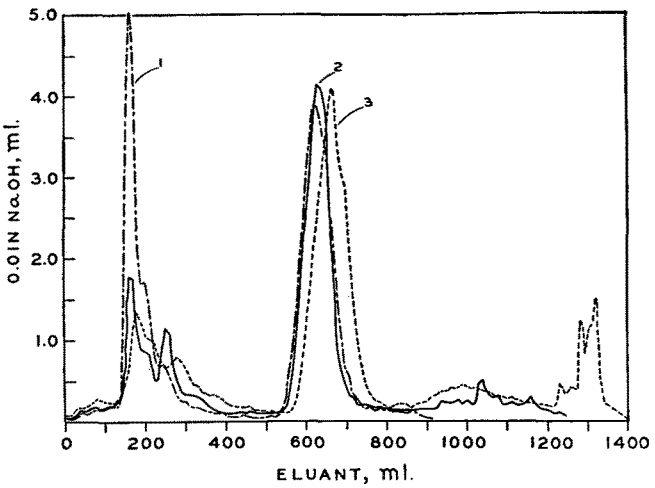

FIG. 2. Chromatograms of commercially disproportionated rosins.
---- Sample 1; ——— Sample 2; ——— Sample 3.

Peak 2, p.e.v. = 170. Fractions 12–25 from the large chromatograms were combined. The acids were recovered by precipitating the cyclohexylamine salt from the isooctane solution. The salt was acidified in ether solution with 3N acetic acid, washed neutral, and evaporated to dryness. When wet with ethanol, the residue yielded crystals with m.p. = 115.5–146° C., $[\alpha]_D = +44.9°$ (2% soln. in 95% EtOH), and no characteristic ultraviolet absorption. The position of the peak effluent volume indicates that this peak consists of di- and (or) tetrahydroresin acids (15). This point is substantiated by the fact that di- and tetrahydroabietic acids have been isolated from disproportionated rosin (1, 3, 4). *Anal.* Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Calcd. for $C_{20}H_{34}O_2$: C, 78.36; H, 11.19. Found: C, 78.75, 78.76; H, 10.92, 11.02.

In order to determine what percentages of di- and tetrahydroresin acids were present in this peak, a 0.5004-g. sample was lactonized according to the procedure of Fleck and Palkin (6): 0.3928 g. (representing 78.5% of the acids) of a lactone were obtained, having a m.p. = 97.5–99°C., $[\alpha]_D = -12.2°$ (2% soln. in 95% EtOH). *Anal.* Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Found: C, 78.90, 78.75,; H, 10.43, 10.49. This product is probably a mixture of the lactones of dihydroabietic and dihydropimaric acids. Since the acids from this peak represented 26% of the total acids present in the disproportionated rosin, the percentage of the acids in the disproportionated rosin that was dihydroresin acids was 20.4%. The remainder of the lactonized product, 0.1073 g. (representing 21.5% of the acids), was isolated as a mixture of tetrahydroresin acids, having a m.p. = 199–

237°C., $[\alpha]_D = -9.5°$ (2% soln. in 95% EtOH). This quantity of tetrahydroresin acids represents 5% of the total acid content of disproportionated rosin.

Peak 3, p.e.v. = 650. Fractions 56–80 were combined. The acid was recovered by precipitation of the cyclohexylamine salt from the isooctane solution. The salt was converted to the free acid in ether solution with dilute HCl. After evaporation of the ether the acid crystallized upon wetting with ethanol. The dehydroabietic acid obtained had a m.p. = 170–172°C., $[\alpha]_D = +61.7°$ (2% soln. in 95% EtOH), and showed maximum characteristic ultraviolet absorption at 276 mμ, $a = 2.37$ and 268 mμ, $a = 2.15$.

Peak 4; p.e.v. = 1040. The acids in this peak were not isolated since they represented only 2% of the acidic portion of the disproportionated product. The position of the peak effluent volume indicates that they are more polar than the characterized resin acids.

Detection of Diene-Resin Acids in Disproportionated Rosin. This chromatographic method is satisfactory for the detection of as little as 1% of the diene-resin acids in a completely disproportionated product since the peak effluent volumes of these acids range from 290 to 510 (Figure 1, curve 1). It is of interest to note that on disproportionation with 5% palladium on carbon catalyst all of the diene unsaturated acids in the rosin were converted to their di-, tetra, and dehydro derivatives. This includes the pimaric as well as the abietic-type acids.

Chromatographic Investigation of Commercially Disproportionated Rosins. The chromatographic curves of three samples of commercially disproportionated rosin are shown in Figure 2. The variations in the extent of disproportionation is apparent from examination of these chromatograms. No attempt was made to isolate the various components of these samples. The degree of separation obtained shows that the method is applicable to all of the products examined and that the percentage of dehydroabietic acid in the acidic portion of the rosin can be determined. On that basis Table I shows the percentages of the various acids or groups of acids divided into three categories: a) acids eluted prior to dehydroabietic acid, b) dehydroabietic acid, c) acids eluted after dehydroabietic acid.

TABLE I

Distribution of Acids in Commercially Disproportionated Rosins

Sample	Acids eluted prior to dehydroabietic acid	Dehydroabietic acid	Acids eluted after dehydroabietic acid
1	26	51	23
2	30	59	11
3	40	58	0

REFERENCES

1. Fieser, L. F., and Campbell, W. P., J. Am. Chem. Soc., *60*, 159–170 (1938).
2. Fleck, E. E., and Palkin, S., Science, *85*, 126 (1937).
3. Fleck, E. E., and Palkin, S., J. Am. Chem. Soc., *60*, 921–925 (1938).
4. Fleck, E. E., and Palkin, S., *ibid.*, *60*, 2621–2622 (1938).
5. Fleck, E. E., and Palkin, S., *ibid.*, *61*, 247–249 (1939).
6. Fleck, E. E., and Palkin, S., *ibid.*, *61*, 3197–3199 (1939).
7. Fleck, E. E., and Palkin, S. U. S. Pat. 2,239,555 (April 22, 1941).
8. Hampton, B. L., (to The Glidden Co.), U. S. Pat. 2,494,550 (Jan. 17, 1950).
9. Hampton, B. L. (to The Glidden Co.), U. S. Pat. 2,497,882 (Feb. 21, 1950).
10. Hasselstrom, T., and Brennan, E. A., U. S. Pat. 2,265,161 (Dec. 9, 1941).
11. Kalman, N. L., and Rutherford, N. J. (to Ridbo Laboratories Inc.), U. S. Pat. 2,395,278 (Feb. 19, 1946).
12. Littmann, E. R., J. Am. Chem. Soc., *60*, 1419–1421 (1938).
13. Littmann, E. R. (to Hercules Powder Co.), U. S. Pat. 2,154,629 (April 18, 1939).
14. Littmann, E. R. (to Hercules Powder Co.), U. S. Pat. 2,201,237 (May 21, 1940).
15. Loeblich, V. M., Baldwin, D. E., and Lawrence, R. V., J. Am. Chem. Soc., *77*, 2823–2825 (1955).
16. Mills, J. S., and Werner, A. E. A., J. Oil & Colour Chemists' Assoc., *37*, 131–142 (1954).
17. Ramsey, L. L., and Patterson, W. I., J. Assoc. Offic. Agr. Chemists, *31*, 441–452 (1948).

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The Antioxidant Properties of Some 6-Hydroxychromans And 5-Hydroxycoumarans

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H. S. OLCOTT AND O. H. EMERSON (1) related the antioxigenic properties of the unsaponifiable matter of wheat germ oil to its tocopherol content. They noted the great difference in the antioxidant power of β and α tocopherols which differ chemically only by the reversal of the methyl group and the unsubstituted position on both sides of the phenolic hydroxyl. C. Golumbic (2) investigated the relation between antioxidant activity and constitution in the case of hydroquinone and 6-hydroxychroman, the basic ring system common to all tocopherols. He compared the effect that C-methylation of the aromatic ring had on the antioxidant properties of hydroquinone and 6-hydroxychroman in lard. He concluded that methylation is detrimental, especially in the case of hydroquinone, which becomes practically inactive in lard. The 6-hydroxychroman still retains some activity even when completely methylated in the aromatic ring. In 1943 R. H. Rosenwald and J. A. Chenicek (3) showed that the introduction of a tert-butyl group ortho to the free hydroxyl into the monomethyl ether of hydroquinone greatly increased the inhibitor activity over that of the parent compound. The introduction of two tert-butyl groups in the 2 and 5 positions does not improve the low inhibitor potency of methoxyphenol. The 6-hydroxychroman may be considered structurally related to a monoalkylated alkoxyphenol, in which the introduction of a tert-butyl group should depress the inhibitor activity. Therefore the effect of the introduction of a tert-butyl group into a 6-hydroxychroman could not be predicted and could only be determined empirically. The 5-hydroxycoumaran was investigated also because of its close chemical relation.

The chromans and coumarans selected were the 2,2-dimethyl-6-hydroxychroman and the 2,2-dimethyl-5-hydroxycoumaran. The two compounds were prepared as suggested by C. D. Hurd and W. A. Hoff-