Method for Determination of Combined Maleic Anhydride in Rosin-Maleic Anhydride Adducts by Chromatographic Techniques

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Abstract

A new analytical method for the determination of combined maleic anhydride in rosin maleic anhydride adducts has been developed. The method is based on the use of chromatographic techniques for separating the rosin acids and the rosin maleic anhydride adduct using silicic acid-celite as the adsorbent and benzene and acetone as solvents. An acid number is determined on the adduct which is used to calculate the combined maleic anhydride in the sample. Free maleic anhydride does not interfere in the analysis. Data are presented showing good agreement with the results obtained on known blends by infrared spectroscopy and chromatography.

Introduction

Harris and Sanderson (4) and Harris (5) reported when maleic anhydride is added to a rosin, the trace amount of levopimaric acid in equilibrium mixture of rosin acids is assumed by the evidence presented in Figure 1. Pure levopimaric acid by virtue of its double bond configuration, conjugated within one ring, reacts with maleic anhydride at room temperature to form a crystalline Diels-Alder adduct in quantitative yields.

Under similar conditions abietic acid and neoabietic acids do not react with maleic anhydride. However, if maleic anhydride is added to the equilibrium mixture of abietic type acids, a reaction takes place at once with the trace amount of levopimaric acid that is formed. Excellent yields of levopimaric acid-maleic anhydride adduct can be obtained by carrying out the reaction in benzene in the presence of a strong acid at room temperature. Similar results can be obtained by heating a mixture of rosin acids and maleic anhydride at temperatures above 100 C.

Rosin-Maleic anhydride adducts (maleopimaric acid) have been analyzed by determining the extent of anhydride formation which is measured by the acid number of an ethanol and 80% aqueous acetone solvent system. Acid number is defined as the number of milligrams of KOH required to neutralize the acids in 1 g of sample (6,8). This method is based on the fact that the anhydride will react with the alcohol to form a half ester. Maleopimaric acid is then titrated as a dicarboxylic acid. The amount of maleic adduct can also be determined by gas chromatography using the methyl ester (3,7).

In addition to the above methods for determining rosin maleic anhydride adducts, all anhydrides can be characterized in the infrared by two absorption bands in the 5 to 6 μ region due to the asymmetric and symmetric carbonyl vibrations (1,2).

The method presented in this paper for the determination of combined maleic anhydride in rosin-maleic anhydride is based upon the separation of rosin acids and rosin-maleic anhydride adducts on a silicic acid-celite column, using benzene and acetone as solvents.

Experimental Procedures

Apparatus

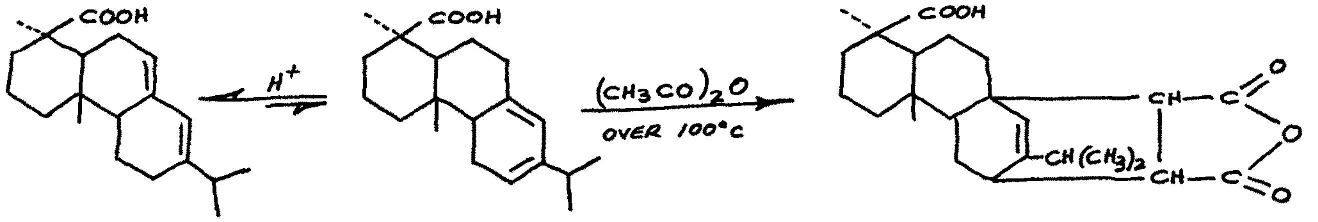
Chromatographic column, size III, 38 × 230 mm column (Scientific Glass Apparatus, Bloomfield, N.J.); round wood rod ½ × 15 in. A suitable length of a wooden dowel may be used; Fisher Filtrator (Fisher Scientific Co.).

Materials and Reagents

Acid, silicic-Merck reagent (Powder); celite analytical filter-aid (John-Mansville Co.); benzene, ACS reagent grade; acetone, commercial C.P. grade; cotton, absorbent; alcoholic KOH, approximately 0.1 N, accurately standardized.

Preparation of Chromatographic Column

Thoroughly mix equal parts by weight of silicic acid and celite. (It is convenient to prepare sizable quantities of this mixture ahead of time.) Assemble the column on the Fisher Filtrator and put a small plug of cotton in the bottom of the tube, then add a sufficient amount of the silicic acid-celite mixture to the tube so that a packed column height of about 5 cm will be obtained. The column is packed under full suction of a water aspirator, aided by slight tapping of the sides of the tube with the wooden rod. Do not tamp the column, simply level the top with the end of a small rod after packing has been completed.



ABIETIC ACID

LEVOPIMARIC ACID

LEVOPIMARIC ACID-MALEIC ANHYDRIDE ADDUCT

FIG. 1

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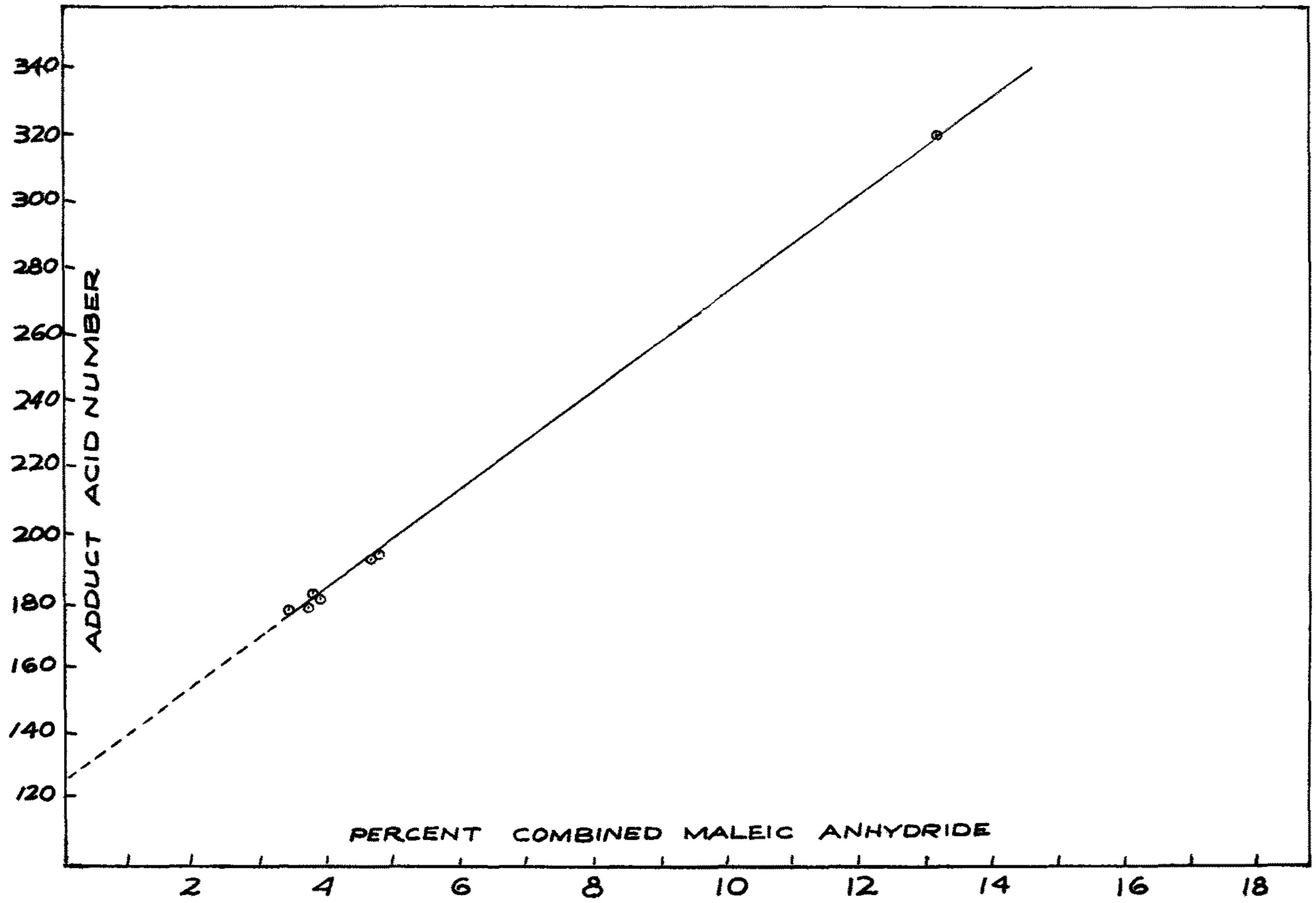

Fig. 2

Procedure

Weigh accurately about 1.2 g sample of a 3% adduct or 0.4 g sample of a 12% adduct and dissolve in 5 ml of benzene. Place a clean, dry, 150 ml beaker in the Fisher Filtrator. Turn the suction on and pour the sample solution into the top of the column. Rinse the beaker with 10 ml of benzene. As the top of the benzene solution reaches ⅛ in. above the top of the column packing, pour the rinse benzene into the top of the column and again allow the surface of the benzene to come within ⅛ in. above the surface of the packing. Rinse the beaker with a second 10 ml portion of benzene, add to the column, draw down to ⅛ in. above the packing, and finally add 80 ml of benzene to the column and draw down to ⅛ in. above the packing and turn off suction. Make certain that the top of the column is always covered with benzene and does not suck dry during the operation. Remove the beaker with the benzene solution and replace with another clean, dry tared 150 ml beaker. Discard the benzene solution containing the rosin acids.

Turn on the suction and add 10 ml of acetone to the top of the column. When the top of the liquid is ⅛ in. above the top of the packing, add 10 ml of acetone and drawn down to ⅛ in. above the top of the packing. Then finally add 55 ml of acetone and allow the column to suck dry. Disconnect the suction and remove the beaker. Evaporate the acetone on a steam bath using a gentle stream of clean, dry air directed into the top of the beaker to speed evaporation. Finally, heat the beaker containing the adduct in a 100 C oven for 15 min, cool and weigh.

Dissolve the separated adduct (from the acetone solution) in about 50 ml of neutral acetone, add 5 drops of 1% thymol blue indicator solution, and titrate with approximately 0.1 N alcoholic KOH solution to a blue end point permanent for 30 sec. Estimate readings to the nearest 0.05 ml.

Calculations

Figure 2 is a typical curve prepared by plotting the acid number of the fraction separated from standard adducts versus per cent combined maleic anhydride in the original sample. Before the calibration curve can be used, the adduct must be separated from the rosin chromatographically and the acid number is calculated on the adduct as follows: ml × N × 56.1/g of adduct = acid.

Number of Adduct

The per cent combined maleic anhydride is read directly from the calibration curve prepared using pure samples of maleopimaric acid or is calculated using the equation developed from the curve as follows: Acid number − 127.5/14 = per cent combined maleic anhydride in the sample.

Discussion of Results

A new method for the determination of combined maleic anhydride in rosin-maleic anhydride adducts by chromatographic techniques has been developed. The method is based on the separation of rosin acids and rosin-maleic anhydride adducts on a silicic acid-celite column. After the separation, the acid number is determined on the rosin-maleic anhydride adduct. Using this acid number, the per cent combined maleic anhydride can be read directly from a calibration

TABLE I

Chromatographic Determination of Combined Maleic Anhydride Adduct in Wood Rosin and Gum Rosin

Sample	Per cent maleic anhydride adduct prepared	Per cent adduct found
Gum rosin		
B179-6-1[a]	3.7	3.7 3.6
B189-6-1	3.3	3.3 3.1
U559-6-1[b]	4.6	4.5 4.5
U582-6-1	4.8	4.5 4.6
U625-6-1	2.9	2.7 2.8
2-36	9.5	9.3 9.4
2-40	13.2	12.3 12.5
Wood rosin		
65-3682-1	3.9	3.5 3.6
65-3682-2	3.9	3.4 3.5

[a] B, from longleaf pine trees which grew on an area of land that was burned over annually for many years.

[b] U, from longleaf pine trees which were never subjected to burning.

TABLE II

Correlation of Infrared and Chromatographic Analysis of Rosin Maleic Anhydride Adducts

Sample	Per cent maleic anhydride prepared	Per cent by chromatography	Per cent by infrared
B179-6-1	3.7	3.6 3.7	3.8
B189-6-1	3.3	3.1 3.3	3.3
U559-6-1	4.6	4.5 4.5	4.4
U582-6-1	4.8	4.6 4.5	....
U635-6-1	2.9	2.8 2.7	3.3
2-36	9.5	9.3 9.4	8.7
2-40	13.2	12.3 12.5	13.2
65-3682 (N-Wood rosin)	3.9	3.4 3.5	3.4

curve or by a calculation using the equation derived from the curve. The calibration curve in Figure 2 was made by analyzing known blends of rosin and rosin-maleic anhydride adduct.

This chromatographic technique was applied to a series of rosin-maleic adducts prepared in the laboratory. The results of their separations are presented in Table I. An observation of these data will show that the amount of combined maleic anhydride found by the separation procedure agrees very well with the amount of maleic anhydride added. These results correlate very well with the results obtained by infrared spectroscopy and are presented in Table II.

In order to demonstrate the complete chromatographic separation of the rosin acids and the rosin-maleic anhydride adduct, a sample of rosin-maleic anhydride adduct (B179-6-1) was separated into rosin acids and adduct on a 3 × 30 cm silicic acid-celite column. These results are shown in Figure 3. One can observe from this figure that some separation of the rosin acids was indicated in the early part of the total solids curve. However, the most important feature of this curve is that it shows a complete separation of the anhydrides from the acids in the benzene-

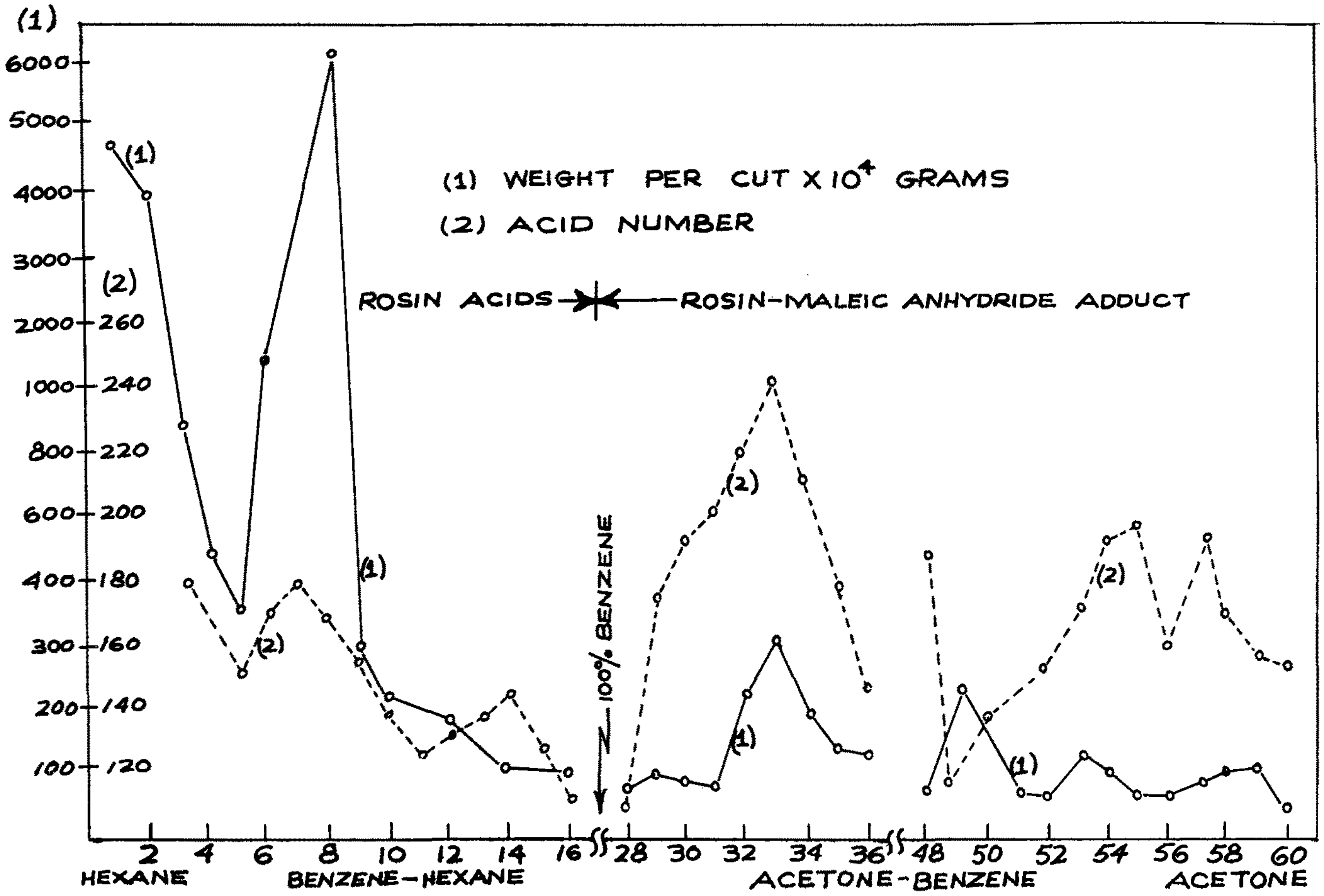

FIG. 3

hexane wash. Upon increasing the polarity of the developing solvent by the addition of acetone to the system solvent, the adduct began to leave the column and practically all of it was eluted within a range of 5% acetone.

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