Isolation of Palustric Acid from Tall Oil Rosin by Partition Chromatography *

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In 1954 Loeblich, Baldwin and Lawrence isolated a new rosin acid of the abietic series from gum and wood rosins of two American pine species; the new acid they named palustric acid [1]. In this isolation the authors employed, with minor modifications, the chromatographic method developed by Ramsay and Patterson [2] for the separation of straight-chain fatty acids. We have applied the same method to isolate the components of Finnish tall oil rosin and have also found palustric acid among the rosin acids and in amounts of 14—15 % of the total rosin acids in the tall oil rosin. In the light of previous analytical data for tall oil rosins (see references in Ref.[3]), this finding is surprising and of significance from the standpoint of the industrial utilization of tall oil rosin.

By means of the chromatographic technique we were able to separate the components of artificial binary, ternary and quaternary mixtures of rosin acids in the following order (the volume given is peak volume of the eluant): tetrahydroabietic acid 95 ml, dihydroabietic acid 150 ml, palustric acid 190 ml, dextropimaric acid 225 ml, *iso*dextropimaric acid 225 ml, *l*-abietic acid 240 ml, levopimaric acid 285 ml, neoabietic acid 360 ml, dehydroabietic acid 490 ml. As will be noted, the hydrogenated rosin acids are eluted first, followed by palustric acid which is clearly separated from these acids and from dextro- and *iso*-dextropimaric acids and *l*-abietic acid, which are eluted next. It was found that when the abietic acid content was many times as large as the pimaric acid content, the peak for dextropimaric acid was not separated from the abietic acid peak but merged with the latter so that the peak for abietic acid was wider at the left face in the chromatogram. Likewise levopimaric acid expanded the right face of the peak for abietic acid when the levopimaric acid content was much lower than the abietic acid content. The next fraction eluted consists of neoabietic acid and this is clearly separated from dehydroabietic acid which follows it. These observations are in essential agreement with the findings of Loeblich, Baldwin and Lawrence [1].

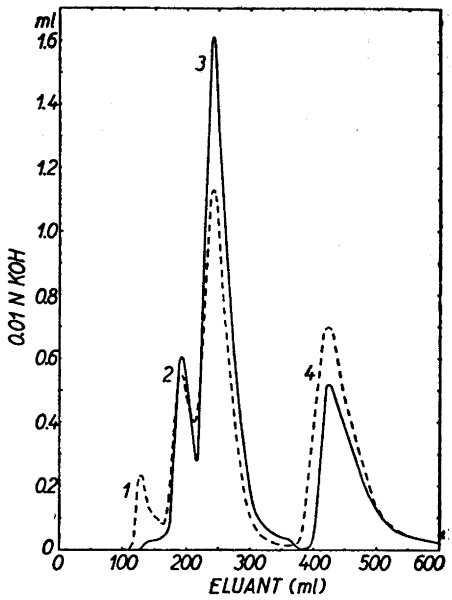

Fig. 1. Chromatogram of tall oil rosin showing the presence of palustric acid (peak 2). Ordinate: consumption of 0.0100 N alcoholic potassium hydroxide in titration of 5 ml eluant volumes (phenolphthalein as indicator). Sample *a* (———), tall oil rosin obtained by continuous distillation. Sample *b* (— — —), tall oil rosin obtained by batch distillation. For the other peaks, see text.

The chromatograms of two samples of crystalline tall oil rosins distilled by different methods are shown in Fig. 1. The samples have yielded chromatograms with four peaks. The first of these coincides with an eluant volume of 130 ml and according to the peak volumes given consists of hydrogenated rosin acids (which are present in only small quantities in sample *a*). The second peak at 190 ml lies at the peak volume for palustric acid. The third, the largest peak, undoubtedly refers to abietic acid and any small amounts of pimaric acids possibly present. We

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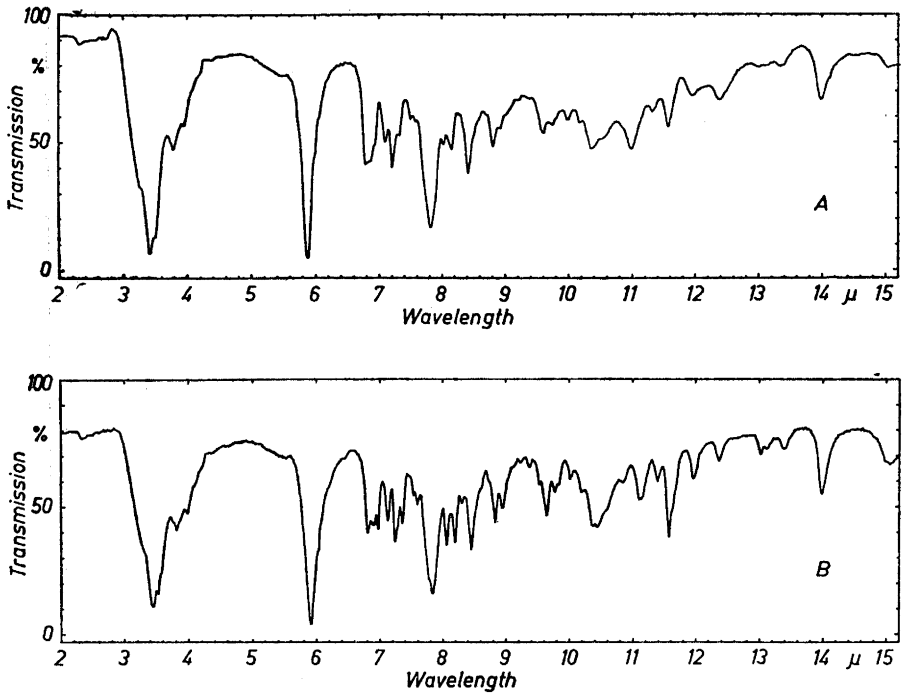

Fig. 2. Infrared absorption spectra of (A) palustric acid isolated from tall oil rosin sample *a* (peak 2 in curve for sample *a* in Fig. 1) and (B) authentic palustric acid.

have found that the addition of dextropimaric acid in an amount corresponding to 8 % of the abietic acid content to an artificial mixture of palustric and *l*-abietic acids in the proportions corresponding to those of the acids yielding peaks 2 and 3 in Fig. 1 leads to a filling up of the area between the peaks for palustric and *l*-abietic acids in the chromatogram. The dextropimaric acid contents of samples *a* and *b* are hence according to Fig. 1 in all probability less than 8 % of the abietic acid content. The shoulder at 360 ml in the chromatogram of sample *a* coincides with the peak volume of neoabietic acid. The fourth peak at 425 ml appears appreciably earlier than the peak for dehydroabietic acid in the chromatogram of the artificial mixture. The tall oil rosin thus evidently contains dehydrogenated rosin acids that differ in type from the dehydrogenated acids in the artificial mixture. The amounts of material in the peaks of the chromatogram are given in Table 1. The material of peak 2, which in view of its location in the chromatogram refers to palustric acid, represents 14—15 % of the rosin acids in both samples.

Table 1. Rosin acid contents (in g.equiv.) in peaks 1—4 in Fig. 1 as percentages of the total content of eluted rosin acids computed from the areas under the peaks.

Peak No.	Sample *a*	Sample *b*
1	< 1 %	5 %
2	14 »	15 »
3	58 »	41 »
4	27 »	39 »

In order to confirm the identity of the palustric acid (peak 2), chromatography of tall oil rosin (sample *b*) was carried out on a ten times larger scale than the above separations to obtain enough of the acid to permit the measurement of its infrared absorption. Although it was not possible

to carry out six recrystallizations from methanol as Loeblich, Baldwin and Lawrence [1] had done to obtain a constant specific rotation and melting point, but only one, the similarity of the recorded infrared absorption spectra reproduced in Fig. 2 clearly indicates that the isolated rosin acid of peak 2 consisted of palustric acid. It may be noted that the band at 12.37 μ is specific for palustric acid when the absorptions of the other rosin acids for which the eluant peak volumes were determined are taken into account (*cf.* Refs.[3-5]).

The infrared absorption spectra of rosin acid fractions of crystalline tall oil rosin (of the same origin as sample *b*) recorded by Bruun and Jalava [6] contained bands due to *l*-abietic and dehydroabietic acid but no bands characteristic of tetrahydroabietic, dihydroabietic and dextro- and *iso*dextropimaric acids (acc. to Refs.[3-4]). The chromatographic data obtained in the present study are in agreement with these observations. It may be difficult to determine from their infrared absorption the identity of the substances yielding peak 1 which amount to 5 % of the rosin acid mixtures and which possibly consist of isomeric rosin acids. This may be true also for dextropimaric acid when its content is as low as in the samples studied (according to the chromatograms of rosin acid mixtures, its content is less than 4 % of the total acids, and according to chromatograms of tall oil rosin samples from which the major part of the *l*-abietic acid was precipitated with diamylamine before chromatography, at the most 4—5 % of the total acids). — The infrared absorption spectrum of palustric acid, which spectrum was not known when the previous infrared absorption study was carried out, has its strongest bands at 8.46, 8.83, 9.65, 10.38 + 10.44, 11.11, 11.57, 11.97, 12.37 and 13.98 μ [5]. With the exception of the band at 12.37 μ, the strong and moderate bands are seen at or close to the same wavelengths as in the spectra of *l*-abietic and dehydroabietic acids, the two major components of tall oil rosin (*cf.* Refs. [3-4]). For this reason, it is difficult to detect from infrared spectra even relatively high contents of palustric acid in mixtures containing these acids. The content of 14—15 % of palustric acid deduced from the chromatographic analysis of the tall oil rosin is thus not necessarily at variance with the results of the infrared spectral studies of tall oil rosin acids [6].

Chromatographic data. Column diameter (inside): 11 mm. Adsorbent: 15.0 g of Mallinckrodt's silicic acid, A.R. Immobile solvent: 9 ml of a mixture of equal parts of furfuryl alcohol (B.D.H., technical, vacuum distilled after treatment with sodium hydroxide) and 2-aminopyridine (B.D.H., Laboratory Reagent). Eluting solvent: 2,2,4-trimethylpentane (B.D.H., Laboratory reagent): purified by distillation and passage through a column of aluminium oxide and saturated before use with the immobile solvent. The fraction volume was 5 ml. Data relating to the acid samples examined will be given in a forthcoming publication.

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