

Thermal Behavior of Certain Resin Acids

WALTER H. SCHULLER

Naval Stores Laboratory, Olustee, Fla.

CARL M. CONRAD

Plant Fibers Pioneering Research Laboratory, New Orleans, La.

Differential thermal analysis and thermogravimetric analysis measurements are reported for the seven pure major resin acids found in pine oleoresin.

DIFFERENTIAL thermal analysis (DTA) and thermogravimetric analysis (TGA) were applied to the seven pure major resin acids found in pine oleoresin. The acids studied fall into two categories: those which isomerize on heating—namely, levopimaric (2), neoabietic (3), and palustric (1) acids; and those which are stable to heat—namely, abietic, dehydroabietic, pimaric, and isopimaric acids. Five of the acids have previously been studied by DTA (4, 5); isopimaric and palustric acids were not included. However, no TGA analyses were reported.

Curves of the three acids which undergo isomerization are shown in Figure 1, while Figure 2 presents those which are stable toward isomerization. The characteristics shown by the curves may be summarized in Table I.

EXPERIMENTAL

The DTA curves were recorded with a Robert L. Stone Differential Thermal Analysis apparatus at a rate of temperature rise of 7.5° C. per min. in a slow current of prepurified nitrogen and with fine granular quartz as reference material. With the aid of highly purified samples of β -D-glucose (m.p. 150°) and cellobiose (m.p. 225°), it was determined that melting temperatures corresponded to the beginning of the appropriate

endotherm and not with its minimum. The increase of temperature between beginning and minimum of an endotherm averaged 13° C. The accuracy of the DTA determinations of the melting point probably did not exceed plus or minus 3° C.

The TGA curves were recorded on the Thermo-Gravimetric unit of the Stone apparatus at a heating rate of 3.5° C. per min. in a slow carrier stream of prepurified nitrogen. Fine granular quartz was used as a support for 0.1 gram samples of the acids. The resin acids were highly purified materials reflecting the highest m.p.'s, $[\alpha]_D$, and ϵ values at their λ_{\max} , reported in the current literature.

DISCUSSION

The DTA thermogram of levopimaric acid (Figure 1a) shows two distinct endotherms, the second of which, with minimum of 154°, is associated with the melting point. The cause of the first minimum, which was reproducible, is not clear. This first minimum was shown, though less prominently, by Sandermann, Weismann, and Augustin's (4, 5) thermogram for this acid. A similar situation was observed in the present work for isopimaric acid (Figure 2c), with minima of 153° and 175° C. These double minima may be due to crystal or molecular transformations. All of the thermograms of Figure 1 show considerable exothermic

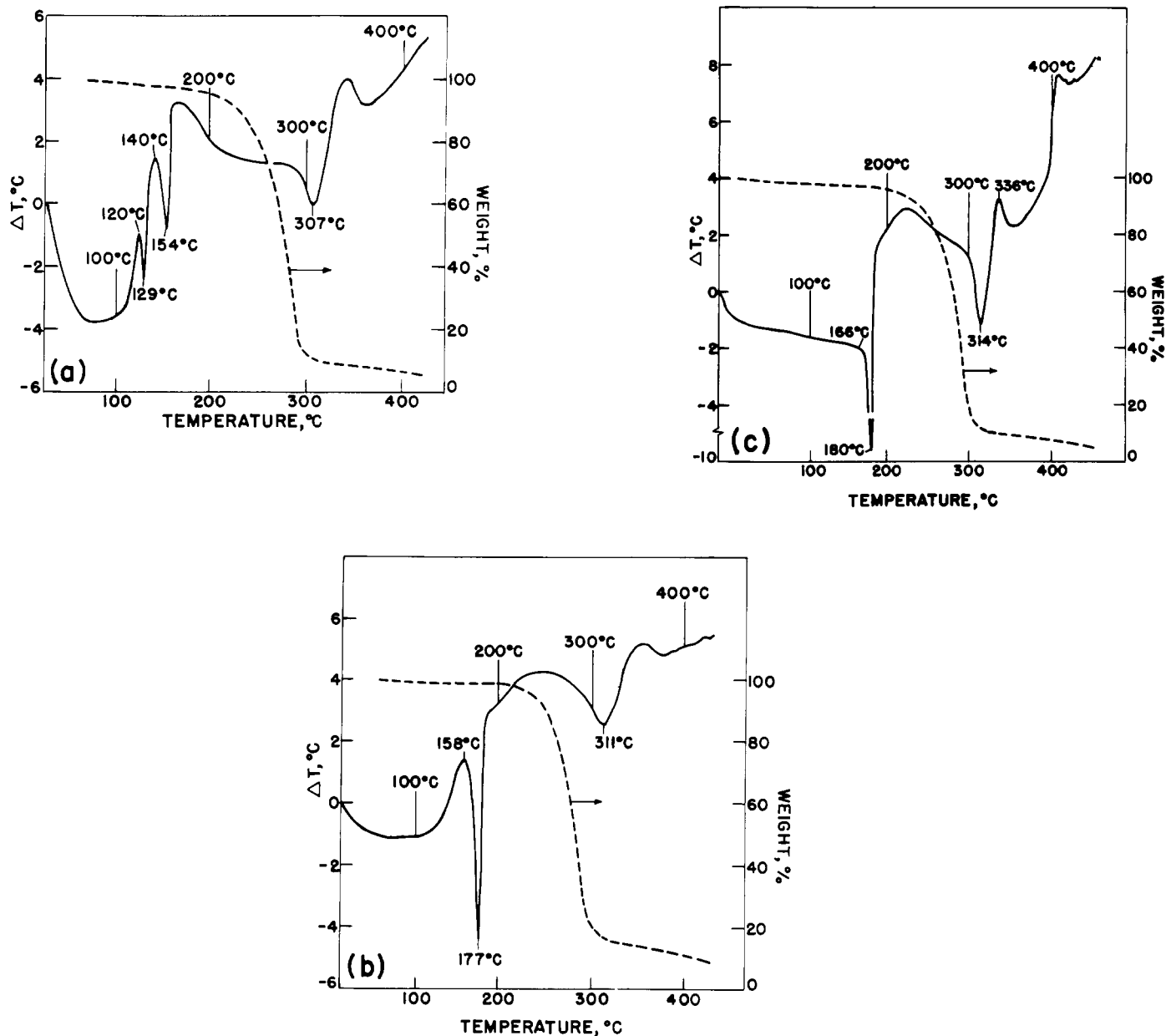


Figure 1. Differential thermal analysis (solid lines) and thermogravimetric analysis (broken lines) curves of resin acids (a), levopimaric acid; (b), neoabietic acid; (c), palustric acid

Table I. Thermal Characteristics of Resin Acids

Name of Acid	Figure	M.P., °C.		Temp., °C., of Per Cent Loss (TGA)		
		Lit.	DTA	10%	50%	90%
Levopimaric	1a	150-2	140	241	288	402
Neoabietic	1b	171-3	158	251	281	424
Palustric	1c	162-7	166	247	286	410
Abietic	2a	172-5	175	258	293	312
Dehydroabietic	2b	171-3	175	252	292	323
Isopimaric	2c	162-4	156	236	279	428
Pimaric	2d	217-9	187-194	241	277	298

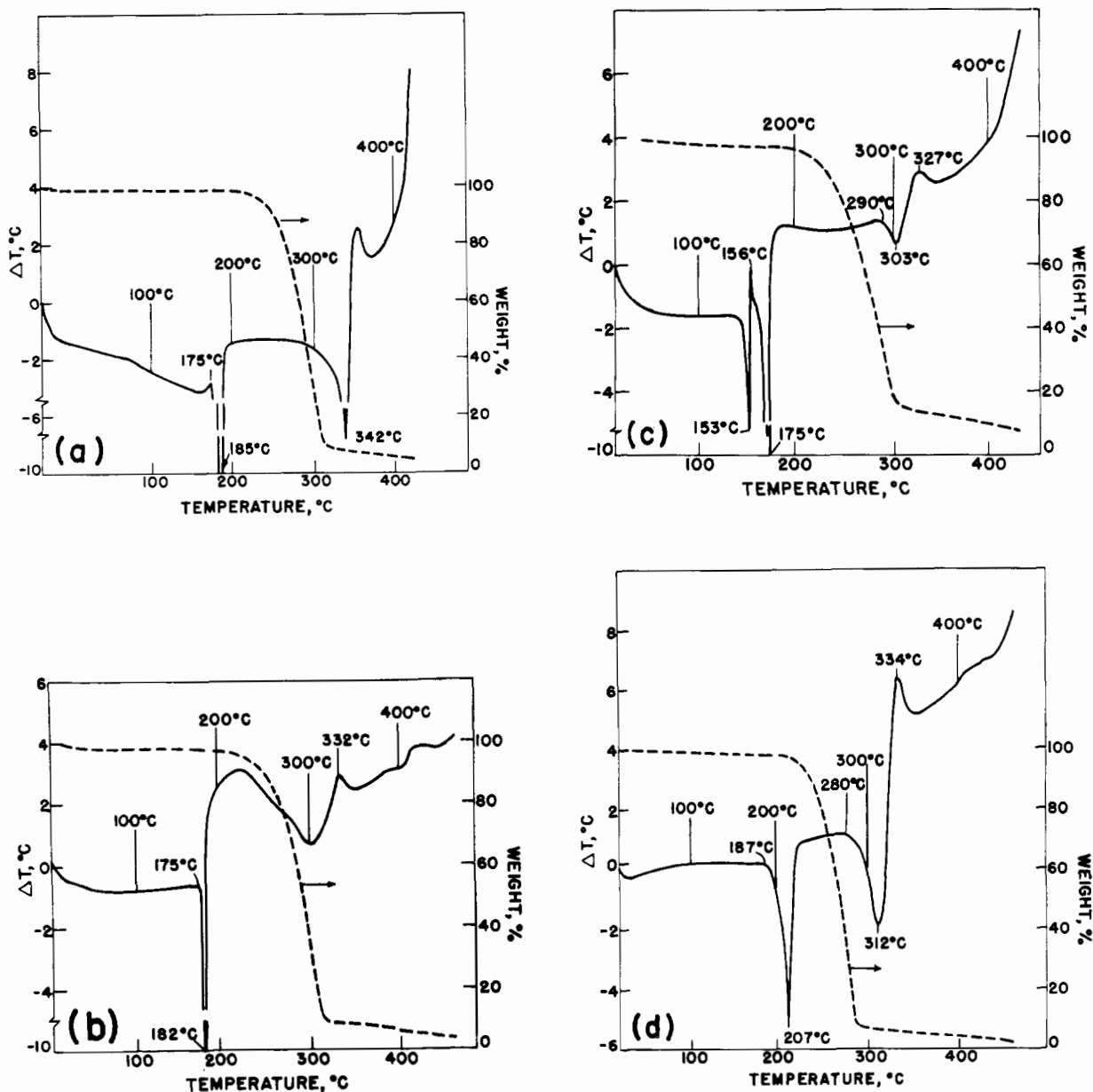


Figure 2. Differential thermal analysis (solid lines) and thermogravimetric analysis (broken lines) curves of resin acids

a, abietic acid; b, dehydroabietic acid; c, isopimaric acid; d, pimaric acid

trend above the melting points which may be associated with their isomerization processes. The boiling temperatures are indicated in all cases by more or less broad DTA endotherms.

The TGA curves of the different acids (Figures 1 and 2, Table I) show relatively small differences associated with temperature. Probably for evaluation purposes, the temperature corresponding to 50% mass loss is most significant for a particular acid. The relatively high temperatures for 90% loss are in most cases due to small differences in rate of loss of the residual portions of the acids.

CONCLUSIONS

The seven pure resin acids examined in this paper together comprise the major part of the rosin portion of pine gum. Pine gum consists of about 80% resin acids and 20% turpentine and is one of the major sources of rosin. Rosin is used in the manufacture of paper size, surface coatings, and other industrial applications. The processing of pine gum into rosin involves a distillation in which the rosin is heated close to 170° C., and in

many cases the rosin is shipped at about this temperature. The present study sheds some light on the thermal behavior of the pure components of rosin.

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