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Thermal Isomerization of Levopimaric Acid

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The thermal isomerization of levopimaric acid has been studied in a temperature range of 150 to 200°. The isomerization was found to be a first-order reaction with respect to the levopimaric acid and catalyzed by the carboxyl group in the resin acid molecule. Palustric, *l*-abietic and neoabietic acids have been identified as the products of the isomerization at 155 and 200° by partition chromatography. This study accounts for the major changes taking place in the conversion of pine oleoresin to rosin and turpentine. The isomerization rate of the levopimaric acid was found to be more than fifty times faster than the rate of methyl levopimarate.

The work described in this paper was undertaken in order to obtain a better understanding of the reactions that take place when pine oleoresin is processed into rosin. The acid portion of commercial pine oleoresins contains from 23 to 40%[2] levopimaric acid which is completely isomerized to other resin acids during gum distillation. It has been shown that the major end product of the thermal isomerization of levopimaric acid is *l*-abietic acid.[3,4] The formation of an intermediate acid or acids is strongly indicated by two observations: (1) a comparison of the ultraviolet absorption spectra of gum and rosin does not show a sufficient increase in *l*-abietic acid content in the rosin to allow for the complete conversion of the levopimaric acid to *l*-abietic acid, and (2) the specific rotation of the thermally isomerized levopimaric acid passes through a minimum before rising to a value which approaches the specific rotation of *l*-abietic acid.

The thermal isomerization of pure levopimaric acid has been studied by Kohler[3] and Ruzicka.[4] Most of their work was done at temperatures of 200° or above, and under these conditions *l*-abietic acid was the major product formed. Kohler carried out a few isomerizations at 150–160° for 7 to 10 minutes, but the only product isolated was unchanged levopimaric acid.

The present paper describes a study of the thermal isomerization of pure levopimaric acid. The rate of isomerization was determined at 120, 130, 140, 145, 155 and 200°. Very little, if any, isomerization of the crystalline acid occurred below its melting point, 150–152°, even after long periods of heating.[5]

It was found that temperatures of 155 and 200° gave measurable rates of isomerization. The temperature of 155° was chosen for the most detailed part of the study because pine oleoresin is processed into rosin at 150–160°.

In the 155° series, the data obtained on each sample included the specific rotation, chromatographic analysis, ultraviolet absorption analysis and the percentage levopimaric acid content. This information furnished a complete analysis of the components of thermally isomerized levopimaric acid and showed that on heating at 155°, levopimaric acid isomerized to palustric, *l*-abietic and neoabietic acids. During the first three hours the concentration of palustric, neoabietic and *l*-abietic acids increased as the specific rotation decreased until a maximum of 37% palustric and 15% neoabietic acid was formed. At the end of four hours, the levopimaric acid was completely isomerized, the specific rotation reached a minimum, −5.6°, the palustric and neoabietic acid content decreased slightly and the *l*-abietic acid content increased to 52%. After the disappearance of the levopimaric acid, the percentages of palustric and neoabietic acids continued to decrease slowly accompanied by a slow increase in *l*-abietic acid content until after 221 hours of isomerization the product contained 7% palustric, 86% *l*-abietic and 8% neoabietic acids.

The isomerized samples were separated by chromatography into three groups of acids—the first, palustric acid; the second, levopimaric and *l*-abietic acids; and the third, neoabietic acid (Fig. 1). The percentage of levopimaric acid was determined by the volumetric method of Fleck and Palkin.[6] The specific rotation and specific extinction coefficient, α, of the isomerized samples were calculated and found to be in good agreement with the observed values (Table I), indicating that no appreciable quantities of other acids are formed by isomerization.

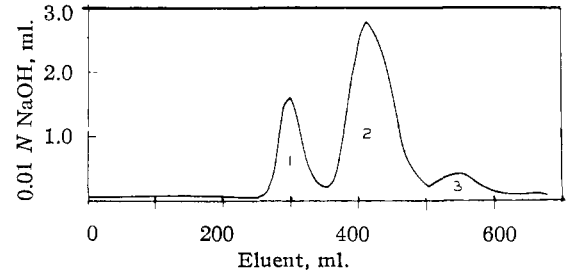

Fig. 1.—Chromatogram of levopimaric acid isomerized for three hours at 155°; peak 1, palustric acid; peak 2, levopimaric and *l*-abietic acids; peak 3, neoabietic acid.

The change in the composition of the isomerized levopimaric acid may be followed by a comparison of the ultraviolet absorption spectra of the samples (Fig. 2). In 45 minutes the sample had changed

(1) One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) Benjamin L. Davis and Elmer E. Fleck, *Ind. Eng. Chem.*, **35**, 171 (1943).

(3) John Kohler, *J. prakt. Chem.*, **86**, 534 (1912).

(4) L. Ruzicka, F. Balas and F. Vilim, *Helv. Chim. Acta*, **7**, 458 (1924).

(5) This evidence is contradictory to statements often found in the literature attributing the wide range in the melting point of levopimaric acid to its isomerization while the melting point was being determined. Most instances of a broad melting range for levopimaric acid that have been observed in this Laboratory were caused by traces of low molecular weight acids.

(6) Elmer E. Fleck and Samuel Palkin, *Ind. Eng. Chem.*, **14**, 146 (1942).

TABLE I

SUMMARY OF DATA ON THERMAL ISOMERIZATION OF LEVOPIMARIC ACID AT 155°

Time, hr.	$[\alpha]_D$, 2% EtOH	α at 241 mμ	Palustric, %	Levopimaric, %	*l*-Abietic, %	Neoabietic, %	Calcd. $[\alpha]_D$	Calcd. α at 241 mμ
1/2	−208	15	11	76	8	4	−203	14
3/4	−151	23	19	56	19	5	−152	24
1	−116	27	24	43	22	11	−106	23
2	−33	41	34	16	35	15	−32	43
3	−9	46	37	5	42	15	−9	47
4	−6	52	35	0	52	14	−7	54
5	−6	53	35		52	14	−7	54
9	−18	56	28		59	14	−19	59
15	−28	57	20		67	12	−36	63
24	−52	60	12		74	12	−49	67
48	−62	69	9		79	10	−60	69
120	−69	70	9		81	9	−63	70
221	−70	69	7		86	8	−70	72

from levopimaric acid with a maximum at 272 mμ, α 18.7, to a mixture of acids having maxima at 262–265 mμ, α 18.7; 251 mμ, α 23.0; and 242 mμ, α 23.2, indicating the presence of palustric, neoabietic and *l*-abietic acids. After 24 hours of isomerization, the ultraviolet spectrum of the sample is quite similar to the spectrum of *l*-abietic acid with the exception that the extinction coefficient at 241 mμ is lower than the specific extinction coefficient for pure abietic acid and in the range of 260–280 mμ the absorption is higher than the absorption of pure *l*-abietic acid.

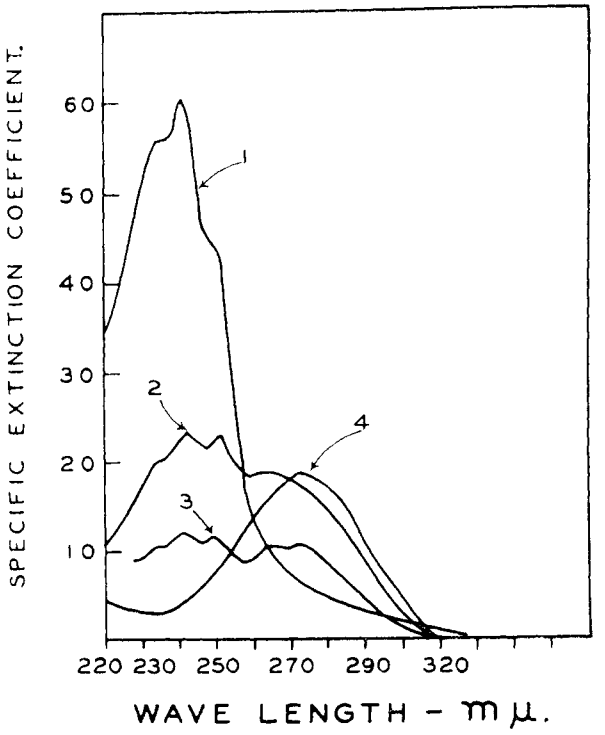

Fig. 2.—Ultraviolet absorption spectra: 1, levopimaric acid isomerized at 155° for 24 hours; 2, levopimaric acid isomerized at 155° for 45 minutes; 3, methyl levopimarate isomerized at 155° for 18.5 hours; 4, levopimaric acid.

It was found that, within the limits of experimental error, the isomerization of levopimaric acid was a first-order reaction since a plot of the logarithm of the concentration of levopimaric acid as the ordinate *vs.* time as the abscissa was essentially a straight line. The line intersected the *x*-axis at 12 minutes indicating that 12 minutes was the time required for the samples to melt and reach the isomerization temperature of 155°. Assuming 12 minutes as zero time and replotting the values, the average specific rate constant, K, in the equation for a first-order reaction $K = 2.303/t \log C_0/C$, is 0.069 min.$^{-1}$.

In a recent publication,[7] it was shown that palustric acid comprised 9–10% of the acidic portion of pine oleoresin and 18–19% of the acidic portion of rosin. The increase in the palustric acid content of the rosin is in good agreement with the work reported in this paper since the heating of the oleoresin during processing appears to be about equal in isomerization effect to the 3- to 5-hour isomerization of the levopimaric acid in sealed tubes. Therefore, the increase of 9% palustric acid content in the rosin may be explained by the fact that 35–37% of the levopimaric acid in the oleoresin is isomerized to palustric acid in three to five hours.

The rate of isomerization of levopimaric acid at 200° was found to be approximately eight times as fast as the isomerization at 155°—the minimum $[\alpha]_D$ being reached in 30 minutes at 200° in comparison to 4 hours at 155° (Table II). Chromatographic analysis of the products from the isomerizations at 155 and 200° with minimum specific rotations showed that the composition of the samples was essentially the same.

Temp., °C.	Time, hr.	Palustric, %	*l*-Abietic, %	Neoabietic, %
155	4	35	52	14
200	0.5	34	52	14

The rate of isomerization of methyl levopimarate was also measured by the change in the specific rotation. The carboxyl group was blocked in this manner to determine whether the isomerization of the acid was truly due to heat or whether the carboxyl group provided a sufficient concentration of hydrogen ions to cause isomerization which would then be effectively of acid character. It was found that isomerization did occur but at a much slower rate than the rate of the free acid. A comparison of the ultraviolet spectrum of methyl levopimarate isomerized for 18.5 hours with the spectrum of levopimaric acid isomerized for 0.75 hr. shows that after 18.5 hours about 50% methyl levopimarate is still present in the sample (Fig. 2).

Experimental

Preparation of Levopimaric Acid.—A modification of the procedure of Harris and Sanderson[8] was used to separate levopimaric acid from pine oleoresin. A solution of 110 ml. of 2-amino-2-methyl-1-propanol dissolved in 110 ml. of 95% ethanol was added to a solution of 500 g. of pine oleoresin in 400 ml. of 95% ethanol. The amine salt was allowed to precipitate at room temperature overnight; then filtered and redissolved in 900 ml. of boiling ethanol, the minimum amount required to effect solution of the salt. After cooling in the refrigerator, the salt was again filtered and recrystallized from 700 ml. of ethanol. A third recrystallization

(7) Virginia M. Loeblich, Doris E. Baldwin and Ray V. Lawrence, THIS JOURNAL, **77**, 2823 (1955).

(8) G. C. Harris and T. F. Sanderson, *ibid.*, **70**, 334 (1948).

from 400 ml. of ethanol yielded a salt with $[\alpha]_D$ −212° (calculated $[\alpha]_D$ −216°).

The salt was suspended in ether, washed twice with 100-ml. portions of 3*N* acetic acid, twice with distilled water, once with 50 ml. of 0.5% aqueous sodium bicarbonate to remove the last traces of acetic acid, then once with distilled water. The ether solution was dried over sodium sulfate and filtered. Two-hundred ml. of 95% ethanol was added to the ether solution and the ether was removed by distillation at atmospheric pressure. On cooling, levopimaric acid with an $[\alpha]_D$ −268° precipitated from the alcohol solution. One recrystallization from ethanol raised the $[\alpha]_D$ to −275° Based on the acid number of the oleoresin, the yields of levopimaric acid varied from 13% using slash gum to 18% using longleaf gum. The yield of levopimaric acid may be raised to 21–24% by working up the mother liquor.

Thermal Isomerization of Levopimaric Acid.—The levopimaric acid used for the thermal isomerization studies had an $[\alpha]_D$ −275° and was shown by chromatographic and ultraviolet absorption analysis to contain more than 97% levopimaric acid.

The levopimaric acid was placed in constricted tubes and the air replaced with nitrogen by thorough flushing and repeated evacuation. The tubes were sealed off under high vacuum and then heated in an oil-bath at the desired temperature for specified lengths of time. For studies from 30 minutes through 4 hours at 155°, 10 g. of acid was used. Beyond 4 hours, 5-g. samples were used. For the 200° series, 1-g. samples were isomerized.

Analysis of the 155° Thermally Isomerized Products.—The data obtained on each sample included the specific rotation, chromatographic analysis, ultraviolet absorption analysis and the percentage levopimaric acid content.

The chromatographic procedure used is described by Loeblich, Baldwin and Lawrence.[7] Three minor changes were made in the technique for this work: (1) the diameter of the chromatographic column was changed from 18 mm. i.d. to 10 mm. i.d., thereby tripling the height of the silicic acid bed; (2) the ratio of 2-aminopyridine to furfuryl alcohol was changed from a 1:1 weight ratio to a 1:3 weight ratio. These two modifications improved the degree of separation considerably. The third modification, using 1 g. of Celite and 19 g. of silicic acid, increased the flow rate without altering the efficiency of the column. A summary of the data on the thermal isomerization of levopimaric acid at 155° is given in Table I.

The identity of the palustric, *l*-abietic and neoabietic acids was confirmed by separating 3.5 g. of a 4-hour isomerized sample on a large (200-g. silicic acid) chromatographic column.[7] Acids having the following physical constants were isolated: palustric acid, m.p. 162–167°, $[\alpha]_D$ +71.5°, α 31.0 at 265–266 mμ; *l*-abietic acid, m.p. 175–182°, $[\alpha]_D$ −105.1°, α 77.2 at 241 mμ; neoabietic acid, m.p. 167–169°, $[\alpha]_D$ +159°, α 80 at 251 mμ.

Biot's relationship[9] was used to calculate the specific rotations of the isomerized products. The specific extinction coefficient at 241 mμ also was calculated. The values used for these calculations were: palustric acid, $[\alpha]_D$ +71.6°, α at 241 mμ 12.8; *l*-abietic acid, $[\alpha]_D$ −105°, α at 241 mμ 77; neoabietic acid, $[\alpha]_D$ +160°, α at 241 mμ 70.6; and levopimaric acid, $[\alpha]_D$ −275°, α at 241 mμ 5.1.

Thermal Isomerization of Levopimaric Acid at 200°.—The rate of isomerization of levopimaric acid was observed by the change in the specific rotation and the ultraviolet absorption of the isomerized samples (Table II).

TABLE II

THERMAL ISOMERIZATION OF LEVOPIMARIC ACID AT 200°

Time, hr.	$[\alpha]_D$, 2% EtOH	α at 241 mμ	Time, hr.	$[\alpha]_D$, 2% EtOH	α at 241 mμ
0	−275	..	4	−43	62
0.25	−19	45	6	−46	64
0.50	−7	46	8	−45	65
0.75	−12	53	24	−54	65
1	−21	55	48	−52	64
2	−35	57	120	−51	64

Chromatographic analysis of the 0.5-hour isomerized sample showed that it contained 34% palustric, 52% *l*-abietic and 14% neoabietic acids.

Thermal Isomerization of Methyl Levopimarate at 155°.—Methyl levopimarate was prepared by treating an ether solution of levopimaric acid with an excess of an ether solution of diazomethane. Removal of the ether by distillation, followed by crystallization of the product from methanol, yielded the ester, m.p. 64–65°, $[\alpha]_D$ −270°, acid number = 0. The rate of isomerization was observed by the change in specific rotation (Table III).

TABLE III

THERMAL ISOMERIZATION OF METHYL LEVOPIMARATE AT 155°

Time, hr.	$[\alpha]_D$ (2% EtOH)	Time, hr.	$[\alpha]_D$ (2% EtOH)	Time, hr.	$[\alpha]_D$ (2% EtOH
0	−270	14	−130	64	−45
2	−221	18.5	−111	137	−28
5	−196	24	−86	165	−25
8.5	−169	36	−78	272	−15
11.5	−156	50	−68	296	−12

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(9) Biot, *Ann. chim. phys.*, [3] **59**, 206 (1860).