[CONTRIBUTION FROM THE NAVAL STORES RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Catalytic Isomerization of the Acids of Pine Oleoresin and Rosin[1]

BY E. E. FLECK AND S. PALKIN

The acids so far isolated from pine oleoresin and rosin are isomeric decahydrophenanthrene monocarboxylic acids ($C_{20}H_{30}O_2$) of varying degrees of stability. One of these, dextro- or α-pimaric acid, can be distilled (in vacuum), and its rotation is not altered even at 250°, whereas the sapinic acids isomerize rapidly above 50–55°. *l*-Abietic acid, although considered to be relatively stable, isomerizes readily, and is highly susceptible to atmospheric oxidation. The purification and separation of the pure abietic acid (Schulz)[2] from the accompanying intermediate isomers is a relatively laborious task.

The means heretofore used in effecting isomerization of the labile resin acids[3] involve the action of: (1) acids; (2) heat without chemical agents; (3) ultraviolet light.

In a previous publication[4] it was shown that palladium carbon also isomerizes, as well as dehydrogenates, the rosin acids yielding α-pyroabietic acid.

The pyroabietic acids,[5] which represent a stage of isomerization beyond that of *l*-abietic, have heretofore been produced by heat only (fifty to one hundred hours at 250°). The resulting reaction product consists largely of a complex mixture of isomeric acids, and is further complicated by the presence of considerable neutral material, due to pyrolytic decomposition. The yield of pyroabietic acid is generally poor, and the task of separating it from the reaction mixture is difficult.

TABLE I

ROTATION AND MELTING POINTS OF PYROABIETIC ACIDS REPORTED BY VARIOUS AUTHORS

Rotation	Melting point, °C.	Source	Author	
$[\alpha]_J$ +60°	172–173	*Pinus halepensis* (*Aleppo pine*)	Fanica (1)	
$\alpha]_J$ +62.5°	172–173	*Pinus halepensis*	Fanica (2)	
$[\alpha]_J$ +47.5°	155–159	Rosin oil	Dupont and Dubourg	(3)
$[\alpha]_J$ +51°	155–159	*Pinus halepensis*	Dupont and Dubourg	
$[\alpha]_D$ +53°	171–173	Rosin oil	Schulz (4)	
$[\alpha]_D$ +37.5°	156–158		Greth (5)	
$[\alpha]_J$ −15°	194	*Pinus pinaster* (*Maritime pine*)	Fonrobert and Greth (6)	
$[\alpha]_D$ −62.5°	189–190		Greth (6)	
$[\alpha]_J$ −52.8°	185–190	*l*-Abietic acid from *Pinus pinaster*	Greth (7)	
$[\alpha]_D$ −50 to 60°	196–198		Klason and Köhler (8)	
$[\alpha]_J$ −30°	176–182	*Pinus halepensis*	Fanica (9)	

(1) *Bull. inst. pin*, 158 (1933). (2) *Ibid.*, 183 (1933). (3) *Ibid.*, 181 (1928). (4) *Chem. Zeit.*, **41**, 666 (1917). (5) *Bull. inst. pin*, 86 (1935). (6) *Chem. Umschau Fette, Öle, Wachse Harze*, **36**, 93 (1929). (7) Citation 6, page 86. (8) *Monit. Sci.*, **21**, July, 1907. (9) Citation 2, page 188.

As in the case of resin acids in general, considerable confusion exists in the literature regarding the pyroabietic acids (Table I).

In the present investigation, a study has been made of the action: (1) of metal catalysts (with and without carriers); (2) of non-metal catalysts; (3) metallic oxides and other types of catalysts frequently used as carriers for catalysts.

Experimental

Preparation of Resin and Rosin Acids.—The *l*-abietic acid used in these experiments was prepared from gum rosin by the method previously described.[2] It had a rotation $[\alpha]^{20}D$ −86° in absolute alcohol and a melting point of 162–167°. The α-(dextro-)-pimaric acid and the β-(levo-)-pimaric acids were prepared by the method described in another publication.[6] The β-(levo-)-pimaric acid had a rotation $[\alpha]^{20}D$ −274° in absolute alcohol and a melting point of 143–148°. The α-(dextro-)-pimaric acid had a rotation $[\alpha]^{20}D$ +74° in absolute alcohol and a melting point of 212–214°.

The sapinic acids were prepared from the liquid portion of settled longleaf pine oleoresin. The gum was neutralized with normal sodium hydroxide and then extracted exhaustively with ether to remove resenes, esters, and other neutral material. This solution was concentrated at 50° by spraying it into a vacuum chamber. In order to effect a separation from oxidation products, the sapinates were then precipitated by addition of strong sodium hydroxide and separated by the centrifuge. These soaps were further purified by redissolving in water and re-precipitating with sodium hydroxide. This process was repeated several times. The final product was neutralized carefully in dilute solution (in the cold) with an equivalent quantity of dilute acetic acid (determined by titration of an aliquot), filtered by suction, washed and dried in vacuum at 40°, $[\alpha]^{20}D$ −39°.

Conditions of Isomerization.—A few preliminary experiments were made with several catalysts, varying the time and temperature. A uniform heating period of five

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(1) Presented before the Organic Section, Chapel Hill meeting of the American Chemical Society, April 12–15, 1937.

(2) Palkin and Harris, THIS JOURNAL, **56**, 1935 (1934).

(3) S. Palkin, *J. Chem. Ed.*, **12**, 35 (1935).

(4) E. E. Fleck and S. Palkin, *Science*, **85**, 126 (1937).

(5) Dupont and Dubourg, *Bull. inst. pin*, 181 (1928).

(6) Palkin and Harris, THIS JOURNAL, **55**, 3677 (1933).

hours and temperature of 250° were chosen for testing the effect of variation of catalysts. These conditions were found, on the average, best suited for obtaining adequate comparison of the various catalysts, in view of wide differences in catalytic activity. As will be shown, a considerably shorter heating period and lower temperatures are possible with palladium carbon as the catalyst. All preparations of α-pyroabietic acid were carried out under thermostatic control.

Extraction of the Isomerized Acids from the Reaction Product.—The cooled reaction mass was shaken with ether until the catalyst was completely in suspension. The catalyst was filtered off with suction and then washed with ether. The ether solution was extracted twice with quarter normal sodium hydroxide. The combined alkaline extracts were shaken twice with ether. The aqueous solution was then made acid to congo red by addition of dilute hydrochloric acid, and the isomerized acids were extracted with ether. The ether solution was shaken out with water until the extracts were neutral to congo red. The ether was then distilled and the residue was dried at 80° in vacuum to constant weight. The optical measurements were made on this material in a 2% solution in absolute alcohol.

Isomerization of *l*-Abietic Acid.—As may be seen from Table II, the oxides and other non-metallic catalysts were, with the exception of fuller's earth (at 200°) and charcoal, productive of little or no dextro- or α-pyroabietic acid, the product being mainly levorotatory. Fuller's earth and Wilkinite at 250° cause complete decarboxylation. Similar decarboxylating action was noted by Palmer and Powers[7] by partially esterified rosin with fuller's earth or active clay at 260–325° for several hours. Palladium–, platinum–, and nickel–carbon are effective in varying degrees, palladium–carbon being by far the best agent. The different charcoals show considerable variation in catalytic action, Carbex being the most effective.

TABLE II

CATALYTIC ISOMERIZATION OF *l*-ABIETIC ACID

2 g. of *l*-abietic acid ($[\alpha]^{20}\text{D}$ −86°) and 1 g. of catalyst heated at 250° for five hours.

Catalyst	Yield of acid, %	$[\alpha]^{20}\text{D}$ of acid
Pd–C[a] (0.5 g. catalyst used)	85	+53°
Carbex	70	+53°
Carboraffin	65	+53°
Sumacarb	65	+53°
Fischer's activated charcoal	50	+45°
Pt–C[a] (0.5 g. catalyst used)	65	+44°
Fuller's earth (at 200°)	35	+42°
Fischer's absorbing charcoal	55	+23°
Darco	80	+19°
Ni–C[a] (0.5 g. catalyst used)	55	+13°
Norite	75	+ 8°
Silica gel	55	0°
Silica	60	− 9°
Copper chromite[b]	40	−26°
Graphite (flake)	85	−28°
Heat (without catalyst)	80	−28°
Alumina	70	−30°
Calcium sulfate (anhyd.)	75	−31°
Carbex ash	50	−35°
Wilkinite	Trace	
Fuller's earth	Complete decarboxylation	

[a] Diels, *Ber.*, **58**, 1231 (1925). Catalyst made with Fischer's Activated Charcoal and with Carbex.

[b] Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1138 (1932).

Uniformity in the production of α-pyroabietic acid by the catalytic method was observed also with rosins from different sources (Table III). This finding is in marked contrast with that reported by Fanica[8] and Fonrobert and Greth[9] for isomerization by heat alone.

TABLE III

ISOMERIZATION OF ROSINS FROM DIFFERENT SOURCES

Conditions: rosin, 2 g.; Pd–C catalyst, 0.5 g., heated for 5 hrs. at 250°.

Rosin	$[\alpha]^{20}\text{D}$ of rosin	Acids Yield, %	Acids $[\alpha]^{20}\text{D}$
P. pinaster (French)	− 5°	70	+54°
P. pinaster (bleached French)	−11°	75	+53°
P. pinaster (Portuguese)	+13°	70	+51°
P. longifolia (Indian)	+ 2°	70	+51°
P. palustris and *P. caribaea* (American wood)	−18°	70	+52°
P. palustris and *P. caribaea* (American wood)	+ 2°	70	+53°
P. palustris (American)	− 4°	75	+55°
P. caribaea (American)	+16°	70	+55°
P. caribaea (American) (No catalyst—heat alone)	+16°		+ 1°

Catalytic Action on Primary Resin Acids.—Similar findings are to be noted with respect to the primary resin acids, β-pimaric and the sapinic acids, as may be seen from data in Table IV. With regard to α- or dextro-pimaric acid, which has heretofore been regarded as unisomerizable,[8b] the situation is somewhat obscured by the production of a mixture of acids which thus far has resisted separation into isomerically homogeneous compounds. It is interesting to note, however, that even with this very stable acid an isomerizing action by catalytic means does take place.

TABLE IV

ISOMERIZATION OF VARIOUS PRIMARY RESIN ACIDS WITH PALLADIUM–CARBON CATALYST

Sample	Temp., °C.	Acids Yield, %	Acids $[\alpha]^{20}\text{D}$	Acids M. p., °C.
α-Pimaric	250	60	+45°	178–195
α-Pimaric	275	55	+53°	179–192
α-Pimaric	300	40	+49°	184–203
α-Pimaric	250		+54°	173–186
			(recryst.)	232–237
β-Pimaric	250	70	+54°	171–172
"Sapinic acids" $[\alpha]^{20}\text{D}$ −39°	250	75	+55°	166–167

Preparation of α-Pyroabietic Acid from *l*-Abietic Acid.—Twenty-five grams of *l*-abietic acid and 0.5 g. of palladium

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(7) U. S. Patent 2,022,973 (December 3, 1935).

(8) Fanica, *Bull. inst. pin*, (a) 155 (1933); (b) 181 (1933).

(9) Fonrobert and Greth, *Chem. Umschau Fette, Öle, Wachse Harze*, **36**, 93 (1929).

carbon catalyst were heated at 240–245° (inside temperature) for one hour. The product was stirred mechanically. The product was allowed to cool until it solidified, and 100 cc. of alcohol was then added. The reaction mass was heated on the steam-bath until the catalyst was completely in suspension. It was then filtered hot, and the catalyst washed with 25 cc. of hot alcohol. The hot filtrate was diluted with 50 cc. of warm water. Crystallization took place at once, and the mass set to a paste. The cooled mass was filtered with suction, washed with 50 cc. of 50% alcohol, and dried at 80° in vacuum to constant weight. The yield was 23 g. or 92%. This crude product melted at 169–170°. For further purification, it was recrystallized from alcohol or ligroin (b. p. 60–90°). The recrystallized product[10] melted at 171–172°; $[\alpha]^{20}_D$ +55° in absolute alcohol.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.41; H, 10.01. Found: C, 80.00, 80.09; H, 9.61, 9.62.

Speed of Isomerization with Palladium-Carbon.—Twenty-five grams of *l*-abietic acid and 0.5 g. of palladium-carbon catalyst were heated in a 200-cc. three-necked distilling flask equipped with mechanical stirrer, in a bath brought to 250 ± 5°. Samples were then withdrawn at intervals, the isomerized acids extracted in each case with alkali from the ether solution of the reaction products as previously described, and rotations and melting points taken. The point of highest rotation is reached after a heating period of thirty-six minutes from the time the charge attained a temperature of 250°. Within the six minutes required to reach the bath temperature, a very substantial part of the isomerization had already taken place. The reaction was found to be exothermic.

Data from this experiment are shown graphically in Fig. 1 [graph (b)], and some indication of the relative speed of isomerization obtainable with this catalyst, as compared with the usual long heating period without catalyst, may be had from the comparative graphs (a) and (b) of Fig. 1. Graph (b) was plotted from experimental data given in the publication by Dupont and Dubourg.[5]

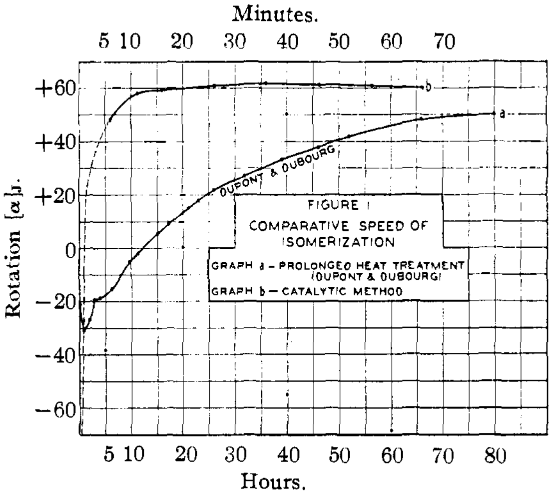

Fig. 1.

In view of the great difference in time factor, graph (a) is shown in terms of hours and graph (b) in terms of minutes.

Summary

A rapid method for the isomerization of resin and rosin acids by catalytic means has been described. Palladium–carbon, platinum–carbon, and certain brands of charcoal have been found effective catalysts, the palladium–carbon, however, being by far the best.

The catalytic method of isomerization has been found to be selective, α-(or dextro-)-pyroabietic acid being formed from the several resin acids and rosins from different sources used.

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[10] Combustion data kindly furnished by W. G. Rose of the Division of Insecticide Investigations, Bureau of Entomology and Plant Quarantine, Department of Agriculture.

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Sterols. XVIII. Preparation of *epi-allo*-Pregnanolone from *allo*-Pregnandiol

BY RUSSELL E. MARKER, OLIVER KAMM AND DAVID M. JONES

Recently we reported the isolation of *epi-allo*-pregnanolone,[1] an androgenic principle from human pregnancy urine, and later its preparation from chloro-*allo*-cholanic acid.[2] We have now prepared this product from *allo*-pregnandiol, obtaining it in good yields. Upon partial acetylation by refluxing a solution of *allo*-pregnandiol in acetic acid with one equivalent of acetic anhydride, the OH group in the 3-position is acetylated, leaving the OH group in the 20-position free. The OH group in the 20-position is then oxidized to a ketone, giving the acetate of *epi-allo*-pregnanolone, which is separated and purified by means of Girard's reagent, its half succinic ester and its semicarbazone.

In the course of this work some other unrelated derivatives of pregnandiol were prepared for biological assays, including the diacetate of preg-

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[1] Marker, Kamm and McGrew, THIS JOURNAL, **59**, 616 (1937).

[2] Marker, Kamm, Jones, Wittle, Oakwood and Crooks, *ibid.*, **59**, 768 (1937).