A solution of this monothioanilide in excess caustic potash did not hydrolyze upon standing in the cold for three days, since upon acidification the original material was recovered unchanged. Upon boiling a solution in excess caustic potash some hydrolysis with formation of aniline occurred but the main product was the potassium salt of the monothioanilide of methylmalonic acid, m. p. 118°. This upon melting gave thiopropionic anilide, m. p. 67°, which further confirmed the structure of the original addition compound.

Summary

1. Whereas the sodium enolates of malonic and cyanoacetic esters combine readily with phenyl isothiocyanate to form approximately 100% yields of the sodium enolates of the corresponding monothioanilides, the sodium enolates of methylmalonic and α-cyanopropionic esters give only very small yields (5–15%) of the simple addition products and the major portion of the reactants is unchanged.

2. A modification of the theory of the mechanism of this addition reaction is consequently necessitated and an explanation is offered.

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The Resin Acids of American Turpentine Gum. The Preparation of the Pimaric Acids from Pinus Palustris[1]

BY S. PALKIN AND T. H. HARRIS

The resin acids of *Pinus maritima*, the principal French gum, have been given considerable study by Vesterberg,[2] Aschan,[3] Dupont[4,5] Ruzicka[6] and others.

The acids of the American gums, *Pinus palustris* and *Pinus carribea*, from which the bulk of the world's supply of rosin and turpentine are obtained, have received less attention.[7,8]

Pinus maritima[5,9] contains two general types of isomeric acids of the empiric formula $C_{20}H_{30}O_2$—the sapinic and the pimaric acids. The sapinic, of which two have been described (α and β), have been estimated by Dupont to represent about 70% of the total acids. These are levorotatory, very susceptible to oxidation, and easily isomerized by heat and

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(1) Presented before the Cellulose Division, Washington Meeting of the American Chemical Society, March 26–31, 1933.

(2) A. Vesterberg, *Ber.*, **18**, 3331 (1885); **19**, 2167 (1886); **20**, 3248 (1887); **38**, 4125 (1905).

(3) O. Aschan, "Naphthen Verbindungen, Terpene und Campherarten," 251–319 (1929).

(4) G. Dupont, *Bull. soc. chim.*, **29**, 718 (1921).

(5) G. Dupont and Douberg, *Bull. Inst. du Pin*, **31**, 581 (1926).

(6) L. Ruzicka, *Bull. Inst. du Pin*, **59**, 112 (1929).

(7) A. W. Schorger, *Trans. Wisconsin Acad. Sci.*, **19**, 728 (1919).

(8) Fr. Balas, "Casopis Ceskoslovenskeho Lekarnictva," **7**, 320 (1927); *Chem. Zentr.*, **100**, 2530 (1929).

(9) P. Klason and J. Köhler, *J. prakt. Chem.*, **73**, 337 (1904).

mineral acids to abietic acid, and they do not form crystalline salts. The pimaric, of which two also have been prepared, one levo (β) and the other dextro-(α)-rotatory, do possess the property of forming crystalline salts, a property which has thus far served as the principal means for their isolation from the complex acid mixture.

While the actual steps involved in the preparation of the resin acids are relatively simple, their isolation in a reasonable state of purity is rendered exceedingly difficult by a number of factors including the physical character of the gum, close similarity of their properties, their instability, and their great tendency to form isomorphous crystals.

Considerable advance in the methods of preparation was made by Dupont,[4] and later by Ruzicka and Balas,[10] and by Aschan,[3] over those of the earlier investigators. But even their improved procedures when applied to *Pinus palustris* were found to lead to certain difficulties, indicating the need for a more dependable working scheme in which greater flexibility of method as applied to acid mixtures of varying composition is provided.

By extending the observations of Ruzicka, data on the behavior of the sodium salts on fractional crystallization under certain conditions of temperature, concentration and alkalinity have been worked out. These data, together with an improved technique for obtaining the original crude acids and for liberating the acids from the sodium salts, have made possible a more expeditious separation of the pimaric and the sapinic, and the α- and β-pimaric acids from one another, than by previous means.

As shown in this paper, levo-pimaric acid from *Pinus palustris* agrees well in properties with that derived from *P. maritima*, but dextro-pimaric acid from the two sources differs markedly in rotation and melting point.[11]

The *P. palustris* gum was found to contain appreciable quantities of the two pimaric acids.

Their relative proportions, as indicated by calculations from the rotation of the mixture, was about two parts of levo to one part of dextro, a ratio similar to that observed in the French gum.[5]

Experimental Part

Treatment of the "Galipot."—The thick sirupy character of the gum turpentine medium, containing the settled crystalline acids or so-called "galipot," renders the ordinary laboratory filtration apparatus and processes inapplicable. Since the task of removing the crystalline mass from this medium is in this case attended with such extraordinary difficulties and constitutes an unavoidable step in the preparation of initial mixed acids, a convenient device providing a large filtering surface is here shown in detail in Fig. 1. A small quantity of turpentine gum spread evenly over the surface of the cloth before suction is applied will serve to seal the rim and the hood. The "galipot" mass is distributed evenly over the filter cloth in a layer about 5 cm. thick, and

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[10] L. Ruzicka, Fr. Balas, and Fr. Vilim, *Helv. Chim. Acta*, **7**, 458 (1924).

[11] The latter, unless that from *P. palustris* is found to be a new isomer, has been prepared by this means in a higher state of purity than hitherto obtained from any other source, or by other means.

smoothed over with a wide spatula to insure uniform suction. Where the crystalline "galipot" is relatively coarse, the filtration proceeds rapidly. The product obtained is relatively dry to the touch.

Preparation of the Mixed Acids.—Two extractions of the filtered product with 80% alcohol, and one crystallization from 95% alcohol, were found adequate to provide white crystalline pimaric acids in sufficient concentration to give a crystalline ammonium salt.[12]

The white crystalline acids yielded a pearly mass of sodium salts in one crystallization, as described later.[13]

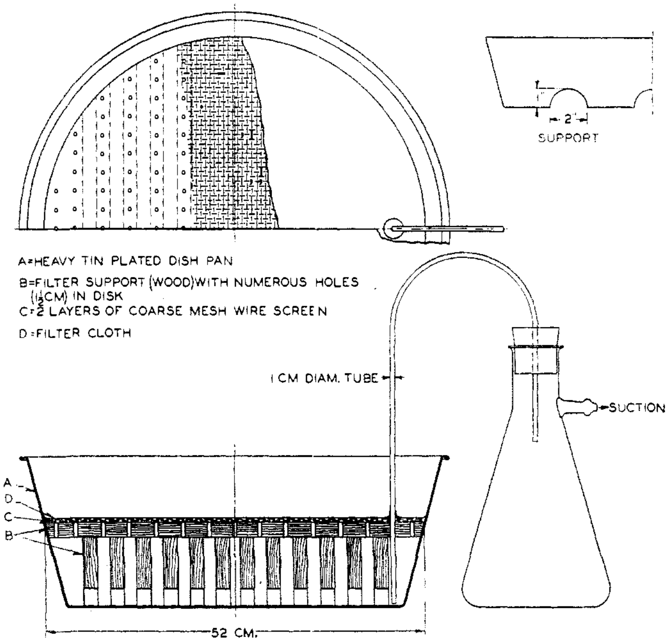

Fig. 1.—Large filter.

The extractions with the 80% alcohol were carried out at room temperature, 500 cc. per kilogram being used each time. The "galipot" acids were thoroughly disintegrated in these two extractions and filtered by suction.

The acids so obtained (containing also chips, bark, etc.) were then crystallized once from 95% alcohol, the alcohol being warmed 50° to effect the solution. This was carried out in several stages, treating with the alcohol, filtering by suction and re-treating the residue each time with fresh alcohol to bring it into solution with a minimum of solvent. About one liter per kilogram of acids was required. The chips, bark, etc., were thus eliminated in this step.

Preparation of Crystalline Sodium Salt.—The resulting white crystalline acids were converted to the salt with warm *N*/2 sodium hydroxide (not over 50°). After cooling somewhat, the soap was precipitated with an excess of alkali (using 2 or 3 normal)

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(12) Unless the sapinic acids have been sufficiently removed, the ammonium salt test cannot be obtained and subsequent preparation of the crystalline sodium salt is much more difficult.

(13) This preparatory treatment of the acid may be compared with the ten treatments of the pressed "galipot" found necessary by Dupont as follows: four extractions with 75% alcohol; one crystallization from 75% alcohol; three crystallizations from 80% alcohol; two crystallizations from 95% alcohol.

more or less as described by Dupont[5] in connection with the preparation of sapinic acids. The soap was either centrifuged or filtered by suction, a filter cloth disk being used instead of paper. The resulting white soap, thus freed from oxidation products, was redissolved in a minimum quantity of warm water (about 50°), diluted with about one-half the volume of additional water and allowed to crystallize in cold storage (about 0°) for twenty-four hours. The mass of pearly crystalline pimaric acids thus obtained was either centrifuged or filtered by suction.[14]

12.03 Kilograms of "galipot" yielded in this manner 2375 g. of crystalline sodium salt having a rotation $[\alpha]_D$ $-173°$ in terms of its corresponding acids. In another experiment 6.78 kilograms yielded 1265 g. having a rotation $[\alpha]_D$ $-164.6°$ in terms of its acids. Assuming the pure acids to have the specific rotations $[\alpha] = -279°$, and $+73°$, respectively, their relative proportions would be about 71% levo and 29% dextro in the first instance, and 68% levo and 32% dextro in the second.

Separation of Levo from Dextro Pimaric Acid.—In the following scheme for the separation of the respective pimaric acids, due consideration is given to the composition of the acid mixtures or fractions in question, rotation being the criterion as to the applicability of any particular method used. Actual composition of any given fraction (assuming only the two compounds dextro and levo pimaric acid present) may be calculated from Biot relationship as follows: $Px(\mathrm{LR}) + (1-P)x(\mathrm{DR}) = \mathrm{OR}$ where P is % levo pimaric acid; LR is specific rotation of pure levo pimaric acid; $1-P$ is % dextro pimaric acid; DR is specific rotation of pure dextro pimaric acid; OR is observed rotation of mixture.

Two general procedures were found useful for effecting a concentration of the respective acids: (1) one leading in a few steps to levo pimaric acid and applicable to pimaric acid mixtures having a rotation of $-160°$ or above. This was found more convenient and effective than fractionation from acetone as described by Ruzicka, *et al.*[10] The resin acids were liberated (quantitatively) from the sodium salts in an alcoholic solution in the cold with an equivalent of acetic acid in alcohol. (2) Another procedure leads more or less rapidly to dextro pimaric acid and is applicable to pimaric acid mixtures having rotations below $-160°$. In this method the sodium salts were subjected to a systematic crystallization in a manner similar to that described by Ruzicka,[10] modified to include fractionating advantages incident to low temperature and alkalinity. This scheme was found particularly useful for acid mixtures in which fractionation of the free acids from organic solvents was ineffective.

Method 1.—The sodium salt was dissolved in warm alcohol (about 45°), filtered by suction (paper washed with alcohol) and brought to a concentration (in a volumetric flask) of not more than 500 g. per liter. The calculated equivalent of 2 N acetic acid in alcoholic solution (using 3 or 4 cc. excess), ice cooled, was added to the previously cooled solution of sodium salt. This quantity was calculated from analytical determination of an aliquot. Crystallization (aided by stirring) soon took place. The acid filtered by suction was washed with a little ice cold 75% alcohol, and finally with water to remove all traces of acetic acid. Successive crops were obtained by progressive dilution with water. The yields and rotations of the acids so obtained are shown in Table I.

Method 2. Systematic Fractional Crystallization of the Sodium Salts.—The sodium salts were dissolved in warm water (about 50°) and diluted with cool water, the dilution depending upon the relative proportions of the respective acids as determined by the rotations of the fractions treated. In these experiments the temperature was generally not allowed to go above 50° to avoid isomerization.[5]

The progress of the fractional crystallization is indicated in the diagram (Fig. 2A). The approximate dilutions (volume of water per gram of sodium salt) are shown on the continuous lines of the chart. Except as indicated three fractions were generally ob-

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[14] In some instances repetition of this step may be desirable.

TABLE I

RESULTS OBTAINED WITH METHOD 1

Sodium salt taken Fraction No.[a]	$[\alpha]$[b]	Crop	Free acid obtained by direct neutralization $[\alpha]$	Yield, g.
256 EFC	−277	1st	−244.3°	255
172 EFCD	−215			
60 CCD	−208			
25 EFC	−215	2d	−142	60
		3d		5
75 ED	−247	1st	−268.6	27
		2d	−228.7	5
		1st	−219	135
565 G	−173	2d	−121	155
		3d	−132	30
		1st	−251	85
500 G[c]	−175	2d	−156	180
		3d	−142	40

[a] Numerical portions of fraction numbers also represent weights of fractions. [b] Spec. rotation in terms of the corresponding acid. [c] Used *N* acetic instead of 2 *N* acetic acid for neutralization.

tained, (1) at room temperature, (2) by cooling, (3) by the slow addition of alkali (about 5 *N*) until precipitation was fairly complete. These crops are indicated by the designations "r. t.", "ice," "alk.," respectively. The numerical part of the experiment numbers (just preceding the letters), represents the approximate weights of the respective fractions. Specific rotations are given directly below each experiment number. Various fractions, whose rotations were not markedly different, were combined in the usual way for further fractionation, such combinations being indicated by dotted lines connecting them. In order to render the diagram less confusing, some of the intermediate fractions are not shown.

Rotations of the various crops of sodium salt are given in terms of their corresponding acids. These we determined as follows. A weighed quantity of sodium salt (1 or 2 g.) was dissolved in a minimum quantity of alcohol and to this solution (ice cooled) was added slightly more than an equivalent of a cool alcoholic solution of 2 *N* acetic acid. (Approximately 1.2 cc. to 1.4 cc. of 2 *N* acetic acid per gram of sodium solution is generally sufficient.) A fine granular crystalline precipitate formed on stirring. Cool water was then added, drop by drop, with stirring, to effect a complete precipitation. This product, after filtration by suction and washing with water, was dried in the air and then in vacuum (at 45°). The specific rotation was generally made on a 1% alcoholic solution in a 2-decimeter tube.

This procedure was generally preferred to the liberation of the acids by way of carbon dioxide, as the latter, even when heated to 60° during precipitation, as suggested by Ruzicka, were frequently found to filter poorly.

There was virtually no isomerization by the acetic acid under the special conditions described above, as may be seen by the following determinations (Table II).

TABLE II

Experiment		1	2	3
Acids liberated with	AcOH $[\alpha]_D$	−207°	−286°	−251°
	CO_2 $[\alpha]_D$	−205°	−286°	−250°

In Experiment 3 an excess of acetic acid, over 60% more than the required equivalent, was used without any apparent isomerization.

Enrichment of the sodium salts in terms of dextro pimaric acid proceeds fairly rapidly with fractions of rotation below −100°, as may be seen from fractions $158C_{400}$, 80CCD and 92CCD, etc. (Fig. 2A).

High concentration of dextro acid tended markedly to hydrolyze. Gradual addition of a small quantity of $N/2$ alkali to the suspension in the hot water generally cleared the solution. The progress of the purification of the levo and dextro acids may be seen from the diagram in Fig. 2B.

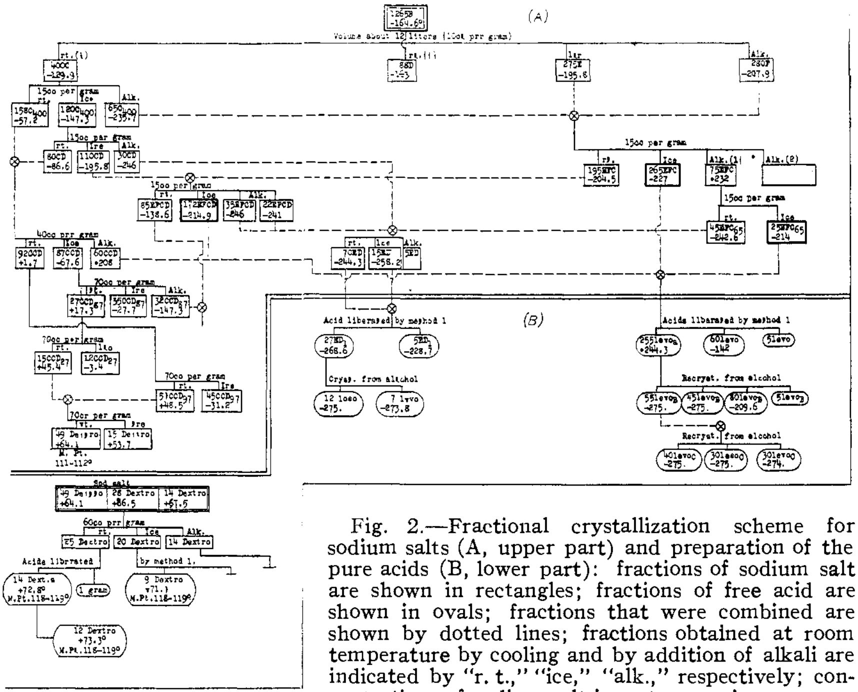

Fig. 2.—Fractional crystallization scheme for sodium salts (A, upper part) and preparation of the pure acids (B, lower part): fractions of sodium salt are shown in rectangles; fractions of free acid are shown in ovals; fractions that were combined are shown by dotted lines; fractions obtained at room temperature by cooling and by addition of alkali are indicated by "r. t.," "ice," "alk.," respectively; concentrations of sodium salt in water are given on continuous lines; numerical part (to left) of experiment numbers indicates approximate weights of fractions; specific rotation given for each fraction.

The properties of the purified levo and dextro pimaric acids obtained from longleaf pine (*Pinus palustris*) are given in Table III.

Catalytic Hydrogenation

Dihydro-levo-pimaric Acid.—Ten grams of the pure levo-pimaric acid in 85 cc. of ethyl acetate with 0.5 g. of palladium–barium sulfate catalysts,[15] absorbed 820 cc. of hydrogen in a total of two and one-half hours, 800 cc. having been absorbed in the first half hour. (Calculated volume for the dihydro compound is approximately 810 cc.)

The hydrogenated product, after removal of the catalyst and solvent, was crystallized several times from diluted alcohol (85%) as described by Ruzicka, Balas and Vilim.[10] Several isomers were apparently formed as reported by these authors, of which only one was obtained in pure form, as indicated by constancy of the melting point (m. p. 144–146°).

Dihydro-dextro-pimaric Acid.—Four grams of dextro-pimaric acid in 110 cc. of

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[15] Houben–Weyl, 2d ed., p. 500.

TABLE III

COMPARISON OF PROPERTIES OF THE PIMARIC ACIDS

Acid prepd. by		Levo pimaric acid			Dextro pimaric acid		
Balas[8]		150°			213°		
		$[\alpha]_D$	−280.4	(1.5% alcohol)		$[\alpha]_D$ + 79.3°	(0.57% alc.)
	M. p., °C.[a]	148–151			211		
Ruzicka[9]	Rotation	$[\alpha]^{17}_D$ (in 2% abs. alcohol)	−279.2°			$[\alpha]^{18}_D$ + 57°	0.48% abs. alc.
		$[\alpha]^{19}_D$ (In 5% $CHCl_3$)	−266.6			$[\alpha]^{19}_D$ + 59.7°	2.9% abs. alc.
						$[\alpha]^{17}_D$ + 74.7°	(5% $CHCl_3$)
	M. p., °C.	150–152			211–212		
Dupont[4]	Rotation	$[\alpha]_J$	−282.4°			$[\alpha]_J$ + 63.5°	
	M. p., °C.	150–152			218–219		
Palkin	Rotation	$[\alpha]^{20}_D$	−274.5°	In abs. alc. 2 g. per 100 cc.		$[\alpha]^{20}_D$ + 73.3°	In abs. alc. 2 g. per 100 cc.
		$[\alpha]^{20}_J$	−290.7°			$[\alpha]^{20}_J$ + 77°	
		$[\alpha]^{20}_D$	−258.5°	In $CHCl_3$ 5 g. per 100 cc.		$[\alpha]^{20}_D$ + 87.3°	In $CHCl_3$ 5 g. per 100 cc.
		$[\alpha]^{20}_J$	−273°			$[\alpha]^{20}_J$ + 91.8°	
Cryst. examination[b]	Crystal form	Colorless rods and plates				Colorless rods and plates	
	Refr. index.	α = 1.537; β = 1.588; γ = 1.620				α = 1.556; β = 1.564; γ = 1.606	

[a] Levo pimaric acid isomerizes rapidly as the melting temperature is approached. Softening takes place before substance melts to an oil. Ruzicka and Frank,[16] prepared a dextro pimaric acid, melting at 215°, by way of the dihydromethyl ester. No rotation for this is given.

[b] The crystallographic data were furnished by G. L. Keenan of the Food and Drug Administration.

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(16) L. Ruzicka and M. W. Frank, *Helv. Chim. Acta*, **15**, 1925 (1932).

ethyl acetate with 0.1 g. of palladium-barium sulfate catalysts (warmed somewhat), absorbed a total of 340 cc. of hydrogen in five hours, 270 cc. having been absorbed in the first two hours (calculated volume for dihydro compound, 325 cc.).

The reaction product after removal of the catalyst and solvent was recrystallized from ether to a constant melting point which was over 10° higher than that reported by Ruzicka and Balas[17] (m. p. 249–250°).

Anal.[18] Calcd.: C, 78.88; H, 10.60. Found: C, 78.87; H, 10.63.

The authors wish to express their appreciation to Mr. R. R. Long, of Atmore, Ala., for his coöperation in furnishing the turpentine gum.

Summary

An investigation of the pimaric acids in *P. palustris*, an improved systematic procedure for their preparation from the "gum," as well as the preparation of catalytic hydrogenation products of these acids are described.

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[17] L. Ruzicka and Fr. Balas, *Helv. Chim. Acta*, **6**, 677 (1923).

[18] These analytical data were kindly determined by J. R. Spies, Department of Chemistry, University of Maryland.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Carbon Syntheses with Malonic and Related Acids. I

BY ARTHUR MICHAEL AND JOHN ROSS

In 1879[1] it was shown that mixtures containing benzoic, or cuminic, aldehyde with phenylacetic acid and sodium acetate heated in sealed tubes gave stilbene, or propylstilbene, evidently by loss of carbon dioxide from the first-formed cinnamic acid derivatives. Subsequently,[2] this modification of the Perkin synthesis, using an acid instead of an acid anhydride, was extended to malonic acid, when, with benzoic aldehyde, cinnamic acid was obtained without use of acetate. This synthesis was not extended, as, simultaneously, Claisen and Crismer[3] found that benzalmalonic acid was formed on heating malonic acid with benzoic aldehyde in acetic acid solution, with or without acetic anhydride, and Komenos[4] that replacement of aromatic by fatty aldehydes led to the formation of aliphatic α,β,Δ-dibasic acids, or corresponding monobasic acids through loss of carbon dioxide. A large literature now exists on the use of malonic acid for the preparation of mono- and dibasic α,β,Δ-acids.[5]

Komenos[4] was unable to condense malonic acid with acetone, using acetic anhydride, but Meldrum[6] observed that addition of a little sulfuric acid

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[1] Michael, *Am. Chem. J.*, **1**, 312 (1879).

[2] *Ibid.*, **5**, 14 (1883).

[3] Claisen and Crismer, *Ann.*, **218**, 135 (1883).

[4] Komenos, *ibid.*, 149 (1883).

[5] Beilstein, Vol. II, p. 245; Suppl., Vol. II, p. 235 (1920). Thirty researches are listed. Knövenagel used pyridine instead of acetic acid and anhydride to induce the reaction.

[6] Meldrum, *J. Chem. Soc.*, **93**, 605 (1908).