[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

An Investigation of Certain Sapinic Acids Obtained from Various Species of Pine and Spruce

BY TORSTEN HASSELSTROM AND MARSTON TAYLOR BOGERT[1]

It has been observed frequently[2] that when the solid portion of the oleoresins of pine and spruce is subjected to fractional crystallization from anhydrous solvents at temperatures below 60°, there are obtained the so-called sapinic acids. These are resin acids of the molecular formula $C_{20}H_{30}O_2$, with melting points in the neighborhood of 142–144°, which are very sensitive to oxidation, and easily isomerized by heat or by mineral acids to an abietic acid.[2e,g,h,3]

In optical rotation, they vary greatly, not only as between different tree species, but even in the case of different trees of the same species (see Table I).

This labile acid, however, is not the true optical antipode of the well-known *d*-pimaric acid. In fact, the real *l*-pimaric acid apparently has not yet been described. It has for some time been the approved usage of investigators in the resin acid field, to classify as "pimaric" acids only those resin acids which yield pimanthrene when fused with sulfur or selenium; and as "abietic" acids, those which when similarly treated give retene.

Since this so-called "*levo*-pimaric" acid yields retene when fused with sulfur,[4b] it belongs to the abietic and not to the pimaric class of resin acids. The name "*levo*-pimaric," originally given to it by Vesterberg,[8] therefore should be replaced by one more in agreement with our present knowledge, and we suggest in its place the designation "*l*-sapietic" acid. This name we have coined to recall its occurrence in the original sapinic acids of the gum and its belonging to the abietic group.

TABLE I

The optical rotations on the crude gums were determined upon selected samples carefully dried between filter papers.

Oleoresin	$[\alpha]_D$	Sapinic acid, m. p., °C.	$[\alpha]$	Calculated composition of the sapinic acids: $[\alpha]_D$ +79.3 *d*-Pimaric acid	$[\alpha]_D$ −280.4 *l*-Sapietic acid	Reference
Pinus palustris	−131.0	142–144.5	− 22.36	71.7	28.3	This paper
Pinus caribbea	− 31.96	142–144.5	− 47.01	64.9	35.1	This paper
Pinus taeda	− 74.50	141–143.5	− 69.38	58.8	41.2	This paper
Pinus serotina	− 56.42	142–143.5	−112.11	46.8	53.2	This paper
Pinus silvestris	.....	142–144	−105.3	49.0	51.0	Leskiewicz[2b]
Pinus silvestris	− 40.14	148.5–150.5	− 46.88	64.9	35.1	This paper
Pinus densiflora	.....	141	− 63.1	61.4	39.6	Suzuki[2d]
Picea excelsa	−126.6	137–139	− 35.2	68.2	31.8	Aschan[2f]
Picea excelsa	−111.5	140–144.5	− 93.33	48.0	52.0	This paper
Picea excelsa	−238	138–151	−278	1.0	99.0	Köhler[2c]
Picea excelsa	.....	142–143	−101.97	49.6	50.4	Nordström[3]

The sapinic acids of *Pinus maritima*,[4] and of *Pinus Palustris*,[5] have been separated into *d*-pimaric and "*levo*-pimaric" acids. The former is stable;[6] whereas the latter is quite unstable, for it is easily oxidized, and is isomerized by heat or by mineral acids to abietic acids.[2c,3,4a,7]

The crystals found by Köhler[2c] between the sapwood and the bark of *Picea excelsa* and which, therefore, had not been exposed to light and air, were probably fairly pure *l*-sapietic acid, containing relatively small amounts of *d*-pimaric acid. Köhler recorded their rotation as $[\alpha]^{20}_D$ −238° and, after four recrystallizations from methanol, as $[\alpha]^{20}_D$ −278°. Subsequent investigators have reported the rotation of the pure acid as $[\alpha]^{17}_D$ −279.4,[4b] −280.4,[9] and −274.5°.[5] Assuming

(1) Presented in abstract before the Division of Organic Chemistry at the New York meeting of the American Chemical Society, April 23, 1935.

(2) (a) Klason and Köhler, *J. prakt. Chem.*, [2] **73**, 337 (1904); (b) Leskiewicz, *ibid.*, **81**, 403 (1910); (c) Köhler, *ibid.*, **85**, 534 (1912); (d) Suzuki, *J. Pharm. Japan*, **515**, 49 (1925); (e) Suzuki, *ibid.*, **524**, 888 (1925); (f) Aschan, *Naftenföreningar, Terpener och Kamferarter*, Helsingfors, 367 (1926); (g) Dupont and Dubourg, *Bull. Inst. Pin*, **31**, 581 (1926); (h) Nordström, *J. prakt. Chem.*, [2] **121**, 206 (1929); (i) Vocke, *Ann.*, **508**, 11 (1933).

(3) Nordström, *Finska Kem. Medd.*, No. 4 (1929).

(4) (a) Dupont, *Bull. soc. chim.*, [4] **29**, 718 (1921); (b) Ruzicka, Balaš and Vilim, *Helv. Chim. Acta*, **7**, 458 (1924).

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

(6) (a) Vesterberg, *Ber.*, **18**, 3331 (1885); (b) *ibid.*, **19**, 2167 (1886); (c) *ibid.*, **20**, 3248 (1887); (d) *ibid.*, **38**, 4125 (1905); etc.

(7) (a) Fanica, *Bull. inst. pin.* **44**, 151 (1933); (b) *ibid.*, **45**, 181 (1933).

(8) Vesterberg, "Kemiska studier öfver några hartser," Diss., Upsala, 1890.

(9) Balaš, *Časopis Československeho Lekarnictva*, **7**, 320 (1927).

that the crude crystals contained only *l*-sapietic and *d*-pimaric acids, and taking Balas' figure[9] for the rotation of the latter ($[\alpha]_D$ + 79.3°), their composition as calculated from Biot's relationship,[10] $-280.4x + (1-x)\ 79.3 = -238°$, would be approximately 88.2% of *l*-sapietic and 11.8% of *d*-pimaric acid.

It is the hypothesis of the authors that most of the so-called "sapinic acids" of the oleoresins of conifers are mainly isomorphous mixtures of *l*-sapietic and *d*-pimaric acids, the differences in optical rotation being due to the relative amount of *d*-pimaric present in the unoxidized and unisomerized acid mixture.

All of the sapinic acids examined by us, when hydrogenated in the presence of the Adams platinum oxide catalyst, yielded large quantities of dihydropimaric acid, which was easily isolated by virtue of its sparing solubility in methanol. Our experiments show that this is a satisfactory solvent for accomplishing the separation of a mixture of the dihydropimaric from the dihydroabietic type of acid.

Attempts to isolate dihydrosapietic acid,[4b,5] m. p. 144–146°, from the mother liquors were unsuccessful. There was obtained a low-melting acid mixture containing some dihydropimaric acid. As noted by previous investigators,[4a,5] catalytic hydrogenation even of pure *l*-sapietic acid yields a mixture of isomers difficult to separate.

As Palkin and Harris[5] have shown, and as we ourselves had observed in the course of some experiments carried out a year before the appearance of their paper, *d*-pimaric acid is readily identified by catalytic hydrogenation to its dihydro derivative.

The presence of *l*-sapietic in the original sapinic acid was established by refluxing the latter with glacial acetic acid, as described by Steele,[11] a treatment which isomerizes the *l*-sapietic to abietic, but leaves the *d*-pimaric acid unaltered. The solids obtained from the mother liquors of the abietic acid, when subjected to catalytic hydrogenation, yielded dihydropimaric acid in considerable amount.

It is generally recognized that the "abietic acids" constitute the major portion of ordinary colophony. Our demonstration of the occurrence of *d*-pimaric in the sapinic acids, indicates its presence also in rosins produced by the usual methods.

Acknowledgments.—For samples of oleoresins supplied, our thanks are due especially to Messrs. I. A. von Julin, Fiskars, Finland; William F. Allen, of Dr. Charles H. Herty's laboratory, Savannah, Ga.; and Edward A. Brennan, of the G. & A. Laboratories, Savannah, Ga.

Experimental

Preparation of the Sapinic Acids.—The semi-solid oleoresin, or the press-cake obtained therefrom by expressing, was dissolved in an anhydrous solvent (ethyl acetate), using approximately 1 part gum to 2–3 parts of solvent, at a temperature not exceeding 60°, and filtered from chips, bark, dirt, etc. The filtrate was concentrated to a sirup by evaporation under diminished pressure at a temperature below 60°, since above that temperature the *l*-sapietic acid begins to isomerize. This sirup was seeded with a few selected dry crystals of the sapinic acid obtained directly from the original gum and, on standing for from four to twelve hours, set to a semi-solid crystalline mass which was easily filtered. The crude sapinic acid so obtained was colorless. It was purified by successive crystallization from ethyl acetate, acetone and methanol.

The *Picea excelsa* oleoresin (from Finland) contained considerable oxidation products. These were removed by adding petroleum ether to the viscous ethyl acetate solution of the gum until no more dark colored precipitate separated. The filtrate from this precipitate was concentrated under reduced pressure at a temperature below 60°, and this process of purification was repeated thrice. The final sirup was then seeded and the crude product recrystallized as noted above.

Further details concerning the preparation of these sapinic acids and their properties, are given in Table II.

Hydrogenation of the Sapinic Acids.—To one part of sapinic acid in 20 of ethyl alcohol, there was added one-twentieth to one-tenth of a part of Adams platinum oxide catalyst and the hydrogenation was conducted at room temperature and a pressure of 7–25 lb. per sq. in. When approximately one mole of hydrogen per mole of acid had been absorbed, the hydrogenation was interrupted, the alcoholic solution concentrated to incipient crystallization and let stand for some time at room temperature. The separated solid was removed and crystallized from methanol until the product showed a m. p. of about 240°. Further crystallization to the m. p. of 249–250°, the figure given by Palkin and Harris[5] for pure dihydropimaric acid, was not undertaken since 240–241° has been generally accepted[12] as the m. p. of a practically pure acid.

From the mother liquors, by fractional crystallization, more dihydropimaric acid was recovered, but no constant melting product which could be identified as a dihydrosapietic acid.

The results of these hydrogenation experiments are presented in Table III.

By crystallization of a mixture of the oleoresins of *Pinus palustris* and *P. carribea*, Vocke[21] obtained a levo-

(10) Biot, *Ann. chim. phys.*, [3] **59**, 206 (1860); etc.

(11) Steele, THIS JOURNAL, **44**, 1333 (1912).

(12) Tschugaeff and Tearu, *Ber.*, **46**, 1769 (1913).

TABLE II

SAPINIC ACIDS

	Pinus palustris	*Pinus caribbea*	*Pinus taeda*	*Pinus serotina*	*Pinus silvestris*	*Picea excelsa*
Initial subs.	Crude gum[a]	Crude gum[b]	Press-cake[c]	Press-cake[d]	Crude gum[e]	Crude gum[f]
Its rotation	$[\alpha]^{30}D$ −131	$[\alpha]^{31}D$ −31.96	$[\alpha]^{30}D$ −74.60	$[\alpha]^{27}D$ −56.42	$[\alpha]^{30}D$ 40.14	$[\alpha]^{31}D$ −111.5
Times crystallized	6	8	4	5	7	6
Solvents used	AcOEt, AcMe, MeOH	AcOEt, MeOH, AcMe	AcOEt, AcMe	AcOEt, AcMe	AcOEt, AcMe	AcOEt, AcMe
Oxid. products removed	No	No	No	No	No	Yes
Yield sapinic acid, 1st crystallization, g.	190	130	130	120	25	15
M. p. after 2d crystallization, °C.	137.5–139.5	134–137	139–141	134–137	135.5–137.5	134.5–137.5
M. p. after final crystallization (corr.), °C.	142–144.5	142–144.5	141.5–144	142–144	148.5–150.5	140–144.5
Final yield, g.	2	3	22	12	3.5	1.5
Final rotation	$[\alpha]^{33}D$ −22.36	$[\alpha]^{33}D$ −47.01	$[\alpha]^{30}D$ −69.38	$[\alpha]^{27}D$ −112.11	$[\alpha]D^{31}$ −46.88	$[\alpha]^{33}D$ −93.33
M. p. of solids from mother-liquor (corr.), °C.	140.5–142.5		140.5–142.5	139.5–143.5		
Their rotation	$[\alpha]^{33}D$ −31.08		$[\alpha]^{30}D$ −59.94	$[\alpha]^{27}D$ −92.37		

[a] From E. A. Brennan, Savannah, Ga.; May, 1932 = 400 g. [b] From E. A. Brennan, Savannah, Ga.; May, 1932 = 312 g. [c] From William F. Allen, Savannah, Ga.; Dec., 1934 = 320 g. [d] From William F. Allen, Savannah, Ga.; Dec., 1934, = 190 g. [e] From I. A. von Julin, Fiskars, Finland; July, 1932 = 50 g. [f] From I. A. von Julin, Fiskars, Finland; July, 1932 = 112 g.

TABLE III

HYDROGENATION OF SAPINIC ACIDS

	Pinus palustris	*Pinus caribbea*	*Pinus taeda*	*Picea serotina*	*Pinus silvestris*	*Picea excelsa*	Tschugaeff and Tearu[12]	Ruzicka and Balaš[14]	Palkin and Harris[6]
Initial subs., g.	5	5	10	10	3	1.5			
Yield crude acid m. p. <200°, g.	2.79	2.2	3.5	4.5	1.5	0.6			
M. p. (corr.) of dihydropimaric acid, °C.	241–242.5	241–242	241.5–242.5	239–241	239–240	198–203[a]	240–241	239–240	249–250
Rotation of acid	$[\alpha]^{32}D$	$[\alpha]^{33}D$	$[\alpha]^{29}D$	$[\alpha]^{29}D$	$[\alpha]^{33}D$		$[\alpha]D$	$[\alpha]D$	
M. p. <215°	+18.78	+14.01	+12.42	+19.98	+22.93		+19.43	+14.5	
Calcd. for $C_{20}H_{32}O_2$ %C = 78.88	78.57	78.91			78.66	78.30	78.74	79.05	78.87
Calcd. for $C_{20}H_{32}O_2$ %H = 10.60	10.82	10.87			9.77	10.68	10.60	10.68	10.63
Dihydropimaric acid recovered from mother liquors	Yes	Yes	Not examined	Not examined	Yes	Not examined			

[a] The quantity of material available was insufficient for further recrystallization, but the presence of dihydropimaric acid seems evident from the analysis and from the fact that no dihydroabietic acid is known with a m. p. above 175°.[2e,2f,2g,5,13]

rotatory sapinic acid, m. p. 143°, which, on hydrogenation, yielded a dihydro acid. This latter was purified by crystallization from ethyl alcohol, in which it was but slightly soluble, and then melted at 195°. On further hydrogenation, there was obtained a tetrahydro acid (m. p. 173°, not sharp) which he assumed to be of abietic type. It is our belief that if Vocke had used methyl instead of ethyl alcohol for the purification of his dihydro acid, he would have discovered the presence therein of dihydropimaric acid.

Formation of Steele's Abietic Acid from Sapinic Acids.—A mixture of 10 g. of the sapinic acid with 10 cc. of glacial acetic acid was refluxed for four hours, then allowed to cool and left overnight at room temperature. The abietic acid which separated was purified by crystallization from alcohol.

The original acetic acid mother liquor was poured into water and the precipitated resin acid mixture removed and hydrogenated catalytically in alcoholic solution as described above. Dihydropimaric acid was thus secured, the mother liquors from which contained a low melting dihydro acid, which could not be obtained of constant melting point and was not identified. It may have been the dihydro Steele abietic acid described beyond.

The results of these experiments are given in Table IV.

TABLE IV

ACTION OF GLACIAL ACETIC ACID UPON SAPINIC ACIDS

Steele's abietic acid (m. p. 161–165°, $[\alpha]D$ −80°)	*Pinus taeda*	*Pinus serotina*
Yield of crude acid, g.	4.5	4.8
M. p. of purified acid, °C.	163.5–165.5	163.5–165.5
$[\alpha]_D$	−79.89	−87.3
Hydrogenation of solids from mother liquor		
Total solids, g.	5.5	4.2
Yield of dihydropimaric acid m. <200°, g.	1.5	1.2
M. p. (corr.) of purified dihydropimaric acid, °C.	238.5–240.5	240.5–242.5
$[\alpha]_D$	$[\alpha]^{27}D$ +18.67	$[\alpha]^{29}D$ + 12.50

Hydrogenation of Steele's Abietic Acid.—Steele's abietic acid was prepared from the press-cake from sulfate "black liquor" tall oil[15] and the crude product was crystallized fifteen times from methanol, acetone and ethyl acetate. After eleven crystallizations, the melting point remained constant at 164.5–165.5°; $[\alpha]^{32}D$ −53.9°.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 79.41; H, 10.01. Found: C, 79.25; H, 10.03.

(13) (a) Johansson, *Arkiv f. kemi*, **6**, 19, 20 (1917); (b) Ruzicka and Meyer, *Helv. Chim. Acta*, **5**, 324 (1922).

(14) Ruzicka and Balaš, *Helv. Chim. Acta*, **6**, 677 (1923).

(15) Hasselstrom, U. S. Patent 1,986,817 (1934).

A solution of 3 g. of this acid in 50 cc. of alcohol was hydrogenated catalytically as described for the sapinic acids, interrupting the operation when one mole of hydrogen had been added (ten minutes). The product was worked up in the usual way, as in the case of the hydrogenated sapinic acids. The crude solid acid was crystallized first from methanol and then from acetone, six times in all. It formed colorless needles, m. p. about 154.5–157° (corr.), $[\alpha]^{32}_{D}$ +17.54°.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.60. Found: C, 78.46; H, 10.50.

In view of the unsatisfactory melting point, it is unlikely that this is the pure dihydro derivative of Steele's abietic acid. More probably, it is a mixture of isomers.

Summary

1. The sapinic acids of *Pinus palustris, P. caribbea, P. taeda, P. serotina, P. silvestris* and *Picea excelsa*, consist chiefly of a mixture of *d*-pimaric and *l*-sapietic acids. This is in accord with the findings of Palkin and Harris[5] in the case of *P. palustris* and of Dupont,[4a] and Ruzicka, Balaš and Vilim[4b] for *P. maritima*.

2. The presence of the former is proved by the formation of dihydropimaric acid when the sapinic acids are hydrogenated catalytically; and, of the latter, by the fact that, when refluxed with glacial acetic acid, the sapinic acids yield Steele's abietic acid as one of the products.

3. The stability of *d*-pimaric acid and its existence in the sapinic acids explains its presence in ordinary colophony.[16]

(16) (a) Rimbach, *Ber. pharm. Ges.*, **6**, 61 (1896); (b) Hosking and McFadyen, *J. Soc. Chem. Ind.*, **53**, 195T (1934).

NEW YORK, N. Y. RECEIVED JUNE 11, 1935

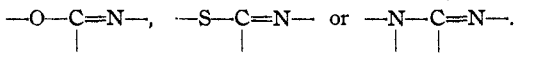
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

The Synthesis of Certain Phenylated Benzoxazoles and Derivatives[1]

BY VLADIMIR J. MIKESKA AND MARSTON TAYLOR BOGERT

The investigations of thiazole compounds conducted in these laboratories, especially on the connection between chemical constitution and tinctorial properties,[2] have made it seem worth while to carry out some similar studies in the closely related oxazole series.

The structural similarity between the oxazoles, thiazoles and imidazoles is paralleled by a close resemblance in methods of preparation and in properties of analogous compounds in the three series. Thus, in the basicity of their salts, the fluorescence of their solutions,[3] and odors, they are much alike. Auwers and Ernst,[4] who examined a large number of analogous compounds in the three groups in the helium region of the spectrum at 20°, found that their dispersion spectra corresponded closely, and that it seemed to make but little difference in the spectrum whether the grouping present in the cycle was



In all three series, the monocyclic types are most easily hydrolyzed, then the aliphatic 2-R derivatives of the benzo (dicyclic) type, the most stable derivatives being the 2-aryl compounds, like 2-phenylbenzoxazole. Of the three series, the oxazoles are most easily hydrolyzed,[5] even methylation breaking open the ring when 2-methylbenzoxazole is heated with methyl iodide.[6]

Clark[7] has carried out some interesting experiments on the opening of the cycle by the action of potassium hydroxide upon the methiodide.

Böttcher[8] was unable to effect ring closure by reduction of $CH_3COOC_6H_4NO_2$-(*o*), although this was accomplished easily by reduction of either $C_6H_5COOC_6H_4NO_2$-(*o*) (2) or $C_6H_5COOC_{10}H_6NO_2$ (3).

For our attack upon the problem, the 2-R-5-phenyl and 2-R-7-phenylbenzoxazoles were used, because of the availability of the important industrial by-products *p*- and *o*-hydroxy diphenyls, from which they are easily synthesized. These syntheses are recorded in the present paper. The production of dyes from the phenylated benzoxazoles so obtained and a discussion of the tinctorial properties of these dyes, will form the subject of another communication.

(1) Based upon the dissertation submitted by V. J. Mikeska, June, 1934, for the Ph.D. degree under the Faculty of Pure Science, Columbia University, New York, N. Y., to which dissertation the reader is referred for further experimental details and literature citations.—M. T. B.

(2) (a) Bogert and Bergeim, *Color Trade J.*, **15**, 63 (1924); (b) Bogert and Chertcoff, THIS JOURNAL, **46**, 2864 (1924); (c) Bogert and Allen, *Ind. Eng. Chem.*, **18**, 582 (1926); (d) Bogert and Allen, THIS JOURNAL, **49**, 1315 (1927).

(3) Henrich, *Ber.*, **54**, 2492 (1921).

(4) Auwers and Ernst, *Z. physik. Chem.*, **122**, 217 (1926).

(5) Skraup, *Ann.*, **419**, 33 (1919).

(6) Fischer, *J. prakt. Chem.*, [2] **73**, 436 (1906).

(7) Clark, *J. Chem. Soc.*, **129**, 232 (1926).

(8) Böttcher, *Ber.*, **16**, 629, 1933 (1883).