sodium hypobromite (1.7 g. of sodium hydroxide, 2 g. of bromine in 23 ml. of water) for two hours. The excess sodium hypobromite was decomposed with a small amount of sodium bisulfite. After removing the neutral fraction containing bromoform, the alkaline solution was acidified with sulfuric acid and an acid fraction was extracted with ether. The major portion (0.39 g.) distilled at 0.1 mm. and a bath temperature of 190-200°.

Anal. Fr. b. p. (0.1 mm.) 190-200° after redist.: calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44 (dicarboxylic acid). Found: C, 64.34; H, 9.52.

Reaction of Dicarboxylic Acid with Acetic Anhydride.[5]—A mixture of 0.3 g. of dicarboxylic acid obtained from fraction b. p. (0.1 mm.) 190-200° and 0.5-0.7 ml. of acetic anhydride was heated in a sealed tube for half an hour at 240° (bath temperature).

After removal of the acetic anhydride, the reaction mixture was distilled under high vacuum. A fraction of approximately 50 mg. which distilled at 0.01 mm. pressure and a bath temperature of 200-210° was obtained.

Anal. Calcd. for $C_{14}H_{24}O_4$ (acid): C, 65.60; H, 9.44. For $C_{14}H_{22}O_3$ (anhydride): C, 70.55; H, 9.30. For $C_{13}H_{20}O$ (ketone): C, 80.35; H, 11.41. Found: C, 68.17; H, 9.17.

Acknowledgment.—The authors appreciate the coöperation and interest of Dr. A. C. Hildreth, Dr. H. Trent and Dr. J. Kirchner during the course of this work.

Summary

The structure of partheniol, a sesquiterpene alcohol isolated from guayule, *Parthenium argentatum, Gray*, has been determined.

PASADENA, CALIFORNIA RECEIVED DECEMBER 22, 1947

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

Resin Acids. III. The Isolation of Dextropimaric Acid and a New Pimaric-type[1] Acid, Isodextropimaric Acid

BY GEORGE C. HARRIS AND THOMAS F. SANDERSON

The history of the discovery and isolation of dextropimaric[2] acid parallels that of levopimaric[2] acid by virtue of one property common to both acids, namely, the insolubility of their crystalline sodium salts. In other physical and chemical properties, they are significantly different. Dextropimaric acid is not susceptible to oxidation by air or isomerization by heat or dilute mineral acid, whereas levopimaric acid is relatively sensitive to both changes.

Previous methods of isolation of dextropimaric acid depended on fractional crystallization as its insoluble sodium salt from mixtures of resin acids such as "galipot"[3] or on recrystallization after oxidation of the more susceptible acids.[4] We have obtained a fraction containing dextropimaric acid and related acids by removal of the two-double-bond abietic-type acids by reaction with maleic anhydride after acid isomerization. The unreacted acids were separated from the maleic anhydride adduct by precipitation from aqueous alkaline solution by adjustment of the *p*H to 6.2.[5] Ultraviolet absorption spectra showed the absence of two-double-bond abietic-type acids in this fraction.

Further fractionation of this mixture has not only given relatively large amounts of dextropimaric acid but also yielded a new pimaric-type acid. When this resin acid fraction was dissolved in acetone and treated with butanolamine, an insoluble salt was obtained and recrystallized to constant rotation $[\alpha]^{20}\text{D}$ 0°. When the salt was decomposed with mineral acid, the resin acid was obtained which was crystallized first from alcohol and water as thin plates and finally as needles after standing in the mother liquor; $[\alpha]^{24}\text{D}$ 0°; m. p. 162-164°; neutral equivalent 302. The yield was 8% of the total oleoresin acids of *Pinus palustris.* The physical constants indicated a new resin acid. The isolation of formaldehyde as its "dimedon" derivative, m. p. 190-191°, on ozonolysis at −60° and of pimanthrene as its trinitrobenzolate,[6] m. p. 158-160°, on dehydrogenation with palladium-carbon catalyst at 330° proved it to be a pimaric-type acid. The homogeneity of the acid was proved by the preparation and purification of the methyl ester, m. p. 61.5-62°, and the butanolamine salt, $[\alpha]^{24}\text{D}$ 0°, and the regeneration of the acid with the same physical constants. The ultraviolet absorption spectrum, like that of dextropimaric acid, showed no maximum, indicating the absence of a conjugated double bond system.[7] This new pimaric-type acid has been termed isodextropimaric acid.

Dextropimaric acid was isolated from the acids regenerated from the residual salts, after that of isodextropimaric acid was separated, by crystallization first from acetone and then from glacial acetic acid in 4% yield with rotation, $[\alpha]^{24}\text{D}$ + 79°, m. p. 213-215°. The isolation of dextro-

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[1] We wish to designate by this term that type of resin acid which yields pimanthrene (1,7-dimethylphenanthrene) upon complete dehydrogenation, and that has the gem configuration of methyl and vinyl groups at C-7. Evidence for this will be shown in a subsequent publication: G. C. Harris and T. F. Sanderson, Resin Acids. IV. THIS JOURNAL, **70**, 2081 (1948). The abietic-type acids are those that yield retene (1-methyl-7-isopropylphenanthrene) upon complete dehydrogenation and have an isopropyl or isopropylidene group at C-7.

[2] These words have purposely been written as one word since the compounds are not stereoisomers as the prefixes *levo-* and *dextro-* would imply.

[3] A. Vesterberg, *Ber.*, **20**, 3248 (1887).

[4] E. Knecht and E. Hibbert, *J. Soc. Dyers Colourists*, **38**, 221 (1922).

[5] A method developed by W. P. Campbell of this Laboratory.

[6] L. Ruzicka and L. Sternbach, *Helv. Chim. Acta*, **23**, 124 (1940).

[7] V. N. Krestinskii, S. S. Malevskaya, N. F. Komshilov and E. V. Kazeeva, *J. Applied Chem.* (*U. S. S. R.*), **12**, 1840 (1939).

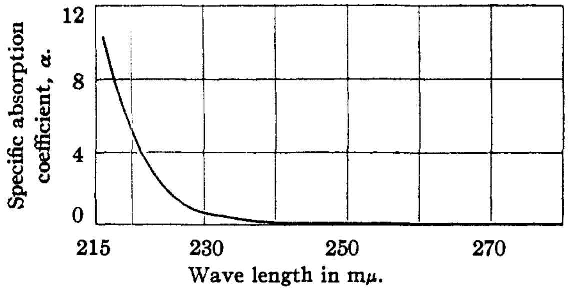

Fig. 1.—Ultraviolet absorption spectra (identical) of dextropimaric and isodextropimaric acids.

pimaric acid of high purity from this source supports the supposition that two-double-bond pimaric-type acids were not altered by the action of mineral acid in boiling benzene, the conditions used in the removal of the two-double-bond abietic-type acids.

The separation of both dextropimaric and isodextropimaric acid from wood or gum rosin was possible after observation was made of their very high volatility. It was found that in the course of the fractional distillation of rosin, these acids distilled with the more volatile constituents, the neutral bodies, at 136–200° with 1.0 mm. pressure. The total acids were separated by an alkaline extraction to obtain a mixture of resin and non-resin acids from which the isodextropimaric acid was separated as the insoluble butanolamine salt, and the dextropimaric acid crystallized as in the foregoing mixture of oleoresin acids in about 4 and 2% yield, respectively.

Experimental[8]

Isolation of Resin Acids from Oleoresin.—The procedure for the isolation of the resin acids from oleoresin was described in a previous publication.[9] It is carried out in the same manner with the exception that the temperature can be raised above 50° and dilute hydrochloric acid, *ca.* 10%, can be used in place of boric acid solution.

Separation of the Two-Double Bond Abietic-Type Acids.—A solution of 200 g. of oleoresin acids and 200 g. of maleic anhydride in one liter of dry benzene was saturated with dry hydrogen chloride and refluxed for forty-eight hours. At the end of this time, the benzene was steam distilled and the residue washed twice with hot water to remove the excess maleic anhydride. It was dissolved in a concentrated solution of 67 g. of sodium hydroxide, and, after complete solution, diluted to 6 liters. This solution was titrated to a *p*H of 6.2 with dilute hydrochloric acid and the precipitated resin acids were filtered, dissolved in ether, the ether solution washed free of acid, dried over sodium sulfate, and the ether evaporated. To assure the complete removal of two-double-bond abietic-type acids, the reaction with maleic anhydride was repeated to obtain 48 g. (24% yield) of maleic anhydride–unreactive acids with neutral equivalent of 304. An ultraviolet absorption curve showed the absence of these abietic-type acids.

Isolation of Isodextropimaric Acid.—The resin acids (48 g.) were dissolved in 96 g. of acetone and treated with a solution of 14.7 g. of butanolamine (2-amino-2-methyl-1-propanol, Commercial Solvents, Inc.) in 14.7 g. of acetone. A very vigorous reaction resulted with the simultaneous precipitation of the crystalline salts. In subsequent experiments, methyl acetate was used as the precipitating solvent. The salts were filtered and recrystallized three times from large volumes of methyl acetate to the constant rotation, $[\alpha]^{24}\mathrm{D}$ 0°.[10,11] A few drops of amine were added after the salts were dissolved and the solution concentrated to compensate for that lost by evaporation. This was found necessary for complete recovery.

The salts were then suspended in ether and decomposed by shaking with 10% hydrochloric acid. To assure complete decomposition, two fresh portions of acid were used after the salts were in solution. The ether solution containing the resin acid was washed free of mineral acid with water, dried over sodium sulfate, and the ether evaporated. The residue was dissolved in acetone and crystallized from the hot solution by the addition of water to incipient turbidity, first as thin platelets and then, on long standing in the solution, as shiny needles, with rotation $[\alpha]^{24}\mathrm{D}$ 0°, melting point 162–164°, and neutral equivalent 302 (theory 302). The yield was 8% (16.0 g.) based on the total oleoresin acids.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.37; H, 10.00. Found: C, 79.48, 79.40; H, 9.90, 9.95.

Preparation of the Methyl Ester of Isodextropimaric Acid.—A 20-g. sample of isodextropimaric acid was dissolved in 100 cc. of ether and the solution treated with an excess of an ether solution of diazomethane. The isolation was carried out in the usual manner to obtain an excellent yield (20 g.) of the ester melting at 61.5–62°.

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.69; H, 10.19. Found: C, 79.70, 79.65; H, 10.27, 10.30.

The purity and homogeneity of the acid was established in the following manner. Material with rotation $[\alpha]^{24}\mathrm{D}$ 0° and melting point 162–164° was used to prepare the butanolamine salt which was recrystallized three times to constant rotation $[\alpha]^{24}\mathrm{D}$ 0°. The resin acid was regenerated in the usual manner with no change in rotation, $[\alpha]^{24}\mathrm{D}$ 0°, or melting point, 162–164°. The methyl ester prepared as above was recrystallized to the constant melting point of 61.5–62°. Saponification in alcoholic alkali with subsequent acidification with mineral acid resulted in the isolation of isodextropimaric acid with rotation $[\alpha]^{24}\mathrm{D}$ 0° and melting point 162–164°.

Ozonization of Isodextropimaric Acid; Isolation of Formaldehyde.—A 1.0-g. sample of pure isodextropimaric acid, rotation $[\alpha]^{24}\mathrm{D}$ 0°, was dissolved in 50 cc. of dry ethyl chloride and treated with 3–5% ozone at −60° for two hours. The solvent was evaporated over water at room temperature and the ozonide decomposed in boiling water in an apparatus so arranged that the escaping gases were passed through an aqueous alcohol solution of "dimedon" (dimethyldihydroresorcinol). Upon standing, needles of the dimedon derivative of formaldehyde precipitated, m. p. 190–191°. A mixed melting point with an authentic sample showed no depression.

Dehydrogenation of Isodextropimaric Acid.—A 1.0-g. sample was mixed with 1.0 g. of 5% palladium–carbon catalyst and heated at 300–330° for four hours using carbon dioxide gas to sweep the gaseous products out of the reaction flask. After cooling, the catalyst was filtered from an ether solution of the reaction product and the ether evaporated. The trinitrobenzolate of pimanthrene, melting point 158–160°, crystallized upon heating the residue with a saturated alcoholic solution of trinitrobenzene.

Isolation of Dextropimaric Acid.—The acetone solution of the residual salts was evaporated to dryness, the residue dissolved in ether, and washed with dilute (10%) aqueous hydrochloric acid to decompose the salts. The ether solution containing the resin acids was washed free of mineral acid and water, dried over sodium sulfate, and the ether evaporated to obtain 32 g. of resin acids. The latter were dissolved in 30 cc. of acetone and cooled to

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[8] All melting points are corrected.

[9] G. C. Harris and T. F. Sanderson, This Journal, 70, 338 (1948).

[10] All rotations are of 1% solutions in absolute ethanol.

[11] Same rotation, $[\alpha]^{24}\mathrm{D}$ 0°, in chloroform and dry benzene.

−20° to obtain crystals of dextropimaric acid. Recrystallization from glacial acetic acid gave 8.0 g. (4% yield) of pure acid with rotation $[\alpha]^{24}\mathrm{D}$ +79°, and melting point 217–219°.

Isolation of the Pimaric Acids from Wood or Gum Rosins.—A 1000-g. charge of wood or gum rosin was distilled fractionally at 1.0-mm. pressure in a 10-plate column and the fraction, 120 g., boiling between 136 and 200° was taken. It was found to be composed of nonacidic material and of resin and nonresin acids. The total acids were separated from the neutral bodies by extraction with a 2% aqueous alkaline solution from an ether solution of the mixture. The alkaline solution was acidified, the resin acids dissolved in ether, and the ether solution washed free of mineral acid, dried, and the ether evaporated.

The total acids (65 g.) were dissolved in 200 cc. of acetone and treated with 20 g. of butanolamine in 20 g. of acetone. The pure salt of isodextropimaric acid, $[\alpha]^{24}\mathrm{D}$ 0°, was isolated and decomposed with mineral acid as before to obtain 39 g. (*ca.* 4%) of isodextropimaric acid. The acetone solution of the residual salts was evaporated, the salts decomposed, and dextropimaric acid crystallized as above to obtain 20 g. (2%) of the pure acid with rotation $[\alpha]^{24}\mathrm{D}$ +79°, and melting point 217–219°.

Summary

1. A new, pimaric-type resin acid, termed isodextropimaric acid, has been isolated from the oleoresin of *Pinus palustris* and from wood or gum rosin.

2. Dextropimaric acid has also been isolated from these sources.

WILMINGTON 99, DELAWARE RECEIVED[12] AUGUST 9, 1947

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[12] Original manuscript received August 9, 1946.

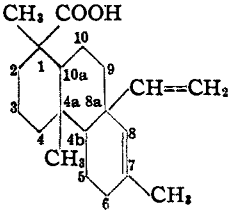
[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

Resin Acids. IV. The Position of the Ring Double Bond in Dextropimaric[1] Acid and the Structure of Isodextropimaric[1] Acid

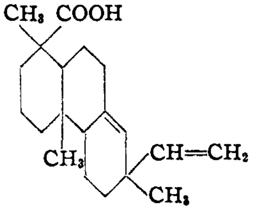
BY GEORGE C. HARRIS AND THOMAS F. SANDERSON

Ruzicka and Sternbach[2] have recently advanced Formula I and suggested Formula II as possible structures for dextropimaric acid.

I



II



Their argument against the latter was the fact that upon dehydrogenation of tetrahydrodextropimaric acid only pimanthrene (1,7-dimethylphenanthrene and no 1-methyl-7-ethylphenanthrene) was obtained. However, Formula II cannot be eliminated on this basis because the latter hydrocarbon may have been formed in such low yield as to escape detection. Experience shows that the isolation of pure hydrocarbons even as their solid derivatives from dehydrogenation mixtures is difficult, and especially so, if they are only minor constituents.

Formula II was proposed and preferred by Fleck and Palkin[3] in explaining the structure of a lactone obtained from dextropimaric acid treated with sulfuric acid at −20 to −30°. Lactonization at 4b position was suggested by the comparable stability of this lactone to that of hydroxytetrahydroabietic acid. If Formula I is assumed for dextropimaric acid, the necessary shift of the double bond to the bridgehead position, 4b,8a, is not possible; whereas if Formula II is assumed, the shift can be brought about by mineral acid so that lactonization of the carboxyl group can occur at C-4b.

Ruzicka and co-workers[4] have shown on the basis of experimental results that the vinyl group must be on a tertiary carbon atom, either 7 or 8a, however, not 4b, and still be compatible with the isoprene rule. Since the endocyclic double bond can be at the 7,8 or 8,8a position, the vinyl group must be on C-8a carbon atom for the former and on C-7 carbon atom for the latter position. The experimental evidence described herein will show the vinyl group to be at C-7 carbon atom, and, hence, the endocyclic double bond at 8,8a position.

Dextropimaric acid, I or II, $[\alpha]^{24}\mathrm{D}$ + 75°, melting point 217–219°,[5] was hydrogenated selectively to the dihydro stage in absolute ethanol with 5% palladium–carbon catalyst. The reaction proceeded smoothly to the absorption of 1.0 mole of hydrogen yielding the insoluble dihydro acid, III or VII, in excellent yield.[6] The dihydro acid was ozonized in dilute carbon tetrachloride solution at −20° and the ozonide decomposed in boiling water in the presence of zinc powder to obtain a ketoaldehyde, IV or VIII. If the endocyclic double bond in dextropimaric acid is in 7,8 position, Formula I, a methyl ketone, IV, would be obtained and detected by the liberation of iodo-

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(1) These words have purposely been written as one word since the compounds are not stereoisomeric with levopimaric acid as the prefixes *levo-*, *dextro-*, and *isodextro-* would imply.

(2) L. Ruzicka and L. Sternbach, *Helv. Chim. Acta*, **23**, 124 (1940).

(3) E. E. Fleck and S. Palkin, THIS JOURNAL, **62**, 2044 (1940).

(4) L. Ruzicka, G. B. R. de Graaff, M. W. Goldberg, and B. Frank, *Helv. Chim. Acta*, **15**, 915 (1932).

(5) G. C. Harris and T. F. Sanderson, Resin Acids III, THIS JOURNAL, **70**, 2079 (1948).

(6) It was also found (reference below) that the crystals formed from rosin hydrogenated in the presence of platinum oxide were those of the dihydrodextropimaric acid. This afforded an abundant source of the material. T. Hasselstrom and B. L. Hampton, *ibid.*, **61**, 967 (1939).