$-20°$ to obtain crystals of dextropimaric acid. Recrystallization from glacial acetic acid gave 8.0 g. (4% yield) of pure acid with rotation $[\alpha]^{24}\text{D}$ $+79°$, 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, $[\alpha]^{24}\text{D}$ 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 $[\alpha]^{24}\text{D}$ $+79°$, 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

---

[12] Original manuscript received August 9, 1946.

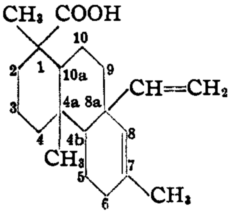
[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

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

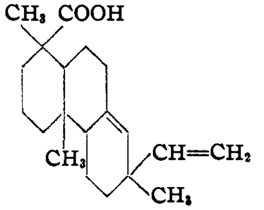
BY GEORGE C. HARRIS AND THOMAS F. SANDERSON

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, $[\alpha]^{24}\text{D}$ $+ 75°$, 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-

---

[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).

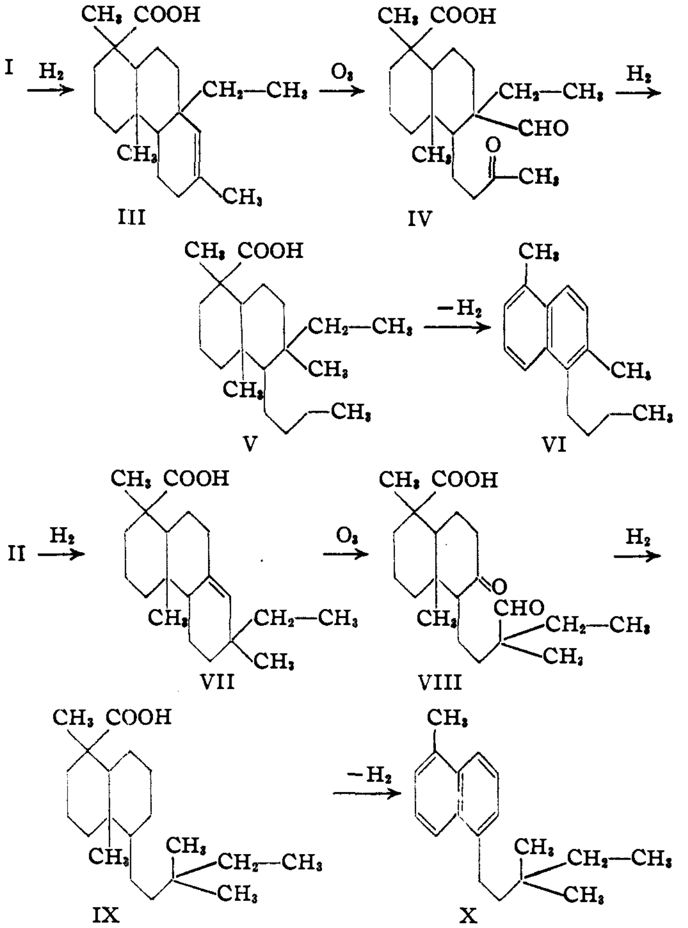
[3] E. E. Fleck and S. Palkin, THIS JOURNAL, **62**, 2044 (1940).

[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).

form from a sodium hypoiodite solution of the substance. A negative iodoform test indicated that the endocyclic double bond is at 8,8a position, Formula II, hence a ketoaldehyde of structure VIII.



The latter compound, VIII, was reduced to the hydrocarbon by the Wolff–Kishner method. The non-crystalline product was dehydrogenated, the hydrocarbon isolated, and its trinitrobenzolate prepared and recrystallized to a constant melting point, 113–116°. Analyses for carbon, hydrogen, and nitrogen content and molecular weight determinations, obtained ebullioscopically with acetone as solvent, of the solid derivative showed it to be conclusively the trinitrobenzolate of a C_{18} hydrocarbon. The derivative was decomposed over activated alumina and the hydrocarbon isolated. Carbon and hydrogen analyses and molecular weight determination showed it to be a C_{18} hydrocarbon. Attempts to oxidize the hydrocarbon to the 1,5-dicarboxylic acid with potassium ferricyanide were unsuccessful, possibly because of the long alkyl chain at the 5 position. The ultraviolet absorption curve[7] of the isolated hydrocarbon, Fig. 1, Curve 2, demonstrates absorption that is characteristic of dialkylated naphthalenes, with intense band at 228 mμ, for example, 1,5-dimethylnaphthalene, Fig. 1, Curve 1 (see below). The height of the maxima of the C_{18} hydrocarbon is not so intense as those of the 1,5-dimethylnaphthalene because of the larger molecular weight of the former.

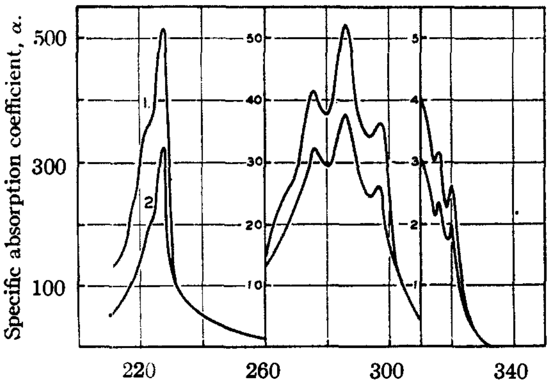


Fig. 1.—Ultraviolet absorption spectra of (1) 1,5-dimethylnaphthalene, and (2) the C_{18} hydrocarbon (X) from both dextropimaric and isodextropimaric acids.

If the vinyl group is on C-8a carbon atom, Formula I, dehydrogenation of V should give a C_{16} hydrocarbon, VI; whereas, if the vinyl group were on C-7 carbon atom, Formula II, dehydrogenation of IX would give a C_{18} hydrocarbon. Since a C_{18} hydrocarbon was isolated, the vinyl group is placed at 7 position and the endocyclic double bond at 8,8a position. Hence Formula II is concluded to be that for dextropimaric acid.

The same series of experiments was carried out with pure isodextropimaric acid, $[\alpha]^{24}\text{D}$ 0°, and melting point 162–164°,[5] to obtain the trinitrobenzolate of the same hydrocarbon, X, with melting point 113–116°. A mixed melting point with the corresponding derivative from dextropimaric acid showed no depression, 113–116°. The identity of the two substances was *further* supported by the identity of their X-ray diffraction patterns and identity of their ultraviolet absorption spectra (Fig. 1, Curve 2).

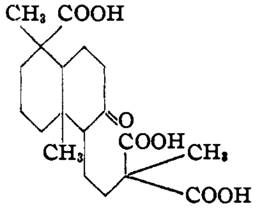
From this, it was concluded that the two acids, isodextropimaric and dextropimaric acid, are dissimilar only with regard to the difference in the configuration of the methyl and vinyl groups about the asymmetric C-7 carbon atom. If this is the case, a similar decomposition product, in which the asymmetry at C-7 carbon atom was destroyed, should be obtained from each acid. Formula IX represents such a compound; how-

---

(7) The ultraviolet absorption data were determined by Dr. Evelyn V. Cook of this Laboratory.

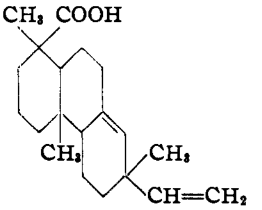
ever, it was not possible to crystallize either it or an acid derivative thereof.

Another approach for eliminating the asymmetry at 7 position is to ozonize the intact acids to obtain a tricarboxylic acid of Formula XI.



XI

This scheme was followed successfully to obtain the crystalline 2,4-dinitrophenylhydrazones and semicarbazones of triacids XI, which were proved to be identical by comparison of X-ray diffraction patterns and mixed melting points that showed no depression as compared with those of the individual derivatives. Therefore, the indication is that isodextropimaric and dextropimaric acids are dissimilar only with respect to the configuration of the methyl and vinyl groups at C-7 carbon atom. If Formula II is assumed for dextropimaric acid, Formula XII is that for isodextropimaric acid.



XII

Further evidence for Formula II as that for dextropimaric acid was obtained by the partial dehydrogenation of the pure acid.

The dehydrogenation was carried out in the usual manner at 300–330° with palladium–carbon catalyst, but the products were isolated by fractionation through a column of silica gel with hexane as solvent. The first product of dehydrogenation was a trisubstituted naphthalene, a C_{18} hydrocarbon (XIII). Its most intense band in the near ultraviolet (Fig. 2) is at 232 mμ, characteristic of trialkylated naphthalenes,[8] a shift of 4 millimicrons from that of dialkylated naphthalenes (Fig. 1). An intense band at 325 mμ, absent in the spectrum of the dialkylated naphthalenes, is also characteristic of the trisubstituted naphthalenes. If Formula I is that for dextropimaric acid, a C_{16} hydrocarbon would be isolated with only one substituent, a methyl group, at C-7. This structure would not be expected to be stable so that further dehydrogenation would give pimanthrene (XV) at once.

The C_{18} hydrocarbon was further dehydrogenated under the same conditions to obtain pimanthrene (XV).

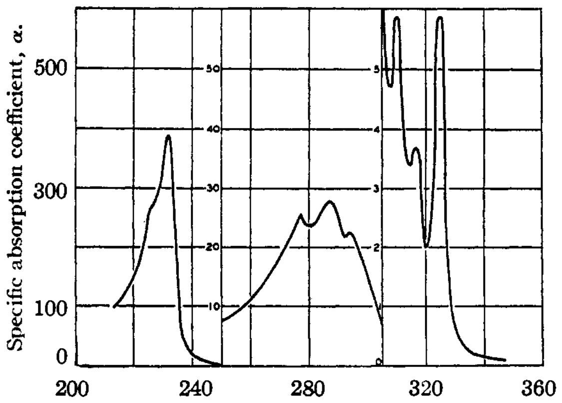
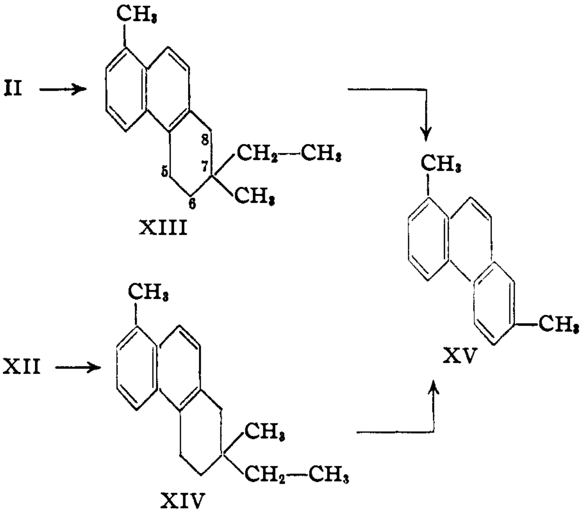


Fig. 2.—Ultraviolet absorption spectrum of C_{18} hydrocarbon (XIII and/or XIV).



Isodextropimaric acid (XII) was treated in a similar manner to obtain the C_{18} hydrocarbon, XIV, whose trinitrobenzolate had the same melting point as that of hydrocarbon XIII, m. p. 122–123°. Further dehydrogenation of hydrocarbon XIV also gave pimanthrene in good yield. No difference in spatial configuration of the two hydrocarbons (XIII and XIV) was detected by a mixed melting point of their trinitrobenzolates, optical rotation of the pure substances, or X-ray diffraction patterns of the trinitrobenzolates. It, therefore, can be assumed that racemization took place during the dehydrogenation so that hydrocarbons XIII and XIV are identical. Racemization during partial dehydrogenation is further evidence for the asymmetry at C-7. The identity of the hydrocarbon derivatives was substantiated by identical X-ray diffraction patterns. The synthesis of the C_{18} hydrocarbon is now in progress.

The known and new derivatives of the two acids and their melting points are:

---

(8) The characteristic absorption maxima of mono- and polyalkylated naphthalenes will be the subject of a future publication.

		Melting point, °C.
1	Methyl isodextropimarate	61–62
2	Methyl dextropimarate	68–69
3	Dihydroisodextropimaric acid	173–175
4	Dihydrodextropimaric acid	243–245
5	Lactone of 3	109–110
6	Lactone of 4	98–99
7	Methyl ester of 3	75–76[a]
8	Methyl ester of 4	78–79

[a] Mixed melting point with 8 shows a marked depression.

Experimental[9]

Hydrogenation of Dextropimaric Acid (II).—A 5.0-g. sample of dextropimaric acid, $[\alpha]^{24}\text{D}$ +75°,[10] melting point 217–219°, was dissolved in 50 cc. of absolute ethanol and the solution agitated in a hydrogen absorption apparatus in the presence of 1.0 g. of 5% palladium–carbon catalyst until 408 cc. (1.0 mole) of hydrogen was absorbed. The reaction was carried out at room temperature and atmospheric pressure and stopped completely after the absorption of 1.0 mole of hydrogen. The catalyst was removed by filtration, and the dihydro acid watered out of the warm alcoholic solution to obtain 4.9 g. of acid (98% yield) with rotation, $[\alpha]^{24}\text{D}$ +19°, and melting point 243–245°.

Hydrogenation of Isodextropimaric Acid (XII).—The reaction was carried out in the same manner to obtain the dihydroisodextropimaric acid in the same yield with rotation, $[\alpha]^{24}\text{D}$ 0°, and melting point 173–175°.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.88; H, 10.54. Found: C, 78.91, 78.95; H, 10.66, 10.60. Hydrogen absorption calcd. 0.66; found, 0.66.

Ozonization of Dihydrodextropimaric Acid (VII).—A 1.0-g. sample of dihydrodextropimaric acid, $[\alpha]^{24}\text{D}$ 0°, was dissolved in 50 cc. of boiling carbon tetrachloride and the solution allowed to cool to room temperature and eventually to −20° in an acetone–Dry Ice-bath. The ozonolysis reaction was carried out for two hours with an oxygen throughput of 20–25 liters per hour using a generator issuing 3–5% ozone. At the end of this time, the solvent was evaporated in vacuum at room temperature, the residue dissolved in a minimum amount of ether, water added, and the suspension boiled for four hours in the presence of 1.0 g. of powdered zinc. The reaction product was isolated in ether, the ether solution washed, dried, and the ether evaporated to obtain 0.80 g. (77% yield) of the ketoaldehyde, VIII, with neutral equivalent 330 (theory 336). It was not possible to crystallize the ketoaldehyde or a derivative thereof.

Anal. Calcd. for $C_{20}H_{32}O_4$: C, 71.38; H, 9.60. Found: C, 70.40, 70.49; H, 9.41, 9.38.

The product gave a negative iodoform test.

Ozonization of Dihydroisodextropimaric Acid.—The results with this acid were almost identical with those of dihydrodextropimaric acid. A non-crystalline substance was obtained giving approximately the same analytical data and a negative iodoform test.

Anal. Calcd. for $C_{20}H_{32}O_4$: C, 71.38; H, 9.60. Found: C, 70.20, 70.43; H, 9.45, 9.50.

Wolff–Kishner Reduction of the Ketoaldehyde, VIII, and of the Corresponding Product from Isodextropimaric Acid.—The disemicarbazones were prepared by dissolving 2 g. of the ketoaldehyde in an alcoholic solution of semicarbazide acetate, adding a few drops of pyridine and allowing the solution to stand for two days. The noncrystallizable derivative was then extracted in ether after the reaction solution was poured into a large volume of water. The ether was evaporated, the residue taken up in 35 cc. of alcohol containing 3.0 g. of sodium metal, and the solution heated at 200° for eight hours under 1800 p. s. i. of nitrogen pressure.

The solution was poured into water and acidified with dilute mineral acid, and the organic material was dissolved in ether. The ether solution was washed free of mineral acid, dried, and the ether evaporated. The crude product, IX, 0.9 g. (50% yield) was dehydrogenated.

The corresponding product from isodextropimaric acid was treated in a similar manner to obtain a crude product in the same yield.

Dehydrogenation of the Crude Product IX.—A 2.0-g. sample of the powdered material was mixed intimately with 2.0 g. of 5% palladium–carbon catalyst and heated at 300–325° for four hours under a stream of carbon dioxide gas. At the end of this time, the dehydrogenated product was dissolved in ether and the catalyst filtered. The residue was dissolved in 1 cc. of 95% ethanol and treated with 10 cc. of a saturated solution of trinitrobenzene. Upon concentrating to 5-cc. volume and cooling, light-yellow needles of the trinitrobenzolate of hydrocarbon X precipitated in 35–40% yield. The derivative was recrystallized to a constant melting point of 113–116°.

Anal. Calcd. for $C_{18}H_{24}$ (X) + $C_6H_3N_3O_6$, $C_{24}H_{27}N_3O_6$: C, 63.56; H, 6.00; N, 9.27. Found: C, 63.76, 63.43; H, 5.75, 5.67; N, 9.14, 9.20. Molecular weight Calcd.: 227. Found (ebullioscopic method): 225, 229. Calcd. for $C_{16}H_{20}$ (VI) + $C_6H_3N_3O_6$, $C_{22}H_{23}N_3O_6$: C, 62.11; H, 5.44; N, 9.88. Molecular weight calcd.: 213.

Dehydrogenation of Compound, Corresponding to IX, from Isodextropimaric Acid.—This reaction was carried out in the same manner to obtain a trinitrobenzolate of the hydrocarbon that melted at 113–116°. The identity of the two substances was shown by a comparison of their X-ray diffraction patterns, ultraviolet absorption curves, and a mixed melting point that showed no depression.

Anal. Calcd. for $C_{18}H_{24}$ + $C_6H_3N_3O_6$ or $C_{24}H_{27}N_3O_6$: C, 63.56; H, 6.00; N, 9.27; mol. wt., 227. Found: C, 63.60, 63.40; H, 5.85, 5.65; N, 9.22, 9.17; mol. wt., 227, 230.

Isolation of Hydrocarbon X.—The trinitrobenzolate derivative (2.0 g.) was dissolved in 5 cc. of benzene and placed on a column of alumina (30 × 320 mm.). Upon elution with benzene, the hydrocarbon was washed through the column and the trinitrobenzene remained adsorbed. The benzene was evaporated under vacuum to obtain 1.0 g. (95% yield) of a fluorescent hydrocarbon that could not be made to crystallize.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.92; H, 10.08; mol. wt., 240. Found: C, 89.84, 89.87; H, 10.10, 10.10; mol. wt., 237, 242.

Complete Ozonization of Dextropimaric Acid, II.—A 1.0-g. sample was dissolved in 30 cc. of ethyl chloride and the solution cooled to −60° in an acetone–Dry Ice-bath. The reaction was carried out for two hours with an oxygen throughput of 20–25 liters per hour using a generator issuing 3–5% ozone. At the end of this time, the solvent was evaporated in vacuum, the residue dissolved in a minimum amount of ether, water added, and the suspension boiled for four hours in the presence of 1.0 g. of powdered zinc. Upon isolation in ether, the decomposed ozonide was dissolved in 5% alkali, and 2% hydrogen peroxide solution was added to oxidize the aldehyde to carboxyl groups, XI.

The aqueous solution was acidified and the precipitate dissolved in ether. The ether solution was extracted with bicarbonate solution and the product isolated in ether upon careful acidification of the bicarbonate solution. It could not be made to crystallize, so the data were obtained on the powdered material.

Anal. Calcd. for $C_{19}H_{28}O_7$ (XI): C, 61.82; H, 7.89. Found: C, 62.29, 62.89; H, 8.28, 8.00. Molecular weight, calcd.: 368. Found: 373 (ebullioscopically).

Its 2,4-dinitrophenylhydrazone was prepared in the usual manner, melting point 185–188°. The semicarbazone was also prepared, m. p. 223–225°, and analyzed for nitrogen content. Calcd., 9.9; found, 10.35, 10.12.

Complete Ozonization of Isodextropimaric Acid, XII.—The reaction was carried out in the same manner to obtain

---

(9) All melting points are corrected.

(10) All rotations are of 1% solutions in absolute ethanol.

a product of the same nature. Its dinitrophenylhydrazone also melted at 185–188° and its semicarbazone at 223–225°. The identity of the two derivatives with the corresponding ones from dextropimaric acid was shown by mixed melting points that showed no depression and also by the fact that their X-ray diffraction patterns were identical.

Dehydrogenation of Dextropimaric and Isodextropimaric Acids.—A 2.0-g. sample of the pure acid was mixed intimately with 1.0 g. of 5% palladium–carbon catalyst and heated at 300–330° for four hours. The catalyst was filtered from an ether solution of the mixture of hydrocarbons.

Isolation of the Trinitrobenzolate of C_{18} Hydrocarbon (XIII or XIV).—The dehydrogenation product (1.4 g.) was dissolved in 10 cc. of hexane and transferred to a column of silica gel. The chromatogram was developed with hexane and followed with ultraviolet light. The fraction (0.6 g.) taken was that which preceded the blue fluorescence due to pimanthrene.

The same trinitrobenzolate, m. p. 122–123°, was isolated from the corresponding fraction obtained from each of the two resin acids as shown by identical X-ray diffraction patterns and no depression in a mixed melting point. Once their identity was established, they were mixed and analytical data obtained.

Anal. Calcd. for $C_{18}H_{22}$ + $C_6H_3N_3O_6$ (T. N. B.), $C_{24}H_{25}N_3O_6$: C, 63.56; H, 6.00; N, 9.27. Found: C, 64.16, 64.10; H, 5.75, 5.75; N, 9.18, 9.34.

Isolation of Hydrocarbon XIII or XIV.—The procedure is the same as that described for the isolation of hydrocarbon X. The first experiments were done with the pure trinitrobenzolates of the hydrocarbons obtained from each acid. Each was found to have a rotation of 0° in absolute ethanol or benzene.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.65; H, 9.35. Found: C, 90.23, 90.64; H, 9.30, 9.35.

Dehydrogenation of Hydrocarbon XIII or XIV.—The same procedure was used as in the section on the dehydrogenation of the free acids. The trinitrobenzolate of pimanthrene, m. p. 158–160°, was isolated in good yield.

Summary

The positions of the vinyl group and of the endocyclic double bond of dextropimaric acid have been established, hence the structure of the acid completed.

The structure of isodextropimaric acid has been determined and the stereoisomerism of the two acids demonstrated.

WILMINGTON, DELAWARE RECEIVED[11] AUGUST 12, 1947

---

(11) Original manuscript received August 9, 1946.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK & CO., INC.]

Streptomyces Antibiotics. XVI. The Structures of bis-Desoxystreptose, Dihydrodesoxystreptose and Tetraacetyl-bis-desoxystreptobiosamine

BY NORMAN G. BRINK, FREDERICK A. KUEHL, JR., EDWIN H. FLYNN AND KARL FOLKERS

Treatment of ethyl tetraacetylthiostreptobiosaminide diethyl mercaptal,[1,2] I, with Raney nickel catalyst gave tetraacetyl-bis-desoxystreptobiosamine, II, and tetraacetyldesoxystreptobiosamine, III. Acid hydrolysis of tetraacetyl-bis-desoxystreptobiosamine yielded N-methyl-L-glucosamine,[3] IV, and bis-desoxystreptose, a 3,4-dihydroxy-2,3-dimethyltetrahydrofuran,[4] V. Details of these investigations and an account of the analogous degradation of pentaacetyldihydrodesoxystreptobiosamine[5,6] to dihydrodesoxystreptose are described herein.

When a solution of ethyl tetraacetylthiostreptobiosaminide diethyl mercaptal in 70% ethanol was refluxed in the presence of Raney nickel catalyst (not freshly prepared) and the products of the reaction were chromatographed on alumina, two compounds were isolated. The first crystalline fractions from the chromatogram consisted of tetraacetyl-bis-desoxystreptobiosamine, m. p. 159–160°, $[\alpha]^{25}$D − 85°. The second product melted at 166–167°, $[\alpha]^{25}$D − 81°, and was isolated from later fractions. It differed by the presence of one additional oxygen atom, and was designated tetraacetyldesoxystreptobiosamine. A mixture of the two compounds did not give a mixed melting-point depression, and the close correspondence of their physical properties added to the difficulties of separation. The bis-desoxy derivative was unchanged by acetylation treatment, but the desoxy derivative on acetylation gave a pentaacetyl derivative, VI, which melted at 111–112°. The pentaacetyldesoxystreptobiosamine was considerably more soluble than either of the tetraacetates. This observation was of value for the purification of tetraacetyl-bis-desoxystreptobiosamine, because after acetylation it could be separated readily from pentaacetyldesoxystreptobiosamine by recrystallization. Crude tetraacetyldesoxystreptobiosamine was purified by repeated chromatography.

The conversion of tetraacetyldesoxystreptobiosamine to pentaacetyldesoxystreptobiosamine indicated that the additional oxygen atom in the desoxy compound was present as a hydroxyl group, and it seemed likely that this group had been introduced by hydrolysis which competed with the hydrogenolysis during the treatment with Raney nickel catalyst. In support of this interpretation was the observation that when the reaction was carried out with Raney nickel catalyst which had been prepared immediately before use,

---

(1) Kuehl, Flynn, Brink and Folkers, THIS JOURNAL, **68**, 2096 (1946).

(2) Hooper, Klemm, Polglase and Wolfrom, *ibid.*, **68**, 2120 (1946).

(3) Kuehl, Flynn, Holly, Mozingo and Folkers, *ibid.*, **68**, 536 (1946).

(4) Brink, Kuehl, Flynn and Folkers, *ibid.*, **68**, 2405 (1946).

(5) Brink, Kuehl, Flynn and Folkers, *ibid.*, **68**, 2557 (1946).

(6) Lemieux, Polglase, DeWalt and Wolfrom, *ibid.*, **68**, 2747 (1946).