(200 ml. in all) of ethyl ether. The combined ether extracts were fractionated (final temperature 230°). Since no principal fraction boiling at 126°, the boiling point of *n*-amyl mercaptan, was found, the combined distillate was extracted with sodium hydroxide, the alkali solution then acidified and extracted with ether. The ether was evaporated and the residual foul-smelling liquid treated with 2,4-dinitrochlorobenzene, which produced a few crystals of the *n*-amyl 2,4-dinitrophenyl thioether melting at 80–81° (recorded[10] value 80°). The material left after extraction with alkali was treated with picric acid in hot alcoholic solution. A few yellow crystals melting from 268–273° were obtained. Had the amyl group been substituted in the indented position, the product should have been naphthalene picrate, melting at 149–150°. Several experiments using decalin showed that the above process would give good yields of naphthalene and naphthalene picrate.

Summary

A series of studies on the reaction of amyl-

(10) Bost, Turner and Norton, THIS JOURNAL, **54**, 1986 (1932).

sodium with bicyclic compounds showed that metalation occurred readily in a considerable number of places. The positions of attack were shown by examination of the products of carbonation.

The end-products from naphthalene were both mono-carboxylic acids, at least three dicarboxylic acids, and some tricarboxylic acid.

Acenaphthene was attacked readily; the only product which could be isolated was a dicarboxylic acid, either 1,6- or probably 1,5.

Decalin was attacked very easily and a considerable variety of products was formed. A small amount of the dianhydride of a tetracarboxylic acid was separated. The tertiary hydrogen atom in decalin may be attacked but does not appear to be a favored position.
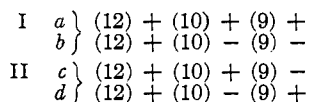
CAMBRIDGE, MASS.   RECEIVED MARCH 18, 1942

The Diastereoisomerism of the 9,10,12-Trihydroxystearic Acids and the Geometric Configurations of Ricinoleic and Ricinelaidic Acids

BY J. P. KASS AND S. B. RADLOVE

In the course of an investigation of the dehydration of ricinoleic and ricinelaidic acids to isomeric linoleic acids, it became necessary to identify the parent 12-hydroxy-9,10-octadecenoic acids by means of their partial oxidation to the 9,10,12-trihydroxystearic acids. Theoretical considerations[2,3,4] indicate that each of the geometrically isomeric, dextrorotatory monohydroxy acids should yield two diastereoisomeric trihydroxystearic acids, with the following configurations of the initially dextrorotatory twelfth carbon atom and the newly asymmetric ninth and tenth carbon atoms

$$
\begin{array}{llll}
\text{I} & \left.\begin{array}{l} a \\ b \end{array}\right\} & \begin{array}{l}(12)+(10)+(9)+ \\ (12)+(10)-(9)-\end{array} \\
\text{II} & \left.\begin{array}{l} c \\ d \end{array}\right\} & \begin{array}{l}(12)+(10)+(9)- \\ (12)+(10)-(9)+\end{array}
\end{array}
$$

Moreover, assuming that no inversion occurs during oxidation, the pairs of the derivatives should be

related in such a manner that the products of the *cis*-hydroxylation of one of the unsaturated acids must correspond to the products of the *trans*-addition to its geometric isomer; specifically, the mild alkaline permanganate oxidation of ricinoleic acid should yield two trihydroxystearic acids identical with the pair resulting from the oxidation of ricinelaidic acid with acid hydrogen peroxide, and *vice versa*. This relationship has been shown to obtain uniformly in the monoethenoid[5,6] and linoleic acid[7] series.

The older literature[8] reports the preparation of three of the trihydroxystearic acids under consideration, and intimates the existence of the fourth isomer. The oxidation of ricinoleic acid with cold alkaline permanganate was first shown by Hazura and Grüssner[9] to produce two trihydroxystearic acids, m. p. 110–111° and 140–142°, for which Dieff[10] later reported m. p. of 100–114° and 137–140°. From similarly treated ricinelaidic

(1) The Northern Regional Research Laboratory is one of four regional laboratories authorized by Congress in the Agricultural Adjustment Act of 1938 for the purpose of conducting research to develop new uses and outlets for agricultural commodities. These laboratories are administered by the Bureau of Agricultural Chemistry and Engineering of the U. S. Department of Agriculture. (Not subject to copyright.)

(2) Mangold, *Monatsh.*, **13**, 326 (1892).

(3) Walden, *Ber.*, **27**, 3471 (1894).

(4) Smit, *Rec. trav. chim.*, **49**, 675 (1930).

(5) Hilditch, *J. Chem. Soc.*, 1828 (1926).

(6) Braun, THIS JOURNAL, **51**, 228 (1929).

(7) Kass and Burr, *ibid.*, **61**, 1062 (1939).

(8) *Cf.* Lewkowitch and Warburton, "The Chemical Technology and Analysis of Oils, Fats and Waxes," 6th ed., Vol. 1, The Macmillan Co., London, 1938, p. 236.

(9) Hazura and Grüssner, *Monatsh.*, **9**, 475 (1888).

(10) Dieff, *J. prakt. Chem.*, [2] **39**, 339 (1889).

acid, Grüssner and Hazura[11] and Dieff[10] succeeded in isolating only one trihydroxystearic acid, m. p. 114–115°, although Mangold[2] claimed that he obtained two substances, m. p. 113–116° and 117–120°, in amounts too small for further identification. The optical activity of only the first isomer, m. p. 110–111°, has been determined by Walden,[3] who found $[\alpha]D$ −6.25 to −6.0° (c = 10–15 in glacial acetic acid).

However, Dean[12] apparently assumed the identity of the two possible pairs of derivatives, while Brady[13] recently repeated the earlier work and stated that the mild alkaline permanganate oxidation of both ricinoleic and ricinelaidic acids produced the same two trihydroxystearic acids, m. p. 110 and 141°, albeit in different proportions. His statement has been accepted by Henshall and Smith.[14] Furthermore, Scanlan and Swern[15] implied that the single trihydroxystearic acid, m. p. 108–109°, which they obtained through the oxidation of the ricinoleic acid of castor oil with hydrogen peroxide in acetic acid, was presumably identical with Hazura and Grüssner's[9] product, m. p. 110–111°, of the alkaline permanganate oxidation of ricinoleic acid, rather than of ricinelaidic acid. Previously, Smit[4] had shown that the oxidation of ricinelaidic acid with perbenzoic acid yielded two trihydroxystearic acids, m. p. 112 and 137°, presumably identical with the compounds formed by the alkaline permanganate oxidation of ricinoleic acid. The latter did not, however, yield any identifiable trihydroxystearic acids with the perbenzoic acid.

In view of the unsatisfactory state of the experimental data and the apparent contradiction between some of the more recent work and the theoretical expectations, it was considered desirable to characterize more fully the trihydroxystearic acids derived from the oxidation of ricinoleic and ricinelaidic acids with both alkaline permanganate and acid hydrogen peroxide. Contrary to the findings of Brady,[13] four distinct diastereoisomers were obtained, the behavior of which was in complete agreement with the theoretical considerations outlined in the introductory section, as shown in the accompanying table. In line with a previous suggestion,[7] each acid has

(11) Grüssner and Hazura, *Monatsh.*, **10**, 196 (1889).

(12) Dean, "The Utilization of Fats," A. Harvey, London, Eng., 1938, p. 18.

(13) Brady, This Journal, **61**, 3464 (1939).

(14) Henshall and Smith, "Annual Reports of the Chemical Society of London for 1940," **37**, 213 (1941).

(15) Scanlan and Swern, This Journal, **62**, 2309 (1940).

been designated with a Greek letter prefix, the lower-melting isomer in each pair having the lower designation. It is probable that the hitherto unreported γ-trihydroxystearic acid, m. p. 86.8–87.4°, has been overlooked by previous workers because of its relatively pronounced solubility in organic solvents, while the failure of the recent workers[13,15] to recognize the distinction between the α- and δ-trihydroxystearic acids may have been due to the close similarity of the melting points of these substances.

Correlation of the specific rotations of the individual trihydroxystearic acids with their possible stereochemical configurations indicated in the introductory discussion offers corroborative evidence for the *cis*-configuration of ricinoleic acid and the *trans*-configuration of ricinelaidic acid; at least, it presents an analogy between the fatty acids and maleic and fumaric acids, respectively. Where fumaric acid on oxidation with alkaline permanganate yields racemic tartaric acid, ricinelaidic acid similarly produces the strongly dextrorotatory γ-trihydroxystearic and the even more strongly levorotatory δ-trihydroxystearic acid, which are diastereoisomeric because of the presence of the already asymmetric dextrorotatory twelfth carbon atom (structures *a* and *b*, respectively). Conversely, where maleic acid forms *meso*-tartaric acid, ricinoleic acid yields the two weakly levorotatory α- and β-trihydroxystearic acids, the comparatively slight levorotations of these diastereoisomers being due to the partial internal compensation of the strong levorotation of either the ninth or tenth carbon atoms by the other newly asymmetric carbon atom possessing a relatively weaker dextrorotation (either of structures *c* and *d*).

Experimental

Preparation of Ricinoleic and Ricinelaidic Acids.— Castor oil (900 g.) was extracted five times with 500-cc. portions of petroleum ether (b. p. 30–60°). The residue, freed from solvent on the water-bath *in vacuo*, was saponified by boiling for one-half hour with a solution of 360 g. of potassium hydroxide in 243 cc. of water and 1800 cc. of alcohol. The acids were liberated in the usual manner, washed three times with hot water, and dried over sodium sulfate in diethyl ether solution. After filtration and evaporation of the solvent *in vacuo*, the residual acids, which did not solidify completely in the refrigerator at 3°, were extracted four times with large volumes of cold petroleum ether. Evaporation (*in vacuo*) of the solvent from the insoluble acids left 623 g. of an amber oil; I. V. 86.3 (theory for ricinoleic acid, I. V. 85.1). This crystallized completely in the refrigerator.

CONSTANTS OF THE 9,10,12-TRIHYDROXYSTEARIC ACIDS

Trihydroxystearic acids produced by oxidation

Parent acid		M. p., °C. from literature[a]	M. p., °C. from present work	with alkaline permanganate $[\alpha]^{28}D$ in ethanol	in acetic acid	with hydrogen peroxide in acetic acid M. p., °C. from present work	$[\alpha]^{28}D$ in ethanol	in acetic acid
Ricinoleic	$\alpha112^4$		112	$-2.9\ (c=5)$	$-6.6\ (c=4)$	$\delta110$	-26.6	-38.7
	$\alpha111^{3,9}$							
	$\alpha100{-}114^{10}$							
	$\alpha110^{13}$							
	$\beta137^4$		138	$-3.9\ (c=2)$	$-11.6\ (c=2)$	$\gamma87$	$+19.1$	$+21.8$
	$\beta140{-}142^9$							
	$\beta137{-}140^{10}$							
	$\beta141^{13}$							
Ricinelaidic	γ		87	$+19.1\ (c=4)$	$+21.8\ (c=2)$	$\beta138$	-3.9	-11.6
	$\delta113{-}116^2$							
	$\delta115^{11}$		110	$-26.6\ (c=2)$	$-38.7\ (c=4)$	$\alpha112$	-2.9	-6.6
	$\delta110^{13}$							
	$\delta109^{15}$							

[a] To avoid confusion arising from the multiplicity of melting points cited and the similarity of the m. p. of the α and δ acids, the previously published m. p. are recorded here with regard to the correct isomeric relationships of the trihydroxystearic acids, rather than their source as reported by the original investigators.

Further purification was effected by treating an alcoholic solution of the potassium salt of the crude ricinoleic acid with an equivalent aqueous solution of barium chloride and recrystallizing the precipitated and washed barium salt three times from 95% alcohol. The barium ricinoleate was then extracted with diethyl ether and the dried, finely powdered salt was suspended in the ether and decomposed by vigorous shaking with successive small portions of dilute hydrochloric acid. Evaporation (*in vacuo*) of the washed and dried ether solution left a colorless oil which solidified in the refrigerator to a crystalline mass, m. p. about 5°. (The crude acid polymerizes very rapidly, for the addition of aqueous barium chloride to the alcoholic solution of the potassium soap of a portion of the acid which was left at room temperature for several weeks produced only a gummy precipitate. However, preliminary saponification of the estolide with an excess of alcoholic alkali and the subsequent isolation of the free acid permitted the recovery of the crystallizable barium salt.)

The ricinelaidic acid was prepared by the action of nitric acid and sodium nitrite on the crude ricinoleic acid which was obtained by the saponification of castor oil previously extracted with petroleum ether as described above. The acids from 1000 g. of castor oil were warmed without preliminary drying to 60° and mixed during vigorous mechanical stirring with 400 cc. of 50% nitric acid at the same temperature. A solution of 30 g. of sodium nitrite in 200 cc. of water was added at once through a delivery tube reaching to the bottom of the reaction flask, and the mixture was vigorously stirred for ten minutes at 60°. The flask was then transferred to an icebath and the stirring continued for several hours until the supernatant layer solidified. The product was washed several times with hot water and taken up in five volumes of diethyl ether. The solution was washed with water, dried with sodium sulfate, filtered and chilled. To facilitate the filtration of the voluminous material which separated on chilling, the cooling and filtrations were performed at 10° intervals to −30°. Two recrystallizations of the combined material from diethyl ether yielded 220 g. of white ricinelaidic acid, m. p. 50–51°.

The combined mother liquors from the recrystallizations of the ricinelaidic acid were completely freed from solvent, and the liquid residue was again treated with nitric acid and nitrite exactly as before. An additional 185 g. of ricinelaidic acid was thereby obtained, having a m. p. of 50–51° after a single recrystallization from diethyl ether.

The 405 g. of the crude ricinelaidic acid was taken up in a large volume of boiling petroleum ether, which left undissolved 5 g. of a white crystalline solid, m. p. 134–136°, presumably the natural dihydroxystearic acid.[16] This residue was reserved for future study. Recrystallization of the ricinelaidic acid from petroleum ether raised the m. p. of the main product to 51–52°.[17]

(1) **Oxidation with Alkaline Potassium Permanganate** (a) **Ricinoleic Acid.**—The procedure followed was that of Lapworth and Mottram[18] exactly as employed by Brady.[13] A solution of 5 g. of ricinoleic acid in 2500 cc. of water containing 1.6 g. of potassium hydroxide was stirred for ten minutes at 0° with 5.3 g. of potassium permanganate dissolved in 250 cc. of water. Decolorization was effected with 15 g. of sodium sulfite and an excess of dilute sulfuric acid. The flocculent precipitate was permitted to settle for several hours in the cold, when it was filtered, washed thoroughly with cold water, and finally dried in a vacuum desiccator. After exhaustion with petroleum ether, it was extracted with boiling chloroform. The chloroform-soluble fraction (α-trihydroxystearic acid) was recrystallized from alcohol, then aqueous acetic acid, and again from alcohol; m. p. 109–111.5°; yield, 1.1 g. as a micro-crystalline powder.

The chloroform insoluble fraction (β-trihydroxystearic acid) was similarly recrystallized to yield 1.2 g. of a white powder, m. p. 136–138°.

(16) Ref. 8, p. 226.

(17) Subsequent work in this Laboratory has shown that pure methyl ricinoleate may be very simply prepared by the fractional distillation of the crude mixed methyl esters of castor oil fatty acids through a packed, electrically heated fractionating column. The final purification of ricinelaidic acid is also greatly facilitated by a preliminary fractional distillation of its crude methyl ester. Details of the separations will be described in a forthcoming publication.

(18) Lapworth and Mottram, *J. Chem. Soc.*, **127**, 1628 (1925).

(b) **Ricinelaidic Acid.**—The identical procedure was applied to ricinelaidic acid, 15 g. of which was dissolved with slight warming in a solution of 4.8 g. of potassium hydroxide in 100 cc. of water. (The solid acid is not easily wet and care must be taken to ensure complete solution.) The soap solution was diluted with 2.5 l. of cold water and treated with 16 g. of potassium permanganate in 1 l. of water. After decolorization with 50 g. of sodium sulfite and 250 cc. of 1:4 sulfuric acid, the washed and dried white precipitate was extracted with ligroin. The mixture of crude acids obtained weighed 10.5 g. and melted indefinitely above 70°. The entire product dissolved easily and completely in 100 cc. of warm chloroform. Cooling to approximately 0° precipitated 6 g. of a partially crystalline solid, melting indefinitely above 86° after removal of the stubbornly adhering chloroform with petroleum ether. The chloroform mother liquor was chilled to −40°, at which temperature it deposited about 1 g. of a powder having a m. p. of 83–86° after thorough drying in the vacuum desiccator. The substance remaining in the chloroform was precipitated with ligroin as a waxy solid which melted on rubbing. This was discarded after futile attempts to crystallize it from ether and alcohol.

The main fraction, melting above 86°, was recrystallized twice from chloroform at 0° to yield 3.5 g. of large lustrous plates having a m. p. of 109–110° after washing with ligroin. This compound (δ-trihydroxystearic acid) differed markedly in appearance from the microcrystalline α-trihydroxystearic acid (m. p. 109–111.5°); the m. p. of a mixture of the two was 97–104°.

The solid obtained at −40° was combined with the residue left by the evaporation of the chloroform mother liquors of the δ-trihydroxystearic acid, and the crude product (2.5 g.), m. p. 82–86°, was recrystallized several times from chloroform, aqueous alcohol, and finally from ether, when its m. p. became constant at 86.8–87.4°; the neut. equivalent was 336 (calcd. for trihydroxystearic acid, 332).

Anal.[19] Calcd. for $C_{18}H_{36}O_5$: C, 65.06; H, 10.84. Found: C, 65.20; H, 10.94.

The new acid (γ-trihydroxystearic acid) precipitated on cooling its solutions as a micro-crystalline powder, but slow evaporation left clusters of feathery crystals.

(2) **Oxidation with Hydrogen Peroxide in Acetic Acid. (a) Ricinoleic Acid.**—As already pointed out by Scanlan and Swern,[15] whose procedure was used, free ricinoleic acid reacted very sluggishly with the reagent in comparison with its glyceride, despite the purification of the acid immediately before use. Nevertheless, significant amounts of γ- and δ-trihydroxystearic acids were obtained. However, the proportions were different from those obtained with the parent castor oil, which readily produced good yields of the δ-isomer but only small amounts of the γ-acid.

Forty-five grams of pure ricinoleic acid was stirred with a solution of 36 g. of 30% hydrogen peroxide in 50 cc. of glacial acetic acid which had previously been heated for one hour at 80–85° and then cooled to room temperature. The temperature of the mixture rose slowly and spontaneously to 42° in the course of several hours and then

(19) Micro analyses by C. H. Van Etten, Division of Analytical and Physical Chemistry, Northern Regional Research Laboratory.

dropped without causing the mixture to become homogeneous. The viscous mixture was poured into 400 cc. of hot water. The aqueous layer was siphoned off, and the residue was then refluxed for one hour with 400 cc. of a normal solution of sodium hydroxide. Acidification precipitated the trihydroxystearic acids, which were taken up in chloroform, filtered through decolorizing charcoal and crystallized in the ice-bath to yield 3.35 g. of a crystalline solid having a m. p. of 108.5–110° after one crystallization from alcohol. The m. p. of a mixture of this product with α-trihydroxystearic acid produced by the permanganate oxidation of ricinoleic acid (m. p. 109–111.5°) was 97–100°; that of a mixture with δ-trihydroxystearic acid (m. p. 109–110°) obtained by the permanganate oxidation of ricinelaidic acid was 109–110°.

After evaporation of the mother liquor under vacuum, the residue was extracted with ligroin and finally taken up in diethyl ether. On cooling to below 0°, the ether solution deposited 1.5 g. of a white solid, m. p. 78.5–82.5°. This was dissolved in 50 cc. of ether and cooled to 0°, when a small amount of the δ-acid precipitated. At −40°, the remainder crystallized with a m. p. of 83–87°; this was recrystallized from aqueous alcohol and ether to a m. p. of 86–87°, showing no depression with the γ-trihydroxystearic acid obtained by the permanganate oxidation of ricinelaidic acid.

Equally poor yields of the γ- and δ-trihydroxystearic acids were similarly obtained from ricinoleic acid oxidized with hydrogen peroxide in glacial acetic acid at 0° in the course of one week, according to the method of Hilditch.[5]

The oxidation of about 300 g. of castor oil with 225 g. of 30% hydrogen peroxide in 820 cc. of glacial acetic, previously warmed and cooled as before, duplicated all the observations of Scanlan and Swern,[15] the temperature of the reaction mixture rising quickly to 70°, at which point the mixture became homogeneous. The crude trihydroxystearic acids, obtained after saponification of the reaction product with dilute alkali and subsequent acidification, were recrystallized from alcohol and then toluene to yield about 90 g. of a beautifully crystalline solid, m. p. 109–110°, which was identical with the higher-melting compound produced in the similar oxidation of the free ricinoleic acid and in the permanganate oxidation of ricinelaidic acid. It caused a marked depression in m. p. when mixed with α-trihydroxystearic acid. The mother liquors of the above crystallization were combined and evaporated to a small volume from which about 5 g. of solid material precipitated on cooling. This product was recrystallized from aqueous alcohol, exhaustively extracted with boiling water in which the δ-acid is somewhat soluble, and finally fractionally crystallized from diethyl ether. The first crop, obtained at 0°, melted at 108–110°; the residue melted at 81–85°. Further fractionation of this residue narrowed the m. p. to 85–87°, which was unaffected by admixture with γ-trihydroxystearic acid.

(b) **Ricinelaidic Acid.**—The *trans*-isomeride reacted with the acid hydrogen peroxide as sluggishly as did ricinoleic acid but produced relatively better yields of α- and β-trihydroxystearic acids, which were easily purified. Thirty grams of ricinelaidic acid was stirred into a solution of 22.7 g. of 30% hydrogen peroxide in 32 cc. of glacial acetic which had been warmed for one hour at 80° and

cooled to room temperature. An additional 18 cc. of the acetic acid was added to facilitate the solution of the solid acid. The temperature of the mixture rose only to 43°. After standing at room temperature for two days, the substantially homogeneous solution was filtered to remove a slight amount of waxy solid and the free acids were recovered from the filtrate by dilution with water, saponification with 100 cc. of 1 N sodium hydroxide and acidification as in the procedure followed with ricinoleic acid. The dried crude acids were separated with boiling chloroform, which left undissolved about 4 g. of a white powder, m. p. 137–138.5° without further purification. This proved to be β-trihydroxystearic acid, identical with the corresponding product of the permanganate oxidation of ricinoleic acid.

The chloroform solution readily deposited 4 g. of a white solid, m. p. 110–111°. The mixed m. p. showed no depression with α-trihydroxystearic acid (obtained by the permanganate oxidation of ricinoleic acid) and a wide range in m. p., beginning below 100°, with the δ-trihydroxystearic acid (m. p. 109–110°, derived from the permanganate oxidation of ricinelaidic acid or the peracetic acid oxidation of ricinoleic acid).

Further Purification of the Trihydroxystearic Acids and the Determination of their Specific Rotations.—Prior to the determination of their optical activities, the corresponding lots of trihydroxystearic acids were combined and purified as follows, the m. p. being determined with calibrated Anschütz thermometers: the α-acid was recrystallized from aqueous alcohol and then fractionated from successively smaller volumes of ether, which left undissolved small residues, m. p. 110–124° and 110–114°. The fractionation of the more soluble portion was continued from diminishing volumes of ether until both the insoluble and soluble portions melted at 109.6–112.4°. This substance was readily soluble in chloroform and benzene, which, however, were found to be unsuitable for recrystallization because the substance separated from such solutions carried much solvent and was difficult to filter off. A 95% alcoholic solution containing 5.562 g./100 cc. at 23° showed a rotation in a 2-dm. tube of −0.32°, $[\alpha]^{23}D$ −2.87°; for a glacial acetic acid solution containing 4.497 g./100 cc., the angle of rotation was −0.60°; $[\alpha]^{23}D$ −6.67°. Considering the difference in concentrations, the latter value agrees well with Walden's[3] figure of $[\alpha]D$ −6.25°.

The β-acid was thoroughly extracted with boiling toluene, and then with ether; it was recrystallized from alcohol, 50% acetic acid, again from alcohol, and was finally dried with diethyl and petroleum ethers. The purified acid was a microcrystalline powder which was poorly soluble in acetone, from which it precipitated in a form difficult to filter. The m. p. was 137.6–138.2°. Three additional crystallizations from alcohol followed by another from a large volume of water failed to change its m. p. or appearance. The rotation in a 4-dm. tube of an alcoholic solu-

tion containing 1.992 g./100 cc. was −0.31°, $[\alpha]^{23}D$ −3.89°; for the acetic acid solution of 2.152 g./100 cc. it was −1.0°, $[\alpha]^{23}D$ −11.62°.

The combined portions of the γ-acid were treated as before by exhaustion with boiling water and recrystallization from aqueous alcohol and finally from ether. It was the most soluble of the four isomers described; m. p. 86.8–87.4°. The rotation in a 2-dm. tube of an alcoholic solution containing 3.581 g./100 cc. was +0.37°, $[\alpha]^{23}D$ +19.13; for glacial acetic acid (c = 2.039), the rotation was +0.89°, $[\alpha]^{23}D$ +21.82°.

The δ-isomer is readily distinguished from the α-trihydroxystearic acid by its relatively poorer solubility in organic solvents, and by the fact that it is the only one of the four diastereoisomers which readily forms large crystals. It is best recrystallized from toluene. Its m. p. was 109.4–110.4°. The rotation in a 4-dm. tube of a 95% alcoholic solution containing 2.440 g./100 cc. was −2.60°, $[\alpha]^{23}D$ −26.63°; in a 2-dm. tube, for an acetic acid solution containing 4.311 g./100 cc. the angle was −3.34°, $[\alpha]^{23}D$ −38.85°.

Summary

1. The partial oxidation of ricinoleic and ricinelaidic acids with alkaline permanganate and with peracetic acid has been shown to result in four distinct diastereoisomeric 9,10,12-trihydroxystearic acids formed in two inter-related pairs, as expected from theoretical considerations but contrary to statements in the recent literature.

2. The α- and β-trihydroxystearic acids, m. p. 112 and 138°, and $[\alpha]^{23}D$ −6.6 and −11.6° in acetic acid (or −2.9 and −3.9° in ethanol), respectively, were obtained by the oxidation of ricinoleic acid with alkaline permanganate or of ricinelaidic acid with hydrogen peroxide in acetic acid. The γ-trihydroxystearic acid, previously unreported, and the δ-isomer, m. p. 87 and 110°, and $[\alpha]^{23}D$ +21.8 and −38.7° in acetic acid (or +19.1 and −26.6° in ethanol), respectively, were obtained by the oxidation of ricinelaidic acid with alkaline permanganate or of ricinoleic acid with hydrogen peroxide in acetic acid.

3. The optical activities of the four trihydroxystearic acids, previously unreported for three of them, were related to the *cis*- and *trans*-structures of the parent ricinoleic and ricinelaidic acids, respectively.