# DIHYDROXYSTEARIC ACID IN CASTOR OIL.*

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The presence of a dihydroxystearic acid $C_{18}H_{36}O_4$ melting at 141–143° as a minor constituent in castor oil was first pointed out by Juillard.(1) Since then Haller,(2) Meyer,(3) Eibner and Münzing,(4) Myddleton, Berchem and Barrett,(5) Panjutin and Rapoport,(6) Heiduschka and Kirsten(7) also found this acid in castor oil, but there has been lacking of investigation in detail on this acid, and its constitution remained quite unknown. Lewkowitsch(8) stated in his classical work that this acid—being a natural product—is probably optically active, but this interesting account seemed to be overlooked by subsequent investigators, and there has been no work containing the optical rotation of this acid.

A few years ago we found that methyl or ethyl esters prepared by the methanolysis or ethanolysis of castor oil deposited a minor quantity of laminar crystals at the room temperature in winter, which were confirmed to consist mainly of methyl or ethyl ester of dihydroxystearic acid by examining their characteristics. Afterward we were supplied with a sufficient quantity of crystalline deposit which was separated from the methyl ester of castor oil by the courtesy of the Taisho Kagaku Kogyo K.K. From this crystalline deposit, dihydroxystearic acid was obtained in a pure state, and its properties were examined with a special reference to the constitution and the optical rotation. For the determination of the constitution of dihydroxystearic acid, it was oxidised with sodium bichromate and sulphuric acid, and *n*-nonoic acid $CH_3{\cdot}(CH_2)_7{\cdot}COOH$ and azelaic acid $HOOC{\cdot}(CH_2)_7{\cdot}COOH$ were identified among the oxidation products. Hence the dihydroxystearic acid was found to be 9,10-dihydroxystearic acid having the formula $CH_3{\cdot}(CH_2)_7{\cdot}CHOH{\cdot}CHOH{\cdot}(CH_2)_7{\cdot}COOH$. This formula was verified also in another way; methyl dihydroxystearate was converted into methyl dibromostearate by the action of

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* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **57** (1936), 976.

(1) *Bull. soc. chim.*, [3], **13** (1895), 238.

(2) *Compt. rend.*, **144** (1907), 462.

(3) *Arch. Pharm.*, **235** (1897), 184.

(4) *Chem. Umschau Fette, Öle, Wachse Harze*, **32** (1925), 153, 166.

(5) *J. Am. Chem. Soc.*, **49** (1927), 2264.

(6) *Chem. Umschau Fette, Öle, Wachse Harze*, **37** (1930), 130.

(7) *Pharm. Zentralhalle*, **71** (1930), 81.

(8) "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th Edition, Vol. I, p. 226.

hydrogen bromide, the latter was debrominated, and the octadecenoic acids were liberated on saponification followed by acidulation of the debrominated product. The octadecenoic acids thus obtained were found to be a mixture of two geometrical isomerides (oleic and elaidic acids) of $\Delta^{9:10}$-octadecenoic acids. The optical rotation of dihydroxystearic acid was examined in methanol or chloroform by using a 40 cm. tube, and the solutions were found to be slightly dextro-rotatory, but an accurate measurement was difficult due to an extremely small angle of rotation.(9) Solutions of methyl dihydroxystearate showed also very small dextro-rotation, but the determination of the angle of rotation was difficult.

The acetylated product of methyl or ethyl ester of dihydroxystearic acid was a liquid at the ordinary temperature, and the specific rotation was measured without using solvent; $[\alpha]_D^{30}$ +0.19° for diacetyl ester of methyl dihydroxystearate and $[\alpha]_D^{30}$ +0.31° for diacetyl ester of ethyl dihydroxystearate.

It is thus confirmed by the foregoing results that dihydroxystearic acid in castor oil is *d*-9,10-dihydroxystearic acid. As for the racemic 9,10-dihydroxystearic acid derived from $\Delta^{9:10}$-octadecenoic acids (oleic and elaidic acids), there are known two isomerides. The one melts at 130° and is obtained from oleic acid by Hazura's oxidation method; the other melts at 100° and is obtained from elaidic acid by Hazura's oxidation method. Resolution of these racemic acids into optically active isomerides has hitherto been studied by Freundler(10) and Inoue and Suzuki.(11) Freundler resolved 9,10-dihydroxystearic acid of higher melting point into optically active isomerides by means of its strychnine salt. Ethyl ester of *d*-isomeride had m.p. 98–99° and $[\alpha]_D$ +1.6°, while ethyl ester of *l*-isomeride had m.p. 98–99° and $[\alpha]_D$ −2.1°. Since, however, the solubility of both isomerides was very small, the specific rotation was not measured accurately, and the above figures were stated to show only approximate values. Also Inoue and Suzuki resolved 9,10-dihydroxystearic acids derived from oleic and elaidic acids by means of strychnine salt. The specific rotation observed by these authors were as follows: $[\alpha]_D$ +23.20° and −23.60° for *d*- and *l*-isomerides obtained from 9,10-dihydroxystearic acid of m.p. 130°; $[\alpha]_D$+27.60° and −27.45° for *d*- and *l*-isomerides obtained from 9,10-dihydroxystearic acid of m.p. 100°. The melting points of optically active isomerides were not recorded in their paper.

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(9) The angle of rotation greater than 0.25° was clearly discriminated by the polariscope used, but a 4% solution of dihydroxystearic acid in a 40 cm. tube showed an angle of rotation smaller than +0.25°, and it was difficult to measure it accurately. Roughly speaking, the specific rotation of dihydroxystearic acid should not be greater than +1.6° (0.25÷4÷0.04).

(10) *Bull. soc. chim.*, [3], **13** (1895), 1052.

(11) *Proc. Imp. Acad.* (Tokyo), **7** (1931), 261.

In comparison of *d*-acid separated from castor oil in these experiments and *d*-acids obtained from racemic 9,10-dihydroxystearic acids by the above cited authors, *d*-acid obtained by Freundler has an appreciably lower melting point than *d*-acid of castor oil, while *d*-acids obtained by Inoue and Suzuki show exceedingly greater specific rotations than *d*-acid of castor oil. After it has been confirmed in these experiments that *d*-acid of castor oil is 9,10-dihydroxystearic acid and its specific rotation is very small (not exceeding $+1.6°$), the discrepancy between the results of our experiments on *d*-acid of castor oil and those of above cited authors on *d*-acids obtained from racemic 9,10-dihydroxystearic acid is not explainable. In order to gain a fuller information regarding this point, we have prepared racemic 9,10-dihydroxystearic acid by oxidation of oleic acid and attempted to resolve it into optically active isomerides by means of its strychnine salt. For the preparation of the strychnine salt of dihydroxystearic acid, strychnine nitrate was added to an alcoholic solution of potassium dihydroxystearate following the method of Freundler with a modification that strychnine nitrate instead of sulphate was used in our experiment. In another experiment dihydroxystearic acid and free strychnine were heated in chloroform solution following the method of Inoue and Suzuki. It was, however, found that no substantial amount of strychnine and dihydroxystearic acid combined by these methods, and the products contained large amount of free strychnine and dihydroxystearic acid. Resolution of dihydroxystearic acid as its strychnine salt was not attained. It should also be noted here regarding the stability of *d*-acid separated from castor oil. According to Inoue and Suzuki the optically active isomerides obtained from racemic 9,10-dihydroxystearic acids had a strong tendency to undergo racemisation. When they were heated in alcoholic solutions for 30 minutes they were completely converted into racemic compounds. Aqueous solutions of their potassium salts were quite inactive. Similar facts were reported by Grün(12) in the case of *d*-isomeride (m.p. 90°) obtained from racemic 9,12-dihydroxystearic acid. Its alcoholic solution became inactive on standing for some time; on heating at 130–140° it became rapidly inactive. The *d*-acid of castor oil is, however, very stable. Even after prolonged heating of its alcoholic solution, the crystals separated on cooling showed the same melting point. After the elapse of several months the melting point of dihydroxystearic acid remained unaltered. Even when dihydroxystearic acid of castor oil was converted into its methyl or ethyl ester and then reconverted into free acid by saponification followed by acidification, there was no indication of racemisation. It is thus seen that contrary to the observations of previous investigators on the optically active isomerides obtained by the resolution of

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(12) *Ber.*, **39** (1906), 4400.

racemic compounds, the *d*-acid of castor oil is quite stable and shows no tendency to undergo racemisation.(13)

## Experimental.

1. **Separation of Dihydroxystearic Acid.** The starting material used in these experiments was supplied by the courtesy of the Taisho Kagaku Kogyo K.K. It was a crude deposit which was separated in a yield of ca. 3% from the methyl esters prepared by the methanolysis of castor oil on cooling at 0–5°. Since the removal of the liquid esters was incomplete, the crude deposit formed a pasty mass at the ordinary temperature. In these experiments 1 kg. of the crude deposit was first mixed with 1 l. of methanol and after heating on the water bath for a short time, a small amount of flocculent precipitate was removed by filtration. The clear solution was allowed to stand at the room temperature, and the crystalline deposit was filtered off. The filtrate formed a further quantity of crystalline deposit on ice-cooling. The crystalline deposits thus obtained were united and redissolved in 1 l. of methanol by warming. A small amount of flocculent precipitate was again removed by filtration, and the clear solution was ice-cooled to separate the crystalline deposit which was filtered and treated with methanol as before. After repeating the methanol treatment five times there were obtained finally 89 g. of methyl dihydroxystearate in lustrous laminar crystals which had m.p. 111–112°(14) and saponification value 167.5 (calc. for methyl dihydroxystearate $C_{19}H_{38}O_4$ : 170.9). The optical rotation of methyl dihydroxystearate was examined in a 4% solution in methanol by using a 40 cm. tube, but an accurate measurement was difficult due to an extremely small dextro-rotation (less than +0.25°).

On heating methyl dihydroxystearate with twice its weight of acetic anhydride at 140° for 2 hours and subsequently washing the product with boiling water, diacetyl ester $C_{19}H_{36}O_2(OCOCH_3)_2$ was obtained. It formed a colourless liquid and had the following constants : $d_4^{15}$ 0.9826, $n_D^{15}$ 1.4498, $[MR_L]_D$ 113.3 (calc. 113.4), $[\alpha]_D^{30}$ +0.19°, saponif. value 403.7 (calc. 408.2).

For the preparation of dihydroxystearic acid the methyl ester was saponified with alcoholic potash, the product was diluted with water and then acidulated with hydrochloric acid. The dihydroxystearic acid liberated was separated by filtration, washed with water and recrystallised from ether-alcohol (1 : 1), yielding laminar crystals; m.p. 142-143°, neutralisation value 177.5 (calc. for $C_{18}H_{36}O_4$ : 177.4). A 1% solution in chloroform and a 4% solution in methanol showed only a very slight rotation in a 40 cm. tube, but the determination of specific rotation was difficult due to an extremely small angle of rotation.

Dihydroxystearic acid was dissolved in alcohol, and after addition of a small amount of sulphuric acid the solution was refluxed on the water bath in order to complete esterification. The product was taken up with ether, the ethereal solution was first washed with a solution of potassium carbonate in order to remove sulphuric acid and unchanged dihydroxy-

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(13) S. Ishikawa and G. Maeda presented a paper at the 29th meeting of the Institute of Physical and Chemical Research held on May 22, 1936, in which the separation of methyl dihydroxystearate from commercial methyl ester of ricinoleic acid and the constitution of this dihydroxystearic acid were dealt with. According to these authors this acid seems not to be 9, 10-dihydroxystearic acid. The present investigation showed, however, that the dihydroxystearic acid of castor oil is *d*-9,10-dihydroxystearic acid, but the presence of any other dihydroxystearic acid was not ascertained.

(14) Juillard (*loc. cit.*) gave m.p. 104–106°. Haller (*loc. cit.*) gave m.p. 107–108°.

stearic acid as their potassium salts. The ethereal solution was then washed thoroughly with water, and after distilling off a portion of the solvent from the solution, it was allowed to cool when the crystals of ethyl dihydroxystearate $C_{20}H_{40}O_4$ separated ; m.p. 104–105°, saponif. value 161.9 (calc. 162.9).

Diacetyl ester of ethyl dihydroxystearate $C_{20}H_{38}O_2(OCOCH_3)_2$ was obtained by heating ethyl dihydroxystearate with acetic anhydride. It formed a colourless liquid having the following constants : $d_4^{15}$ 0.9743, $n_D^{15}$ 1.4485, $[MR_L]_D$ 117.8 (calc. 118.0), $[\alpha]_D^{30}$ +0.31°, saponif. value 392.6 (calc. 392.9).

2. **Oxidation of Dihydroxystearic Acid.** Fifteen grams of dihydroxystearic acid was mixed with 30 g. of sodium bichromate, 75 g. of sulphuric acid and 300 g. of water, and the mixture was heated in an oil bath, the temperature of which was kept at 110°, for 30 minutes and then subjected to steam distillation by which about 1 l. of distillate was collected. The distillate (a) consisted of a minor proportion of oily substances together with aqueous solution. The residue (b) from steam distillation was a dark green liquid. The distillate was saturated with sodium chloride and shaken with petroleum ether. The petroleum ether solution was separated, and after distilling off petroleum ether there remained 6.4 g. of colourless oil which had $d_4^{15}$ 0.9038, $n_D^{15}$ 1.4336, $[MR_L]_D$ 45.53 (calc. for $C_9H_{18}O_2$ : 45.30), neutral. value 350.8 (calc. for $C_9H_{18}O_2$ : 354.8). This oil was converted into the acid chloride by heating with thionyl chloride on the water bath. The acid chloride formed was dropped into ice-cooled ammonia and the precipitated acid amide was filtered and washed with water. It was dissolved in 50% alcohol, treated with active carbon and cooled down to separate the crystals which were identified with *n*-nonoic acid by its m.p. and mixed m.p. 98.5–99°.

The residue (b) from steam distillation was shaken with 2 l. of ether. The ethereal solution was separated and after washing with saturated brine the ether was distilled off leaving 4 g. of bluish-green coloured crystalline solid as residue. This was dissolved in boiling water, in which a small amount of green coloured substances remained insoluble. The clear solution was separated and cooled down to deposit laminar crystals which on recrystallisation from water gave pure azelaic acid ; yield 2 g., m.p. 106–107°, neutr. value 593.0 (calc. for $C_9H_{16}O_4$ : 596.5). It showed no depression of melting point when admixed with an authentic specimen of azelaic acid.(15)

3. **Preparation of Oleic and Elaidic Acids from Methyl Dihydroxystearate.** Ten grams of methyl dihydroxystearate was heated in a flask for 30 minutes by means of an oil bath, the temperature of which was kept at 140°. During heating a current of hydrogen bromide was passed through the melted mass. The methyl dibromostearate thus formed was a viscous oil. Ten c.c. of methanol and 13 g. of zinc powder were added to the product and the mixture was refluxed on the water bath. Ten c.c. of 5 N hydrogen chloride in methanol was added in the course of 20 minutes, and the heating was continued for another 20 minutes, after which the product was taken up with ether. The ethereal solution was washed with water, the ether was distilled off, and the residue consisting of methyl octadecenoate was saponified with alcoholic potash. The soap solution was acidified with

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(15) The specimen of azelaic acid used for the mixed melting point test was prepared by the ozonolysis of oleic acid and had m.p. 105–106°. Azelaic acid obtained in these experiments from dihydroxystearic acid in castor oil is believed to have a higher purity than the specimen from oleic acid.

hydrochloric acid, and the separated free acids were taken up with petroleum ether. The petroleum ether solution was washed with water, the solvent was distilled off, and there remained 8 g. of residue which had neutral. value 196.0, iodine value 84.1 and m.p. 35–36°. On cooling the solution of the residue in 80% alcohol, there was formed about 5 g. of crystalline solid which yielded on recrystallisation from 80% alcohol crystals having neutral. value 198.7 (calc. for $C_{18}H_{34}O_2$ : 198.8), iodine value 87.6 (calc. for $C_{18}H_{34}O_2$ : 89.9) and m.p. 44.5–45°. No depression of melting point was observed when this substance was added to an authentic specimen of elaidic acid.(16) The mother liquor separated from crystals of elaidic acid contained a liquid fatty acid which deposited only a minute amount of solid after standing for several days at the room temperature. The liquid portion was found to consist of oleic acid, since it was converted into a solid mass by the action of nitrous acid and the latter yielded after purification elaidic acid having neutral. value 197.1, iodine value 88.3 and m.p. 44.5–45°.

**4. Preparation of Dihydroxystearic Acid from Oleic Acid and Attempt to Resolve it into Optically Active Isomerides by Means of its Strychnine Salt.** Fifteen grams of oleic acid prepared from tsubaki oil was mixed with 18 c.c. of potassium hydroxide solution (ca. 28%) and then diluted with 1 l. of water. To this solution of potassium oleate, 1 l. of potassium permanganate solution (1.5%) was gradually added with constant stirring, and then sulphur dioxide was passed through the solution until the excess of potassium permanganate and the insoluble oxides of manganese disappeared completely. Dihydroxystearic acid was separated by filtration, and after being washed with water it was recrystallised from 95% alcohol yielding 11.2 g. of crystals having m.p. 129.5–130°. By repetition of these operations a further quantity of dihydroxystearic acid was prepared.

Thirty-six grams of dihydroxystearic acid and 45 g. (ca. 20% in excess) of strychnine were refluxed on the water bath when a clear solution was obtained. After heating for 30 minutes, 2 l. of chloroform was added to the solution, and it was kept at the room temperature over a night. A large amount of crystals (27 g.) separated, but these were found to be unchanged dihydroxystearic acid by their neutr. value and melting point. This experiment was then discontinued.

Thirty-eight grams of dihydroxystearic acid was dissolved in 1.7 l. of alcohol and neutralised with alcoholic potash. Fifty grams of strychnine nitrate (in small excess) was added to the solution, and it was refluxed on the water bath for 1 hour. There was formed a considerable amount of precipitate which seemed to be potassium nitrate. The substances contained in the clear solution separated from the precipitate were subjected to fractional crystallisation, and there were obtained 4 fractions $F_1-F_4$. The first fraction $F_1$ was separated further into 8 fractions $F_{1-1}-F_{1-8}$ by means of fractional crystallisation from chloroform. The fraction $F_{1-6}$, which was most abundant in quantity, was separated further into 5 fractions $F_{1-6-1}-F_{1-6-5}$ from chloroform solution. The fraction $F_4$ obtained by the first fractional crystallisation was separated into 6 fractions $F_{4-1}-F_{4-6}$ from chloroform solution. Fractions thus obtained were separately examined, but they were found to contain a considerable amount of strychnine and dihydroxystearic acid in free state, and to what extent dihydroxystearic acid was resolved into the optically active isomerides as their strychnine salts was difficult to know.

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(16) The specimen of elaidic acid used for the mixed melting point test was prepared from oleic acid separated from tsubaki oil and had m.p. 43.5–44°.

## Summary.

A dihydroxystearic acid, which is contained as a minor component in the fatty acids of castor oil, has been separated and proved to be identical with *d*-9,10-dihydroxystearic acid.

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