CRYSTALLINE DEPOSIT FROM CASTOR OIL

YOSHIYUKI TOYAMA and HIDEKO TAKAI

Department of Applied Chemistry

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Castor oil as compared with other ordinary fatty oils has characteristic properties. In spite of its relatively low unsaturation, it has a low cloud point. It is generally a clear oil without solid deposit even in the winter season in our country. However, samples of castor oil which contain crystalline solid and are turbid in the winter season have recently been submitted to this laboratory for examination from oil mills in this district. The oil samples still contain crystalline solid even at a room temperature of 20° C. But they, once heated until they become clear, deposit no solid even when they are kept at 0° C for a short time. The crystalline solid in the oil samples should have been formed after a long standing in the cold place. Since methyl or ethyl ester of mixed fatty acids of castor oil deposits in the cold methyl or ethly ester of 9, 10-dihydroxystearic acid[1] which is contained in castor oil as a minor component of fatty acids, the authors presumed at first the crystalline solid in the oil samples to consist of glycerides or other esters of 9,10-dihydroxystearic acid. However, the crystalline solid in the oil samples was found to consist chiefly of stearo-diricinolein in these studies. Although this stearo-diricinolein is slightly dextro-rotatory, its structure, whether 1-stearo-diricinolein or 2-stearo-diricinolein, could not be determined by optical activity, since stearo-diricinolein contains optically active ricinoleic acid radical. In order to determine the structure of stearo-diricinolein, it was oxidized with potassium permanganate in acetone, and stearo-diazeleo-glyceride was separated from the oxidation product. An examination of its optical activity indicated that it was very slightly optically active, if at all, so that it was quite difficult to decide convincibly whether it is optically active or inactive, though it appeared to be slightly dextro-rotatory. On the other hand, the melting point 36°–37° C of stearo-diricinolein is considerably higher than the melting point 22.5°–23.5° C of 1-stearo-diolein[2] which, like stearo-diricinolein, contains one stearic acid radical and two unsaturated acid radicals. It is rather close to the melting point 38.5° C of 1-oleo-distearin[3] or the melting point 42.5°–43° C of 2-oleo-distearin.[4] The relatively high melting point of stearo-diricinolein seems to suggest that this glyceride is symmetrical 2-stearo-diricinolein. In short, the structure of stearo-diricinolein could not been determined in these experiments. It is to be noted that stearo-diricinolein like castor oil is miscible with ethanol and glacial acetic acid, while stearo-diricinolein like other ordinary fatty oil, in contrast to castor oil, is miscible with hexane.

Oil No. 1. This sample is a refined castor oil of light yellow color produced by the expression method in Dec. 1951-Jan. 1952 from the seeds imported from Siam. It deposited crystalline solid in the winter season. The solid remained undissolved even at a room temperature of about 20° C in April. The oil sample

(50 g) was filtered by suction. The solid remaining on the filter was recrystallized from 20 cc of acetone under cooling with ice, yielding 1.4 g of crystalline solid which was again recrystallized from acetone. The final product melted at 34.5°-37° C and had the following constants: A.V. 1.4, S.V. 174.0, Acetyl S.V. 274.4.

Calc. for $C_3H_5(OCOC_{17}H_{35})(OCOC_{17}H_{32}OH)_2$: A.V. 0, S.V. 183.1, Acetyl S.V. 279.5.

Although the saponification value of the crystalline solid is considerably lower than the calculated value for stearo-diricinolein, saponification of the crystalline solid followed by removal of unsaponifiable matter from soap solution yielded a fatty acid mixture which solidified at ordinary temperature and had N.V. 189.0 and I.V. 56.3 (Calc. for a mixture of 1 mole of stearic acid and 2 moles of ricinoleic acid, N.V. 191.0 and I.V. 57.8). On cooling the fatty acid mixture in acetone, there separated a crystalline acid which had M.P. 68°-68.5° C and N.V. 196.7 and showed no depression of melting point when mixed with stearic acid (M.P. 70° C and N.V. Calc., 197.2). These results indicate that the crystalline solid of M.P. 34.5°-37°C consists chiefly of stearo-diricinolein.

The mother liquors of recrystallization of stearo-diricinolein were concentrated, and a further quantity (0.9 g) of crystalline solid was separated. Recrystallization of this crystalline solid yielded eventually stearo-diricinolein of M.P. 34.5-36.5° C. Solutions of stearo-diricinolein in absolute ethanol, 90% ethanol, glacial acetic acid and hexane (0.5 g in 20 cc) are perfectly clear at 20° C.

Oil No. 2. This sample is a refined oil produced by the expression method in April, 1951 from Indian seeds. It deposited crystalline solid in the cold. The supernatant clear oil was removed, and the bottom portion containing a relatively large amount of solid was submitted to this laboratory. The bottom portion melted at 35° C to a clear oil which deposited no solid by cooling for several hours at about 0° C. Further cooling for two days at 0°--5° C formed crystalline solid so that the entire material became a semi-solid. A solution of 80 g of the bottom portion in 240 cc of acetone was cooled to −10° C, but no crystals separated after one hour. When the solution was inoculated with several small pieces of crystalline solid obtained from Oil No. 1, it deposited immediately a considerable amount of crystalline solid. The crystalline solid melted at about 35° C. After three recrystallizations, it showed M.P. 36°-37° C and $[\alpha]_D^{26} = +4.22°$ (in acetone).

To a solution of 2.4 g of crystalline solid in 48 cc of acetone was added 24 g of powdered potassium permanganate in small portions, and the mixture was refluxed for 2 hours in order to complete the oxidation. The acetone was then distilled, water was added to the residue, and the mixture was decolorized with a solution of sodium bisulfite. The oxidation product was extracted with ether, The ether solution was shaken with a solution of potassium carbonate, by which acidic oxidation product entered into the solution of potassium carbonate. After acidification of the carbonate solution with hydrochloric acid, the resulting acidic oxidation product was extracted with ether. Since the acidic oxidation product thus obtained had an odor of lower fatty acids, it was washed with hot water in order to remove water-soluble components, and there was obtained an viscous oil of N.V. 157.3, S.V. 384.9 and $[\alpha]_D^{25} = +0.74°$ (in acetone).

Calc. for stearo-diazeleo-glyceride $C_3H_5(OCOC_{17}H_{35})(OCOC_7H_{14}COOH)_2$: N.V. 160.5, S.V. 401.4.

Summary

Crystalline solid which separated from castor oil in the cold has been found to consist chiefly of stearo-diricinolein of M.P. 36°-37° C and $[\alpha]_D^{26} = +4.22°$. It is completely miscible with each of ethanol, glacial acetic acid and hexane.

References

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