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THE PURIFICATION OF SODIUM RICINOLEATE¹

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Sodium ricinoleate is prepared from castor oil, which is composed largely of ricinoleic acid glyceride. There are also present, however, small amounts of two saturated fatty acids, stearic and dihydroxystearic, and two acids more unsaturated than ricinoleic, namely, oleic and linolic. The quantitative composition of castor oil is still open to question, and undoubtedly varies considerably with the grade of oil, but the qualitative presence of these five fatty acids and the absence of significant amounts of other fatty acids seem to be well established.²

The earliest attempt to prepare a purified ricinoleic acid was that of Krafft,^{2d} who in 1888 cooled the free fatty acids obtained from castor oil to 0°, and pressed the solid fatty acids at gradually rising temperatures, obtaining a solid acid melting near room temperature. Juillard^{2g} later showed that this method gave a product containing stearic and dihydroxystearic acids. Juillard attempted the purification of ricinoleic acid by filtering the crude acids, at ordinary temperature, to remove the insoluble solid fatty acids, then prepared the barium soaps, which he purified by recrystallization from alcohol. Haller^{2h} alcoholized castor oil and fractionated the resulting ester before saponifying. Kozlowski and Halvorson,³ by recrystallizing the barium soaps from alcohol, decomposing with strong acid and resaponifying, obtained fractions of sodium soaps which had the theoretical iodine numbers for sodium ricinoleate. This fact is not a complete criterion of purity, however, since a combined contamination with saturated fatty acids and a more unsaturated acid than ricinoleic might also give a product with the theoretical iodine number. Fahrion,²ⁱ and Panjutin and Rappoport⁴ described methods for the partial purification of castor oil and its derivatives by extraction with petroleum ether and benzene.

¹ A preliminary report of this research was made before the Organic Section of the American Chemical Society, Indianapolis, Indiana, April, 1931.

² (a) Saalmüller, *Ann.*, **64**, 108 (1848); (b) Bussy and Lecanu, *J. Pharm.*, **8**, 57 (1857); (c) Hazura and Grüssner, *Monatsh.*, **9**, 475 (1888); (d) Krafft, *Ber.*, **21**, 2730 (1888); (e) Mangold, *Monatsh.*, **15**, 307 (1894); (f) Meyer, *Arch. Pharm.*, **235**, 185 (1897); (g) Juillard, *Bull. soc. chim.*, [3] **13**, 240 (1895); (h) Haller, *Compt. rend. acad. sci.*, **144**, 462 (1907); (i) Lifschutz, *Z. physiol. Chem.*, **56**, 446 (1908); (j) Chonowsky, *Ber.*, **42**, 3339 (1909); (k) Rubinsky, *Z. angew. Chem.*, **26**, 316 (1912); (l) Fahrion, *Chem. Umschau*, **23**, 60, 71 (1916); (m) Eibner and Münzing, *ibid.*, **32**, 153, 166 (1925); (n) Myddleton, Berchem and Barrett, *THIS JOURNAL*, **49**, 2264 (1927); (o) Heiduschka and Kirsten, *Pharm. Zentralhalle*, **71**, 81 (1930).

³ Kozlowski, *J. Bact.*, **16**, 203 (1928); Halvorson, *Proc. Soc. Exptl. Biol. Med.*, **22**, 553 (1925).

⁴ Panjutin and Rappoport, *Chem. Umschau*, **37**, 130 (1930).

The purity of various fractions of sodium ricinoleate cannot be checked accurately by determinations of the iodine number, due to the original presence of such varied contaminants. The presence of small amounts of sodium stearate or sodium dihydroxystearate in a sample of purified sodium ricinoleate can be detected, however, by virtue of the fact that a 1% aqueous solution of sodium ricinoleate containing traces of these soaps of solid fatty acids clouds on standing in the cold. Using this clouding as a criterion of the presence of saturated fatty acid, the writer found that none of the above described methods of purification was capable of satisfactorily removing these saturated acids, and that even the ether extraction of the combined lead soaps often failed to give a sharp separation of the lead soaps of saturated and unsaturated fatty acids.

The solid acids appear to precipitate quantitatively when the mixed fatty acids are chilled, but the liquid acids become so viscous that they cannot be filtered. It was found, however, that after adequately chilling a solution of the fatty acids in an equal volume of alcohol, the solid acids still appeared to precipitate quantitatively and left a supernatant liquid which could be easily filtered. A soap prepared from fatty acids purified in this manner gave an aqueous solution which remained clear even when frozen.

The solid fatty acids separated by this procedure amounted to 2.5-3% of the total. Since stearic acid is ether soluble while dihydroxystearic acid is difficultly soluble in ether, an attempt was made to separate these two compounds from their mixtures by prolonged extraction by ether in a Soxhlet extractor. The ether solution was then chilled and filtered. A precipitate of crude dihydroxystearic acid, m. p. 138-141°, was obtained. The resulting filtrate, upon removal of the ether and recrystallization of the residue from alcohol gave stearic acid, m. p. 65-68°. The material which had not dissolved in ether during the extraction process melted at 190-208°, and upon further recrystallization from alcohol melted at 210-212°. This product contained few free carboxyl groups, yet upon saponification and reacidification gave an equal weight of dihydroxystearic acid. It is probable that this high melting compound is an anhydride of dihydroxystearic acid, and it is undoubtedly formed during the chilling in alcoholic solution.

The ratio of dihydroxystearic acid to stearic acid was approximately 2:1, indicating respective concentrations in the original castor oil of approximately 1.7 and 0.8%. This estimation of dihydroxystearic acid is considerably higher than reported for previous determinations, probably due to the fact that earlier workers have isolated the acid by the barium salt method, which does not give a quantitative separation.

Ricinoleic acid is the only hydroxylated liquid fatty acid present in castor oil and this property makes possible a simple method for its separa-

tion from the other liquid fatty acids. The methyl esters of ricinoleic, oleic and linolic acids have boiling points falling within a rather narrow range (225, 212 and 208°, respectively, at approximately 10 mm.), and when a mixture of the three is distilled there is no clean cut separation. When such a mixture of esters is acetylated, the methyl oleate and methyl linolate are unchanged, while the methyl ricinoleate is converted into its acetyl derivative, thus raising its boiling point by about 35°. It is now possible by a single distillation to separate a pure fraction of methyl acetylricinoleate having both the theoretical iodine number and the theoretical acetyl number.⁵ From material prepared in this manner, C. P. ricinoleic acid and C. P. sodium ricinoleate were prepared as described below.

Experimental

Preparation of Ricinoleic Acid Free from Saturated Fatty Acids.—Castor oil is saponified with concentrated aqueous potash and the free fatty acids liberated by the addition of a slight excess of dilute hydrochloric acid. The free fatty acids are separated and dissolved in an equal volume of 95% alcohol. This solution is then chilled to -15°, kept at that temperature for a sufficient time to complete the precipitation of the insoluble acids (four days) and filtered in the cold. The alcohol is removed by washing with a large amount of dilute hydrochloric acid, thus liberating the free fatty acids which are further washed with water and separated. A small amount of esterification or anhydride formation occurs during the solution of the fatty acids in the alcohol. This ester or anhydride is reconverted into free acid by resaponification, and the free purified fatty acids liberated by the acidification of an aqueous solution of the resulting soap.

Examination of the Solid Fatty Acids.—The solid fatty acids separated in the above process, amounting to 2.5–3% of the total fatty acids, are subjected to a prolonged extraction with ether in a Soxhlet extractor. In this manner all of the stearic acid and free dihydroxystearic acid are extracted. The ethereal extract is chilled, precipitating crude dihydroxystearic acid, m. p. 141–142° (from alcohol). The ether filtrate is evaporated and the residue recrystallized from alcohol, yielding stearic acid, m. p. 65–68°. If the ether extraction has been carried to completion, an ether-insoluble residue remains which melts, after recrystallization from alcohol, at 210–212°. This material is probably an anhydride of dihydroxystearic acid, since when saponified with alcoholic potash and thrown out by pouring into dilute hydrochloric acid, an identical weight of dihydroxystearic acid is obtained which melts at 141–142°. The relative amounts of the two saturated acids vary considerably, depending upon the composition of the original oil and losses during the handling of the large amounts worked with. The average ratio of dihydroxystearic acid to stearic acid is 2:1.

Preparation of the Methyl Esters of the Liquid Fatty Acids of Castor Oil.—The free fatty acids from which the solid acids have been removed are dissolved in three times their volume of absolute methyl alcohol, a little dry gaseous hydrogen chloride is added, and the solution refluxed for several hours.

The crude free fatty acids may, of course, be dissolved originally in absolute methyl alcohol, chilled, filtered and esterified without the necessity of isolating the partially purified fatty acids. The excess of methyl alcohol from the esterification mixture is

⁵ An apparent acetyl number was obtained by saponification with alcoholic potash, acidification with an excess of dilute sulfuric acid, distillation and titration of the acetic acid

removed by distillation or by washing with water, after which the methyl ricinoleate is distilled and a fraction collected boiling at 188–193° under a pressure of 4 mm.

Preparation of Methyl Acetylricinoleate.—Methyl ricinoleate as described above is mixed with two parts by weight of acetic anhydride and refluxed for several hours, after which the excess of acetic anhydride and the by-product acetic acid are distilled off. The residue is fractionally distilled under a low vacuum. The separation is not sharp, but if the distillation is carried out slowly, at least the last half of the distillate, boiling at 195° under a pressure of 1 mm., is pure methyl acetylricinoleate.

Anal. Calcd. for $C_{21}H_{38}O_4$: I₂ no., 71.7; acetyl no.,⁵ 158.5. Found: I₂ no., 71.4, 71.5; acetyl no., 157.2, 158.2.

Preparation of C. P. Ricinoleic Acid.—Methyl acetylricinoleate with the theoretical iodine and acetyl numbers is saponified with an excess of alcoholic potassium hydroxide, the free fatty acids are liberated by the addition of dilute hydrochloric acid and washed thoroughly with water to remove the acetic acid. The fatty acid is then separated, dried over anhydrous sodium sulfate and filtered. Ricinoleic acid so prepared is of a light straw-yellow color, rather viscous and perfectly clear. The acid solidifies in an ice-salt bath to a waxy solid mass which melts, as marked by a return to transparency, at approximately 5°. After standing for six weeks the acid melts in the same manner at 4–5°.

Preparation of C. P. Sodium Ricinoleate.—Ricinoleic acid, c. p., prepared as above described is neutralized with the stoichiometric amount of c. p. sodium hydroxide dissolved in hot alcoholic solution. The resulting solution is allowed to cool and gel and is then broken into small pieces which are dried in a vacuum desiccator over calcium chloride. The resulting soap is a brittle solid of a faint lemon-yellow color. A 1% aqueous solution of this soap has a *P_H* of 8.3–8.5 (determined by the quinhydrone electrode).

Summary

Methods are given for the removal of the saturated fatty acids from the fatty acids of castor oil and attention is called to the existence of a larger proportion of dihydroxystearic acid than has been heretofore recognized. A satisfactory method is given for the preparation of c. p. ricinoleic acid and c. p. sodium ricinoleate.

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