

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, THE OHIO STATE UNIVERSITY]

**Studies on the Chemistry of the Fatty Acids. V. The Preparation of Methyl Ricinoleate and Ricinoleic Acid by Fractional Crystallization Procedures**

BY J. B. BROWN AND NAOMA D. GREEN

Ricinoleic acid,  $C_{18}H_{34}O_3$ , occurs in castor oil to the extent of 80–86% of the total fatty acids.<sup>1,2</sup> The valuable medicinal and commercial properties of this oil are due in large part to this unsaturated hydroxy acid which occurs in the oil as tri-ricinolein and as mixed triglycerides with oleic, linoleic and stearic acids. According to Goldsobel<sup>3</sup> and others<sup>4,5,6,7</sup> ricinoleic acid is 12-hydroxy-*cis*-9-10-octadecenoic acid. Although numerous attempts have been made in the past to prepare the pure acid for use in preparation of derivatives and to study its properties, few, if any, pure preparations, especially of the acid, are described; in most cases analytical criteria of purity are quite inadequate. Methods of preparation up until 1931 have been reviewed by Rider.<sup>8</sup> They have included cold-pressing of the acids of castor oil, and crystallization of the barium soaps of the resultant acids from alcohol; direct alcoholysis of castor oil with methyl alcohol and distillation of the methyl esters; removal of olein, linolein, dihydroxystearin and unsaponifiable from the original oil by repeated extraction with benzine, the final product being 98.5% ricinoleic acid and various combinations of procedures. Rider prepared the pure acid by chilling the fatty acids of castor oil, dissolved in an equal volume of 95% alcohol, to  $-15^\circ$  when the solid acids precipitated. The liquid acids were then converted into methyl esters, acetylated with acetic anhydride and the acetylated esters fractionally distilled at 4 mm. The pure acetyl ester was thus isolated. It was converted into ricinoleic acid by saponification. The acid melted at  $4-5^\circ$ . The melting point was the only criterion of purity reported. A more recent preparation by Straus, Heinze and Salzmänn<sup>9</sup> employs Rider's method of removing the saturated fatty acids and in addition crystallization of the

lead soaps from ether and preparation of the benzoyl methyl ester.

The object of the present work was to apply low-temperature fractional crystallization methods, previously developed in this Laboratory for the purification of oleic, linoleic and linolenic acids,<sup>10</sup> to the preparation of ricinoleic acid and its methyl ester. Since it has long been known that the free acid cannot be distilled without decomposition even at very low pressures, the preparation of pure methyl ricinoleate was first attempted. A specimen of castor oil was converted into methyl esters by direct alcoholysis. The distilled esters were fractionally crystallized from acetone or from methyl alcohol. Fractions were isolated in good yield which analyzed as methyl ricinoleate of high purity. Four such preparations are described. Attempts to prepare pure ricinoleic acid from the pure ester were unsuccessful because the product could not be distilled and because during saponification, even in the cold, the acid was partly dehydrated with the formation of octadecadienoic acids. A specimen of ricinoleic acid of 95% purity was prepared by cold saponification of the crude methyl esters, followed by direct fractional crystallization of the acids from acetone.

**Experimental Part**

**Equipment.**—For low temperature work the special equipment described in our previous work was used, namely, a room in which a temperature of  $-20$  to  $-25^\circ$  was continuously maintained and a well insulated dry-ice-alcohol apparatus designed to accommodate a 2-liter Erlenmeyer flask. In the latter part of this work, a similarly constructed bath for a 4-liter Erlenmeyer flask was used. All filtrations were carried out by suction in the  $-20^\circ$  room.

**Procedures. A. Preparation of Pure Methyl Ricinoleate.**—(1) One kilogram of castor oil (iodine number 87.9; saponification number 179.7) was esterified with 1500 cc. of methyl alcohol containing 2% dry hydrogen chloride by refluxing on a hot water-bath for twenty-four hours. The crude esters were then distilled at a pressure of 2–3 mm., the boiling point range being  $185$  to  $212^\circ$ ; yield 810 g.

Eighty grams of the esters was dissolved in 4 liters of C. P. acetone in 2-liter Erlenmeyer flasks (more concen-

(1) Eibner and Munzing, *Chem. Umschau. Fette Öle Wachs Harze*, **32**, 153 (1925).

(2) Panjutin and Rapoport, *ibid.*, **37**, 130 (1930).

(3) Goldsobel, *Ber.*, **27**, 3121 (1894).

(4) Kasansky, *J. prakt. Chem.*, **62**, 363 (1900).

(5) Haller and Brochet, *Compt. rend.*, **150**, 496 (1910).

(6) Chonowsky, *Ber.*, **42**, 3339 (1909).

(7) Noorduyt, *Rec. trav. chim.*, **38**, 317 (1919).

(8) Rider, *THIS JOURNAL*, **53**, 4130 (1931).

(9) Straus, Heinze and Salzmänn, *Ber.*, **66B**, 631 (1933).

(10) Brown and Stoner, *THIS JOURNAL*, **59**, 3 (1937); Brown and Shinowara, *ibid.*, **59**, 6 (1937); **60**, 2734 (1938); Brown and Frankel, *ibid.*, **60**, 54 (1938).

TABLE I  
 ANALYTICAL DATA ON FOUR SPECIMENS OF METHYL RICINOLEATE

M. p., °C.	Mean mol. wt.	Iodine number	$n_D^{20}$	Acetyl number	$[\alpha]_D^{25}$ —Acetone	$[\alpha]_D^{25}$	% Purity <sup>a</sup>	
Theory, calcd.	312.0	81.34	....	137.71	....	....	..	
Haller <sup>b</sup>	....	...	1.4645 <sup>15</sup>	....	....	+5.3 <sup>d</sup>	..	
Leathes <sup>c</sup>	....	...	....	....	....	+3.8	..	
Straus, <i>et al.</i>	....	...	1.4626 <sup>21</sup>	....	....	....	..	
Sample (1)	313.44	81.01	1.4627	136.65	....	....	99.2	
Sample (2)	307.30	82.43	....	135.28	....	....	98.2	
Sample (3)	-4.0	303.66	81.05	1.4628	133.75	+7.41°	+4.82°	97.1
Sample (4)	-4.5	311.60	80.71	1.4628	137.05	+5.19° <sup>a</sup>	....	99.5

<sup>a</sup> Purity based on acetyl number. <sup>b</sup> Haller, *Compt. rend. acad. sci.*, **144**, 462 (1907). <sup>c</sup> Leathes, "The Fats," Longmans, Green and Co., New York, N. Y., 1925. <sup>d</sup> At 20°. At 27°.

trated solutions, 4, 8 and 10% were tried and found to give too bulky precipitates for efficient fractionation. No precipitate formed at -20° after standing seventy-two hours. The solution was therefore cooled with constant stirring to -50° at which point a small precipitate (approx. 1%) was removed by suction on a large Buchner funnel (-20°). This fraction was solid at room temperature and probably contained most of the saturated esters. The filtrate was further cooled with vigorous stirring to -60 to -62° and the precipitate at this temperature separated by filtration as above. Solvent was then removed from the precipitate by warming under reduced pressure. The residual product was distilled at 3.6 to 4 mm. pressure in an all-glass apparatus. It was water-white; yield 62 g. Constants on this sample, no. 1, together with those of other specimens of methyl ricinoleate prepared are given in Table I.

(2) In an attempt to find a solvent in which more concentrated solutions could be handled, 400 g. of the original methyl esters was dissolved in 4000 cc. c. p. methyl alcohol and allowed to stand overnight at -20°. The precipitate was filtered off and the filtrate was further cooled with continuous stirring to -40° and a second small precipitate removed. Upon cooling to lower temperatures, it was found that this solution was too concentrated for further fractionation; so it was diluted with an equal volume of methyl alcohol making the solution approximately 5%. A large precipitate came down at -65° and was filtered off. This specimen was treated in a manner similar to the first. The yield of the distilled ester, specimen 2, was 328 g.

(3) Six hundred and forty grams of original esters was dissolved in 32 liters of c. p. acetone in eight 4-liter flasks and treated as sample (1) with the following differences.

The precipitation was carried out in 4-liter flasks in the dry ice-alcohol bath and it was found (perhaps due to slight supercooling with somewhat less efficient stirring in the larger volume of solution) that precipitation corresponding to that in (1) occurred at -55 and -65° instead of -50 and -60° as before. After filtering at -65°, the precipitate was allowed to melt, made up to approximately 2% solution and recrystallized at -65°.

The yield of distilled specimen (3) was 283 g.

(4) An additional sample of methyl ricinoleate was prepared in the same manner as sample (3) except that the recrystallization at -65° was from a 4% solution in acetone instead of 2%.

Analytical data on the four specimens are given in Table I. Molecular weights were determined by saponification; iodine numbers by the Wijs method with one hour reaction time. Acetyl numbers were determined essentially by the method of West and co-workers.<sup>11</sup> The acetyl value was defined as the number of mg. of acetyl radical taken up by 1 g. of sample. In our work we have allowed one and a half hours reaction time and one-half hour decomposition time.

The analytical data in Table I, especially the iodine and acetyl numbers, show the four specimens to be methyl ricinoleate of high purity. The molecular weights by saponification are also in excellent agreement with the theory in specimens (1) and (4). They are not so satisfactory in (2) and (3), which may be due to side reactions with alkali. We have repeatedly obtained low results for molecular weight by the saponification method. In fact it has been difficult with some specimens to obtain checks on this account. From these experiments it may be concluded that it is possible to prepare methyl ricinoleate of high purity by the low temperature crystallization methods described above, either methyl alcohol or acetone being satisfactory solvents.

**B. Preparation of Ricinoleic Acid.**—It would seem that the preparation of pure ricinoleic acid from the pure ester would be a comparatively simple procedure, but in actual attempts to saponify the ester the resultant acids gave constants which were far from satisfactory. In three such experiments the pure ester was saponified with boiling alcoholic potash, most of the alcohol distilled off, and the soaps decomposed with hot hydrochloric acid. The temperatures of most of these operations were kept below 60°. The resultant acids were analyzed directly or crystallized from ether or acetone at very low temperature. Attempts to distil the acid even at 0.5-1.5 mm. pressure gave products with iodine numbers of 92-113. The undistilled product invariably gave molecular weights by titration 20 to 30 units high, up to 330 (theory 298). Also high iodine

(11) West, Hoagland and Curtis, *J. Biol. Chem.*, **104**, 627 (1934); Hafner, Swinney and West, *ibid.*, **116**, 691 (1936).

numbers were obtained.<sup>12</sup> These high values, however, are not due to abnormal reaction with the Wijs reagent used but to the formation of octadecadienoic acids by the dehydration of methyl ricinoleate or soap during the saponification and subsequent treatment. High molecular weights on the other hand are caused by formation of polyricinoleic acids, to incomplete saponification, or to the presence of residual solvent which is difficult to remove without distillation. Since hot saponification caused definite alteration in the product, two attempts at cold saponification were tried in which the ester was treated with a large excess of alcoholic potash at 0–4° for 101 and 285 hours, respectively. The products again had iodine numbers and mean molecular weights which were indicative of incomplete saponification.

These experiments made it obvious that cold saponification of the pure ester was not complete and hot saponification did not give a pure acid and that the product would have to be fractionally crystallized to remove poly acids and dienoic acids formed in the process. Since fractional crystallization was necessary, obviously it was practical to start with more crude ester which had not been so highly purified. Accordingly a number of samples of less pure methyl ricinoleate were mixed and saponified with hot alcoholic potash. The resultant acids, 359 g., were then dissolved in 7180 cc. of C. P. acetone. No precipitation occurred at –20° and the solution was cooled to –70°. A copious precipitate was removed by filtration and an acid recovered by warming under reduced pressure, taking care to keep the temperature below 60°. Apparently this procedure was successful in removing the

(12) Cf. Caldwell and Piontkowski, *THIS JOURNAL*, **56**, 2086 (1934).

last traces of solvent, because the product gave a molecular weight by titration in neutral alcohol of 298 (theory 298.3). The other constants were iodine number (Wijs) 88.52 (theory 85.1), acetyl number 137.9 (theory 144.2), m. p. 5.5°. (The literature reports various melting points from 4–5° (Leathes) to 17°);  $n^{20}$  1.4697 (Straus, Heinze and Salzmann, report 1.4716);  $\alpha^{26D}$  (acetone) +7.15°; sp. gr. 27.4°, 0.940. The thiocyanogen number of this specimen of acid was 85.34 (theory 85.09). On the basis of acetyl number, the product was 95.6% ricinoleic acid. On the basis of iodine number and assuming the mixture to consist of ricinoleic and octadecadienoic acids, the purity was 97%.

In the above experiments we have given only a résumé of many of our attempts to prepare ricinoleic acid from its methyl ester and details only in our most successful preparation. We conclude that it is a comparatively simple procedure to prepare the ester in high purity and in very good yield, but, even with pure ester available, it is quite difficult to prepare an acid of satisfactory purity. Ricinoleic acid, itself, appears to be even more difficult to prepare than oleic acid, not because of difficulty of separation from other acids but because of its own reactivity.

### Summary

1. Low temperature fractional crystallization procedures have been applied successfully to the preparation of methyl ricinoleate from castor oil.

2. Saponification of methyl ricinoleate and isolation of the resultant acid does not yield a pure ricinoleic acid.

3. Analytical constants of pure methyl ricinoleate and of 95.6% ricinoleic acid are given.

COLUMBUS, OHIO

RECEIVED JANUARY 22, 1940