REFERENCES

1. Duncan, I. J., J. Am. Oil Chem. Soc., *25*, 277-278 (1948).
2. Gerhardt, Fisk, Ind. Eng. Chem., *22*, 160-163 (1930).
3. Hollowell, E. G., "Commercial Extraction of Soybean Oil Using Non-Inflammable Solvents," Ph.D. Thesis, Iowa State College (1947).
4. Karnofsky, George, J. Am. Oil Chem. Soc., *26*, 564-569 (1949).
5. Milkweed Seed Collection Discontinued. Oil, Paint, and Drug Reporter, 148 (No. 1) July 2, 1945.
6. Moore, N. H., Oil Mill Gazetteer, p. 13-16, April 1950.
7. Neish, A. C., and Burns, J. W., Can. Chem. and Met., *5*, 316-319 (1921).
8. Persell, R. M., Pollard, E. F., and Gastrock, E. A., "Problems and Progress in the Solvent Extraction of Cottonseed," Cotton Gin and Oil Mill Press, December 23, 1950.
9. Rea, H. E. Jr., and Wamble, A. C., "The Extraction of Oil from Oil-Bearing Materials by Prepressing Followed by Solvent Extraction," Texas Eng. Exp. Sta. Research Report No. 11, February 1950.
10. Sweeney, O. R., and Arnold, L. K., J. Am. Oil Chem. Soc., *26*, 697-700 (1949).
11. Tray, S. E., and Bilbe, C. W., Chem. Eng., *54* (No. 5), 139-141, 153, 160-163 (1947).

[Received December 29, 1952]

Composition of Castor Oil by Optical Activity

DON S. BOLLEY, The Baker Castor Oil Company, Bayonne, New Jersey

CASTOR oil occupies a unique position in the field of natural fats and oils. While, like other common oils, it is a glyceride, it is unusual in that the acid components of the glyceride are primarily hydroxy compounds. No other common natural fat or oil contains an appreciable quantity of combined hydroxy acids. This acid in castor oil has been named ricinoleic acid.

The exact amount of ricinoleic acid that occurs in the mixed acids from castor oil has been the subject of a number of analytical investigations. The methods used have been all chemical and involved the determination of acetyl or hydroxyl values as well as the use of the thiocyanate procedure. The values obtained for the percentage of ricinoleic acid by the various investigators are as follows:

Investigator	Date	Ricinoleic Acid
A. Eibner and E. Munzing (4)	1925	84.0%
P. Ponjutin and M. Rappoport (12)	1930	87.5
H. P. Kaufmann and H. Bornhardt (7)	1939	87.0
G. W. McBride (11)	1940	90.0
H. G. Kirschenbauer (8)	1944	87.8
H. K. Dean (3)	1946	87.0
R. L. Terrill (15)	1950	88.0
S. S. Gupta and T. P. Hilditch (5)	1951	93.1
J. P. Riley (13)	1951	92.6

It may be noted there has been a trend towards higher values in later years. This could be explained by the composition of castor oil tending towards higher ricinoleic acid content, but a more likely explanation is simply experimental error or refinement of analytical procedures. As far as is known, no attempt had previously been made to determine the percentage of ricinoleic by physical means, such as optical activity, refractive index, specific gravity, etc.

The formula for ricinoleic acid is: $CH_3(CH_2)_5CHOHCH_2CH{:}CH(CH_2)_7COOH$. It may be noted ricinoleic acid is identical with the more common vegetable fatty acid, oleic acid, except that it has a hydroxyl group on the 12th carbon atom. This atom is therefore asymmetric and should give the molecule optical activity since the oil is also a natural product. Actually castor oil and its ricinoleate derivatives have a pronounced ability to rotate a plane of polarized light. The observed specific rotation should therefore be adaptable for use as a measure of the ricinoleic content. It should also be highly specific since no other common fatty acid has an asymmetric carbon atom and thus optical activity. Although most natural vegetable oils contain unsymmetrical triglycerides and thus an asymmetric carbon atom in the glyceryl radical, no optical activity has been noted due to this structure (2).

The nonricinoleate components of castor oil are linoleic, oleic, stearic, and some dihydroxystearic. The actual amounts reported by different investigators varies considerably. The relative amounts should be further investigated by the newer analytical techniques. Actually dihydroxystearic acid has two asymmetric carbon atoms and could be optically active. Apparently the two sources of optical activity are nearly internally compensating, and the optical activity is slight. Since only small amounts of this acid are present, their effect on total optical activity has been disregarded in this paper. Thus the mixed fatty acids of castor oil are considered to be ricinoleic acid and nonricinoleic acid. This paper is concerned only with their relative proportion.

The optical activity of castor oil and its derivatives has been recognized for some time. In 1905 Lythgoe (9) measured the optical rotation of 44 samples of castor oil at 20° C. He reported that they varied in specific optical rotation from +8° to +9°. Markley (10), in his book on "Fatty Acids" published in 1947, reported the specific optical rotation of ricinoleic acid to be +6.7°. Hawke (6) in 1949 reported +7.79° and Brown and Green (1), +6.25°. It is suspected all these values are high and their variation due to some lactone or estolide formation. Brown and Green (1) in an excellent article on the "Preparation of Pure Methyl Ricinoleate," reported the optical rotation with the sodium line at 20° to be +5.19° for the pure methyl ester. There was apparently no attempt to determine the ricinoleic acid content of castor oil or its derivatives by this means.

Measurement of Optical Activity

The optical rotation of castor oil and its various derivatives described below was measured with a Rudolph Precision Polarimeter, Model 70, using the standard technique. This polarimeter is stated to have an accuracy of 0.01°. It was used with a 200 cm. tube and mercury arc lamp. Thus the data given are in terms of the 5461 Å mercury line as recommended by the Bureau of Standards instead of the usual sodium line. All readings were made at 25°C or corrected to 25°C. The correction was made by observing the change in specific rotation with temperature from which the necessary correction factor was readily calculated. The total rotation observed was calculated to specific rotation, alpha. The formula used was:

$$\text{Alpha} = \frac{\text{Observed Angle of Rotation}}{\text{Length in Decimeters} \times \text{Density}}$$

Castor Oil

Both the specific optical rotation (alpha) and the chemical hydroxyl value would measure the same functional group if all the hydroxyl group was present as ricinoleates. However there are dihydroxystearic and possibly some mono- or diglycerides present which are measured by the chemical value and not by the optical method. It has been noted that the dihydroxystearic present in castor has very little optical activity which may be disregarded. If we assume the dihydroxystearic content is fairly constant and there is little mono- or diglyceride present, then the specific optical rotation and the chemical hydroxyl values would be directly related. These assumptions seem reasonable. In order to establish this relationship two castor oils were chosen, one from Brazilian seed and one from domestic. These were carefully analyzed and the following results obtained:

	Brazilian	Domestic
Color at 470 mμ	85.5%	90.6%
Color at 550 mμ	97.7%	98.6%
Viscosity (GH)	U +	U +
Refractive Index at 25°	1.4774	1.4772
Volatile	0.17%	0.12%
Iodine Value	86.3	86.4
Acid Value	1.6	0.7
Unsaponifiable	0.36%	0.30%
Sap. Value	180.3	179.8
Acetyl Value	145.9	146.4
Acetyl Sap. Value	306.5	306.4
Hydroxyl Value	164.5	164.5
Average Specific Rotation	5.24	5.22

The values for the average specific rotation were taken from over a dozen readings of the Brazilian and Domestic Oils at different temperatures and corrected to 25° C. From the above values the two oils appears to be very close to each other in composition.

Since the hydroxyl value is a straight-line function of the specific rotation, the so-called alpha hydroxyl value may be calculated from the specific rotation by multiplying by a constant. This constant was determined by dividing the hydroxyl value of 164.5 by the average specific rotation of 5.24. This gave 31.4. In other words, alpha hydroxyl value = 31.4 × specific rotation.

In the same manner the alpha hydroxyl value may be calculated from acetylated castor oil. The acetylated standard Brazilian castor oil was found to have a specific rotation of 26.21. From this the alpha hydroxyl value = 6.276 × specific rotation. The following table gives the hydroxyl value of a number of oils calculated both from the nonacetyl and acetylated specific rotation and compared to the chemical method of determining hydroxyl value:

	Alpha Hydroxyl	Alpha Acetyl Hydroxyl	Chemical Hydroxyl
Standard Brazilian	164.5	164.5	164.5
Standard Domestic	163.9	165.7	164.5
Domestic No. 1	159.8	163.8	163.8
Domestic No. 2	160.5	165.0	162.2
Domestic No. 3	161.0	158.6	164.1
Domestic No. 4	166.9	164.2	163.4
Domestic No. 5	166.6	160.2	163.0

There does not seem to be any definite trend or correlation between the variation in results. The difference probably represents experimental error and possibly some variation in nonricinoleic hydroxy groups. A large number of other castor oils were determined by both the optical and chemical method for hydroxyl value and compared. Substantially the same type of results were obtained. It was interesting to note that there was very little difference in the chemical composition of castor oil from wild Brazilian and Domestic seed as indicated by these values.

The chemical composition of castor oil can be calculated from the chemical hydroxyl value if we disregard the small dihydroxystearic content and any mono- or diglycerides. Taking a molecular weight of 937.6 (90% triricinolein at 943.4 and 10% triolein at 885.4), we obtained a calculated hydroxyl value of 179.5, assuming three hydroxyl groups per molecule. The actual value observed was 164.5, which indicates a purity of 91.6%. Any nonricinoleic hydroxyl would lower the percentage and the unsaponifiable or nonglyceride portion would raise it.

Methyl Ricinoleate

Brown and Green (1) have shown that pure methyl ricinoleate can be prepared from the mixed methyl esters of castor oil by a combination of distillation and fractional crystallization. Since optical activity is an additive property, it should be possible to compute the percentage of ricinoleate in the mixed esters from specific optical rotation, knowing the specific optical rotation of the pure methyl ricinoleate. This was one of the methods used in this study. The mixed methyl esters of castor oil (technical methyl ricinoleate) can readily be prepared by methanolysis (14).

A good grade of castor oil (AA® Oil from the Baker Castor Oil Company) was treated with an excess of methyl alcohol, using sodium hydroxide catalyst. At moderate temperatures the glycerol settles out and can be removed in a separatory funnel. The sodium hydroxide and soaps are neutralized with acid and the excess methyl alcohol distilled out. The salt is removed by filtration giving the mixed methyl esters.

The mixed methyl esters are placed in a regular distillation apparatus equipped with a fractionating column and distilled at approximately 1 mm. Since the nonhydroxylated portion of the methyl esters boil about 30° lower than methyl ricinoleate, these distill over first. The procedure used was to discard the first 20% collecting a 70% second fraction, leaving a 10% residue. The second fraction is then redistilled in a similar manner to obtain the purified methyl ricinoleate. The following results were obtained:

	Mixed Esters	First Distillation	Second Distillation	Theo.
OH Value	176.5	177	179.9	179.5
Melting Point	–25° C	–7° C	–5° C	....
Acid Value	3.0	1.5	0.6	0.0
Iodine Value	84.5	....	81.6	81.2

The fraction from the second distillation was taken as pure methyl ricinoleate.

The optical rotation of the mixed methyl esters of castor oil and the pure methyl ricinoleate was measured with the precision polarimeter. Methyl esters were prepared from both the Brazilian and Domestic castor oils. The following specific rotations were observed:

	Alpha
Pure methyl ricinoleate	5.83°
Brazilian Technical Methyl Ricinoleate	5.42°
Domestic Technical Methyl Ricinoleate	5.42°

It was interesting to note that similar results were obtained from the mixed methyl esters of Brazilian and Domestic castor oil. The ratio of alpha indicates the technical ricinoleates contained 93% pure methyl ricinoleate.

Methyl Acetyl Ricinoleate

Since the methyl ricinoleic has optical activity, its acetylated derivative should also be optically active. In fact, it was observed the acetylated methyl ricinoleate had roughly five times more the specific rotation than the nonacetylated products. This fact offers the possibility of greater accuracy in measurement as well as another check on the composition of castor oil. Thus the mixed methyl esters of castor oil were prepared as before and acetylated. The optical activity of these esters was determined and the following results observed. Both Brazilian and Domestic oils were again used as source material.

	Alpha
Pure Methyl Acetyl Ricinoleate	28.22
Technical Brazilian Methyl Acetyl Ricinoleate	25.37
Technical Domestic Methyl Acetyl Ricinoleate	25.45

The ratio of alphas indicates a 90% ricinoleate content in the technical material.

Dehydrated Castor Oil

There has been considerable discussion as to the amount of ricinoleates that remain in castor oil and castor products after dehydration. Since ricinoleates are optically active and the dehydrated products are not, it was hoped a quantitative measure of the completeness of dehydration could be obtained with the polarimeter. The following table gives the specific rotation obtained:

	Alpha
Castor Oil	5.24
Unbodied Dehydrated Castor No. 1	4.94
Unbodied Dehydrated Castor No. 2	5.05
Bodied Dehydrated Castor	1.26
Soybean Oil	Trace
Tung Oil	Trace

The large value for the dehydrated castor oils was not expected and at first was quite puzzling. The dehydrated castor oils used were of good quality and obviously could not contain the high ricinoleic content the ratio indicated.

In order to find the explanation for the high value, specific optical rotation was run on a dehydrated castor oil fatty acid and two esters. The following values were obtained:

	Alpha
DCO Acids No. 1	1.47
Methyl Esters of DCO Acids No. 1	2.95
Methyl Esters of DCO Acids No. 2	5.44

Again the high values could not be accounted for by nondehydrated ricinoleates.

Since the dehydrated ricinoleates (isometric linoleic acid) boil at a lower temperature than ricinoleic acid, an attempt was made to separate the products by fractional distillation. Accordingly the batch having the optical rotation of 2.95 was distilled at about 1 mm. and the fractions analyzed.

	Percentage	Alpha
First Fraction	9.7	1.10
Second Fraction	13.2	1.63
Third Fraction	18.2	1.51
Fourth Fraction	9.0	1.77
Fifth Fraction	29.8	3.05
Residue	20.0	15.9

From the above it may be seen the optically active material is concentrated in the high boiling fraction. Also the alpha value of the residue was much higher than pure methyl ricinoleate. Moreover it was noted that the boiling point of the residue was considerably over that of methyl ricinoleate. This indicates that the material giving optical activity to the dehydrated castor oil products is a polymer. It has been shown that the acetylated product or ester had five times the optical activity of the nonacetylated product. From these facts it seems quite obvious that the material in dehydrated castor giving optical activity is an estolide or a polyester. This is probably formed during dehydration in the order of about 15%.

Summary

The optical activity of castor oil and its derivatives has been studied. Pure methyl ricinoleate and methyl acetyl ricinoleate were prepared. The mixed methyl esters and acetylated methyl esters of castor oil were also prepared. By the determination of specific rotation of the pure and technical esters, the percentage of ricinoleate fraction can be deduced. This was calculated to be 93% and 90%, respectively. The esters of castor oil were calculated to contain 91.6% ricinoleate from the chemical hydroxyl value. This was about the average of the two values obtained optically and is believed close to the actual value. A number of castor oils were analyzed by both optical and chemical methods and found to be of nearly constant ricinoleic content. Dehydrated castor oil was found to have a comparative high specific rotation. This was believed due to its estolide content formed during dehydration.

Acknowledgment

The writer wishes to express his appreciation to the Baker Castor Oil Company for permission to publish these data, which were obtained in their laboratories. Special thanks are due to Phillip C. Daidone and Frank C. Naughton, who collected most of the results reported.

REFERENCES

1. Brown and Green, J. Am. Chem. Soc., *62*, 738 (1940).
2. Cowan, J. C., Gilman's "Organic Chemistry," *3*, 215 (1953).
3. Dean, H. K., Soaps, Perfumery, and Cosmetics, *19*, 928 (1946).
4. Eibner, A., and Munzing, E., Chem. Umschau., *32*, 153-162 (1925).
5. Gupta, S. S., and Hilditch, T. P., J. Sci. Food Agr., *2*, 245-51 (1951).
6. Hawke, F., J. S. African Chem. Inst. (N.S.), *2*, 125-9 (1949).
7. Kaufmann, H. P., and Bornhardt, H., Fette u. Seifen *46*, 444-6 (1939).
8. Kirschenbauer, H. G., Fats and Oils (125 (1944)).
9. Lythgoe, H. C., J. Am. Chem. Soc., *27*, 887-92 (1905).
10. Markley, K. S., "Fatty Acids" (1947).
11. McBride, G. W., Chem. and Met. Eng., *47*, 830-3 (1940).
12. Ponjutin, P., and Rappoport, M., Chem. Umschau., *37*, 130 (1930).
13. Riley, J. P., Analyst, *76*, 40-4 (1951).
14. Smith, M. K., U. S. Patent 2,486,444 (1949).
15. Terrill, R. L., J. Am. Oil Chem. Soc., *27*, 477-81 (1950).

[Received May 21, 1953]