Acetaldehyde.—Acetaldehyde reacted completely with the fused alkalies at 250°, hydrogen and acetates were the products of the reaction which conformed to the extent of 90% of the calculated amount to the reaction,

$$CH_3CHO + NaOH \longrightarrow CH_3CO_2Na + H_2$$

At 300° and 350° the yields of hydrogen, methane and carbonates were practically those calculated for the reaction,

$$CH_3CHO + 2NaOH \longrightarrow H_2 + CH_4 + Na_2CO_3$$

Acetone.—The reactions of acetone were analogous to those of aldehyde. At 250°, methane and acetates were the chief products of the reaction which conformed, at least to the extent of 70% of the calculated amounts, to the reaction,

$$CH_3COCH_3 + NaOH \longrightarrow CH_3CO_2Na + CH_4$$

At 350°, the yields of methane and carbonates were more than 90% of those calculated for the reaction,

$$CH_3COCH_3 + 2NaOH \longrightarrow Na_2CO_3 + 2CH_4$$

Further applications of this special method of investigating the interactions between carbon compounds and fused caustic alkalies are in progress.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY, No. 506]

A METHOD FOR THE DIRECT IDENTIFICATION OF RAPESEED OIL BY ISOLATION OF ERUCIC ACID

BY ARTHUR W. THOMAS AND MORRIS MATTIKOW

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The purpose of this investigation was to find a method for the direct identification and quantitative estimation of rapeseed oil, the most important of the oils of the general order of *Cruciferae*, by isolating its characteristic acid, erucic acid. The isolation and purification of this acid is described in the literature.[1]

There was no attempt to separate or measure quantitatively erucic acid in rapeseed oil until 1910, when Tortelli and Fortini[2] and Holde and Marcusson[3] proposed their methods.

The method of Tortelli and Fortini depends on the determination of the iodine number and melting point of the fatty acids whose lead soaps are insoluble, or nearly so, in ether and on the critical temperature of solution

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[1] Darby, *Ann. chim. pharm.*, **69**, 1 (1849). Websky, *Jahresber.*, **6**, 443 (1853). Städeler, *Ann.*, **87**, 133 (1853). Otto, *Ann.*, **127**, 182 (1863). Hausknecht, *Ann.*, **143**, 41 (1867). Fitz, *Ber.*, **4**, 442 (1871). Farnsterner, *Z. Nahr. Genussm.*, **2**, 1 (1899). Reimer and Will, *Ber.*, **19**, 3320 (1886).

[2] Tortelli and Fortini, *Chem.-Ztg.*, **34**, 690 (1910).

[3] Holde and Marcusson, *Z. angew. Chem.*, **23**, 1260 (1910).

of the sodium salts produced by the decomposition of the soluble lead soaps. While this method is reliable in giving indications of adulteration of olive oil by rapeseed oil, it has no further application.

The method of Holde and Marcusson is based on the fact that erucic acid is more soluble in chilled 96% alcohol than are the saturated solid acids. It does not give quantitative results.

Biazzo and Vigdorcik[4] have proposed the following method for the detection of rapeseed oil in olive oil: first a lead-soap precipitation with extraction by ether, then a conversion to fatty acids and subsequent precipitation of potassium soaps in acetone; a further decomposition to fatty acids and reconversion to lead soaps with further extraction with ether; then decomposition to fatty acids and finally hydrogenation in ethereal solution. The final criterion is the melting point of the hydrogenated acid, upon fractional crystallization; if it melts at 76–79° the test is a positive one for rapeseed oil.

None of the available methods is quantitative, all having been devised for the detection of adulteration in another oil, usually olive, with rapeseed oil. In extending and developing the magnesium-soap-alcohol method, proposed by Kerr,[5] Thomas and Yu[6] noticed that when the magnesium soaps of rapeseed oil are precipitated and decomposed there results a fatty acid product the constants of which approximate those of erucic acid. The present investigation is the development of this observation into a direct method for determining the purity of rapeseed oil.

Materials Used

Stearic Acid.—The specimen used melted at 69.5°, had a molecular weight of 284.46, and showed no ash or iodine number.

Erucic Acid.—Rapeseed oil was saponified with alcoholic potassium hydroxide solution. Magnesium soaps were precipitated by the addition of alcoholic magnesium acetate solution followed by boiling. The soaps, after being allowed to stand overnight at 10°, were filtered off, washed with 90% alcohol and then decomposed with hydrochloric acid. The clear layer of fatty acids was hardened by cooling, filtered, washed free from chloride and magnesium ions, dissolved in hot 90% alcohol and allowed to remain overnight at 10°. Saturated acids, which crystallized out at 10°, were filtered off. The solution was then refrigerated at 0° and the first batch of crystals was filtered off at that temperature. This process was repeated about five times, the first three lots of crystals being rejected. The final crystallizations and filtrations were made at —10°.

The final product had an iodine number of 75.0 (calcd., 75.2) and melted at 33°.

A small quantity of Kahlbaum's erucic acid (m. p., 34°; iodine no. = 74.2; mol. wt. = 337.8) was also employed as raw material. This was dissolved in 90% (by volume) alcohol and chilled to 0° for one hour. The resulting crystals were discarded. The solution was then left at 0° overnight and the crystallized erucic acid filtered off and dried in a vacuum at 40°. The iodine number and molecular weight were 75.1 and 338.2 (calcd.: 75.2, 338.34) respectively.

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[4] Biazzo and Vigdorcik, *Ann. chim. applicata*, **6**, 185 (1916).

[5] Kerr, *J. Ind. Eng. Chem.*, **8**, 904 (1916).

[6] Thomas and Yu, THIS JOURNAL, **45**, 113, 129 (1923).

Oleic Acid.—A specimen of reagent oleic acid was cooled to 10°, and the solids that deposited were filtered off and discarded. The filtrate had an iodine number of 88.9, a molecular weight of 282.8 (calcd.: iodine no., 90; mol. wt., 282.27) and contained no ash.

Behenic Acid.—Behenic acid was prepared by hydrogenation of erucic acid as described later in this paper. The synthesized acid was washed with 95% alcohol and dissolved in hot absolute alcohol from which it crystallized on cooling. This operation was twice repeated. The final yield of crystals was dried in a vacuum oven at 70°. The product melted at 80-81°, and showed no iodine number or ash.

Preparation and Analysis of Soaps of the Fatty Acids

Lead and Magnesium Soaps of Erucic Acid.—Ten g. of the purified erucic acid was dissolved in 200 cc. of 95% alcohol and converted into the ammonium salt by adding molar ammonium hydroxide solution until alkaline to litmus. Then, upon the addition of 0.5 *M* aqueous solution of lead or magnesium acetate in slight excess, the resulting mixture was boiled for 20 minutes during constant vigorous stirring. Three hundred cc. of distilled water was then poured into the hot mixture and the whole allowed to remain at room temperature for a few hours. The soap was filtered off and washed repeatedly with warm water. It was twice extracted with 150 cc. of 95% alcohol under a reflux condenser and once with 100 cc. of ether. After each extraction the mixture was allowed to cool to room temperature, the insoluble portion was filtered off and washed with the solvent. The final residues of lead erucate or of magnesium erucate were dried in a vacuum oven at 40°. The purity of these soaps was proved by determination of the magnesium and lead contents.

Determination of Solubilities of Fatty Acids and their Soaps in Various Solvents

The alcohol used was distilled over potassium hydroxide and silver oxide, the first and last fractions being rejected. The ethyl ether employed was distilled over sodium.

Technique.—An excess of the solid was placed in a tightly stoppered 250cc. bottle with 150 cc. of the solvent, and agitated for 24 hours at room temperature. It was then placed in a water thermostat at 25 ± 0.01° for 48 hours, being occasionally vigorously shaken for the first 36 hours. As a precaution the tips of the calibrated pipets, used in drawing up the solution, were covered with extracted filter paper.

Twenty-five cc. of the solution at 25° was pipetted into a weighed 30cc. beaker, and slowly evaporated to dryness at a temperature below the boiling point of the solvent. In the case of the unsaturated soaps, the residue was dried in a vacuum oven at 40°, but with the saturated acids, drying to constant weight was effected at 80°.

The density of another portion of the solution was determined at 25 ± 0.01° in the usual way.

Four hours later the determinations were repeated. In the event of failure to check, the whole experiment was discarded and a new one performed.

In determining the solubilities of the fatty acids at lower temperatures, a longer time was allowed for equilibrium to take place.

TABLE I

SOLUBILITY OF STEARIC ACID IN MIXTURES OF WATER AND ETHYL ALCOHOL

		G. of dissolved solid in 100 cc. of soln.	
Alcohol, % by wt.	d_4^{25}	0 ± 1° (*b*)	10 ± 0.5° (*a*)
91.53	0.80935	0.113	0.396
86.16	.82356	0.061	.232
63.07	.87783	...	.031

[a] Left in refrigerator for five and a half days; shaken four times daily; checks taken five and a half days later.

[b] Left in refrigerator for ten days; shaken twice daily; check taken three days later.

TABLE II

SOLUBILITY OF BEHENIC ACID IN MIXTURES OF WATER AND ETHYL ALCOHOL

	G. in 100 cc. of soln.		G. in 100 g. of solvent
Alcohol, % by wt.	0°	25°	25°
91.53	0.013	0.206	0.218
86.16	.010	.111	.116
63.07	.002	.010	.011

SOLUBILITY OF ERUCIC ACID IN A MIXTURE OF ETHYL ALCOHOL AND WATER AT 0 ± 1°

91.53	2.356

Checks were taken three days later.

SOLUBILITY OF LEAD ERUCATE IN ANHYDROUS ETHER AT 25°

d_4^{25} 0.70380	0.340	0.408

The solubility of lead erucate in ether varies considerably with the amount of moisture the ether contains and with the time of contact with the solvent. The solubility of the soap was determined in a commercial sample of anhydrous ether. Only 0.241 g. of lead erucate dissolved in 100 cc. of the solution in the length of time required by the methods described above. After the mixture had stood for five days in the thermostat at 25° the solubility rose to 0.281 g.

To prove that equilibrium is not attained when lead erucate is refluxed for 15 minutes and allowed to remain in a thermostat at 15° for one hour, as prescribed by Tortelli and Fortini, the following experiments were performed. Two flasks, each containing 2.5 g. of lead erucate and 85 cc. of anhydrous ether (over commercial sodium), were heated under a reflux condenser for 15 minutes. One flask was immediately placed in a thermostat at 25° and the other in the refrigerator at 10°. At intervals, 10cc. portions were withdrawn, evaporated to dryness and finally dried in a vacuum oven at 40°: the amounts of lead erucate dissolved in 100 cc. of solution in one and three hours at 25° were 1.626 and 0.844 g., respectively; and in one and two hours at 10°, 0.350 and 0.336 g., respectively.

The equilibrium solubility in this ether was 0.240 g. in 100 cc. of solution at 25°. The procedure of Tortelli and Fortini requires but one hour's standing in a thermostat at 15°. Even at 10° equilibrium is not attained in the short time prescribed.

TABLE III

SOLUBILITY OF MAGNESIUM ERUCATE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 25°

Alcohol % by wt.	d_4^{25}	G. in 100 cc. of soln.	G. in 100 g. of solvent
94.28	0.80176	0.323	0.420
88.38	.81774	.268	.349
75.40	.85038	.179	.240
65.82	.87337	.142	.171
45.67	.91941	.019	.020
28.37	.95351	.007	.008
18.13	.96904	.004	.005
water	.....	.006	.006

It was assumed that the magnesium soap of rapic acid had about the same solubility in 90% alcohol as magnesium oleate and would not be found with the precipitated soaps. Since the molecular weight of the acid product was about 334 and the iodine number 73, the soap evidently acts like magnesium oleate for its presence would be manifested by a higher iodine number and lower molecular weight.

Preparation of Reagents

1. **Alcoholic Potassium Hydroxide Solution.**—Fifty g. of potassium hydroxide was dissolved in 1 liter of alcohol and the solution filtered to remove impurities.

2. **Alcoholic Magnesium Acetate Solution.**—Fifty g. of magnesium acetate [$Mg(C_2H_3O_2)_2$] was dissolved in 100 cc. of boiling distilled water and the solution filtered. To each volume of the cold filtrate, three volumes of 95% alcohol were added.

3. **Alcoholic Acetic Acid.**—Twenty cc. of glacial acetic acid was dissolved in 80 cc. of 95% alcohol. This reagent keeps for about a month.

4. **Ninety % Alcohol.**—Nine hundred cc. of 95% (by volume) alcohol was mixed with 50 cc. of distilled water. The resulting strength was 90.3 ± 0.3% alcohol by volume.

Influence of Saturated and Unsaturated Magnesium Soaps on the Precipitation of Magnesium Erucate

Known mixtures of erucic and oleic and stearic acids were neutralized with *N* alcoholic potassium hydroxide solution. After the magnesium soaps had been precipitated by an excess of alcoholic magnesium acetate solution, they were cooled in the refrigerator at 10° overnight. The insoluble soaps were filtered off, washed with 50 cc. of 90% alcohol and then decomposed with hot 5 *M* hydrochloric acid. The fatty acids were washed free from magnesium and chloride, dissolved with small amounts of hot

95% alcohol into a weighed beaker, the solvent was evaporated and the residue dried to constant weight at 40° in a vacuum oven.

The results showed that there is but a slight loss of magnesium erucate in the presence of large amounts of stearic acid. With mixtures of equal amounts of erucic and oleic acid less than 50% of the calculated amount of erucic acid was recovered but with similar mixtures of stearic and erucic acids, about 96% of the calculated amount of erucic acid was recovered. Hence, in the precipitation of magnesium erucate the determining factor is not the saturated soaps but the unsaturated soaps.

Study of the Conditions Governing the Separation of Erucic Acid from Rapeseed Oil

The complete separation of magnesium erucate depends upon three factors: (1) time of cooling; (2) amount of available magnesium acetate present in solution; and (3) amount of alcohol necessary to wash the insoluble soaps.

1. **Time of Cooling.**—About 10 g. of refined rapeseed oil was accurately weighed and saponified with a mixture of 50 cc. of alcoholic potassium hydroxide solution and 50 cc. of 95% alcohol. The soap solution was neutralized to phenolphthalein with alcoholic acetic acid, and then titrated back to a permanent pink with alcoholic potassium hydroxide. To this was added 25 cc. of magnesium acetate solution. The mixture was placed in the refrigerator at 10° for different intervals. The insoluble magnesium soaps were filtered off, washed with 50 cc. of 95% alcohol, decomposed with 5 *M* hydrochloric acid and analyzed for total fatty acids as shown below. It was found that one night's standing in the refrigerator produces a coarse, granular precipitate which can be filtered rapidly. Allowing the soap to remain longer than 48 hours results in the precipitation of some magnesium oleate. It is therefore inadvisable to refrigerate the solution longer than 24 hours.

TABLE IV

INFLUENCE OF TIME OF COOLING

Time of cooling, hrs.	Amt. of acid obtd., %	M. p., °C.	Iodine no.
2	22.4	34	66.7
4	24.7	33	68.3
6	26.6	30	71.2
12	42.9	28	73.0
18	43.0	27	72.8

The low temperature is essential in the separation of magnesium erucate since at 25° it does not deposit in appreciable quantities. A 10g. sample of oil was saponified, precipitated as before but, instead of being refrigerated at 10°, was placed in a thermostat at 25° overnight. Acid product to the extent of 6.7% crystallized.

2. **Amount of Alcoholic Magnesium Acetate Required for Complete Precipitation of Magnesium Erucate in Rapeseed Oil.**—This series of experiments was carried out as above, except that various amounts of 0.81 *M* alcoholic magnesium acetate were added to the soap solutions obtained from 10 g. of rapeseed oil. The mixtures were allowed to stand overnight at 10°.

Table V

Influence of Amount of Magnesium Acetate

$MgAc_2$ soln., cc.	0	5	10	20	30
Acids obtd., %	61.0	48.9	44.1	43.0	42.9
Iodine no.	90.0	88.8	76.1	74.0	73.0

Twenty-five cc. of the reagent was chosen because it produced the maximum amount of fatty acid product with an iodine number most nearly approximating that of erucic acid.

3. **Amount of Alcohol Used in Washing Soaps.**—The magnesium erucate, when filtered off, has adhering to it other unsaturated soaps. In view of the solubility of the former, however, it is evident that too large a volume of 90% alcohol should not be used. In any case, the volume of wash alcohol should be measured. The effect of different amounts of 90% alcohol is shown in Table VI.

Table VI

Influence of Amount of Alcohol

Alcohol (90%), cc.	50	100	150
Acid product, %	42.4	37.1	33.2
Iodine no.	73	69	67

Hydrogenation of Erucic to Behenic Acid

Stohmann and Langbein[7] transformed erucic to behenic acid by heating with 1.5% of its weight of iodine for four hours at 270°. The product was then reduced with zinc and hydrochloric acid and after being converted to the potassium salt with alcoholic potassium hydroxide was changed to the barium salt, which in turn was decomposed with hydrochloric acid and the fatty acid was crystallized from alcohol. Talanzeff[8] accomplished the conversion by the use of phosphorus tri-iodide. Reychler[9] used 1% iodine and crystallized from ether (m. p., 77°).

Vavon[10] was the first to employ hydrogenation in the presence of an active catalyst. He converted erucic to behenic acid by agitating an ethereal solution of erucic acid in the presence of platinum black in an atmosphere of hydrogen. Boehringer and Söhne[11] accomplished the re-

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[7] Stohmann and Langbein, *J. prakt. Chem.*, **42**, 379 (1890).

[8] Talanzeff, *ibid.*, **50**, 72 (1894).

[9] Reychler, *Bull. soc. chim.*, [3] **1**, 296 (1889).

[10] Vavon, *Compt. rend.*, **149**, 999 (1910).

[11] Boehringer and Söhne, Ger. pat. 187,788, through *Chem. Centr.*, **78**, 1287 (1907).

duction at a platinized platinum cathode electrolytically. Lewkowitsch proposed a method for hydrogenating erucic acid to behenic acid in the presence of nickel as a catalyst.

Mannich and Thiele's method[12] of preparing an active catalyst by the precipitation of palladium on charcoal previously ignited was tried. The hydrogen was passed through a palladous chloride solution in which was suspended charcoal such that the palladium was 2% of the amount of charcoal present. The precipitate of palladium-charcoal was filtered off, washed free from chlorides and then dried in a vacuum. Although Biazzo and Vigdorcik report the favorable use of this catalyst, the writers have found it unsatisfactory. It loses its activity on standing.

Skita[13] and his co-workers have developed an efficient method for the catalytic hydrogenation of organic substances. Palladous or platinum chloride is used with a "protective" colloid such as gum arabic. The catalyst is prepared by simply bubbling hydrogen through the alcoholic solution of the substance to be hydrogenated.

Using Skita's method with slight modification, erucic acid was converted in 95 and 90% alcoholic solutions to behenic acid. About 4 g. of the erucic acid product from the magnesium soap precipitation was dissolved in 80–100 cc. of 95% alcohol in a bottle fitted with a 2-hole rubber stopper. Through one of the holes a glass tube passed into the solution and almost to the bottom of the bottle, while the other served as an exhaust. Hydrogen was passed through the solution. Using a 1% palladous chloride solution, it took three-quarters of an hour for the colloidal palladium to form (increasing the concentration of palladous chloride greatly accelerated the reaction). Then a precipitate of white particles appeared which rapidly collected on the bottom of the bottle. In two to three hours, no more particles were formed and the hydrogenation was stopped. The bottle was placed in a 25° thermostat overnight, the precipitate filtered off, washed with cold 90% alcohol and dissolved with hot alcohol. The filtrate was allowed to remain at room temperature and the crystallized acid again filtered off and washed as before. After two crystallizations, crystals were obtained with a melting point of 79–80°. A third recrystallization yielded a product which melted at 80–81°, exhibited no iodine number and no ash, and had a molecular weight of 339.4.

Gum gamboge was first used as a "protective" colloid. While it is soluble in alcohol, it was found that it did not function so well as gum arabic, although the latter is insoluble in the medium. If too much "protective" colloid is added the formation of the colloidal catalyst is delayed. One-fourth of the weight of catalyst was found to be the most efficient amount of "protective" colloid to use. The gum arabic does not actually

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[12] Mannich and Thiele, *Ber. Pharm. Ges.*, **26,** 36 (1916).

[13] Skita, *Ber.*, **42,** 1627 (1909).

function as a "protective" colloid but provides nuclei for the deposition of the colloidal palladium, since the gum is precipitated by alcohol.

Technique of the Proposed Quantitative Method

Part I.—About 10 g. of oil, accurately weighed, is saponified in a 250cc. Erlenmeyer flask (A) by a mixture of 50 cc. of alcoholic potassium hydroxide solution and 50 cc. of 95% alcohol. Saponification is complete after the mixture has been heated for one-half hour under a reflux condenser.

The soap solution while still warm is neutralized to phenolphthalein with the alcoholic acetic acid reagent and then just enough alcoholic potassium hydroxide solution is added to give a permanent pink color. Twenty-five cc. of alcoholic magnesium acetate reagent is added. The whole is heated to boiling, cooled and left in the refrigerator at 10° overnight. The insoluble soaps are filtered off and washed with 50 cc. of 90% alcohol, the soaps adhering to the flask being first rinsed out.

The insoluble soaps are washed into the original flask A by puncturing the filter paper and spraying with hot 5 *M* hydrochloric acid. The soaps are decomposed by boiling for about 10 minutes when a clear oily layer is formed; this is then cooled to solidify the fatty acids. The solidified acids are filtered off and washed free from chloride and magnesium. The moisture in the flask A is removed by drying at 80–100°. The acid is transferred to a 150cc. beaker (B) and the filter paper washed with 60 cc. of warm 90% alcohol to dissolve any adhering fatty acid. The covered beaker B is allowed to remain in the refrigerator at 10° overnight, when crystals of saturated acids which may have formed are filtered off. The filtrate is caught in a weighed 150cc. beaker (C). The crystals of acid are washed first with 50 cc. of 90% and then 50 cc. of 70% alcohol. The washings are caught in the weighed 150cc. beaker C. A simple test for the thoroughness of the washing is to dry the filter paper in an oven at about 35°. The absence of an oily stain shows that all the erucic acid has been washed out. The solvent is evaporated slowly at about 70° and the drying completed in a vacuum oven at 60° to constant weight. The iodine number, melting point and molecular weight of the acid product are determined. If these conform with the values given later for the erucic acid product isolated from rapeseed oil, then the latter may be termed pure.

A confirmatory test consists in the hydrogenation of the acid product and the isolation of behenic acid.

Part II. Hydrogenation of Erucic Acid Product.—The erucic acid product is dissolved in 80–100 cc. of 90% alcohol in a bottle fitted with a 2-hole rubber stopper. Two cc. of a 1% palladous chloride solution and 0.5 cc. of a 1% gum arabic solution are added. Hydrogen is passed through as described above. When hydrogenation is complete, usually after about three hours, the bottle is placed in a 25° thermostat overnight, the precipitate filtered off, washed with cold 90% alcohol, and dissolved with hot 95% alcohol into a weighed 150cc. beaker. The solvent is slowly evaporated and the behenic acid product dried in an oven at 80° to constant weight.

Application of the Proposed Method to Rapeseed Oil Analysis

A number of analyses were carried out to test the reliability of the proposed method. Constant amounts of fatty acids were isolated, having almost the same composition, as evidenced by the concordance of iodine number, melting point and molecular weight.

Experiments were carried out with a sample of rapeseed oil (refined) with the following alterations: (1) a slight variation in amount of 95% alcohol needed to accompany the saponification of the oil; (2) prolonged cooling (not more than 48 hours); (3) a slight excess of alcoholic acetic acid or slight excess of alcoholic potassium hydroxide solution during neutralization; (4) a variation in the amount of 90% alcohol from which the saturated acids separate; (5) the washing of the saturated acids with 90% instead of 70% alcohol.

The mean error of the mean computed from 13 such analyses of a refined rapeseed oil was ± 0.16, while the percentage errors of average deviation from the mean were ± 0.40.

Constant errors in the proposed method are: (1) loss of erucic acid due to the appreciable solubility of its magnesium soap in 90% alcohol; (2) solubility of the saturated acids in 90 and 70% alcohol when they are washed with those solvents. As to the first error, it may be said that although the loss of magnesium erucate is appreciable, concordant and reproducible results may be obtained if the volume of alcohol is accurately measured and solubility correction for the excess in volume is made; the method does not allow too much freedom in that direction. The second error is very small, the maximum being about 0.020 g. of saturated acids.

The results of the application of the proposed method to samples of crude and refined rapeseed oils are recorded in Table VII.

TABLE VII

YIELD OF ERUCIC AND BEHENIC ACIDS FROM RAPESEED OILS

Sample	Erucic acid yield, %	Iodine No.	Mol. wt.	M. p.	Behenic acid via hydrogenation, %
Refined, East Indian expressed	42.7	73.5	336	27°	..
	42.8	..	...	..	35.9
Refined, Manchurian extracted	44.2	73.2	334	27	..
	44.9	..	...	..	35.4
Crude, East Indian expressed	44.3	74.6	342	26	..
	44.3	..	...	..	35.8
Crude, Manchurian extracted	48.2	73.1	335	26	..
	47.6	..	...	..	36.3
Dutch refined oil at least three years old	43.5	73.0	333	27	...

The results are quite consistent and demonstrate within the limits of the available samples that not only is the amount of erucic acid quite constant but that the amount of saturated acids occurring in rapeseed oils is fairly uniform. The crude oil was found to give a somewhat higher yield, indicating that some of the erucic acid is lost in the refining process.[14]

If an oil be analyzed according to the proposed method and an acid product obtained weighing about 44% and having a melting point of about 26°, an iodine number of about 73, a molecular weight of 336, then the oil may be said to be a genuine, pure, refined rapeseed oil. A further proof is the catalytic hydrogenation of the product, which should yield an acid product, to the extent of 35% of the amount of oil, melting after two fractional crystallizations, at 77–79°. (If not recrystallized twice, it may melt as low as 73°.)

The constants of the erucic acid product isolated compare favorably with those of pure erucic acid.

	Iodine no.	Mol. wt.	M. p., °C.	n^{35}
Pure erucic acid..............	75.12	338	33	1.4580
Acid product by method......	73.0–74.6	333–342	26–27	1.4568

Study of Mixtures of Rapeseed Oil with Other Oils

The magnesium-soap method was applied directly to pure specimens of olive, cottonseed, linseed, soya bean, perilla, corn, wild mustard and peanut oils. None gave an "erucic acid product." When corn oil, after being saponified in the usual manner, was treated with the alcoholic magnesium acetate solution, a small amount of a soap was formed which was insoluble in the boiling solution.

Mixtures of oils with rapeseed oil were analyzed to determine to what extent the amount of acid product (having the approximate constants for pure rapeseed oil) can be used as a criterion of purity of rapeseed oil. In view of the wide range of oils examined, the results obtained, while not quantitative beyond about 20% of adulterant, are consistent and reproducible, as shown for mixtures of olive and rapeseed oils in Table VIII.

TABLE VIII

AMOUNT OF ERUCIC ACID RECOVERED FROM OLIVE-RAPESEED OIL MIXTURES

10 g. of oil mixture taken

Mixture			
Rapeseed, %[a]	Olive, %	Erucic acid product, %	Rapeseed oil indicated, %
89.6	10.4	36.3	85
89.3	10.7	35.8	84
80.0	20.0	30.0	70
79.7	20.3	29.1	70

[a] The rapeseed oil used yielded 42.7% of erucic acid product.

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[14] Thomas and Yu (Ref. 6) found the same to be true in the amount of arachidic-lignoceric acid mixture recoverable from crude and refined peanut oils by the magnesium soap method.

Results obtained with mixtures of linseed and rapeseed oils indicate that oils containing large amounts of unsaturated acids interfere with the precipitation of magnesium erucate. Thus, while it vitiates any quantitative removal of erucic acid, it increases the sensitivity of the proposed method for the criterion of purity of a rapeseed oil.

Where the amount of saturated acids is high, relatively, a quantitative separation is afforded up to about 20% adulteration of rapeseed oil.

Since erucic acid is a "solid" acid of low melting point and its magnesium soap is quite insoluble it will be found with the "solid" acids. It follows, therefore, that the "solid" acids of an oil will in the presence of rapeseed oil show a lower melting point.

Kreis and Roth[15] determined the adulteration of olive by rapeseed oil by fractional precipitation of the lead soaps and determination of the melting points of the resulting fatty acids. The new method herein proposed for rapeseed oil affords a rapid method for detecting the adulteration of olive with rapeseed oil.

Various amounts of a sample of pure, French olive oil were mixed with a genuine refined rapeseed oil to make 10 g. of oil mixture. By the new procedure for rapeseed oil analysis by isolation of the erucic acid product the results shown in Table IX were obtained (the product was not hydrogenated).

TABLE IX

ACID PRODUCT FROM MIXTURES OF RAPESEED AND OLIVE OILS

		Final acid product	
Rapeseed, %	Olive, %	M. p., °C.	Iodine no.
100	..	27	73
73.5	26.5	28	73
66.3	33.7	30	67
50	50	35	63
39.4	60.6	37	57
26.5	73.5	41	55
12.1	87.9	44	38
..	100	48	33

Plotting percentages of olive oil as abscissas and melting points as ordinates, it is seen that the curve is almost linear from 100% olive to 25% olive (Fig. 1) from which it is apparent that the method affords a fairly accurate, and at the same time, rapid way for ascertaining the amount of rape seed oil used to adulterate olive oil. (Rapeseed oil is an important edible oil in certain parts of the world.)

Mixtures of cottonseed and rapeseed oil were analyzed in the same way. The cottonseed oil was a refined oil having an iodine number of 110. The results are noted in Table X.

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[15] Kreis and Roth, *Z. Nahr. Genussm.*, **26**, 38 (1913).

Table X

Acid Product from Mixtures of Rapeseed and Cottonseed Oils

Rapeseed, %	Cottonseed, %	Acid product M. p., °C.	Acid product Iodine No.
100	..	27	73
75.2	24.8	28	67
66.2	33.8	32	58
49.9	50.1	39	51
39.4	60.6	42	46
26.9	73.1	47	41
11.7	88.3	51	34
..	100	55	27

The composition-melting point curve (Fig. 1) indicates a linear relationship between the amount of rapeseed oil added and the melting point of the acid product as determined by the method cited from 100% cottonseed oil to 25% cottonseed oil. Beyond this point there is no appreciable variation. In the case of mixtures of cottonseed and rapeseed oils containing more than 75% of the latter, the resulting acid product behaves almost like that from pure rapeseed oil in its melting point and iodine number.

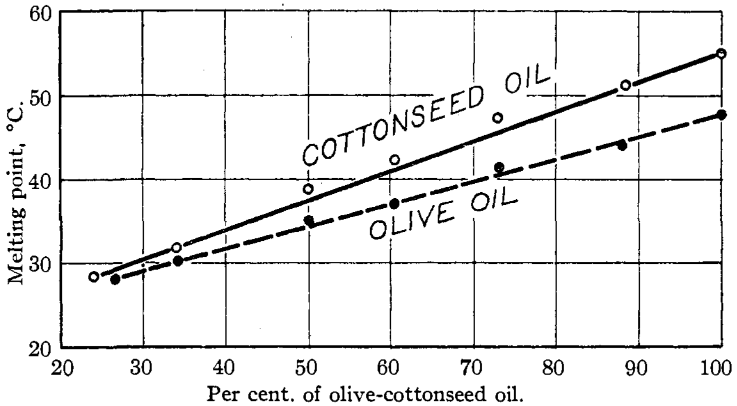

Fig. 1.—Mixtures of olive-rapeseed and cottonseed-rapeseed oils.

In the event of cottonseed being adulterated with 75% of rapeseed oil, the latter can hardly be termed an adulterant. The former should be called the adulterant. In that case the extent of the adulteration could be determined by applying the general method for the rapeseed oils given earlier. The same is true for rapeseed-olive oil mixtures.

Analyses of Mustard-Seed Oils

Genuine black (Sicilian) and yellow (English) mustard seeds were procured. The oils from these were expressed and analyzed for their "erucic acid" content by the proposed method. It would be expected that they should give the same amount of this characteristic acid as rapeseed oil, since the constants of both of these oils are almost alike and the seeds belong to the same botanical family. Such was found to be the case with the oil from yellow mustard seed; but the oil from the black mustard seed yielded less erucic acid. The quantitative results were as follows.

TABLE XI

VALUES FOR MUSTARD-SEED OILS

Seed	Erucic acid product, %	Iodine no.	M. p., °C.	Mol. wt.
Yellow	40.9	71.9	26	331
Black	34.4	79.0	26–27	328

Summary and Conclusions

1. The solubility of magnesium erucate in mixtures of ethyl alcohol and water has been determined and it has been shown that a satisfactory separation from other unsaturated magnesium soaps can be effected.
2. The solubility of lead erucate in anhydrous ether has been measured and the unreliability of anhydrous ether as a solvent demonstrated.
3. The solubilities of behenic, stearic and erucic acids at 10° and 0° have been determined.
4. A new direct criterion of purity of rapeseed oil is proposed based on the separation of magnesium erucate along with the small amounts of saturated soaps present, in 90% alcohol and the subsequent isolation of erucic acid in almost pure form from which behenic acid is obtained by hydrogenation in presence of a catalyst.
5. A semi-quantitative method for olive-rapeseed, olive-cottonseed oil mixtures is suggested.
6. The method does not distinguish rapeseed oil from mustard seed oil, since the latter like the former yields a large proportion of erucic acid.

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

THYMOLSULFONEPHTHALEIN, THE INTERMEDIATE ACID, 4'-HYDROXY - 3' - ISOPROPYL - 6' - METHYL - BENZOYLBENZENE-2-SULFONIC ACID AND SOME OF THEIR DERIVATIVES

BY W. R. ORNDORFF AND RALPH T. K. CORNWELL[1]

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Thymolsulfonephthalein was first made by Lubs and Clark[2] from the chlorides of *o*-sulfobenzoic acid and thymol. They also prepared its di-

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[1] From a dissertation presented by Ralph T. K. Cornwell in partial fulfilment of the requirements for the degree of Doctor of Philosophy. An abstract of this paper was read before the Organic Division of the American Chemical Society at the meeting in Ithaca, N. Y., Sept. 8–13, 1924.

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[2] Lubs and Clark, *J. Washington Acad. Sci.*, **5**, 614 (1915); **6**, 481 (1916).