three replies revealed the preference summarized below on cottonseed and soybean oils, with negligible demand for any other oil samples.

	Cottonseed Oil	Soybean Oil
Highest number favored	10	6
Lowest number favored	3	0
Average number favored	4.2	3.5

While four samples of each of the two oils could be justified by this poll, a majority of the collaborators favored continuing the Referee Board's practice of distributing three samples of each, and this plan was followed again for the past year. Two degummed soybean oil samples were distributed in order to increase the information available to the Refining Committee on results with the tentative method for refining this oil.

In the absence of any better suggestion for tabulating the season's work, collaborators have been "graded" on both oils by the method previously used for the refining tests on cottonseed oil. The tabulation of grades has been furnished to the collaborators and to others closely concerned with the work, and may be considered as a continuation of the present work.

F. G. DOLLEAR
R. T. MILNER
A. S. RICHARDSON, chairman

Grading System

Since there is no approved method for grading our check tests on soybean oil, the above tabulation has no official status. The undersigned has arbitrarily applied to the soybean oil samples the same system which has in recent years been used for grading collaborators on cottonseed oil refining tests, as explained more fully below.

Test	Tolerance	Deductions
F. F. A.	±.1	.3 for each .1% outside tolerance.
Loss, not over 9%	±.3	.1 for each .1% outside tolerance.
Loss, over 9%	±.4	.9/x for each .1% outside tolerance.
Color (Red), not over 7.6	±.3	.1 for each .1% outside tolerance.
Color above 7.6 Red	±.4	7.6/x for each .1% outside tolerance.

x = accepted average corrected to nearest whole number.
Limit of deduction for one determination on one sample = 1.

$$\text{Grade} = 100 - \frac{100 \times (\text{Total Deductions})}{3 \times (\text{Number of samples})}$$

Grades are based as usual on settlement results for loss and for color of refined oil. I.e., the collaborator's settlement result is compared with the settlement result picked from the averages. The settlement loss is simply the lowest loss for soybean oil, and settlement loss and color are fixed by the trading rules for cottonseed oil.

Full credit has been given for all reports received late due to circumstances beyond control of the collaborator.

A. S. RICHARDSON, chairman

Hydrazides of *n*-Aliphatic Acids[1]

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IN the course of an investigation of the composition and nature of the fission products of oxidized fatty esters, it was necessary to identify the *n*-aliphatic acids present in their mixtures. Usually these acids were obtained in the form of esters and often in rather small amounts. It was desirable to have recourse to a derivative that could be prepared directly from the ester in good yield and which would differ sufficiently from adjacent members in melting point and melting point depressions to permit accurate identification of the product or mixture of products.

The work of Sah (6) indicated that the monoacyl hydrazides might be satisfactory derivatives for this purpose, especially since the hydrazides may be analyzed for nitrogen by volumetric methods. The reaction of fatty acid esters with hydrazine may be illustrated by the following equation in which R can be an alkyl or aryl group:

$$RCOOCH_3 + NH_2NH_2 \rightarrow RCONHNH_2 + CH_3OH.$$

Several of the hydrazides of the *n*-aliphatic acids have been prepared (3,6,7) previously as indicated in Table 1. The present series includes the hydrazides of the homologous series, valeric acid through lauric acid as well as those of myristic, palmitic, and stearic acids. Efforts were made to prepare the hydrazides of oleic and elaidic acids. Contrary to the report of Hanus and Vorisek (3) elaidic acid formed a hydrazide in good yield. Oleic acid on the other hand underwent reduction and yielded mainly the hydrazide of stearic acid. A number of diacyl hydrazines of the *n*-aliphatic acids were also prepared but they did not possess sufficiently large differences in melting points between adjacent members of the homologous series to render them satisfactory as characterizing derivatives. The hydrazides can be prepared for purposes of identification with as little as 20 mg. of the parent esters.

Experimental

Materials. In most cases, the saturated fatty acids and esters were obtained from Eastman Kodak Company. They were "white label products" and were used without further purification.

In a few cases the esters were prepared from commercial fatty acids by the method described by Bauer (1). Briefly the procedure consisted of treating commercial fatty acids with concentrated sulfuric acid, removing the sulfo derivatives by repeated washing with water, esterifying with methanol, and fractionally distilling the methyl esters. The fractions conforming most nearly to the calculated values for the saponification equivalent were selected for further purification either by redistillation (liquid

[1] Presented at the 38th Annual Meeting of the American Oil Chemists' Society, New Orleans, Louisiana, May 20-22, 1947.
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TABLE 1.

Constants of the *n*-Aliphatic Acids and Their Hydrazides.

Acid			Nitrogen content of hydrazides [g]		Melting points, °C.		
						Hydrazide mixtures	
Name	No. of carbon atoms	Melting point °C.[a]	Calculated %	Found %	Hydrazides	With next higher homolog	With second higher homolog
Formic	1	8.4	46.65	.....	54[b]	.....	.....
Acetic	2	16.6	37.82	.....	67[b]	.....	.....
Propionic	3	−22	31.80	.....	40[b]	.....	.....
Butyric	4	− 7.9	27.43	.....	44[b]	.....	.....
Valeric	5	−34.5	24.12	23.71	62.6- 63.4[c]	50-52	50-60
Caproic	6	− 3.4	21.52	21.76	73.1- 74 [c]	63-66	57-62
Heptanoic	7	−10.5	19.43	19.43	82.0- 83 [c]	74-78	71-80
Caprylic	8	16.7	17.70	17.65	88.8- 89.6	79-83	77-83
Nonanoic	9	12.5	16.26	16.23	93.5- 94.0	86-89	82-85
Capric	10	31.6	15.04	14.97	98.5- 99.1	92-95	86-90
Undecanoic	11	29.3	13.99	14.01	102.0-102.3	95-97	.....
Lauric	12	44.2	13.07	13.10	104.7-105.5[d]	.....	96-98
Myristic	14	53.9	11.56	11.42	109.4-110	.....	97-100
Palmitic	16	63.1	10.36	10.28	112.2-112.4[d]	.....	103-106
Stearic	18	69.6	9.39	9.29	115.6-116.2[e]	.....	.....
Oleic	18	14	9.39 [f]	9.67	..... [f]	.....	.....
Elaidic	18	44	9.45	9.42	103.0-103.6	.....	.....

[a] See reference (5).

[b] Sah (6).

[c] M.p. of the hydrazides of valeric, caproic, and heptanoic acids reported by Teeter (7) are 60°-61°, 72°-73°, and 81°-82°C., respectively.

[d] M.p. of the hydrazides of lauric and palmitic acids reported by Sah (6) are 104°-105°C. and 111°C., respectively.

[e] Hydrazide of stearic acid reported by Hanus and Vorisek (3) is 114°C.

[f] Oleic acid yields the hydrazide of stearic acid.

[g] Nitrogen determined by the micro-Dumas method.

acids) or by saponification and repeated crystallization from acetone (solid acids). Oleic acid was prepared from a saponified pecan oil by low temperature fractional crystallization and distillation of the methyl esters (8). Elaidic acid was prepared by saponification of a portion of the methyl oleate and the recovered oleic acid was treated with oxides of nitrogen (2). After several recrystallizations from dilute alcohol the elaidic acid was esterified with methanol and the methyl ester distilled.

Melting point determinations. The melting points of the hydrazides were taken by the capillary tube method using a high-speed stirred bath (4) and thermometers calibrated by the National Bureau of Standards at immersion points within the range used in making the melting point determinations. The melting points of the mixed hydrazides were determined with equimolar mixtures of the next higher homolog and in some cases with the second higher homolog. Each mixture was rapidly melted on a micro cover glass, allowed to cool below its freezing point, and the melting range determined with a Fisher-Johns melting point apparatus.

Preparation of hydrazides from esters. The method used was similar to that described by Sah (6). One gram of acid was added to 5 ml. of absolute ethanol containing 0.5 ml. of concentrated sulfuric acid. The solution was refluxed for 30 minutes, cooled, treated with 8 ml. of a saturated solution of calcium chloride, and the ester recovered by extraction with ethyl ether. The ether solution was washed with water, dried with anhydrous sodium sulfate, and the ether removed under vacuum at a low temperature.

One ml. of a 43% aqueous hydrazine hydrate [3] solution was added per gram of ester together with sufficient ethanol to produce a homogeneous solution at reflux temperature. The solution was refluxed for two hours. Upon cooling, the hydrazides of higher molecular-weight fatty acids crystallized whereas those of lower molecular weight remained soluble in the reaction mixture. In the latter case, most of the solvent was removed by distillation after which crystallization also occurred. The crystals were filtered off and recrystallized several times from either dilute or absolute ethanol. The derivatives were dried in an Abderhalden apparatus or under vacuum at room temperature prior to determining their melting points.

Reaction of methyl oleate with hydrazine. Methyl oleate (8.5 g.) was dissolved in 30 ml. of absolute ethanol to which 8 ml. of a 43% aqueous hydrazine hydrate solution was added and the mixture refluxed for two hours. The solution was cooled in an ice box and the solid which separated at this temperature was removed by filtration. The product melted at room temperature. The turbid filtrate deposited crystals during evaporation at room temperature over an interval of three days. These were removed and recrystallized from ethanol whereupon there was obtained 1.08 g. of material melting between 97°-108°C. Further evaporation of the mother liquor from the last mentioned product yielded 3.5 g. of a similar material. Repeated recrystallization yielded a product melting at 115.6°-116.2°C., which produced only a slight depression in melting point of an authentic hydrazide of stearic acid. Upon hydrolysis with alcoholic sodium hydroxide, 1.25 g. of the crude hydrazide yielded 0.58 g. of stearic acid melting at 69.5°-69.8°C., which when mixed with authentic stearic acid (m.p. 69.5°-70°C.) showed no depression of the melting point.

Preparation of elaidic acid hydrazide. Methyl elaidate (10.0 g.) was treated with 10 ml. of 85% hydrazine hydrate and 100 ml. of absolute ethanol. The hydrazide which crystallized directly as colorless plates was separated by filtration, washed with warm commercial pentane-hexane, b.p. 95°-138°F., to remove any unreacted ester. The product was then twice recrystallized from 60 ml. of absolute ethanol and dried under vacuum after which it melted at 103.0°-103.6°C.

Hydrolysis of elaidic acid hydrazide. Elaidic acid hydrazide (1.0 g.) was dissolved in 50 ml. of 50% ethanol containing 5.5 g. of sodium hydroxide, refluxed for two hours, and cooled. The reaction mix-

[3] Precaution should be used in handling hydrazine and its derivatives because they have been shown to be toxic.

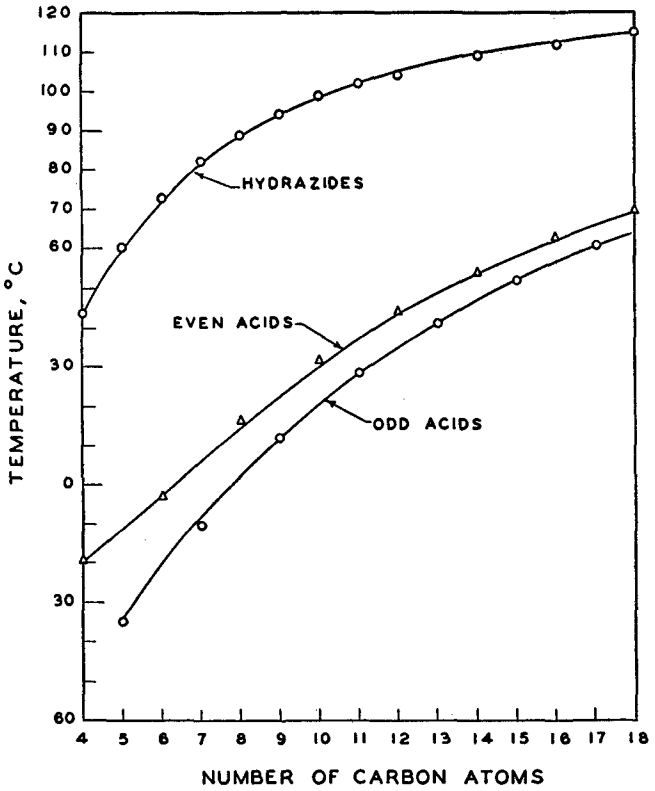

FIG. 1. Melting points of the *n*-aliphatic acids and their hydrazides.

ture was diluted with 50 ml. of water, acidified to pH 3-4 with concentrated hydrochloric acid, and the turbid suspension extracted with ethyl ether. The extract was washed, dried, and the ether removed by evaporation. The product (0.82 g.) was recrystallized from 15 ml. of 60% ethanol which yielded 0.75 g. of elaidic acid melting at 43°-44°C.

Melting points of the fatty acids and corresponding hydrazides are shown in Table 1 and graphically in Fig. 1. The calculated and determined nitrogen contents are also presented in Table 1. Because of the polymorphisom exhibited by the acids they fall on two smooth curves corresponding to the odd- and even-numbered series (5), whereas the melting points of the corresponding hydrazides lie on a single smooth curve, indicating that all members of the homologous series crystallize from ethanol in the same polymorphic form. When the reciprocals of the number of carbon atoms are plotted against the corresponding melting points, the hydrazides of the fatty acids, unlike the fatty acids themselves, fall on a straight line.

Acknowledgment

The authors express their appreciation to L. E. Brown for the nitrogen determinations reported here.

REFERENCES

1. Bauer, S. T., Oil & Soap, *23*, 1-5 (1946).
2. Ellis, G. W., Biochem. J., *26*, 791-800 (1932).
3. Hanus, J., and Vorisek, J., Collection Czechoslov. Chem. Comm., *1*, 223-227 (1929). Chemical Abstracts, *23*, 4443 (1929).
4. Markley, K. S., Ind. Eng. Chem., Anal. Ed., *6*, 475 1934).
5. Markley, K. S., Fatty Acids. Their Chemical and Physical Properties. Interscience Publishers, Incorporated, New York (1947).
6. Sah, P. P. T., Rec. trav. chim., *59*, 1036-1054 (1940).
7. Teeter, Howard M., Bromination of Linoleic Acid Derivatives with N-Bromosuccinimide, Presented at the meeting of the American Oil Chemists' Society, Chicago, Illinois, October 30, 31, November 1, 1946.
8. Wheeler, D. H., and Riemenschneider, R. W., Oil & Soap, *16*, 207-209 (1939).

Report of the Uniform Methods Committee 1946-47

IN PRESENTING the report of the Uniform Methods Committee, we shall try to follow the order in which the reports appeared on the program of the convention. The Soap, Glycerine, and Fat Analysis Committees report at the fall meeting of the Society.

Color Committee:

The Color Committee has done some very fine work investigating new methods of determining colors in oils and has made a report of progress which requires no action.

Refining Committee:

The Refining Committee's report contained a recommendation which was acted upon at the Fall Meeting and is now a tentative method of the Society.

Seed and Meal Analysis Committee:

The Seed and Meal Analysis Committee presented a lengthy report covering various methods, all of which were acted upon by the Uniform Methods Committee but will not be reproduced here as they will be available when published as a report of this committee and will shortly appear as parts of our methods.

a) The Methods of Analysis of Soyflours, covering the determination of moisture and volatile matter, oil, ash and crude fiber, were approved by the Uniform Methods Committee and will be published as tentative methods of the Society.

b) The determination of ash and crude fiber in oilseed meals was approved by the Uniform Methods Committee and will also appear as a tentative method of the Society.

c) On cottonseed and cottonseed meal the committee recommended a quick moisture method which was given considerable consideration by the Uniform Methods Committee. It was decided to approve the insertion of the separate quick moisture method proposed as a tentative method of the Society with the scope and limitations thereof clearly defined by the editor.

d) On peanuts and peanut meal the determination of moisture was approved by the Uniform Methods Committee to be published as a tentative method.

This committee also approved the deletion of the method for determining oil in whole nuts and the revision of the determination of oil in shelled nuts, as described in their report. This is likewise to be published as a tentative method.

Certain changes in the determination of nitrogen, ammonia, and protein, as they appeared in the com-