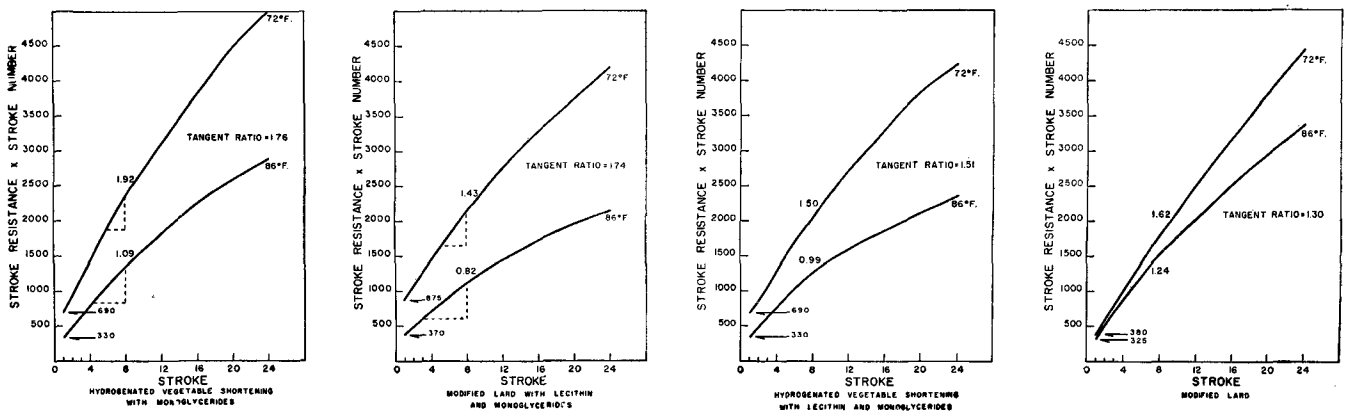

FIG. 9. The linear transformation curves of a) a hydrogenated vegetable shortening with monoglycerides, b) a modified lard with lecithin and monoglycerides, c) a hydrogenated vegetable shortening with lecithin and monoglycerides, and d) a modified lard.

worker. There is evidence of some structure re-establishment in the pumped sample after 24 hrs. as indicated by the slightly different arc at the initial strokes as compared with the end of the worked control.

Many kinds of shortening have been tested, but illustrations of these results would be of limited interest. A few of the typical curves are reproduced in Figure 9 to show differences which can be detected by the instrument. The temperatures used for such testing are 72° and 86°F.(22.2° and 30°C.) only because they are compatible with laboratory schedules and equipment. Any other two temperatures in the approximate range would serve equally well.

Discussion

The shortening rheometer described can be used to determine the flow properties of shortening. The test will establish the following: relative viscosities of shortenings under a single shear application; the change in shortening viscosities as a result of controlled repeated shearing or working; and the relationship of both of these properties as a function of temperature, this providing a simple number index of plastic range.

The test method provides a rapid and accurate method of achieving these results. Duplication is good; repeated tests fall within ± 1 to 5%. The technique is applicable to research, production problems, and quality control. Test output compared to other methods is very high for the amount of information produced. Depending upon the amount of shear given, from two to six minutes are the normal elapsed time of a single determination. With two interchangeable grease workers, the limiting factor is the speed at which the operator can remove, clean, and dry the sensing element. The test is convenient, being self-recording, and requires little or no operator attention. Errors because of operator fatigue are virtually eliminated.

The sample size and shape permits sampling of drums, pails, or cartons by use of open-end molds, from which the sample can be transferred directly to the grease worker. With appropriate segment-forms, chilling molds can be made for laboratory preparation of shortening for tests.

The transformation of the flow-property curves to simple values of initial consistency and tangent ratio at 72° and 86°F.(22.2° and 30°C.) is but one form of describing the flow properties of shortening. Future use of this testing method promises new information unattainable before because of the high cost of analysis and limited interpretation. Standardization of temperatures and sample preparation would establish a common communicative method to describe and control shortening rheological properties.

REFERENCES

1. Clardy, L., Pohle, W. D., and Mehlenbacher, V. C., J. Am. Oil Chemists' Soc., *29*, 591–93 (1952).
2. Dempster, C. J., Hlynka, I., and Anderson, J. A., Cereal Chem., *32*, 241–52 (1955).
3. Feuge, R. O., and Bailey, A. E., Oil and Soap, *21*, 78–84 (1944).
4. Gravenhorst, C. O., Oil and Soap, *11*, 86–87 (1934).
5. Kinney, Paul W., Ind. and Eng. Chem., Anal. Ed., *13*, 178–85 (1941).
6. Rich, A. D., Oil and Soap, *19*, 54–57 (1942).
7. Schlenker, E., and Fidaleo, M., J. Am. Oil Chemists' Soc., *27*, 80–81 (1950).

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Fat Splitting by the Twitchell Process at Low Temperature[1]

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IN THE USUAL Twitchell fat-splitting procedure the reaction is performed at about 100°C. under atmospheric pressure with vigorous stirring. For kinetic studies of the stepwise nature of the hydrolysis a slower rate of reaction was desirable. It seemed possible that this might be achieved if the reaction were performed at room temperature with no shaking or stirring. No data could be found in the literature. Accordingly experiments were conducted to determine the degree of fat splitting at 35°C. without agitation of the mixture. Also determined were the effects of dissolving the catalyst in the water layer or in the oil

[1] Presented at the symposia on fat of the Chemical Society of Japan, Nov. 10, 1954, and Nov. 8, 1955, Nagoya, Japan; and the 8th annual meeting of the Chemical Society of Japan, Apr. 2, 1955, Tokyo, Japan.

layer and of adding glycerol, acetic acid, or fatty acids. The splitting of coconut oil in the presence of a catalyst of the butyl naphthalene sulfonic acid type was studied in greater detail by determining the rates of formation of mono- and diglycerides, free fatty acids, and glycerol.

Experimental

Most of the reactions were performed in test tubes in which the oil layer had a depth of 15.9 mm., and the water layer had the same volume as the oil layer. These were immersed in a thermostat (constant-temperature water-bath) maintained at 35 ± 0.1°C.

The coconut and soybean oils used in this study had the following characteristics, respectively: acid number, 1.74 and 2.06; saponification number, 260.2 and 192.7; hydroxyl number, 1.7 and 2.0; and monoglyceride content 0.2 and 0.3%.

The Twitchell agent used was prepared from n-butanol, naphthalene, and sulfuric acid by the method previously reported by Fukuzumi and Ozaki (2). It consisted mainly of tetrabutyl naphthalene sulfonic acid and was free from sulfuric acid.

In all cases an amount of the sulfonic acid equal to 1% of the weight of oil was used.

Rate of Splitting at 35°C.

The rate of splitting was measured by setting up a series of replicate experiments. The acid numbers were determined at the end of 10 days (Figures 1, 2, and 3) and at intervals up to 30 days (Figure 4). The acid numbers obtained after the same reaction period in the replicate experiments were found to vary within 5 units. The points on the curves represent the averages for replicate experiments.

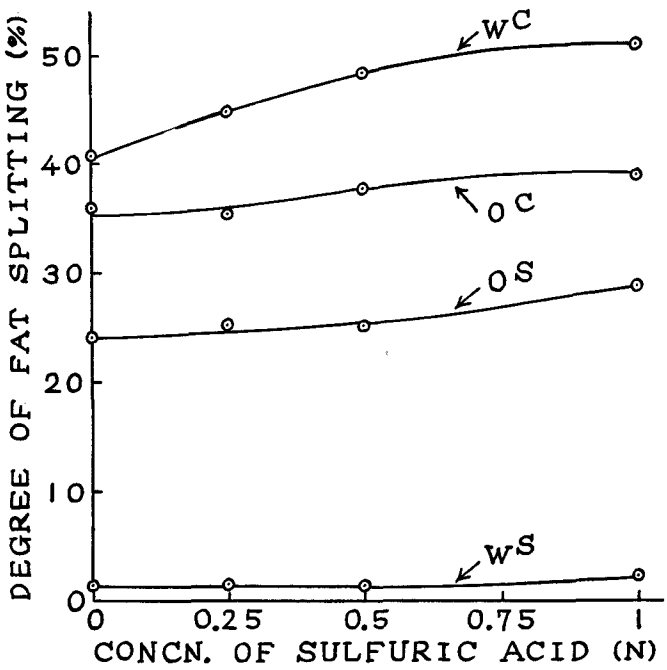

FIG. 1. The difference in the degree of fat splitting at 10 days between the case in which the sulfonic acid is dissolved in the water layer and that in which it is dissolved in the oil layer.

W: The sulfonic acid is dissolved in the water layer
O: The sulfonic acid is dissolved in the oil layer
C: Coconut oil
S: Soybean oil

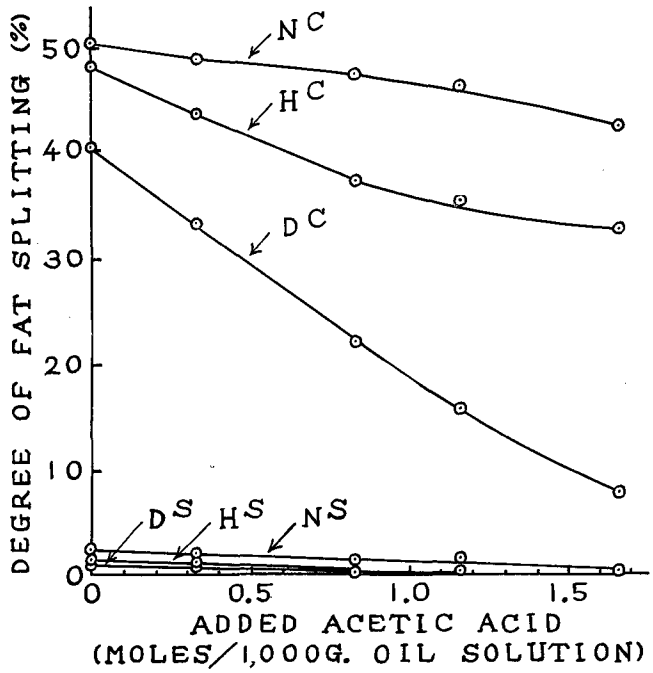

FIG. 2. The variation of the degree of fat splitting at 10 days by adding glacial acetic acid to coconut or soybean oil.

N: 1 *N* sulfuric acid
H: 0.5 *N* sulfuric acid
D: Water
C: Coconut oil
S: Soybean oil

Effect of Sulfuric Acid Concentration

When the sulphonic acid was dissolved in the aqueous layer, the procedure was as follows. The sulfonic acid (1% based on the weight of oil) was dissolved in either 5 ml. of water or 5 ml. of 0.25, 0.5, or 1 *N* sulfuric acid. Over this solution was carefully layered 5 ml. of coconut or soybean oil in such a way that mixing would not occur. Air was displaced with nitrogen, and the tubes were sealed. The tubes were immersed in a thermostat maintained at 35 ± 0.1°C. and allowed to stand for a period of 10 days without agitation.

When the sulfonic acid was dissolved in the oil layer, 5 ml. of water or dilute sulfuric acid were placed in the tube and then 5 ml. of the solution of sulfonic acid in the oil were carefully added.

Results are summarized in Figure 1, which shows that splitting was greatest in 1 *N* sulfuric acid. Furthermore soybean oil was split much less readily than coconut oil and was split to a greater extent when the sulfonic acid was dissolved in the oil than when it was in the water. The reverse was true with coconut oil.

Effect of Added Glycerol

Because glycerol is a fat hydrolysis product, the degree of splitting might be expected to decrease as the concentration of free glycerol increased. To test this idea, reaction systems containing glycerol were used. These reaction systems consisted of 5 ml. of an aqueous solution of the sulfonic acid and glycerol and 5 ml. of coconut or soybean oil. Amounts of glycerol up to 20% (based on the volume of water) were found to have no effect on the degree of splitting of either soybean or coconut oil.

Effect of Added Fatty Acids

As hydrolysis products, free fatty acids would also

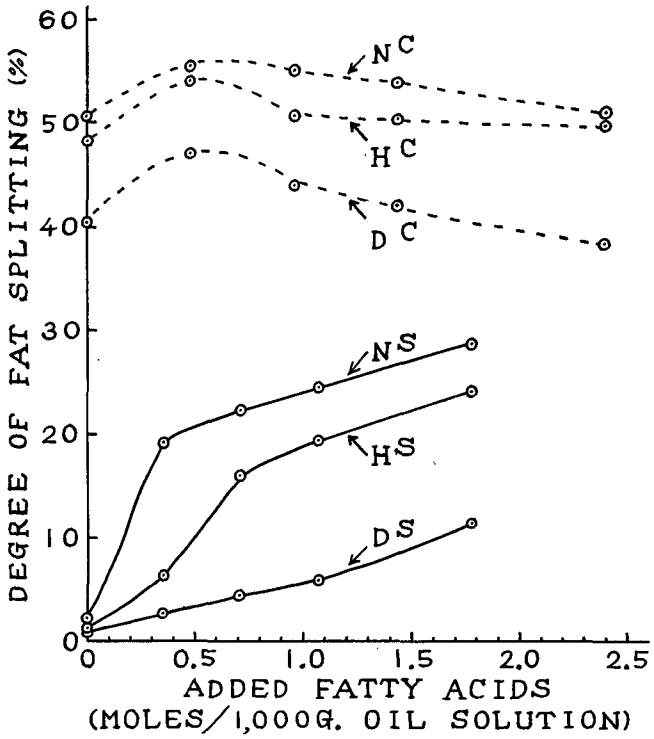

FIG. 3. The variation of the degree of fat splitting at 10 days by adding coconut fatty acids to coconut oil or soybean fatty acids to soybean oil.

N: 1 *N* sulfuric acid
H: 0.5 *N* sulfuric acid
D: Water
C: Coconut oil
S: Soybean oil

be expected to affect the degree of splitting. The effect of added fatty acids is shown in Figures 2 and 3. In Figure 2 the reaction systems consist of 5 ml. of an aqueous solution and 5 ml. of a mixture of coconut or soybean oil plus glacial acetic acid. In Figure 3 coconut or soybean fatty acids are substituted for glacial acetic acid. The data in Figure 2 show that addition of glacial acetic acid had no appreciable effect on the splitting of soybean oil but did markedly decrease the splitting of coconut oil, particularly in the absence of sulfuric acid.

Addition of coconut fatty acids to the coconut oil system (Figure 3) may have increased the degree of splitting slightly. Soybean fatty acids (Figure 3), on the other hand, markedly increased the degree of splitting of soybean oil, particularly when mixtures of the sulfonic acid and sulfuric acid were used as the catalyst.

Products from Coconut Oil

Experiments were made to determine the concentration of the various hydrolysis products at intervals after the start of the splitting of coconut oil in the presence of the sulfonic acid. For this purpose the sulfonic acid was dissolved in 5 ml. of 1 *N* sulfuric acid, and 5 ml. of coconut oil were added. Air in the tube was displaced by nitrogen; the tube was sealed and allowed to stand in a thermostat at 35 ± 0.1°C. without agitation. Three different sizes of tubes were used so as to provide oil layers having a thickness of (I) 15.9 mm., (II) 2.4 mm., and (III) 0.8 mm. This permitted a determination of the effect of the extent of contact between layers on the degree of fat splitting.

When a tube was taken from the thermostat, the acid number in the oil layer was immediately determined by the usual method. Then the glycerides and fatty acids were recovered by evaporating the solvent and acidifying the residue with dilute hydrochloric acid, followed by extraction with ether in the usual way. The hydroxyl number of the oil thus obtained was determined by the usual procedure and the α-monoglyceride content by the periodate oxidation method (3). The β-monoglyceride content was calculated as the difference between total monoglycerides (1) and α-monoglyceride and was found to be small in all cases. The diglyceride content was calculated from the hydroxyl number and monoglyceride content. The triglyceride content was calculated by subtracting the sum of free fatty acids content and mono- and diglycerides contents (%) from 100.

Results of these analyses are presented in Figure 4. Since the curves for II and III were so close together, the curves for II are not shown.

The di- and monoglycerides concentrations increased more rapidly in the thin oil layer than in the thick one. The changes in free fatty acids and triglyceride concentrations also indicated that splitting occurred more rapidly in the thin oil layers, that is, in the systems in whch there was the greater area of contact between the oil and the aqueous solution. Under the experimental conditions at 35 ± 0.1°C. splitting was 90% complete in 15 to 30 days.

Acknowledgment

The authors express their hearty gratitude for the guidance of Y. Toyama.

Summary

A study was made of the degree of splitting of coconut and soybean oils by the Twitchell process at 35 ± 0.1°C. with no shaking or stirring, using an agent consisting mainly of tetrabutyl naphthalene sulfonic acid with water or dilute sulfuric acid. The degree of splitting was greater with sulfuric acid than with water. In general, the degree of splitting of soybean oil was greater when the sulfonic acid was

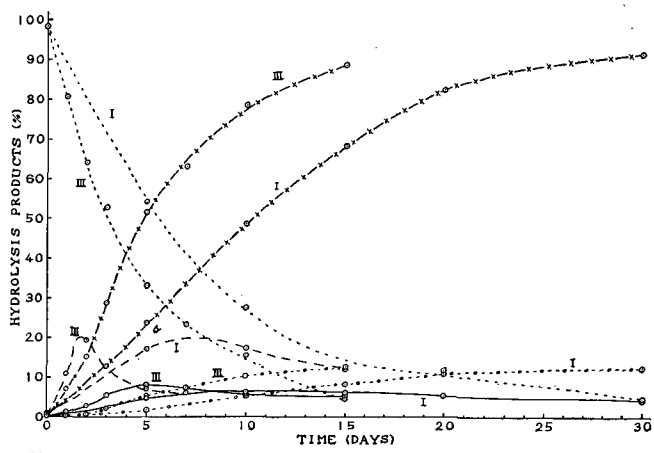

FIG. 4. The concentration of hydrolysis products at various times after coconut oil was placed in contact with a solution of the sulfonic acid in 1 *N* sulfuric acid.

———— Monoglyceride
— — — — Diglyceride
– – – – – – – Triglyceride
—x—x—x— Free fatty acids
– – ⊙ – – ⊙ – – Free glycerol
I: Oil layer 15.9 mm.
III: Oil layer 0.8 mm.

dissolved in the oil layer than when it was in water. The reverse was true with coconut oil. Although addition of glycerol had no effect on the degree of splitting, addition of glacial acetic acid to the coconut oil system decreased fat splitting to a considerable extent. Addition of coconut fatty acids to the coconut oil system had little effect, but soybean fatty acids added to the soybean oil system markedly increased the degree of splitting.

For the first time it has been demonstrated that, at 35 ± 0.1°C., splitting of a fat by the Twitchell process occurs in a stepwise way. Coconut oil in contact with 1 *N* sulfuric acid containing the sulfonic acid, corresponding to 1% by the weight of the oil, was about 90% split in 15 to 30 days, depending on the area of contact of the two layers. The diglyceride concentration reached a maximum during the early days of the reaction and then decreased somewhat. Monoglyceride concentration appeared to reach a maximum more slowly and then continued at that level as the concentrations of free fatty acids and glycerol steadily increased.

REFERENCES

1. Brokaw, G. Y., Perry, E. S., and Lyman, W. C., J. Am. Oil Chemists' Soc., *32*, 194 (1955).
2. Fukuzumi, Kazuo, and Ozaki, S., J. Chem. Soc. Japan, Ind. Chem. Sect., *54*, 727 (1951).
3. Pohle, W. D., and Mehlenbacher, V. C., J. Am. Oil Chemists' Soc., *27*, 54 (1950).

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The Relationship of Diet to Life Expectancy and Atherosclerosis

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THERE HAS BEEN considerable discussion recently concerning the role that dietary fats and fatty foods play in the development of atherosclerosis. Some conclusions have been derived from the comparison of data obtained for various classes of people in carefully selected localities. For example, the Bantus of Africa have been compared directly with the population of the United States, and certain groups in Italy, Spain, and England compared with purportedly similar groups in Minnesota. This has been summarized in a number of review articles (1, 2, 3).

Such comparisons have several obvious and serious limitations. Perhaps the most serious is that of attempting to correlate a specific effect with only one of a large number of potentially causative variables. Thus, whereas dietary fats differed substantially in the groups studied, so too did such factors as total caloric intake, types of all food-stuffs, climate, racial characteristics, energy output, standards of living, sanitation, medical care, economic standards, age of the population, and many others. Another fallacy is that an intermediate factor may be overlooked in such comparisons. For example, any factor that would tend to increase life span would obviously result in more people being susceptible to atherosclerosis. Yet a simple correlation would implicate that factor as a direct cause of the increased incidence of atherosclerosis. Further it can be very misleading to draw conclusions from data of this type unless there are represented many different populations taken on a random basis rather than a few groups selected on some arbitrary basis.

Data are readily available on food consumption

TABLE I
Compilation of Some Components of the Diet and Various Vital Phenomena

Country	Food Consumption Kg./cap./year							Caloric intake per cap. per day	Vital Phenomena				
	Fats and oils					Meat	Eggs		Deaths/ 100,000, arterio-sclerotic heart disease[a]	Deaths/ 1,000, males 40–44 (all causes)[b]	Life expect-ancy, males age 40[c]	Surviv-ors age 40, per 100,000 born (males)[d]	Percent-age of males age 40 and over[e]
	Total	Meat	Veg.	Butter	Marine								
Norway	25	2.5	7.1	5.5	8.6	31	7	3140	135.3	2.8	35.2	90,196	37.0
Netherlands	23	4.5	14.7	3.6	1.8	29	5	2960	147.3	2.7	34.9	91,661	31.3
United Kingdom	22	1.6	10.2	7.4	2.3	50	11	3100	298.0	3.1	31.4	92,430	40.5
Ireland	21	1.3	0.7	18.7	0	56	14	3340	274.8	4.7	30.6	82,462	35.8
Sweden	21	2.5	6.6	14.0	0.7	48	11	3120	229.5	2.8	33.8	91,697	40.0
United States	19	5.6	10.5	4.8	0	74	21	3130	282.3	5.0	31.4	90,207	35.0
Denmark	19	4.7	9.2	4.5	2.6	65	9	3160	202.2	2.7	33.8	90,088	35.2
Belgium	19	5.0	7.2	10.8	0.7	45	13	2770	111.8	3.9	30.6	84,882	41.4
Canada	18	....	....	....	....	69	17	3060	222.9	3.9	32.4	89,649	36.0
Switzerland	16	3.9	8.8	5.8	0	40	9	3150	238.1	3.6	30.4	86,063	38.4
New Zealand	15	....	....	....	....	96	13	3250	252.2	2.7	32.6	92,250	34.1
West Germany	15	5.9	5.3	5.5	0.6	23	4	2640	163.3	3.5	32.3	87,102	40.0
Austria	15	7.9	6.1	3.4	0.1	29	4	2620	195.2	3.7	30.7	85,111	42.2
Israel	15	....	....	....	....	15	12	2630	120.9	2.7	33.1	90,900	27.6
Australia	14	....	....	....	....	108	12	3160	240.9	3.7	31.2	90,823	35.0
Finland	12	....	....	....	....	27	4	3000	191.7	5.5	28.0	86,799	30.0
France	12	4.2	5.9	6.0	0.2	54	10	2770	37.6	4.8	30.4	87,940	41.0
Portugal	10	3.3	9.5	0.4	0	19	2	2110	67.1	5.3	30.3	75,466	28.0
Italy	9	3.4	6.0	1.2	0	18	5	2340	176.3	4.4	32.3	....	....
Cyprus	8	....	....	....	....	17	2	2740	39.9	2.9	32.9	85,159	26.6
Brazil	6	....	....	....	....	39	3	2340	....	14.1	25.4	69,782	18.0
Chile	6	....	....	....	....	38	2	2360	36.2	9.2	27.2	51,210	22.6
Mexico	6	....	....	....	....	23	2	2050	5.5	11.5	24.8	50,376	21.4
Egypt	3	....	....	....	....	10	1	2290	28.2	14.2	26.1	47,243	22.5
Japan	1	....	....	....	....	2	1	2100	44.7	5.1	30.6	84,834	24.8

[a] Number of deaths from arteriosclerosis per 100,000 population.
[b] Deaths of males in age group 40–44 per 1,000 males in that age group.
[c] Average number of years of life remaining for males reaching age 40.
[d] Number of survivors per 100,000 males born 40 years previously.
[e] Percentage of males of all ages that are 40 and more years old.