TABLE III

Moisture in Peanut Butter

Sample No.	A.O.C.S. Official Method Ab 3-49	Vacuum-Oven Method[a]
	%	%
1	2.43	2.31
2	1.45	1.37
3	1.30	1.22
4	1.15	0.96

[a] Sample wt. 5.0 g.; heating period 2 hours at 130°C.; pressure less than 5 mm. of mercury.

dehydration. These differences may be explained by the fact that the whole peanut kernel has a relatively porous structure which permits moisture to escape with comparative ease during oven heating. However this structure is destroyed on grinding, and moisture cannot escape as readily from the resulting viscous compact mass.

The determination of moisture and volatile matter on four samples of peanut butter by heating in a forced-draft oven and in a vacuum oven were performed to ascertain whether peanut butter heated in air increases in weight from oxidation hence appears to have a lower moisture content. The conditions for both determinations corresponded to those of A.O.C.S. Official Method Ab 3-49 except that the pressure in the vacuum oven was reduced to less than 5 mm. of mercury. The slightly lower moisture values for the samples heated in the vacuum oven are not considered significant and probably result from less efficient transfer of heat in the vacuum oven than in the forced draft oven.

Summary and Conclusion

The moisture and volatile content of whole peanuts has been determined by A.O.C.S. Official Method Ab 2-49 and has been compared with the moisture content of the sliced peanuts determined by a toluene distillation procedure described by Tryon (5). For practical purposes the results obtained by these methods are in agreement.

Moisture of peanut butter has been determined by an oven loss-in-weight technique corresponding to the conditions of A.O.C.S. Official Method Ab 3-49 for "second" moisture, and by the toluene distillation method. The results indicate that less dehydration was attained by A.O.C.S. Official Method Ab 3-49 than by the toluene distillation procedure.

Losses in weight of peanut butter samples have been determined in vacuum and forced-draft ovens at 130° C. No differences were observed which would indicate that the conditions of A.O.C.S. Official Method Ab 3-49 produce low results because of oxidation.

It can be concluded that the toluene distillation procedure, using apparatus described by Tryon (5), is suitable for determining the relatively small amounts of moisture present in peanut butter. The unique features of this apparatus seem to make the method particularly adaptable to peanut butter. This information is presented to provide the peanut butter industry with an additional method for use in problems involving determination of small amounts of moisture and for comparison with other prevailing methods.

REFERENCES

1. American Oil Chemists' Society Official and Tentative Methods, American Oil Chemists' Society. Official Methods Ab 2-49 and Ab 3-49.
2. Bidwell, G. L., and Sterling, W. F., Ind. Eng. Chem., *17*, 147 (1925).
3. Dean, E. W., and Stark, D. C., Ind. Eng. Chem., *12*, 486 (1920).
4. Hoffpauir, C. L., Oil & Soap, *22*, 283-286 (1945).
5. Tryon, M., Journal of Research of the National Bureau of Standards, *45*, 362-366 (1950).
6. Willich, R. K., Hall, A. S., Morris, N. J., and Freeman, A. F., Food Technology, *6*, 71 (1952).

[Received March 16, 1953]

The Chemical Utilization of Fats and Oils. I. Preparation of Aralkyl Ketones and Hydrocarbons

R. D. ENGLERT, R. M. SILVERSTEIN, and L. M. RICHARDS, Stanford Research Institute, Stanford, California

CERTAIN studies have been made in these laboratories over the past few years in an effort to utilize fats and oils through chemical modification. One of these studies was on the production of straight chain alkylbenzenes as detergent intermediates.

A detergent intermediate produced in volume is that prepared from benzene and propylene tetramer. The resultant detergent thus contains a branched alkyl chain. It was thought that different and desirable properties might be obtained from a straight alkyl chain. It was also felt that mixtures of alkylaryl sulfonates having alkyl chains of from 14 to 18 carbon atoms might possess desirable detergent and solubility properties even though the individual compounds might not be entirely satisfactory. The use of mixtures would also have economic advantages.

Experimental

A satisfactory general laboratory synthesis of the desired aralkyl compounds consisted in the preparation of the acyl chloride from the fatty acid with phosphorous trichloride, condensation of the acyl chloride with the aromatic compound using aluminum chloride, and hydrogenation of the ketone over nickel on kieselguhr.

Myristic acid was condensed with benzene in the presence of aluminum chloride in the manner described for shorter chain acids (4, 9, 10, 13, 14).

The use of hydrogen fluoride (3, 4, 5, 6, 7, 11, 12, 15) as a condensing agent for the direct acylation of benzene with myristic acid was also studied. Experiments at atmospheric pressure were carried out by introducing hydrogen fluoride through a cooled copper coil into the reactants contained in a copper beaker immersed in an ice bath. The beaker was fitted with a vented copper lid. After the desired time interval the hydrogen fluoride was allowed to evaporate at room temperature from the open beaker. To study reactions under autogenous pressure the reactants were placed in a rocking autoclave, which was cooled in an ice bath, and the hydrogen fluoride was introduced through a cooled copper coil. The autoclave was then sealed and heated to the desired temperature. After the reaction period the autoclave was cooled in an ice bath, and the contents were removed to an open copper beaker from which the hydrogen fluoride was allowed to evaporate.

The crude ketones were usually purified by solution in ether, precipitation of unreacted acid as the ammonium salt, and precipitation of the ketone by the addition of methanol. In some instances the ketones were distilled. The reactions are summarized in Tables I and II.

TABLE I

Condensation of Fatty Acid Chlorides

Exp. No.	Reactants[a]	Conversion[b]	Yield[b]	m.p.
		%	%	
1	300 g. (1.05 moles) stearic acid 75 g. (0.545 mole) PCl_3 800 ml. (8.91 moles) benzene 150 g. (1.12 moles) $AlCl_3$	69	ND[c]	54-56°C.
2	500 g. (1.90 moles) palmitic acid 150 g. (1.09 moles) PCl_3 1600 ml. (17.8 moles) benzene 400 g. (3.0 moles) $AlCl_3$	59	ND	54-55°C.
3	500 g. (2.19 moles) myristic acid 150 g. (1.09 moles) PCl_3 1350 ml. (15.1 moles) benzene 400 g. (3.0 moles) $AlCl_3$	71	79	51-52°C.
4	500 g. (2.50 moles) lauric acid 150 g. (1.07 moles) PCl_3 1350 g. (15.1 moles) benzene 450 g. (3.38 moles) $AlCl_3$	61	72	44-45°C.
5	500 g. (2.19 moles) myristic acid 150 g. (1.09 moles) PCl_3 1350 ml. (15.2 moles) benzene 400 g. (3.0 moles) $AlCl_3$	66	72	ND
6	616.5 g. (3.0 moles) coconut oil acids 206 g. (1.5 moles) PCl_3 1500 ml. (17 moles) benzene 560 g. (4.2 moles) $AlCl_3$	59	76[d]	ND
7	732.5 g. (2.5 moles) palm oil acids 171.8 g. (1.25 moles) PCl_3 1250 ml. (14.1 moles) benzene 456 g. (3.42 moles) $AlCl_3$	59	65	ND
8	731.5 g. (2.7 moles) hydrog. cottonseed oil acids 184.5 g. (1.35 moles) PCl_3 1350 ml. (15.2 moles) benzene 493 g. (3.7 moles) $AlCl_3$	77	91	ND
9	250 g. (1.25 moles) lauric acid 75 g. (0.545 mole) PCl_3 600 ml. (5.65 moles) toluene 225 g. (1.69 moles) $AlCl_3$	58	63	ND
10	250 g. (1.25 moles) lauric acid 75 g. (0.545 mole) PCl_3 600 ml. (4.9 moles) m-xylene 225 g. (1.69 moles) $AlCl_3$	62	64[e]	ND

[a] The acid chlorides were formed during one hour at 70°C. In Experiments 1, 2, 5, 6, 7, and 8 the acylations were conducted at room temperature for an over-night period. In the other experiments the reactions were completed by an additional one hour at steam bath temperatures.

[b] The percentage conversion is based on the quantity of condensation product obtained compared with theory, and the percentage yield is based on the quantity of product and the fraction of acids consumed.

[c] Not determined.

[d] Boiling range 165-215°C. at 4 mm.

[e] Analysis—Calc'd: C, 83.3; H, 11.2. Found: C, 83.7; H, 11.2. Boiling range 165-174°C. at 1 mm., n_D^{22} 1.5000.

Hydrogenation of the ketones to the hydrocarbons over nickel on kieselguhr (2) was preceded by refluxing in methyl alcohol with Raney nickel to remove catalyst poisons. The experiments are summarized in Table III, which also includes the results of a hydrogenation over copper chromite and of a Clemmenson reduction (1).

TABLE II

Direct Condensation of Fatty Acids

Exp. No.	Reactants	Conditions	Conversion
			%
1	50 g. (0.22 mole) myristic acid 135 ml. (1.53 moles) benzene 73.3 g. (0.55 mole) $AlCl_3$	Heat on steam bath for 5 hours	41[a]
2	25 g. (0.11 mole) myristic acid 86 g. (1.1 moles) benzene 200 g. (10.0 moles) HF	Two days at room temp. and atmos. pressure	0
3	25 g. (0.11 mole) myristic acid 86 g. (1.1 moles) benzene 700 g. (35 moles) HF	Overnight at room temp. and atmos. pressure	0
4	45.7 g. (0.2 mole) myristic acid 19.5 ml. (0.22 mole) benzene 277 g. (13.5 moles) HF	Heat in closed bomb in steam bath for 5 hours	0.7[b]
5	45.7 g. (0.2 mole) myristic acid 35.8 ml. (0.4 mole) benzene 170 g. (8.5 moles) HF	Heat in bomb at 100°C. for 5.5 hours	3.6

[a] The yield was 65%.

[b] Product crystallized from methanol had a melting point of 49.5-50.5°C. A mixed melting point with a known sample of myristophenone (mp. 50.5-51°C.) was 49.5-50.5°C.
Analyses—Calc'd: C, 83.3; H, 11.1. Found: C, 83.5; H, 11.2.

The acylations through the acyl chlorides proceeded smoothly in every case to give reasonably good yields.

TABLE III

Preparation of Alkylbenzene

Run No.	Reactions[a]	Conversion	Properties
		%	
1	150 g. (0.48 mole) palmitophenone 10 g. Ni (k) 150 ml. methanol	73	N_D^{23} = 1.4772 166-175°C./0.1 mm.
2	150 g. (0.504 mole) myristophenone 10 g. Ni (k) 150 ml. methanol	59	N_D^{26} = 1.4770 200-205°C./9 mm.
3	175 g. (0.65 mole) laurophenone 10 g. Ni (k) 150 ml. methanol	86	N_D^{28} = 1.4775 148-156°C./2 mm.
4	150 g. (0.504 mole) myristophenone 10 g. Ni (k) 150 ml. methanol	100	196-199°C./9 mm.
5	222 g. coconut phenones 13 g. Ni (k) 160 ml. methanol	98	N_D^{26} = 1.4807 128-223°C./9 mm.
6	195 g. palm phenones 10 g. Ni (k) 150 ml. methanol	78	N_D^{26} = 1.4778 211-240°C./9 mm.
7	286 g. hydrog. cottonseed phenones 15 g. Ni (k) 150 ml. methanol	58	N_D^{26} = 1.4787 215-226°C./7 mm.
8	99.3 g. (0.36 mole) lauroyltoluene 5 g. Ni (k) 70 ml. methanol	73	N_D^{23} = 1.4704 133-135°C./1 mm.
9	110.6 g. (0.38 mole) lauroyl-m-xylene 5 g. Ni (k) 70 ml. methanol	87	N_D^{23} = 1.4635 154-156°C./1 mm.
10	120 g. (0.35 mole) stearophenone 10 g. copper chromite 600 ml. methanol 1-phenyloctadecanol-1 Oxalic acid 1-phenyloctadecene-1 5 g. copper chromite	75	185-208°C./2 mm
11	246 g. (1 mole) stearophenone Amalgamated zinc HCl Xylene	35	N_D^{23} = 1.4810 200-210°C./4 mm.

[a] The *conditions of reaction* were generally 2-6 hours at 200-225°C. The initial H_2 pressure was 1700-2000 psi. Run 11 was carried out as recommended in Reference 1.

There appears to be no economic advantage in the direct acylation with the fatty acids because a larger amount of aluminum chloride is required and a lower yield results. In the direct condensation of myristic acid with benzene at least a 2:1 molar ratio of aluminum chloride to acid was required. The percentage conversion and yield (41 and 65, respectively) were lower than those from two comparable syntheses through the acid chloride (66 and 72; 71 and 79, respectively).

The use of hydrogen fluoride as a condensing agent in the direct acylation with fatty acids was found to be unsatisfactory. No reaction took place at atmospheric pressure; the yields at autogenous pressures and in the temperature range of 80-125°C. were low.

The hydrogenation over nickel on kieselguhr proceeded smoothly in some instances while the yields in other runs were inexplicably low. Further study of this step is indicated. Hydrogenation of stearophenone over copper chromite stopped at the intermediate alcohol which had to be dehydrated to the unsaturated compound before reduction would proceed. Reduction of stearophenone by the Clemmenson method was unsatisfactory. Large amounts of viscous high boiling products were obtained along with the desired hydrocarbon.

Summary

A number of straight chain aralkyl detergent intermediates were prepared from fatty acids. The most satisfactory method of preparation involved a Friedel and Craft condensation of the acyl chlorides with the aromatic followed by catalytic hydrogenation.

Acknowledgment

This work was supported by the Purex Corporation Ltd., Southgate, Calif.

REFERENCES

1. Adams, R., "Organic Reactions," 1st ed., Vol. I, p. 167, New York, John Wiley and Sons Inc. (1947).
2. Adkins, R., "Reactions of Hydrogen," 1st ed., p. 14, Madison, The University of Wisconsin Press (1946).
3. Fieser, L. F., and Herschberg, E. B., J. Am. Chem. Soc., *61,* 1272-1281 (1939).
4. Fieser, L. F., and Johnson, W. S., *ibid.*, *61,* 1647-1654 (1939).
5. Fieser, L. F., and Joshel, L. M., *ibid.*, *61,* 2958-2961 (1939).
6. Fieser, L. F., and Herschberg, E. B., *ibid.*, *62,* 49-53 (1940).
7. Fieser, L. F., and Kilmer, G. W., *ibid.*, *62,* 1354-1360 (1945).
8. Groggins, P. H., and Nagel, R. H., U. S. Patent 1,966,797 (1934).
9. Groggins, P. H., Nagel, R. H., and Stirton, A. J., Ind. Eng. Chem., *26,* 1317-1318 (1934).
10. Groggins, P. H., Ind. Eng. Chem., *42,* 1690-1693 (1950).
11. Ipatieff, V. N., Pines, H., and Olberg, R. C., J. Am. Chem. Soc., *70,* 2123-2128 (1948).
12. Johnson, W. S., Goldman, A., and Schneider, W. P., *ibid.*, *67,* 1357-1360 (1945).
13. Malinoskii, M. S., and Kislova, F. F., J. Gen. Chem. (USSR), *28,* 1643-1644 (1948).
14. Newton, H. P., and Groggins, P. H., Ind. Eng. Chem., *27,* 1397-1399 (1935).
15. Simons, J. H., Randall, D. L., and Archer, S., J. Am. Chem. Soc., *61,* 1795-1796 (1939).

[Received March 18, 1953]

Improvements in the Rapid Refractometric Method of Determining the Oil Content of Olives

SOCRATES A. KALOYEREAS, Louisiana State University, Baton Rouge, Louisiana, and
WILLIAM V. CRUESS, University of California, Berkeley, California

RAPID refractometric tests for determining the oil content of various products such as cotton seeds (4), flaxseed (1), olives (2), and cheese (3) have been developed in the past. The precision of such methods depends largely on the standardization procedure followed by the investigator. Success in practical application and acceptance of the methods by industry require adequate accuracy under standard laboratory conditions and also adaptability to special, local conditions. The authors of the older refractometric tests on olives (2) were conscious of the fact that a lack of a sufficient degree of adaptability in their method proved to be a handicap to its practical application by the olive industry in the United States and abroad. There is a growing demand for a rapid oil test for use in the cooperative olive oil mills of southern Europe.

We have tried to remedy the deficiencies of the older method, first by describing a simple, practical test, and second by discussing the various factors involved in the method.

The simplified procedure involves the use of a Waring blendor for grinding the sample and a method of standardization which does not require corrections for refractive index of the oil of the sample. The use of the Waring blendor is made possible by adding water to the mixture of olive sample and Halowax oil (α-chlor-naphthalene) to make a thin purée or liquid suspension. The addition of water, together with the use of the Waring blendor, also makes possible the use of a larger and more representative sample. Twenty or even 40 grams of olives can be easily handled in the Waring blendor rather than the usual 5-g. sample ground in a mortar. Our standardization involves the addition of 70-80 ml. of water to 10 grams of olive sample and 10 ml. of Halowax oil in the blendor. After running the blendor for five minutes at a speed slow enough to prevent foaming, a portion of the mixed liquids is centrifuged and the refractive index of the clear liquid, a mixture of Halowax oil and olive oil, from the bottom of the tube is determined. By subtracting the refractive index of the mixture from the refractive index of the Halowax

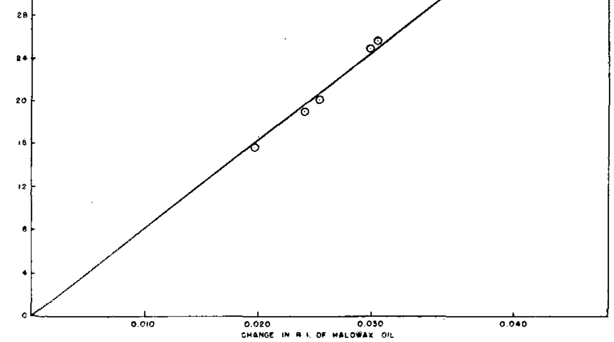

FIG. 1. Change in refractive index of the Halowax oil.