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

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

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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 cordections 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

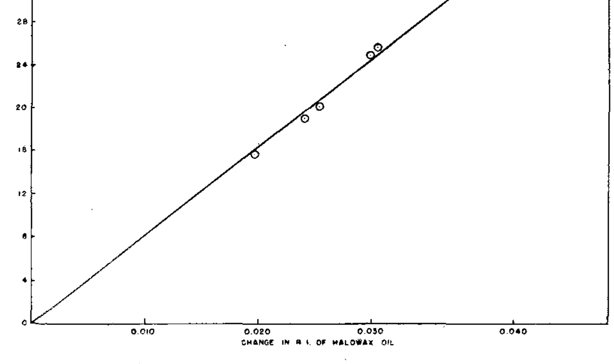

FIG. 1. Change in refractive index of the Halowax oil.

TABLE I

Showing Data Obtained with the New Method on Various Samples of Olives

Samples of Olives	Per Cent Oil by Soxhlet	R. I. at 25°C.		Per Cent Oil in the Mixture	R. I. Change/1% Olive Oil	
		Mixture of Hal. Oil-Olive Oil	Pure Olive Oil		Expt. Values	Theoretical Values
Green (fresh)	15.76	1.6101	1.4711	11.83	0.00165	0.00166
Green Yellow (fresh)	18.91	1.6059	1.4718	13.87	0.00164	0.00165
Reddish (fresh)	20.13	1.6044	1.4690	14.63	0.00165	0.00167
Black (fresh)	25.54	1.5995	1.4741	17.86	0.00168	0.00163
Black (canned)	24.79	1.6003	1.4731	17.43	0.00168	0.00164

oil measured at the same temperature, we obtain the change in the refractive index of the Halowax oil produced by the olive oil dissolved in it. The water, being immiscible with Halowax oil, does not affect the refractive index of the Halowax oil-olive oil solution. On the other hand, it helps to eliminate the effect of other soluble solids besides oil and also the effect of the variation of the refractive index of the oil from different samples (Table I, Figure 1). The interference of these two factors is indeed a great handicap for the introduction of the old method into practical use. By plotting the changes in refractive index obtained from various samples of olives against their oil contents as determined by the Soxhlet extraction method, the curve shown in Figure 1 is obtained. This can serve for rapid determination of the oil content of any olive sample directly from the change of the refractive index of Halowax oil produced by the oil of the sample without any further calculations or corrections, which were required in the previous method.

Some Theoretical Considerations

Contraction in Volume of Oil-Solvent Mixtures

Samples of fresh olives of the Mission variety, the common oil variety of California, at different stages of maturity, were used. The flesh of the ground olive samples (10 gm.) was treated for 5 minutes in a Waring blendor with 10 ml. of Halowax oil and 70-80 ml. water. The refractive index of the separated mixture of Halowax oil-olive oil was accurately determined.

Three factors were involved in the change in refractive index resulting from dissolving olive oil in Halowax oil. These were:

a) The variation of the refractive index of the olive oil of the samples.

b) The effect of other substances dissolved besides oil.

c) The contraction in volume of the mixtures of oil and solvent.

The factors 1 and 2 have been eliminated by the new technique as shown by the close agreement between theoretical and experimental values obtained in the data of Table I and the position of the curve in Figure 1. The third factor, that of contraction in volume, remained to be determined in order to enable the calculation of theoretical values for the change of refractive index of Halowax oil effected by dissolving olive oil in it.

TABLE II

Effect of Contraction of Volume upon Refractive Index of Mixtures of Halowax Oil and Olive Oil

	% Olive Oil in Mixture	Refractive Index at 41°C.	% Contraction in Volume	Effect of Contraction[a]
Halowax oil	0	1.6282	0	none
Olive oil	100	1.4703	0	none
Mixture A	3.1413	1.6224	0.36	0.00007
Mixture B	9.5497	1.6111	0.92	0.00006
Mixture C	24.3245	1.5837	2.50	0.00006

[a] Effect of contraction upon refractive index change per 1% oil in the mixture.

Three mixtures of Halowax oil and olive oil were prepared. The contraction in volume of the three mixtures, their refractive index, and the respective changes of refractive index due to contraction are shown in Table II.

If the values for contraction are plotted against the percentage of oil in the mixture, the corresponding points fall practically on a straight line (Figure 2),

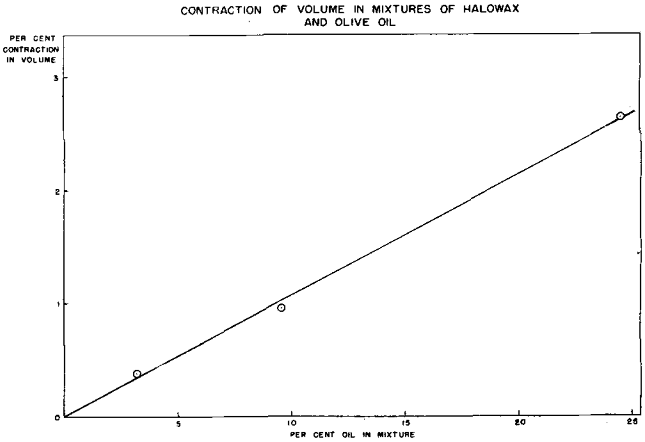

FIG. 2. Contraction in volume of olive oil Halowax oil mixtures.

showing that the effect of contraction is practically uniform, at least between the limits of 0 and 25% oil. The thermal coefficients for volume and refractive index of mixtures of Halowax oil and fat have been determined previously (3) and found equal to 0.69 ml. for the first and 0.00043 for the second. From these values and from the figures obtained here for the change in volume by contraction, the effect of contraction upon the change of refractive index in the various mixtures can be calculated as follows. In mixture A, for instance, the effect will be equal to $0.00043 \times 0.36/0.69 = 0.00022$, and for 1% oil in the mixture will be $0.00022/3.1413 = 0.00007$. Practically the same value is obtained if calculations are carried out on the other mixtures, B and C.

The refractive index of Halowax oil used in this experiment was 1.6297 at 25°C. The refractive index of the olive oil varies according to the sample; therefore it is necessary to calculate the theoretical values for the change in refractive index of the mixtures separately for each sample of olives. For the sample No. 1, for instance, of Table I, the theoretical value will be $1.6297\text{-}1.4711/100 + 0.00007$ (effect of contraction) $= 0.00166$.

In Table I appear the comparative data of the oil content of various samples of olives determined by Soxhlet and the new method as well as theoretical and experimental values for the refractive index change of the mixtures of Halowax oil and olive oil.

Summary

A new standardization of the rapid refractometric method of determining oil in olives has been devised. A theoretical discussion of all the factors involved and the introduction of the use of the Waring blendor in making the treatment with Halowax oil have also been presented.

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ABSTRACTS . . . . E. S. Lutton, Editor

• Oils and Fats

R. A. Reiners, Abstractor
Ralph W. Planck, Abstractor

Fatty alcohols. P. Blaizot and M. Servant. *Oleagineux* 8, 267-271(1953). The commercial preparation of fatty alcohols from natural fatty materials by catalytic hydrogenation and by sodium reduction as well as synthetic methods which include the oxidation of Fischer-Tropsch paraffins and the "Oxo" and "Synol" processes are discussed.

Better utilization of rice bran oil. C. Carola. *Olii Minerali-Grassi e Saponi-Colori e Vernici* 30, 56-61(1953). The uses, methods of extraction and refining, composition, constants, and the storage of rice bran oil are discussed.

The conservation of fats, oils, and soaps. H. J. Henk. *Seifen-Öle-Fette-Wachse* 79, 249-50(1953). The effectiveness of antioxidants in preventing rancidity in fats, oils, and soaps is discussed.

The autoclave splitting of fat. H. Radfang. *Seifen-Öle-Fette-Wachse* 79, 250-52, 273-74(1953). After an historic retrospect the autoclave splitting of fat is described with special consideration being given to the preliminary purification of the material to be treated and the manipulation of the autoclave.

Chemical composition of molds. II. Fatty material of penicillium chrysogenum. Y. Abe. *Proc. Fac. Eng. Keiogijuku Univ.* 2, No. 7, 15-20 (129-34)(1949). *Penicillium chrysogenum* contains water 9, crude fat 2.67, crude protein 33.98, and ash 3.62%. The fat from *P. chrysogenum* melts at 10-12°; specific gravity is 0.9175, acid value 58.8, saponification value 176.7, and iodine value 89.0. Composition of these fatty acids was found to be: saturated acids 19.0% (myristic 3.2, palmitic 10.3, stearic 4.9, and *N*-tetracosanic 0.6%); unsaturated acids 67.2% (oleic 46.2, linoleic 17.5, others 3.5%); unsaponifiable 3.9% (ergosterol 0.62%). (Chem. Abs. 47, 4949)

Fatty acids from Indian cottonseed-oil foots. B. Bhushan, J. P. Phillips and K. C. Gulati (Central Labs. Sci. Ind. Research, Hyderabad). *J. Sci. Ind. Research* (India) 12B, 38-9(1953). A 3-kg. sample of commercial cottonseed-oil foots, containing 66.2% fatty acids, heated for 6-7 hrs. at 100-110 lb./sq. in., and distilled at 240-60° at 400-420 mm., gave 1.4 kg. of fatty acids of acid value 198; and a distillation residue of 0.77 kg. (*Chem. Abs.* 47, 5138)

Synthetic liquid fuel from Indian cottonseed-oil foots. B. Bhushan, J. P. Phillips, and K. C. Gulati (Central Labs. Sci. Ind. Research, Hyderabad). *J. Sci. Ind. Research* (India) 12B, 39-40(1953). Pyrolysis of cottonseed-oil foots 100 with lime 10-20 g. at 450-480° produced 16-21% crude oil. Ca and Na soaps from refined cottonseed oil gave 84 and 82% crude oil, respectively. About 18% wax settled from both oils on standing. They yielded by distillation 31-35% gasoline (70-200°), and 43-50% kerosene (225-325°). (*Chem. Abs.* 47, 5138).

Sunflower-seed oil. Brit. Standards Inst., London, S. W. 1. *Brit. Standard* 1939: 1953, 15 pp. Specifications are given for the volatile matter, color, specific gravity, *n*, iodine no., saponification value, unsaponifiable matter, acidity, and polybromides for crude and semirefined oil. Methods of determination are described. (*Chem. Abs.* 47, 5139)

Chemical composition of the seed oil of Ilex paraguariensis (yerba mate). P. Cattaneo, Germaine K. de Sutton, and Maria L. Rodriguez. *Anales direc. nacl. quim.* (Buenos Aires) 5, No. 9, 9-12(1952). The seed, before and after extraction with ligroin (boils 30-70°) contained, respectively, water 7.2 and 8.6, ash 1.3 and 1.5, protein 6.4 and 7.6, fiber 52.0 and 61.9, pentosans 17.0 and 20.2, and petroleum-ether extract 16.1 and 0.2%. The oil had acetyl no., 8.0; specific gravity ^{25} 0.9152; n^{25} 1.4720; saponificatoin no., 192.7; (Hanus) iodine no., 116.7; acid no. 4.4; Halphen test, negative; unsaponifiable 0.55%. The composition of the fatty acid was: lauric 0.87, palmitic 10.05, stearic 3.79, arachidic 0.58, oleic 34.46, palmitoleic 1.47, and linoleic 49.15%. (*Chem. Abs.* 47, 5139)

Utilization of tensioactive compounds for the extraction of oils. H. Debruyne (Lab. munic., Bordeaux, France). *Bull. mens. inform. ITERG* 7, 56-64(1953). Surface-active compound solutions of, respectively, 2, 0.5, 0.1% concentration on incorporation into test samples of 200 g. of dried peanut-meal in such a quantity as to replace 6-8% of the moisture did not improve oil extraction over that of controls by a laboratory hydraulic press. Actually at short pressing times the oil yield was less with surface-active treatment. (*Chem. Abs.* 47, 5138)

Effect of varying the urea concentration on the efficiency of the extraction of unsaturated fatty acids from corn oil. A. T. Ericson and R. E. Clegg (Kansas State Coll., Manhattan). *Trans. Kansas Acad. Sci.* 55, 493-8(1952). A study was made of the adducts formed from corn-oil fatty acids in diisopropyl ketone as a solvent with increasing amounts of urea. Increasing the concentration of urea increased the probability that the unsaturated fatty acids would form the adduct. Decreasing the temperature increased the formation of adduct with the unsaturated fatty acids at lower urea concentrations. In the case of saturated urea solutions containing a large excess of solid urea, the adduct formed contained the unsaturated fatty acids present in the original sample, and a satisfactory separation from the pigments was possible. (*Chem. Abs.* 47, 5137)

Most suitable solvent for extraction of oils from bagasse (grape, cottonseed, olive, etc., refuse). H. Fontana. *Ion* 13, 574-7(1952). $CHCl:CCl_2$ is favored over CS_2 as an oil-extraction solvent because of favorable insurance rates, lower heat of vaporization (steam saving), does not leave trace of S in the oil, and is more efficient on undried material. (*Chem. Abs.* 47, 5138)

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Composition of the body fat of small green chironomids. D. N. Grindley (Wellcome Chem. Labs., Khartoum, Sudan). *J. Exptl. Biol.* 29, 440-4(1952). The body fat of *Tanytarsus lewisi* (Chironomidae) consists of a mixture of the glycerides of palmitic, stearic, oleic, palmitoleic, linoleic acids, and a polyethenoid acid containing 4 or 5 double bonds. The fat is closely similar to that usually occurring in fresh-water fish. The insect does all its feeding while in the larval stage on the bed of the river, and the body fat resembles that of algae and plankton, which probably are the main sources of food, and differs considerably from that of most terrestrial insects hitherto studied. (*Chem. Abs.* 47, 5032)

The occurrence of *n*-decanoic acid in mutton fat. R. P. Hansen and N. J. Cooke (Dept. Sci. Ind. Res., Wellington, N. Z.). *Biochem. J.* 54, 14-16(1953). *n*-Decanoic acid has been isolated in trace amounts from the external fatty tissue of sheep.

Selective esterification of tall oil with pentaerythritol. P. Kirjakka and E. Turunen. *Teknillisen Kemian Aikakausilehti* 9,