permit evaluation of oils under conditions promoting oxidation catalyzed by metal pick-up and by contact with metal surfaces, situations encountered in commercial operations. It has been shown that a substantial lowering of the A.O.M. values is obtained when the modified test is used.

Data are presented on the reproducibility of the method for evaluating the stability of shortenings and the protective influence of antioxidants. Isopropyl citrate esters, predominantly monoisopropyl citrate, have proved to be superior to other metal sequestering agents in the test described since the esters can be readily added to oils in sufficiently high concentrations to be effective. Isopropyl citrate esters protect the oils not only against the prooxidant effects of dissolved iron but also against contact metal catalysis.

The relative keeping times of fats and oils in actual practice probably fall somewhere between the two extremes predicted from the results of the conventional and the modified A.O.M. tests. Both tests have virtue in evaluating oils; the reproducibility of values by the conventional test, conducted on different batches of a given oil without antioxidants and metal sequestering agents, reflects the reproducibility of the oil produced in the plant with respect to inherent resistance to oxidative deterioration; the values by the iron tube test reflect the degree of resistance of the oil to oxidation, following extreme exposure to metal contamination and contact metal catalysis.

All of the oils tested in the present study have been subjected to flavor evaluations in addition to serial determinations of peroxide value. The former have supported the latter relative to establishing the end-point or first sign when the oils develop rancidity.

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The Composition of Coffee Oil and Its Component Fatty Acids

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COFFEE is a favorite drink almost all over the world. The water-soluble portions of the coffee bean are thus utilized, and the rest is thrown out as waste. The coffee grounds are mainly composed of proteins, carbohydrates, and lipids. About 20-25% of the dry weight of the water-extracted grounds is recoverable as oil. Coffee grounds in enormous amounts are a product of the soluble coffee industry and actually present a problem for industrial disposal. However they are a potential source of protein and carbohydrate and also of oil of possible edible and other uses. The object of the present work was to investigate the composition of coffee oil in relation to its possible uses. The magnitude of the soluble coffee industry makes recovery of the oil practical, provided there are industrial outlets for its use.

Previous work on coffee oil is meager and conflicting. Robiquet and Boutron (1) in 1837 showed that the coffee-bean contains about 10% of fat, which is extractable with ether. From that time until the end of the past century various reports dealing with coffee fat were published by Rochleder (2), Chech (3), De Negri and Fabris (4), Hilger and Tretzel (5), Hilger (6), Spath (7), Herfeldt and Stutzer (8), and Warmier (9). In most cases these investigators reported the determination of certain constants and partial analyses of the fat; few systematic attempts were made to isolate or identify the individual fatty acids. Juckenack and Hilger (10) however made an extensive study of the fat obtained from various kinds of coffee, both raw and roasted, and reported that the fat consisted largely of glycerides of oleic acid and only minor quantities of glycerides of palmitic and stearic acids. Meyer and Eckert (11) fractionally crystallized the acids from the oil of decaffeinized coffee and reported about 40% of saturated acids, consisting of capric (0.5%), palmitic (25-28%), daturic (1-1.5%), and carnaubic (10%) acids; the unsaturated acids were stated to be composed of 2% oleic acid and 50% linoleic acid. Von Noel (12) investigated six oils from several kinds of coffee. The limits of constants observed were: d, 0.9288-0.9453; saponification number, 176.1-179.15; iodine number, 87.1-92.4; Reichert-Meissl number, 0.52-0.66; Polenske number, 0.2-0.25; unsaponifiables, 6.53-13.49%. The fatty acids of the oil were found to be palmitic, daturic carnaubic, oleic, and linoleic acids. He stated that the fatty acids suffer little change during roasting.

The most important work on coffee oil is that of Bengis and Anderson (13), who studied the component fatty acids of coffee-bean oils of different types (green bean, freshly roasted, stale roasted). Separation of the crude acids by the lead soap method gave 54.4% of liquid acids, consisting of linoleic acid 29.5%, oleic acid 21%, and petroleum-ether-insoluble acid designated as hydroxy unsaturated acids (C_{18} or otherwise) 4%; and 37.5% of solid acids, including palmitic 29.2%, stearic 6.4%, and tetracosanoic 1.8%. They were able to identify tectracosanoic acid but found no C_{20} or C_{22} acids. More recently, Bauer and

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Neu (14) in an examination of oils from several kinds of coffee reported 38-41% of saturated acids, 27-31% of oleic acid, and 22-28% of linoleic acid.

In the present work we have shown that coffee oil contains excessive amounts of unusual unsaponifiables, the presence of which makes the oil unfit for most uses. We have also shown that the unsaponifiables can be removed almost completely by molecular distillation. It would appear that it will be impractical to apply this technique economically in the face of the present over-supply of fats and oils. A specimen of the unsaponifiable-free fatty acids of coffee oil was converted to methyl esters, which were submitted to ester distillation. The components of the several fractions were separated by low temperature crystallization and studied by this procedure and others. The oil was shown to contain over 46% of linoleic acid, which places it in the class of semi-drying oils. In the specimen of oil which we examined, we could find no evidence of the presence of hydroxy acids.

Experimental

The coffee oil used in this work was kindly furnished by R. W. Titus of the Nestlé Company, Marysville, O. It was recovered from the grounds from a fresh roasted blend of Brazilian, Colombian, and Venezuelan coffees, which had been dried to a moisture content of 5% and extracted with trichloroethylene. The oil had been treated with Nuchar and Magnesol. The resultant oil was treated with steam and finally dried. It was reddish in color and retained a strong coffee odor. One of its most characteristic reactions was the development of typical color changes when boiled with methanol, acidified with HCl: light purple, changing to brownish purple, and then ending in a deep purple-green. After some time the reaction resulted in formation of considerable amounts of a brown precipitate. This unique reaction is due to certain of the unsaponifiables in the oil, probably to kahweol.[3] Repeated extraction of the oil with 95% ethanol did not remove the color-producing substances.

Analytical data on the oil follow:

Analytical Constants of Coffee Oil

Iodine value (I.V.)	97.6
Sap. No.	180.7
Free acid as oleic	0.27%
Unsaponifiables	5.84%
Peroxide number	5.2
Hydroxyl	0.2450 m. moles/gm.

Infra-red spectroscopic examination of the oil showed no increase in absorption at 10.36 μ indicating the absence of appreciable amounts of trans-acids.

The Unsaponifiables of Coffee Oil

Coffee oil contains an unusually large amount of unsaponifiables, and removal of this material is likely to be necessary before the oil can be used for most purposes.

[3] Bengis and Anderson (15) isolated a crystalline material (m.p., 143.0-143.5°; $[a]^D$ 204.5; highly unsaturated) from the unsaponifiables of coffee oil and called it kahweol (quahweh coffee). It is, according to them, sensitive to atmospheric oxygen and mineral acids changing colors. However Slotta and Neisser (16) isolated a similar sterol from coffee oil unsaponifiables in better purity and established its structure as cafesterol, having three hydroxyl groups. The findings of these latter authors with respect to color change—red, violet, blue, and finally green-blue—agree with our results.

Since it did not seem likely that any of the usual methods of refining would result in satisfactory removal of the unsaponifiable, without actually saponifying the oil and extracting the soaps with solvent, it was decided to attempt the separation by molecular distillation. Consequently a specimen of the oil was distilled at 1.5 microns pressure in the special pot still, described by Findley and Brown (17). Results of the distillation are given in Table I.

TABLE I

Results of Molecular Distillation of Coffee Oil

Fraction No.	Time hrs.	Temperature of pot °C.	Weight g.	Properties
I	0.5	150	0.2	Amber liquid changing to black on exposure to air
II	2.2	150	0.2	Oil
III	2.5	175	0.7	Oil
IV	2.3	210	5.9	Gummy solid
V	7.5	210	3.0	Oil
Pot residue			39.4	Oil
Total recovery			49.4	

Fractions I-IV gave the typical methanol-HCl color reaction with formation of a dark brown precipitate. Most of the unsaponifiable is therefore to be found in these fractions. However the total weight of these fractions, 7.0 g., is more than twice the amount of unsaponifiable in the oil. It must be assumed therefore that fractions IV and V contained considerable amounts of glycerides. The fact that fraction V and the pot residue gave no cafesterol reaction indicates that distillation up to fraction V would constitute a satisfactory procedure for separation of the oil proper from the undesirable unsaponifiable fraction.

The Question of the Occurrence of Hydroxy Acids in Coffee Oil

Bengis and Anderson (13) reported the presence in coffee oil of 4% of petroleum ether insoluble acids, which they designated as hydroxy-acids. We could not verify this finding. After exhaustive extraction of the potassium soaps of the acids of the oil with ether and with petroleum ether to remove all unsaponifiable, the acids were regenerated from the soaps and converted to methyl esters. These esters gave a zero hydroxyl number. The hydroxyls in the original oil (0.2448 millimoles/g.) must therefore have been present in the unsaponifiable fraction. Infra-red analysis on the unsaponifiable-free esters, the original oil, and the unsaponifiables also confirmed these conclusions. Moreover unsaponifiable-free esters did not form any precipitate in petroleum ether, as reported by Bengis and Anderson.

The Component Fatty Acids of Coffee Oil

Because of the large amount of unsaponifiable in the oil, methyl esters were prepared from a specimen of acids, from which most of the unsaponifiable had been removed by extraction of the soaps with ether. A charge of 600 g. of these esters was distilled through a 100-cm. glass helices packed column. The results are shown in Table II.

The Component Fatty Acids in Ester Fractions

Fractions I and II were assumed, on the basis of sap. equiv., to be entirely palmitate and hexedece-

TABLE II

Distillation of Methyl Esters of Coffee Oil

Fraction	Wt. (g.)	Boiling Range (0.2 mm.) °C.	$n^{50°}$	Sap. Equiv.	I.V.	Carbon series g.		
						C_{16}	C_{18}	C_{20} and above
I	18.9	108-116	1.4290	269.8	2.1	18.9	0.0	0.0
II	85.2	112-116	1.4287	269.6	0.6	85.2	0.0	0.0
III	90.0	112-116	1.4287	269.4	1.4	88.5	1.5	0.0
IV	25.4	116-128	1.4432	285.2	127.7	5.2	20.2	0.0
V	138.0	127-128	1.4472	293.5	150.1	0.0	138.0	0.0
VI	177.8	127-128	1.4470	294.4	138.1	0.0	177.8	0.0
VII	18.9	127-134	1.4420	294.3	97.2	0.0	18.9	0.0
VIII	14.8	134-135	1.4402	299.0	66.5	0.0	14.6	0.2
Column Hold-up	10.1	.....	.....	321.4	49.3	0.0	1.3	8.8
Residue	20.9	.....	.....	358.8	42.1	0.0	0.0	20.9
Original Methyl Esters			1.4400	286.9	86.9	197.8	372.3	29.9
Percentage of Original Methyl Esters			.....	.....	.....	32.9	62.1	5.0

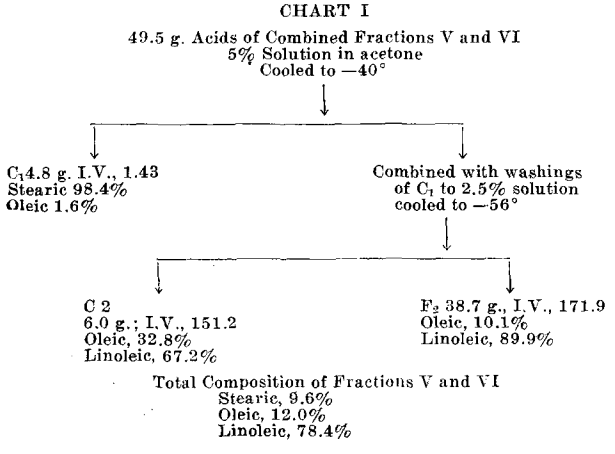
noate. On this basis no C_{14} esters are found in Fraction I. The iodine values of these fractions were assumed to be due to hexadecenoate, and their compositions were calculated accordingly. It was further assumed that Fraction III is methyl palmitate and oleate.

Fraction IV, a comparatively small transition fraction, was converted to acids and separated by crystallization at −40° to yield 4.1 g. crystals; I.V., 7.0. Since linoleic acid does not precipitate at this temperature, the composition was calculated from the I.V. as a mixture of palmitic and oleic acids. The filtrate acids, 10.4 g., I.V. 168.0, were calculated as a mixture of oleic and linoleic acids. No hexabromides were obtained upon brominating a specimen of these acids. Therefore the presence of linolenic acid could not be demonstrated by this procedure. The final composition of Fraction IV was calculated to be: palmitic acid, 20.5%; oleic acid, 18.1%; and linoleic acid, 61.4%. The palmitic acid content checked very closely with the C_{16} component of the original esters of this fraction, as calculated from the s.e. Calculation of the composition of the fraction from the thiocyanogen number gave 58.3% linoleic acid.

Fractions V and VI were assumed to be solely C_{18} esters and were combined. A specimen of the acids of this combined material, on bromination, yielded no hexabromides. The acids present therefore were assumed to be stearic, oleic, and linoleic acids. The acids were separated as shown in Chart I.

The linoleic acid content of the combined acids of Fractions V and VI was also determined from the tetrabromide yields on C_2 and F_2, as described by White and Brown (18) and found to be 73.6%. The discrepancy between this value and the results in Chart I may be due to the presence of about 5% of isomeric octadecadienoic acids in coffee oil or to small amounts of linolenic acid, which could not be detected by the bromination method.[4]

CHART I



Fraction VII on the basis of the sap. equiv. was also assumed to be entirely C_{18} esters and was shown by similar procedures, as described above, to consist of: stearic acid, 38.5%; oleic acid, 12.5%; and linoleic acid, 49.0%. Fraction VIII by the crystallization method was similarly calculated to be composed of the following acids: C_{20} saturated, 0.9%; stearic, 52.9%; oleic, 13.5%; and linoleic, 32.7%.

Column-Hold-Up Acids were crystallized once from acetone at −20° to give a crystal fraction of 3.1 g. (I.V., 0.5; N.E., 310.2) and a filtrate fraction of 2.2 g. (I.V., 117.0; N.E., 305.8). On the basis of certain calculations and assumptions, this fraction was calculated to contain 0.4 g. of methyl stearate, 0.6 g. of methyl oleate, 0.3 g. of methyl linoleate, and 8.8 g. of C_{20} acids. The crystal fraction on the basis of high neutralization equivalent was assumed to contain 92.9% of arachidic acid. This was further verified by repeated re-crystallization of this fraction to give a product melting at 76.0°-76.5°. This showed no melting point depression with a specimen of pure arachidic acid.

On the basis of neutralization equivalent and iodine values, the filtrate fraction was composed of 76.5% of C_{20} unsaturated acids, which were presumably largely eicosenoic acid. There was also good evidence for the presence of eicosadienoic acid. Neither of these was specifically identified because the total Column-Hold-Up Acids amounted to less than 2.0% of the total acids of coffee oil.

Our data on the fatty acids of the still pot residue are incomplete, and we have simply included them in the final calculation of the component acids of oil as C_{20} and above. However we have good evidence for the presence of all three series of acids: C_{20}, C_{22}, and C_{24}. The iodine value of the filtrate fractions from these acids was 102.6, and the neutralization equivalent was high enough to be strongly indicative of the presence of C_{22} and C_{24} monoethenoic acids.

A summary of the calculated composition of the unsaponifiable free methyl ester composition on fatty acids of coffee oil is given as Table III.

[4] Actually, a specimen of the methyl esters of the acids of combined Fractions V and VI was examined for us by S. F. Herb of the Eastern Regional Laboratory at Philadelphia, who found the specimen to contain 68.7% linoleic and 2.9% linolenic acids. However the linolenic acid should have been concentrated in Fraction F_2 above in sufficient amounts to have been detected by the bromination method. If this amount of triene unsaturation is present therefore in this oil, it may occur mainly as isolinolenic acids. In view of this discrepancy between our results and those obtained by spectrophotometry, we prefer to report our polyethenoic acids as linoleic, admitting the possible presence of 1.5% or less of trienoic acids in the original oil.

TABLE III

Component Fatty Acids of Coffee Oil

Fatty Acid	Weight %
Palmitic	32.0
Hexadecenoic	0.9
Stearic	7.6
Oleic	8.2
Linoleic	46.3
C_{20} and above	5.0

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Summary

A specimen of coffee oil has been examined with the objective of determining its composition in the light of possible uses of the oil which is recoverable as a by-product in the soluble coffee industry. The oil, as obtained by extraction of the coffee grounds with solvent, contains over 5% of unique unsaponifiable material which, without preliminary removal, makes the oil unsuitable for many purposes. It has been shown that the unsaponifiable and glyceridic components can be separated by molecular distillation.

A specimen of the methyl esters of the fatty acids of the oil was examined by the ester distillation fractional crystallization techniques. The composition of the component fatty acids has been calculated. The oil contains 46% of linoleic acid. Saturated and unsaturated acids of the C_{20}, C_{22}, and C_{24} series are present in coffee oil in small amounts.

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Edible Spreads of Wide Plastic Range From Vegetable Oils and Monoglycerides[1]

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A problem of the Quartermaster Food and Container Institute for the Armed Forces to which attention has been invited is the development of a spread for bread to be used in combat rations. This fat spread is required to be plastic at the low temperatures of the arctic regions and yet not to melt or separate in the tropics. An obvious solution, one spread for the tropics and one for the arctics, is not feasible for many reasons of military supply. Since our men are stationed in all parts of the world, there is a need for what we characterize as a "global edible spread."

First attempts to prepare spreads of wide plastic range followed the formulation of the wide viscosity range lubricants used by our Armed Forces in Sperry gyroscopes and instruments of the sort. By the use of edible counterparts of ethyl sebacates and lithium soaps, a wide plasticity range fat spread was indeed obtained. A mixture of ethyl esters of soybean fat acids and of calcium soaps properly chilled could be spread at —10°F. and yet retained shape at 140°F. Poor flavor and oxidative stability seemed insurmountable in this product, to say nothing of the questionable merits of feeding the unsuspecting soldier 10-15% of calcium stearate which he could not metabolize.

In the subsequent search for nutritionally acceptable ingredients, mixtures of vegetable oils with relatively large proportions of saturated monoglycerides were found to give solids which possess desirable plastic properties. This composition is the basis of what is described as a global spread. A typical composition is presented in Table I. To the mixture of monostearate and vegetable oils is added antioxidants, vitamins, butter flavor, color, and salt. Because no water is present, no separation of water phase can occur. Because of the lack of water on the other hand, the

TABLE I

Composition of a Global Spread

Ingredients	Parts
Soybean salad oil	84.0
Distilled monostearate	16.0
Salt	3.0
Butter color concentrate [a]	0.2
Butter flavor concentrate [b]	0.2
Propyl gallate	0.01
Citric acid	0.005
Vitamin A	16,500 units/pound
Vitamin D	3,300 units/pound

[a] A mixture of 40% F.D.R.C. butter yellow No. 3 and 60% F.D.R.C. butter yellow No. 4.

[b] "Butr-trate W" made by E. R. Mollner Company, Los Angeles, Calif. The mention of this product does not imply that it is endorsed or recommended by the Department of Agriculture over others of a similar nature not mentioned.

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