4. A concentration of 1% of monoglycerides in the oil phase will lower the interfacial tension at the oil-water interface to approximately one-half that which is observed when no monoglycerides are present. A concentration of 6% of monoglycerides in the oil phase will lower the interfacial tension approximately to zero.

REFERENCES

1. American Oil Chemists' Society, *Official and Tentative Methods*, Revised 1943.
2. Bailey, A. E., and Feuge, R. O., Ind. Eng. Chem., Anal. Ed., *15*, 280-281 (1943).
3. Feuge, R. O., and Bailey, A. E., Oil & Soap, *23*, 259-264 (1946).
4. Harkins, W. D., and Jordan, H. F., J. Am. Chem. Soc., *52*, 1751-1772 (1930).
5. Pohle, W. D., Mehlenbacher, V. C., and Cook, J. H., Oil & Soap, *22*, 115-119 (1945).
6. Smith, L. B., and Matthews, H., Oil & Soap. *17*, 58-67 (1940).
7. Trillat, J. J., and Nardin, Pierre, Compt. rend. *207*, 291-293 (1938).
8. Trillat, J. J., and Nardin, Pierre, Pub. sci. tech. ministere (France) No. 152, 35 pp. (1939).

Oil From Calabash Seed, Crescentia cujete L.

B. A. SMITH and F. G. DOLLEAR

Southern Regional Research Laboratory[1]
New Orleans, Louisiana

DURING the period of extreme scarcity and heavy demand of fats and oils engendered by dislocations in the supply and distribution of these products during World War II the Bureau of Agricultural and Industrial Chemistry was requested to examine a number of oils and oilseeds of Latin American origin with respect to their possible industrial utility. Among the products examined was a sample of seeds and oil obtained from *Crescentia cujete L.* grown in Honduras.

Crescentia cujete L., commonly referred to as calabash or gourd tree, is a native of tropical America and grows wild in Mexico, various Central and South American countries and the West Indies. It is known by a variety of local names, as for example, "tapara" or "totuma" in Venezuela, "jicara" in Cuba and Salvador, "cuia" in Brazil, "calabacero" in Costa Rica, and "guira" in Colombia. It is also known by such names as "calabacillo," "guira de Yucatan," "guira cimarrona," "guacal," "tecomate," and "cutuco."[2]

Crescentia cujete L. is described as a tree of medium to large size bearing globular or elipsoidal fruit approximately the size of a cucumber, the shell of which upon drying becomes as hard as wood. Another description of the plant refers to it as a tree, 5 to 8 feet in height with a tap root one-third to one-half the height of the tree. Although the tree appears to grow wild in great profusion in all of the above-mentioned countries it can be propagated by cuttings which reach fruiting age in four years and from seeds in six years.

Although references to some of the constituents of the calabash fruit or gourd can be found in the literature (1), there appears to be no published information concerning the characteristics of the seed-oil.

The products submitted to the Bureau of Agricultural and Industrial Chemistry for examination consisted of seeds and screw-pressed oil. The seeds were flat and heart-shaped having thin brown hulls. The hulls represented 28% and the kernels 72% of the total weight of the seeds. The seeds ranged from 6 to 10 mm. in length, 5 to 8 mm. in width and 1 to 2 mm. in thickness. One hundred seeds weighed 3.93 grams. The endosperm was very light in color, appearing almost white with a slight greenish cast. The screw-pressed oil, which is referred to as gucha-nut oil by the producers[3] had a greenish color resembling that of olive oil. Oil subsequently obtained in the laboratory by extraction of the seeds with petroleum naphtha (Skellysolve F) was light yellow, resembling refined cottonseed oil.

The characteristics and composition of the screw-pressed oil were determined and compared with those of oil extracted from seed imported from Honduras. Agreement in the characteristics of the screw-pressed and solvent-extracted oils served to establish the authenticity of the former.

Experimental

Composition and Characteristics of Calabash Seed and Crude Oil. The proximate composition of calabash seed is shown in Table I and the characteristics of the crude oil obtained from the seed are shown in Table II. The constants on the oil were determined by the methods of the American Oil Chemists' Society (2), with the exception of the unsaponifiable matter (3), saturated acids (4), tetrabromide value (5), hexabromide value (6), hydroxyl value (7), and peroxide value (8), which were determined by the methods described in the references cited.

Calculation of the composition of the oil on the basis of its iodine and thiocyanogen values, and equations applicable to cottonseed and peanut oils (9) gave results for the content of saturated acids which were not in accord with the experimentally determined values. A determination of the linoleic acid content by a tetrabromide method was made as a

TABLE I.

Analysis of Calabash Seed,[1] *Crescentia cujete L.*

Constituent	As received[2]	Moisture-free
	Per cent	*Per cent*
Moisture	7.80	......
Nitrogen	4.84	5.25
Protein (N × 6.25)	30.25	32.80
Ash	3.34	3.62
Potassium	0.44	0.48
Phosphorus	0.69	0.75
Calcium	0.09	0.10
Crude fiber	12.98	14.07
Total sugar as invert sugar	2.43	2.64
Oil (Skellysolve F extract)	34.10	36.98

[1] Data supplied by the Analytical Section of the Analytical, Physical Chemical, and Physics Division of this Laboratory.

[2] All values reported are averages of closely agreeing duplicate determinations.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Private communication of the Mexican Secretaria de Agricultura y Fomento.

[3] Name coined by Meerbott Associates from whom the original sample of oil was obtained.

TABLE II.

Characteristics of Crude Calabash Seed Oil

Color, Lovibond (5¼" cell)	35 Y, 2.7R
Free fatty acid (as oleic), per cent	0.90
Iodine value, Wijs, 30 minutes	88.7
Thiocyanogen value, 0.2 N, 24-hour reaction period	71.2
Saponification value	191.2
Unsaponifiable matter, per cent (3)	0.81
Saturated fatty acids, lead salt-alcohol, per cent	19.7
Saturated fatty acids, modified Bertram oxidation, per cent (4)	19.6
Tetrabromide value, mixed fatty acids (5)	18.8
Hexabromide value, mixed fatty acids (6)	1.7
Hydroxyl value (7)	2.7
Peroxide value, milliequiv. /kg. (8)	7.6
Reichert-Meissl value	1.3
Polenske value	0.3
Phosphorus, per cent [1]	0.0040
Cloud point, °C.	0.5
Neutral equivalent of solid fatty acids	271.1

[1] Data supplied by the Analytical Section of the Analytical, Physical Chemical, and Physics Division of this Laboratory.

further check on the calculated composition of the oil.

A portion of the mixed fatty acids was brominated at 0° C. in low-boiling petroleum naphtha, following the procedure recommended by Brown and Frankel (5). The brominated product was highly colored and on recrystallization from hot benzene yielded a white crystalline product melting at 180° C. Though the presence of linolenic acid in an oil having an iodine number less than 90 is rare, the melting point of the recrystallized bromide indicated the presence of this acid.

Another portion of the mixed fatty acids was brominated and the petroleum naphtha-insoluble bromides were separated, washed, and dried as recommended by Brown and Frankel (5). In order to separate the hexabromo- and tetrabromostearic acids, the crude brominated acids were extracted with four successive portions of anhydrous ethyl ether in a manner similar to that previously used with petroleum naphtha to purify the mixed bromides. The ethereal washings were collected and the tetrabromides recovered therefrom. The melting point of the crude tetrabromostearic acid was 105-106° C. Recrystallization from a higher boiling petroleum naphtha raised the melting point to 114° C. The ethyl ether-insoluble hexabromostearic acid melted at 181° C. Admixture of these bromides with authentic samples of tetrabromo- and hexabromostearic acids produced no lowering in the melting points.

The tetrabromide value (18.8) and hexabromide value (1.7) of the mixed fatty acids indicated a linoleic acid content of 20.7% and a linolenic acid content of 1.8%, calculated by the equations proposed by Brown and Frankel (5) and Shinowara and Brown (6), respectively.

The fatty acid composition of calabash seed oil, calculated on the assumption that linolenic was present is: saturated 19.7%, oleic 59.4%, linoleic 19.3%, linolenic 1.6%. The calculated composition is based on the iodine and thiocyanogen values of the oil and the percentage of saturated fatty acids of the mixed fatty acids recovered on saponification of the oil. The equations recommended by the American Oil Chemists' Society (9) were used in making these calculations.

Measurement of the ultraviolet absorption spectrum of the oil indicated that less than 0.1% each of diene, triene, and tetraene conjugated constituents were present.

Spectrophotometric analysis of the crude oil by the method of Mitchell, Kraybill, and Zscheile (10), modified by the use of nitrogen to protect both samples and reagent from oxidation during isomerization (11), gave a value of 2.3% for the linolenic acid content, compared to 1.6% calculated from the iodine number, thiocyanogen number and saturated fatty acid content, and a value of 1.8% calculated on the basis of the hexabromide number. The content of linoleic acid (19.3%) obtained by the spectrophotometric method is somewhat lower than that (20.7%) obtained by the tetrabromide method. The values for saturated acids, 19.7% by the lead salt-alcohol method and 19.6% by the modified Bertram oxidation method, are practically identical.

The saturated acids were not fractionated, nor were the components identified, but the average molecular weight (271.1) of the solid acids prepared by the lead salt-alcohol method indicates that they were chiefly palmitic and stearic acids, which is further substantiated by the titer of the mixed acids and the Reichert-Meissl and Polenski values of the oil.

Stability of Calabash Seed Oil. A portion of the crude calabash seed oil was refined with caustic soda and bleached with fuller's earth following the general procedure applied with cottonseed oil of equivalent quality. A 250-ml. portion of the refined and bleached oil was deodorized in a laboratory deodorizer for 0.5 hour at 200° C. and about 2 mm. pressure. The total through-put of steam was about 15 grams. The deodorized oil had a free fatty acid content of 0.044% and a peroxide number of 0.5. It had a bland flavor and a keeping time of 18 hours by the active oxygen method (12) at 97.8° C.

Comparison of Calabash Seed, Peanut, and Olive Oils. The composition and characteristics of calabash seed oil are compared with those of peanut and olive oils in Table III. The iodine value of calabash seed oil indicates that it belongs to the class of non-drying oils. The occurrence of linolenic acid in an oil whose iodine number is less than 90 is rare. Except for the presence of linolenic acid, calabash seed oil is similar

TABLE III.

Comparison of Calabash Seed, Peanut, and Olive Oils.

Oils	Iodine value	Saponification value	Refractive index n_D^{25}	Specific gravity 25°/25°	Titer of mixed fatty acids °C.	Calculated composition of fatty acids			
						Oleic %	Linoleic %	Linolenic %	Saturated %
Calabash seed	88.7	191.2	1.4676	0.9129	27.8	59.4	19.3	1.6	19.7
Olive (minimum)[1]	79	186	....	0.909	17	65	4	....	9
Olive (maximum)[1]	92	196	....	0.915	26	85	15	....	20
Olive, commercial imported [2]	87	190.4	1.4672	....	....	80.9[3]	10.1[3]	....	7.9[3]
Peanut (minimum)[4]	86	189	1.4680	0.912	28	53	13	....	15
Peanut (maximum)[4]	98	196	1.4707	0.915	32	72	27	....	22
Peanut commercial [2]	97.7	191.2	1.4690	....	....	44.1[3]	34.5[3]	....	21.0[3]

[1] See references (2), (13), and (14).
[2] See reference (15).
[3] Calculated as glycerides corrected for unsaponifiable matter.
[4] See references (13), (14), and (16).

to peanut and olive oils both in its general characteristics and composition of fatty acids; hence it can serve to supplement the supplies of the latter.

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Summary

The composition and characteristics of calabash, *Crescentia cujete L.*, seed and oil have been determined. The oil was found to have the following composition calculated from the iodine and thiocyanogen values, and saturated acid content of mixed fatty acids: saturated acids 19.7%, oleic acid 59.4%, linoleic acid 19.3%, and linolenic acid 1.6%. Comparison of the composition and characteristics of calabash seed oil with those for peanut and olive oil indicate that, except for the presence of a small amount of linolenic acid in the former, the oils are similar.

REFERENCES

1. Wehmer, C., Die Pflanzenstoffe, Vol. 2, Gustav Fischer, Jena, 1931, p. 1137.
2. Official and Tentative Methods of the American Oil Chemists' Society (1944).
3. Cocks, L. V., Report of the Sub-committee on Determination of Unsaponifiable matter in Oils and Fats and of Unsaponified Fat in Soaps, Analyst, *58*, 203-211 (1933).
4. Pelikan, K. A., and von Mikusch, J. D., Oil & Soap, *15*, 149-150 (1938).
5. Brown, J. B., and Frankel, J., J. Am. Chem. Soc., *60*, 54-60 (1938).
6. Shinowara, G. Y., and Brown, J. B., J. Am. Chem. Soc., *60*, 2734-2738 (1938).
7. West, E. S., Hoagland, C. L., and Curtis, G. H., J. Biol. Chem., *104*, 627-634 (1934).
8. Wheeler, D. H., Oil & Soap, *9*, 89-97 (1932).
9. Mehlenbacher, V. C., Progress Report of the Committee on Analysis of Commercial Fats and Oils, Oil & Soap, *21*, 143-145 (1944).
10. Mitchell, J. H., Jr., Kraybill, H. R., and Zscheile, F. P., Ind. Eng. Chem., Anal. Ed., *15*, 1-3 (1943).
11. O'Connor, R. T., Heinzelman, D. C., and Dollear, F. G., Oil & Soap, *22*, 257-263 (1945).
12. King, A. E., Roschen, H. L., and Irwin, W. H., Oil & Soap, *10*, 105-109 (1933).
13. Hilditch, T. P., Industrial Fats and Waxes, Bailliere, Tindall, and Cox, London, 1941.
14. Hilditch, T. P., The Chemical Constitution of Natural Fats, John Wiley and Sons, Inc., New York, 1941.
15. Bickford, W. G., Mann, G. E., and Markley, K. S., Oil & Soap, *20*, 85-89 (1943).
16. Jamieson, G. S., Vegetable Fats and Oils, 2nd edition, Reinhold Publishing Corporation, New York, 1943.

A Qualitative Method for Detecting Surface Active Agents*

L. F. HOYT
National Aniline Division, Allied Chemical and Dye Corporation
Buffalo, N. Y.

ABSTRACT

A NEW METHOD is presented for the qualitative detection of small amounts of surface active agents which is generally applicable to all types, i.e. anionic, cationic, and non-ionic. This method is based on the solubilization in aqueous solution of certain oil soluble dyes, particularly Brilliant Oil Blue BMA.

Surface active agents, anionic, cationic, and non-ionic, are finding increasing uses in many products and processes. A large number of surface active agents are commercially available (3, 5, 11, 12, 13). It is often desirable to determine whether or not a product contains a surface active agent, which may be present in a very low concentration.

Very small concentrations of surface active agents, in pure dilute solutions, cause a marked lowering of surface tension, frequently accompanied by persistent foaming, but the presence of soluble extractives from a product under examination for the presence of a surface active compound may also lower the surface tension appreciably and render this criterion valueless.

Methods for the determination of the active component of certain types of concentrated commercial surface active agents are available (2, 6, 7, 9), but these methods do not lend themselves to the detection of small amounts. Methods for the determination of small quantities of sulfonated or sulfated surface active compounds have been offered by Scales (10), Harris (4), and Jones (5), and for the estimation of quaternary surface active agents by Auerbach (1). These methods give satisfactory results with the types of surface active compounds for which they were developed but are not applicable to all types. A quick and easily applied qualitative test is desirable for the detection of a surface active compound, whether anionic, cationic or non-ionic.

Specification No. 100-A (Jan. 18, 1944) of the Office of the Quartermaster General, U. S. Army, entitled "Soap, Toilet, Soft, Hard or Sea Water," specifies, p. 7, section F-13, the use of a 2% solution of di-ortho-tolyl guanidine in 3% acetic acid as a precipitant to remove the synthetic detergent present in such soaps before determining chlorides. This reagent was tried for the qualitative detection of various surface active agents.

With small amounts of some surface active compounds di-ortho-tolyl guanidine reagent gives an opalescence or turbidity. It has been found in our laboratory that this reagent will detect one milligram of a sulfonate type of surface active compound in 100 ml. of solution. Semiquantitative determinations may be made with a turbidimeter if a reference sample of the known surface active compound is available.

We have found, however, that many surface active compounds do not react with this reagent. Among the compounds which give no reaction with di-ortho-tolyl guanidine are Igepon T, and the related Medialan A, Arctic Syntex M, non-ionic products such as Neutronyx 228, Triton NE, Tween 20, Igepal C, Igepal CTA Extra, Leonil FFO and cationic surface active compounds such as Roccal (lauryl benzyl dimethyl-ammonium chloride), Fixanol, Triton K-60, Sapamine MS conc., Sapamine KW, and Retravon.

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