ABSTRACTS

Oils and Fats

Edited by
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Melting and solidifying of cacao butter. W. REINDERS, CH. L. DOPPLER and E. L. OBERG. *Rec. trav. chim.* **51**, 917-39 (1932).—Cacao butter is a mixt. of 2 or more glycerides crystg. together as homogeneous mixed crystals. These mixed crystals can exist in 2 modifications, one stable α-form and one metastable β-form. Usually the cacao butter solidifies first as the metastable β-form, which changes afterward slowly into the stable α-form. The temp. range over which the solidifying and melting takes place may be detd. most sharply dilatometrically and varies for different kinds of cacao butter. For the β-form this range lies from 17° to 24°; for the α-form from about 25° to 35°. The spontaneous building of nuclei of the α-form has a max. below 0°. The linear velocity of crystan. (transition velocity from the β-form) has a max. at about 21°.
E. SCHERUBEL.

Twitchell's fat-splitting reagent. XI. Properties of the principal constituents isolated from the reagent. KYOSUKE NISHIZAWA, MINORN OKUYAMA and TAKAHIDE INONE. *Chem. Umschau, Fette, Oele, Wachse Harze* **39**, 196-202 (1932); cf. *C. A.* **26**, 5778.—From 2 Twitchell reagents ("P" from phenol and "*N*" from naphthalene) 8 constituents (series T_o and T_n) were isolated by Kuriyama's method and their properties examd. with the following results: Addn. of H_2SO_4 increases the emulsifying power of T_o and T_n but the increase lessens with increasing H_2SO_4 addn., the more so the more easily the splitting agent is salted out by H_2SO_4. AcOH poisons the splitting power T_o and T_n in the presence or absence of H_2SO_4. The color of the liberated fatty acids darkens as the reaction progresses, and also with increase in temp.; this is due to some reaction between fatty acid or oil and T_o and T_n. The fat-splitting power increases with the concn. of T_o and T_n; this forces rejection of the theory that the splitting power is due to the non-dissocd. agent. The following relation exists between the fat-splitting powers of the isolated substances: T_o (N) is greater than T_n (N) T_o (P) and T_n (P) in the order named.
P. ESCHER.

Report on [the determination of moisture in] fats and oils. GEO. S. JAMIESON. *J. Assoc. Official Agr. Chem.* **15**, 560-1 (1932); cf. *C. A.* **15**, 5051.—Further collaborative work was done on the vacuum-oven, hot-plate and hot-air oven methods on samples with high (over 1%) and with low (up to about 0.25%) moisture contents. With samples having high moisture and volatile contents, the hot-air oven method gives abnormally high results, and after repeated heating the samples continue to lose wt. indefinitely in the hot-air oven; the method was therefore discarded. In most cases the hot-plate method gave apparently satisfactory results, but several erratic results showed that more details should be given. It is suggested that in using this method the sample to be tested be placed on an asbestos board (under which is a wire gauze to distribute the heat) alongside a "blank" sample of oil in which a thermometer is suspended, so that the temp. can be observed and controlled while the oils are gradually heated to 130° or to incipient smoking. It is recommended that the vacuum-oven method be adopted as official.
A. PAPINEAU-COUTURE.

The polymerization of fatty oils. II. ALPH. STEGER and J. VAN LOON. *Rec. trav. chim.* **51**, 996-1000 (1932); cf. *C. A.* **26**, 4490.—The *true* thiocyanogen no. (Kaufmann method) of a stand oil cannot be detd., on account of decompn. of the thiocyanate; this decompn. does not occur in testing either the total fatty acids obtained from the stand oils or their Me esters. The thiocyanogen-I nos. of the polymerized oils are not const., but vary with the titer of the thiocyanate soln., the reaction time, the excess of thiocyanate, and further factors detg. an equil. reaction. From the thiocyanogen-I nos. given no definite relation can be derived between these nos. and the actual unsatn. of the polymerized oils.
LOUISE KELLEY.

Action of antioxidants in the oxidation of unsaturated fatty oils. V. VI. BUNNOSUKE YAMAGUCHI. *J. Chem. Soc. Japan* **53**, 54-63, 63-70 (1932); cf. *C. A.* **26**, 863.—The rate of oxidation of olive oil at 100° was measured by estn. of the I nos. with or without the addn. of catalysts. The expt. proves that the duration of an incubation period for oxidation of the oil depends on the antioxidizing action of the unsaponifiable substances present in the oil. The same test on pure triolein (**II**) indicates that there is no incubation period and the oxidation started immediately. The action of drying agents such as Cu, Pb and Mn oleates is to shorten this incubation period since they inhibit the action of antioxidants present in the oil. Cu oleate (**I**) and Mn linoleate showed also an antioxidizing action after the incubation period but Pb oleate did not. **I** accelerated the decompn. of the oxidized product of the oil. Stearic acid showed a tendency to shorten the incubation period for the oxidation of the oil but the action was not as great as that of the other drying agents used. When **II** contained α-naphthylamine or hydroquinone (**III**), a similar incubation period for oxidation was observed. When **II** contained **I** and **III**, **I** inhibited the antioxidizing action of **III**, and **I** itself acted as a weak anti-oxidant; **I** also accelerated the decompn. of oxidation products of **II**.
K. KITSUTA.

Potentiometric Titration of Acidity in Oils. *The American Perfumer and Essential Oil Review,* Vol. XXVII, No. 10, Page 568, December, 1932.—R. R. Ralston, C. H. Fellows and K. S. Wyatt (Ind. Eng. Chem. [Anal.], 1932, 4, 109-110). The acidity of oils may be determined by potentiometric titration of the oil (dissolved in isoamyl alcohol saturated with LiCl) with 0.025—0.05 N-KOH in isoamyl alcohol), using a Pt-C electrode couple. A procedure is described, which enables 0.5-g. samples to be used. The existence of more than one inflexion in the titration curves is believed to indicate the presence of acids having widely different dissociation constants.—British Chemical Abstracts.

Air Bleaching of Palm Oil. *Oil and Colour Trades Journal,* Vol. 82, No. 1785, Page 1783, December 30, 1932.—According to E. J. Better ("Allg. Oel. u. Fett. Zeit.," 1932, p. 486) a number of soap factories in Germany have recently built their own palm oil bleaching plants in order to reduce freight and handling costs. Certain precautions against "over-bleaching" with air must be observed. If the treatment at an elevated temperature is continued long after the point at which the color disappears, oxidation of unsaturated fatty acids present result in a darkening of the palm oil. Many samples have been found to contain peroxides and to give a positive Kreis reaction.

Detergents from Fatty Acids. *Chemical Markets,* Vol. XXXI, No. 6, Page 528, December, 1932.—Fatty acids such as oleic acid or those derived from copra, castor, olive, ground nut or palm oil are treated with solution of alkali-metal or ammonium sulfite or hyposulfite to yield sparingly soluble compounds which on subsequent treatment with caustic alkali, alkali-metal, or ammonium carbonates yield soluble crystalline substances suitable as detergents. The detergent may be obtained directly by action upon fatty acids with the two reagents in admixture.

Grease and tallow output in 1931. *Oil, Paint and Drug Reporter,* November 14, 1932.—In a preliminary report on the production of grease, not including lubricating grease and tallow, in 1931 the Bureau of the Census noted a decrease of 51.5 per cent in the value of the output as compared with 1929, the last previous census year. Production in 1931 was valued at $32,936,220 at factory prices, comparing with $67,872,449 in 1929, of the 1931 total $15,546,961 was contributed by establishments engaged primarily in the production of grease and tallow and $17,389,259 by establishments engaged in other lines of manufacture, principally meat packing. This total is made up of 323,454,625 pounds of grease, valued at $11,261,065 and 585,910,262 pounds of tallow, valued at $21,675,155. This industry, as defined for census purposes, embraced establishments engaged primarily in rendering grease, chiefly from animal fat, bones, meat scrap, and so forth, and in rendering tallow from fat.

PATENTS

Neutralizing Fatty Acids. *The National Provisioner,* Vol. 88, No. 1, Page 23, January 7, 1933.—Roy C. Newton, Chicago, Ill., assignor to Swift and Company, Chicago, Ill. This process of removing free fatty acids from oils or fats consists in neutralizing the free fatty acids with sodium bicarbonate under reduced pressure and at a reaction temperature at or above substantially 320° F. Granted November 1, 1932. No. 1,885,281.

Report of the Olive Oil Committee

EARLY in the year 1932, the Committee undertook the study of the Bolton & Williams method for grouping of fatty oils with special reference to the detection of teaseed oil in olive oil.

Briefly stated, the method consists in the determination of iodine values on the unsaponifiable matter of oils. From 2 to 2.5 grams of oil are saponified with alcoholic potash and extracted three times with petrolic ether. The combined extracts are washed twice, filtered into a weighed flask, allowed to evaporate, dried and weighed. The unsaponifiable matter is dissolved in chloroform, an excess of pyridine sulphate bromide reagent added, allowed to stand five minutes and titrated with twentieth normal thiosulphate solution.

According to the authors, the iodine values so obtained cause the oils to fall into four groups. Group I with values 64 to 70 contain kernel oils and the animal fats; Group II with values 90 to 96 include the fish and marine animal oils with cocoa butter; Group III with values 117 to 124 the vegetable oils and fats and Group IV with values 197 to 206 contains olive oil alone. It is claimed that olive oil is thus distinguishable from other oils and in particular from teaseed oil.

It was thought best to run some preliminary experiments on the method before attempting to go into it thoroughly, since a perusal of the procedure above indicates a degree of sensitivity likely to cause large errors in practice. To begin with, the amount of unsaponifiable extracted from so small an amount of oil would seem rather low for reliable iodine absorption values. However, it was believed that an improved procedure could be worked up if the method showed any promise in its present form.

Accordingly samples were sent to the members of the committee with instructions to adhere closely to the conduct prescribed by the authors. These samples were of olive oil containing 20% tea-seed oil in solution. The request was made that the test be made on this as well as on the same diluted down to a 10% teaseed oil content, and in addition to use a pure olive oil of their own choosing.

The results of the preliminary study by the Committee are as follows:

THE BOLTON-WILLIAMS METHOD

Chemist	Olive Oil	20% Teaseed Oil	10% Teaseed Oil
1	189.3	180.6	
2	197.2	231.2	211.3
3		167, 195, 184	
4	No. 1—213, 162 No. 2—255, 244	248, 190, 196, 255, 262	
5	201.2, 197.2	178.5, 181.9	186.5, 190 5
6	204, 225, 212	222, 249, 234, 240	215, 240
8	156, 148.6, 143.5, 141.2	189, 190, 186.8, 187.8	187.6, 215.2 184.8, 195.8

Comments from the members revealed the causes for the above erratic results as follows:

1. The small amount of unsaponifiable matter introduced appreciable errors in weighing, particularly as it oxidizes on drying down, and presents also the question as to which weight to take for the iodine determination, the first weight after evaporation or the last weight when constant.
2. Oxidation of the unsaponifiable matter occurs in drying to constant weight and the iodine values are accordingly lowered.
3. The incomplete washings specified in the method, one with dilute alkali and the second with water, fail to remove soap, alkali or free fatty acids resulting from the hydrolysis of the soap solution, thus giving low and widely varied results.
4. Some trouble is had with emulsification in the extraction with ether.
5. The extraction of the unsaponifiable matter is incomplete, not all is obtained and further extraction shows a selective action, the iodine value based on such progressive amounts varying considerably.

To illustrate the relation of the iodine values to the amount of unsaponifiable, the following experiments are given:

BOLTON-WILLIAMS METHOD
On the 20% Teaseed Oil Sample

Chemist	Unsaponifiable	Iodine No.
1	1.25%	180.6
2	1.12%	231.2
4	0.96%	248
	1.01%	190
	1.06%	196
	0.94%	255
	0.85%	262
8	2.62%	189.0
	2.75%	189.8
	2.65%	186.8
	2.29%	187.8

It is apparent that the lower the unsaponifiable, the higher the iodine value.

Regarding this, one of the chemists pointed out that the unsaponifiable matter of olive oil consists of not just one sterol with an iodine value of 210 but of several, some of which have an iodine value of about 65 and others of about 260; if any sterol is lost in the extraction, it is always the more saturated portion, thus resulting in an abnormally high value in some cases.

As the method stands, therefore, it does not prove sufficiently accurate to be of any practical value in our work of determining teaseed oil in olive oil. As an interesting corollary to our experimental results, it is to be noted that the teaseed oil has a far higher iodine value than the oils of Group III where Bolton & Williams placed it.

Since incomplete extraction and washing are the two major faults of the method, some of the members tried out the Modified Kerr-Sorber and the F.A.C. procedures. The results were more concordant as seen from the table below:

Chemist and Method	——Olive Oil——		20% Teaseed Oil	
	Unsap.	Iodine No.	Unsap.	Iodine No.
2. F.A.C.	1.19%	197.2	1.34%	219.9
3. B. & W. using 5 gms. sample and complete washings	......	205	......	218
	......	225	......	218
F.A.C.	......	220	......	...
	......	224	......	...
4. Mod. Kerr-Sorber	1.14%	205	1.27%	204
	1.10%	208	1.28%	206
	1.10%	207	1.27%	202
	1.08%	209	......	...
	1.14%	213	......	...
	1.14%	211	......	...

In view of our findings, it is evident that work along an improved procedure would be necessary in order to obtain data of value in our investigation in the field of olive oil adulteration and impurities.

M. F. Lauro, Chairman of the Committee, in collaboration with the following members:

Geo. S. Jamieson
A. H. Gill
M. L. Sheely
L. G. Copes
S. Musher
W. H. Dickhart.

Nigeria—Palm Oil Industry

Palm oil and palm kernels are the most important products of Nigeria and constitute almost one-half of the produce exported. Exports of palm oil have averaged 120,000 tons annually since 1924, while the domestic consumption, principally for food, has been estimated by the Department of Agriculture at 100,000 tons annually. A total annual production of over 200,000 tons of palm oil annually may, therefore, be assumed.

Experiments have been made with plants for the mechanical extraction of palm oil on a fairly large scale, but they have been found to be impractical, owing to the high cost of installation and overhead expenses, and the difficulty of obtaining regular supplies of palm fruit. There are no large oil palm plantations and the palm oil producer has to depend on the small lots of fruit brought in irregularly by native farmers.

Palm oil is produced in small quantities by individual natives and by gangs of professional oil-makers, and sold usually through a middleman to European merchants for export. The Department of Agriculture is gradually changing the native farmers to improved methods of hand production, including the use of hand presses, and a slow but steady increase in the use of palm oil presses is anticipated.

Emuwax is the name of a new water-dispersible wax recently introduced by the Glyco Products Co., Inc., of Bush Terminal, Brooklyn, N. Y. It is arousing interest because of its great flexibility, light color and emulsifying properties. It is soluble to a greater extent than natural waxes in organic solvents. It disperses readily in hot water to give milky emulsions. It acts as an emulsifier for oils and waxes for polishes, creams, lotions, textile rubber, softeners and lubricants. Emuwax melts at 115.8° F. and will not turn rancid. It is offered at a lower price than beeswax which it replaces in some cases.