

composition does not allow one to speculate to any great extent on the mechanism of formation of these carbonyl compounds. The mechanisms which have been put forth by other workers (6, 7, 10) suggest that hydroperoxides break down with simultaneous cleavage of the adjacent carbon to carbon bond to form an aldehyde and some unidentified fragment. The specific aldehyde which is formed depends upon the position of the hydroperoxide group on the chain, and the length of the carbon chain which is cleaved from the parent molecule. The formation of acetaldehyde, propionaldehyde, alpha-pentenal, and crotonaldehyde can be postulated from the mechanism by appropriate shifts in double bonds. The formation of methyl ethyl ketone cannot be due to a simple decomposition of a hydroperoxide and cleavage. However the initial cleavage product could be a beta-keto acid, this acid then losing carbon dioxide to form the methyl ketone. The gaseous products are mainly carbon dioxide and water vapor with traces of carbon monoxide and hydrogen. The mechanism whereby these gaseous products are formed is not known.

Three of the compounds which were isolated in the present work, acetaldehyde, propionaldehyde, and alpha-pentenal, have been included among the compounds that have been isolated from reverted soybean oil. The presence of these compounds in the volatile decomposition products of the oxidative polymers of ethyl linolenate indicated that oxidative polymers may serve as precursors of flavor reversion compounds in soybean oil.

Summary

Oxidative polymers which had been isolated from autoxidized ethyl linolenate were oxidatively decomposed in a closed system at room temperature. The

decomposition products were collected in appropriate traps and separated into various fractions on the basis of their volatility and solubility. The aldehydes and ketones thus obtained were converted into 2,4-dinitrophenylhydrazones, chromatographed on silica gel, and the isolated 2,4-dinitrophenylhydrazones identified by standard procedures. Methyl ethyl ketone, propionaldehyde, acetaldehyde, and alpha-pentenal were positively identified, and evidence for the presence of crotonaldehyde and an unknown five-carbon-carbonyl compound was obtained.

Acetaldehyde, propionaldehyde, and alpha-pentenal have been isolated from the decomposition products of oxidatively decomposed reverted soybean oil by previous workers. If oxidative polymers of linolenate are present in reverted soybean oil, they could serve as precursors of the aldehydes and ketones which have been associated with flavor reversion.

REFERENCES

1. Chang, S. S., and Kummerow, F. A., *J. Am. Oil Chem. Soc.*, **30**, 251 (1953).
2. Chang, S. S., and Kummerow, F. A., *J. Am. Oil Chem. Soc.* (in press).
3. Fugger, J., Cannon, J. A., Zilch, K. T., and Dutton, H. J., *J. Am. Oil Chem. Soc.*, **28**, 285 (1951).
4. Golumbic, C., and Daubert, B. F., *Food Industries*, **19**, 1075 (1947).
5. Gordon, B. E., Wopat, F. Jr., Burnham, H. D., and Jones, L. C. Jr., *Anal. Chem.*, **23**, 1754 (1951).
6. Kawahara, F. K., and Dutton, H. J., *J. Am. Oil Chem. Soc.*, **29**, 372 (1952).
7. Kawahara, F. K., Dutton, H. J., and Cowan, J. C., *J. Am. Oil Chem. Soc.*, **29**, 633 (1952).
8. Martin, C. J., Schepartz, A. I., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, **25**, 113 (1948).
9. Rollett, A. Z., *Physiol. Chem.*, **62**, 422 (1909).
10. Schepartz, A. I., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, **27**, 367 (1950).
11. Sims, Rex J., *J. Am. Oil Chem. Soc.*, **29**, 347 (1952).
12. Stapp, R. J., and Daubert, B. F., *J. Am. Oil Chem. Soc.*, **27**, 374 (1950).

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Modification of Vegetable Oils. XIV. Properties of Aceto-Oleins¹

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IN the industrial utilization of fats and oils the need often arises for oils which remain liquid at low temperatures and yet are relatively resistant to oxidative polymerization and other forms of deterioration. In the manufacture of mayonnaise and salad oils, which require oils remaining liquid at the temperature of the domestic refrigerator (4° to 10°C.), these needs can be fulfilled by winterized cottonseed oil, corn oil, and dewaxed soybean oil. However the latter possesses some objectionable characteristics because of its high degree of unsaturation. When oils which remain liquid well below 0°C. and simultaneously possess good stability are needed, few naturally occurring triglycerides can be employed.

The simple triglycerides of saturated fatty acids occurring most profusely in nature, those having 12

to 18 carbon atoms, are solid at temperatures below 46.5°C. Tricaprin and tricaprylin, whose fatty acids occur as glycerides in amounts up to 8% in a few commercially produced oils, are solid below 8.3°C. Tricaproin and tributyrin solidify at temperatures of -25°C. and approximately -60°C., respectively; but their fatty acids occur in natural fats to a very limited degree. Butterfat, the best natural source of caproic and butyric acids, contains from 2 to 4% of each.

Triglycerides of oleic, linoleic, and linolenic acids are, of course, plentiful in nature and are employed where an oil melting at a relatively low temperature is needed. However triolein solidifies at 5.5°C. Trilinolein and trilinolenin solidify at lower temperatures but are more unsaturated, having iodine values of 173.21 and 261.61, respectively, compared to 86.01 for triolein.

In Figure 1 are shown the melting points of triglycerides of naturally occurring fatty acids as a function of chain length and degree of unsaturation.

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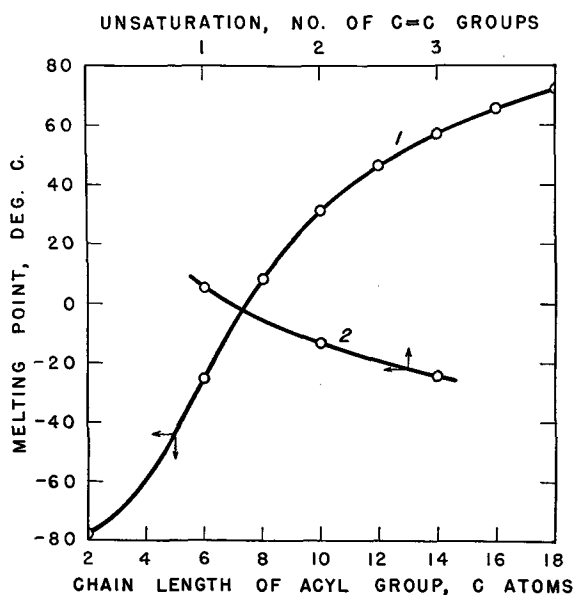


Fig. 1. Melting points of (1) simple, saturated triglycerides as a function of the number of carbon atoms in the acyl groups and of (2) triolein, trilinolein, and trilinolenin as a function of the degree of unsaturation.

While oils of good stability and low melting point do not exist naturally, it should be possible to prepare mixed triglycerides of long and short chain fatty acids having these properties. The long chain fatty acid most suitable for this purpose would be oleic because it occurs widely in natural oils, has a relatively low melting point, and is not highly unsaturated. Acetic acid would best be employed as the short chain fatty acid. It has the lowest molecular weight of any of the saturated fatty acids which might be used; therefore for incorporation in a given number of molecules of fat it will be required in the least amount on a weight basis. For example, to introduce a given number of acyl groups into an oil, 1 part by weight of acetic acid would be equal to 1.47 parts of butyric acid. Acetic acid is readily available in the pure form and relatively cheap. Its odor is not as objectionable as that of some other short chain fatty acids. Acetic acid is edible, and it is anticipated on the basis of preliminary tests that acetoglycerides are edible though their use in foods must await completion of extensive feeding tests.

It has been observed in the laboratory that acetostearins, acetopalmitins, and aceto-oleins are apparently somewhat higher melting than are the corresponding butyric compounds, which is in agreement with observations made in another laboratory (9, 10). However the choice of acetic acid is dictated by the other advantages.

One method of preparing aceto-oleins would be to recombine isolated oleic acid and a certain proportion of acetic acid with glycerol. For other uses it should not be necessary to use pure oleic acid. In such instances a modified oil consisting predominantly of low melting triglycerides prepared from the mixture of fatty acids occurring in oleic-linoleic acid oils should be satisfactory. Such a modified oil would be prepared by interesterifying the natural oil with triacetin and removing the unreacted triacetin, or by reacting the natural oil with glycerol and acylating all or a fraction of the glycerides obtained.

One possible use of aceto-oleins is as a plasticizer of hard fat mixtures to yield products having a good plasticity at low temperatures coupled with a long plastic range.

The present investigation had the following objects: a) to determine the properties of 1,2-diaceto-3-olein, triolein, and a mixture of aceto-oleins; b) to determine the properties of acetylated oils prepared by interesterification with triacetin or by glycerolysis followed by acetylation; and c) to examine the plastic properties of mixtures of highly hydrogenated cottonseed oil and aceto-containing glycerides and to compare the plastic properties of these mixtures with mixtures of highly hydrogenated cottonseed oil and unacetylated oils and with margarine oil.

Materials and Testing Procedures

Materials. Pure 1,2-diaceto-3-olein was prepared by acetylating mono-olein prepared from methyl oleate derived from pecan oil. Pecan oil which has a fatty acid composition of approximately 78% oleic, 16% linoleic, and 6% saturated acids was interesterified at 50°C. in the presence of an excess of methyl alcohol and a small amount of sodium methylate to produce the methyl esters. The latter were treated with acetic acid, washed with water, dried, and then heated for 2 hours at 200°C. with 13% of maleic anhydride, on an ester basis, while under an atmosphere of carbon dioxide (12). The resulting reaction product was fractionated by distillation from a pot still. The second or middle fraction was diluted with 15 parts by weight of acetone and crystallized from the solution at -60°C. To remove any high melting material, another fractional crystallization was performed at -37°C., using 10 parts of acetone. The purified methyl oleate contained 98.8% of methyl oleate, 0.8% of methyl linoleate, and 0.4% of methyl esters of saturated fatty acids, as calculated from iodine and thiocyanogen values.

One part of purified methyl oleate, 0.65 part of U.S.P. glycerol, and 0.001 part of sodium hydroxide were mixed for 15 minutes at 250°C. while under 1 atmosphere of hydrogen. Then a phosphoric acid-glycerol solution containing 2.25 times the amount of acid necessary to react with the sodium hydroxide was added, and the reaction product or crude mono-olein was cooled to room temperature. The crude mono-olein was diluted with ethyl acetate, washed with water, and stripped to remove the ethyl acetate. The mono-olein was further purified by molecular distillation (11) and a single crystallization from acetone (5 parts by weight) at -70°C. to yield a final product having a monoglyceride content of 97.7%.

The mono-olein was mixed with chloroform and pyridine, and a slight excess of acetyl chloride in chloroform solution was added slowly at about room temperature, after which the reaction was allowed to proceed at room temperature for 48 hours. After removal of the unreacted acetyl chloride, pyridine, and pyridine hydrochloride the 1,2-diaceto-3-olein was mixed with hexane, bleached with 5% of neutral, activated clay and 5% of activated carbon, and then crystallized five times from hexane (5 parts hexane to 1 of oil) at -70°C.

The sample of triolein used in the present investigation was prepared from methyl oleate obtained from pecan oil. A 50% excess of the methyl oleate

was reacted with glycerol in the presence of lithium hydroxide (7). The reaction product was purified by acidification, washing, steam stripping at low pressure, molecular distillation to remove diglycerides, and fractional crystallization from solvents.

The aceto-olein product was prepared from a commercial oleic acid (233LL Elaine, Emery Industries³) which was further purified by distillation. The middle portion of the distillate, which contained 97.4% of oleic and iso-oleic acids, 0.3% of linoleic acid, and 2.3% of saturated acids as determined from the iodine and thiocyanogen values, was converted into a technical grade monoglyceride, using the glycerolysis procedure described above. The glycerol-free, technical grade product, containing 62.5% of monoester, the remainder being di- and triglycerides, was acetylated by reacting 1 part with 1.25 parts of acetic anhydride under an atmosphere of hydrogen for 1 hour at 110° C. After the reaction was terminated by the addition of water, the product was washed with water, dried by warming and stripping with hydrogen under vacuum, bleached with clay and carbon, and steam-deodorized (2) for 1 hour at 177°C. and 1 mm. of mercury pressure. The finished product, which was bland in taste and odor, contained no monoglycerides and possessed a hydroxyl value at 6.8.

The acetylated peanut oil was prepared from a refined and bleached oil by the glycerolysis and acetylation procedures used in converting the purified oleic acid into the aceto-olein product. The technical grade monoglyceride resulting from glycerolysis contained 59.0% of monoglycerides, and the acetylated peanut oil had a hydroxyl value of 2.

The two samples of acetylated pecan oil were prepared by different procedures. For acetylated pecan oil A, the original refined and bleached oil was converted into monoglycerides (monoester content 95%) by glycerolysis and molecular distillation. Then the monoglycerides were acetylated and purified by the procedure outlined for the preparation of the 1,2-diaceto-3-olein except that the purification by fractional crystallization from hexane was omitted.

Acetylated pecan oil B was prepared by interestingly approximately equal parts, by weight, of the oil and triacetin for 3 hours at 220°C. in the presence of van Loon's stannous hydroxide catalyst (1). The crude reaction product was washed with dilute acid and then with water, filtered to remove the diatomaceous earth portion of the catalyst, and steam-distilled for 30 minutes at 150°C. and 1 mm. of mercury in order to remove the unreacted triacetin. The finished product had a hydroxyl value of 16.8 and a monoglyceride content of 1.2%.

The sample of acetylated soybean oil was prepared from monoglycerides of soybean oil fatty acids (monoester content, approximately 95%) obtained from Distillation Products Industries, Rochester, N. Y.³ Monoester content of the monoglycerides was approximately 95%. The acetylation and purification procedures were those used to prepare acetylated pecan oil A.

The peanut and pecan oils used in preparing the respective acetylated oils were also examined for purposes of comparison. A typical refined and bleached soybean oil was obtained for comparison with the

acetylated soybean oil. The margarine was a well-known commercial brand. The highly hydrogenated cottonseed oil, which was hydrogenated and steam-deodorized in the laboratory, had an iodine value just below 1.

Testing Procedures. Consistency was measured by one of two different procedures, the choice depending upon the type of material. In one procedure, the micropenetrometer apparatus and technique described by Feuge and Bailey (3) was used. This procedure consists essentially of solidifying the melted samples in copper blocks chilled to 0°C., tempering the samples for 16 hours at 0°C., warming the blocks and samples slowly to the test temperatures, and measuring the depth, in tenths of a millimeter, to which a needle penetrates when dropped under specified conditions.

In the other procedure the cone penetrometer apparatus and technique specified in Method D 217-48 of the American Society for Testing Materials was used except that the weight of the cone and movable attachments was 50 g. instead of 150 g. The cone penetrometer procedure, which was designed for testing petroleum greases, measures the depth in tenths of a millimeter to which a standard cone penetrates a sample in a period of 5 seconds when the cone just touches the surface of the sample at the start of the test.

In obtaining consistencies of the margarine and margarine-like product, each test sample was worked at room temperature, cooled or heated to the test temperature as required, held at the test temperature for a variable length of time, and tested with the penetrometer, which also had been heated or cooled to the test temperature. When making measurements at the lowest temperature (-15°C.), samples of both products were held at this temperature for 100 hours prior to the test. For the test temperature of 4.6°C. a holding time of 20 hours was used while holding times of 4 hours were sufficient to bring the samples to a constant consistency for temperatures above 20°C.

Cloud and solid points were determined by Method D 97-47 of the American Society for Testing Materials except that the sample was examined at 2° instead of 5° intervals in determining the solid point.

Iodine and thiocyanogen values were determined by the methods of the American Oil Chemists' Society, monoglyceride content by the method of Handschumacher and Linteris (8), and hydroxyl value by a modification of the method of West *et al.* (13). Some melting points were determined by the capillary tube method after solidifying the samples slowly by wrapping the capillary tubes in cotton and placing the wrapped tubes in a dry ice chest for 24 hours. Because the aceto-containing products tended to form translucent crystals on cooling, some melting points were determined from heating curves. The melting point of 1,2-diaceto-3-olein was determined from a dilatometric curve.

Properties of Aceto-Oleins

The melting point of 1,2-diaceto-3-olein, as determined from its dilatometric curve, is -18.3°C. and is believed to be that of the high melting form because the sample remained liquid on storage for several weeks at -17°C. The cloud point of 1,2-diaceto-3-olein occurred at -35.6°C., far below the

³This product is named as part of the exact experimental conditions. It does not constitute a recommendation of the Department of Agriculture of this product over that of any other manufacturer.

melting point, as expected, because of the nature of the cloud point test and the habit of glycerides to supercool before solidifying. The solid point occurred at -47.8°C . The melting, cloud, and solid points of 1,2-diaceto-3-olein, together with consistency at -17°C . and iodine value, are recorded in Table I where

TABLE I
Properties of Glycerides Before and After Acetylation

Product	Cloud point, $^{\circ}\text{C}$.	Solid point, $^{\circ}\text{C}$.	Melting point, $^{\circ}\text{C}$.	Consistency, cone penetration, mm./10 at -17°C . ^a	Iodine value
1,2-diaceto-3-olein	-35.6	-47.8	-18.3 ^b	Liquid	57.5 ^c
Aceto-olein product	-22.2	-25.6	-24.0 ^d	Liquid	63.9
Triolein	4.4	-8.9	5.0 ^d	3	84.3 ^e
Acetylated peanut oil	15.6	10.0	16.5 ^f	118	68.3
Peanut oil	3.3	-7.8	5.0 ^d	5	91.6
Acetylated pecan oil A	-11.1	-14.4	-6.5 ^f	233	72.0
Acetylated pecan oil B	-11.1	-13.3	-6.9 ^f	271	78.1
Pecan oil	-13.3	-18.9	-5.0 ^d	3	103.9
Acetylated soybean oil	-4.4	-7.8	4.0 ^d	162	87.9
Typical soybean oil	-6.7	-8.9	-1.7 ^f	110	130.4

^a Unworked consistency. Liquefied samples cooled and held at $-17 \pm 2^{\circ}\text{C}$. for 100 hours.

^b Determined from dilatometric curve.

^c Theoretical value, 57.62.

^d Determined by capillary tube method.

^e Theoretical value, 86.01.

^f Determined from heating curve.

they may be compared with similar values for triolein and the aceto-olein product.

The melting point of 1,2-diaceto-3-olein is about 24° below that of triolein and about half-way between the melting points of trilinolein and trilinolenin. Where triolein has a theoretical iodine value of 86.01, the 1,2-diaceto-3-olein has a theoretical iodine value of 57.62. It is evident that the substitution of acetyl groups for two of the oleoyl groups in triolein results in a modified oil, satisfactory for use where low melting point and a relatively high degree of saturation are required. The acetyl groups in the modified oil constitute only 19.5% of its weight, the other 80.5% may be considered as being derived from triolein.

The aceto-olein product (line 3 of Table I) has physical properties quite similar to those of 1,2-diaceto-3-olein but differs in several respects. The aceto-olein product may be considered as being representative of products manufactured from selectively hydrogenated peanut or cottonseed oils should it become desirable to produce aceto-oleins on a large scale. Glycerides of iso-oleic acids and acetodioleins are present in sizable quantities together with small amounts of trioleins, diglycerides, and glycerides of long chain fatty acids other than oleic. The presence of several types of glycerides is beneficial in that it tends to lower the melting point of the mixture below that of the individual components. The acetyl content of the aceto-olein product was calculated to be approximately 14.3%, on a weight basis, the calculations being based on the calculated hydroxyl value (4) of the technical grade monoglyceride used in the preparation and the hydroxyl value of the final product.

Properties of Acetylated Oils

If a natural oil consisting predominantly of glycerides of oleic acid but containing some glycerides of saturated fatty acids would be modified by the intro-

duction of the acetyl group, either through ester-ester interchange or through glycerolysis and subsequent acetylation, the proportion of lower melting components would increase, but a small amount of higher melting components also would be produced. For example, extensive acetylation of peanut oil would convert one mole of a component like 1-stearo-2,3-diolein (melting point, 23.5°C .) into two moles of a diaceto-olein, possibly 1,2-diaceto-3-olein (melting point, -18.3°C .), and one mole of a diacetostearin, possibly 1,2-diaceto-3-stearin (melting point, 48°C .).

As a result the cloud and solid points and the point of complete melting may be expected to be raised in most instances even though the oil is of a softer consistency at low temperatures. The extent to which these changes occur in any given natural oil depends upon a complex interplay of its composition and the degree and method of acetylation.

In Table I are recorded the physical properties of peanut and pecan oils before and after acetylation and of a typical soybean oil and an acetylated soybean oil. Examination of these data confirms the prediction made concerning changes in physical properties. In most instances acetylation raised the cloud, solid, and melting points but improved greatly the consistency at the low temperature.

None of the acetylated oils behaved like ordinary oils on being cooled to the solid point. Instead of crystallizing into white solids, they appeared merely to congeal and form viscous, translucent liquids. Actually they formed translucent crystals. This behavior is in agreement with observations made on diacetostearins (5, 6). When the latter are cooled from the liquid state, they solidify to a waxy, translucent polymorphic form which is quite stable at room temperature.

The acetylated peanut oil contains only about 14% of acetyl and may be regarded as being representative of a product which can be prepared easily by partially acetylating a semi-drying oil containing a relatively large proportion of glycerides of oleic acid and a relatively small proportion of glycerides of saturated fatty acids. Acetylated pecan oil A represents about the purest diaceto-olein which can be prepared from an unfractionated natural oil. The soybean oils were included in the table to show that plasticity at low temperature apparently can be improved by acetylation even when glycerides of linoleic acid predominate in an oil.

Mixtures of Aceto Compounds and Hard Fat

One of the possible uses of aceto-olein and acetylated oils is in the preparation of plastic fats having a very long plastic range. In such plastic fats the aceto-compound would be the liquid phase or plasticizing component while the solid phase would consist of a relatively hard fat melting well above the desired plastic range.

To test the suitability of aceto compounds as plasticizers, mixtures of a highly hydrogenated cottonseed oil with several of the products listed in Table I were prepared and their consistency measured by the needle penetrometer method of Feuge and Bailey. The results obtained are recorded in Figure 2 where they may be compared with measurements published previously (3) for a typical butterfat (curve 1) and

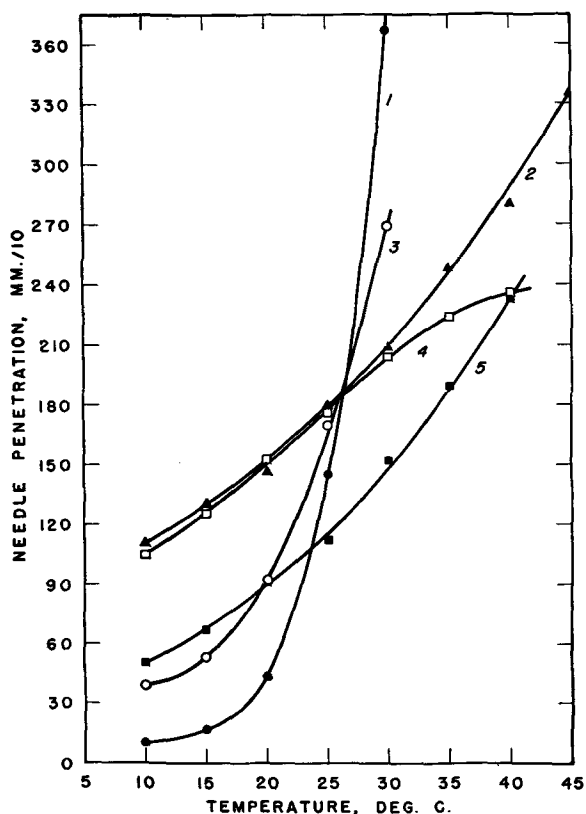


FIG. 2. Consistency vs. temperature curves: (1) butterfat; (2) 86% aceto-olein product, 14% hydrogenated cottonseed oil; (3) 92% cottonseed oil, 8% hydrogenated cottonseed oil; (4) 85% acetylated pecan oil A, 15% hydrogenated cottonseed oil; and (5) 85% pecan oil, 15% hydrogenated cottonseed oil.

for a mixture containing 92% of cottonseed oil and 8% of highly hydrogenated cottonseed oil (curve 3).

If a fat is to be incorporated in a margarine-like product, its consistency at room temperature should be about equal to that of butterfat; that is, the needle penetration should be about 185 at 26°C. If the fat is to have a longer plastic range than does butterfat, it must be softer than the latter at lower temperatures and firmer at higher temperatures. A mixture containing 86% of aceto-olein and 14% of hydrogenated cottonseed oil (curve 2) possesses these properties; and it possesses them to a degree not attainable by mixing a natural oil like cottonseed oil with hydrogenated cottonseed oil (curve 3). The consistency of the latter mixture, while it does not change as rapidly with temperature as does that of butterfat, changes much more rapidly than does the consistency of the aceto-olein mixture.

A mixture containing 85% of acetylated pecan oil A and 15% of hard fat (curve 4) behaves very much like the aceto-olein mixture over the temperature range shown except that it is firmer above 30°C. Mixing 15% of hard fat with the original pecan oil (curve 5) resulted in a mixture having a consistency at room temperature which about equaled the consistency of the acetylated pecan oil mixture at 10°C.

In Figure 3, curve 1, which is from a previous publication (3) and represents a typical all-hydrogenated margarine oil, is quite similar to the curve for butterfat. Curve 2 of Figure 3, which is practically like curve 4 of Figure 1, represents a mixture

containing 85% of acetylated soybean oil and 15% of the hydrogenated cottonseed oil. Curve 3 represents a mixture containing 85% of a typical soybean oil and 15% of hydrogenated cottonseed oil. The difference between curves 2 and 3 is surprising because the acetylated soybean oil and the typical soybean oil were completely liquid over the temperature range shown. Not only does the acetylated soybean oil mixture show less change in consistency over the temperature range covered, but at 40°C. where the soybean oil mixture melts rapidly with increasing temperature, the mixture containing acetylated soybean oil appears to melt quite slowly. The consistency of the mixture containing 86% of partially acetylated peanut oil and 14% of hydrogenated cottonseed oil (curve 4) changes less between 10° and 40°C. than does the mixture containing 85% of soybean oil and 15% of hydrogenated cottonseed oil.

It must be concluded that a mixture of an aceto-olein compound or acetylated oil and a hard fat possesses unusual plastic properties which cannot be duplicated by mixtures of ordinary oils and hard fats, partially hydrogenated oils, or natural fats.

Margarine-like Product

One potential application of these unusual properties is in the preparation of a special margarine-like product which remains spreadable over a wide temperature range and possesses marked resistance to deterioration, as would be expected from its low iodine value. Such a product was prepared con-

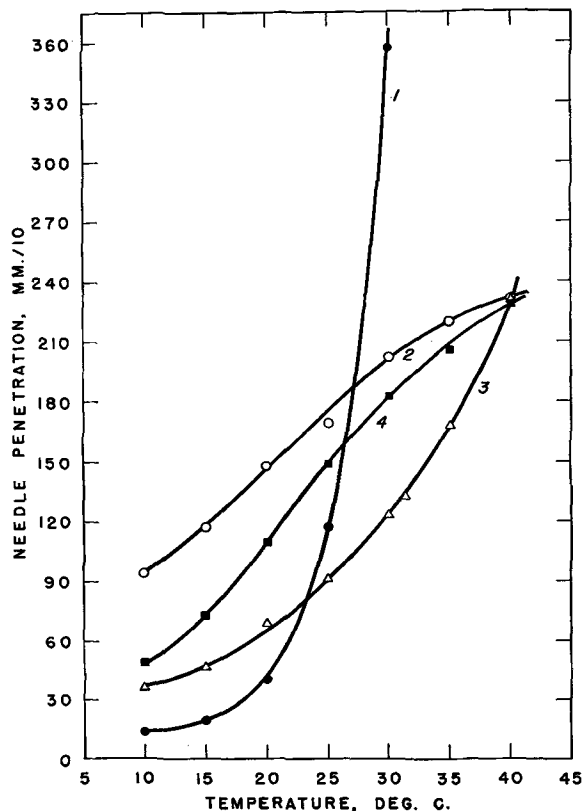


FIG. 3. Consistency vs. temperature curves; (1) all hydrogenated margarine oil; (2) 85% acetylated soybean oil, 15% hydrogenated cottonseed oil; (3) 85% typical soybean oil, 15% hydrogenated cottonseed oil; and (4) 86% acetylated peanut oil, 14% hydrogenated cottonseed oil.

taining 79% of the aceto-olein product, 18.5% of the highly hydrogenated cottonseed oil, 2.5% of finely ground salt, and traces of antioxidant, imitation butter flavor, and butter color. The ingredients were mixed at a temperature just above the melting point of the hard fat, and then chilled to 0°C. while being worked or mixed. The resultant product was allowed to warm to room temperature and again worked until a smooth consistency was attained.

The margarine-like product resembled ordinary margarine in appearance and taste. Because it contained no moisture or milk solids, it is to be expected that there would be little tendency for spoilage by hydrolysis or bacterial action. The iodine value of the fatty portion was 52.0, which is far below that for margarine oil, and it contained 11.6% of the acetyl group. When the margarine-like product was stored for 3 days at 48.9°C., the solid and liquid phases did not separate. The most remarkable property of this product was its almost constant consistency over the temperature range of -15° to 49°C. (5° to 120°F.). The consistency curve obtained with

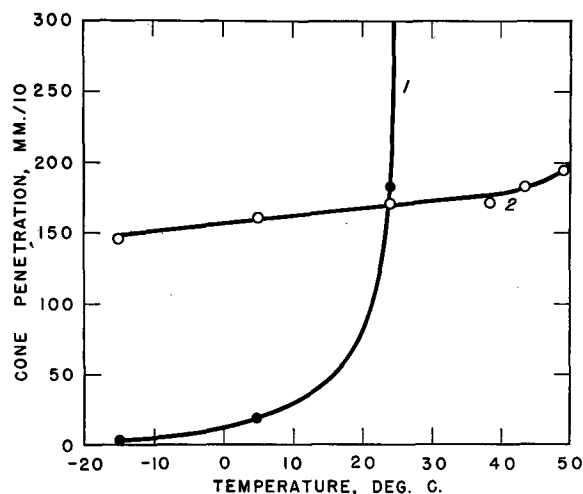


Fig. 4. Consistency vs. temperature curves: (1) margarine, and (2) margarine-like product containing essentially 79% aceto-olein product, 18.5% hydrogenated cottonseed oil, and 2.5% salt.

the cone penetrometer is recorded in Figure 4, which also contains a consistency curve for a commercial margarine.

Letter to the editor

IN the last copy of J.A.O.C.S. (Volume XXX, No. 6) on page 247 there is an error. Below table I the phrase: "Coconut oil contains approximately 94.3% fatty acids . . ." does not have the correct value.

Coconut (and palm kern) oils are among the oils highest in glycerol content and lowest in fatty acids content. All kinds of coconut oil (with low free acids content of about 1-2%) have fatty acids contents around 92% (the average of my analytical determinations) and give the highest yields of glycerol and the lowest yields of fatty acids by splitting. Below

Summary

Pure 1,2-diaceto-3-olein was prepared by acetylating mono-olein. A mixture of aceto-oleins was prepared by acetylating a mixture of mono-, di-, and trioleins derived from commercial oleic acid. Several natural oils were acetylated either by ester-ester interchange with triacetin or by glycerolysis followed by acetylation. The various products were examined for cloud and solid points, point of complete melting, and consistency.

The 1,2-diaceto-3-olein, which contains 19.5% of acetyl group on a weight basis, has a melting point of -18.3°C. while the mixture of aceto-oleins, which contained 14.3% of acetyl on a weight basis, melted at -24°C.

Acetylation of the natural oils raises in most instances their cloud and solid points and point of complete melting, but it also greatly increases their plasticity at lower temperatures.

Aceto-compounds were used to plasticize highly hydrogenated cottonseed oil. These mixtures were prepared so that they possessed the consistency of margarine oil at room temperature. These mixtures, when compared with partially hydrogenated oil, butterfat, or a mixture of cottonseed oil and hydrogenated cottonseed oil, were softer below room temperature and firmer above room temperature.

A margarine-like product containing 79% of aceto-olein and 18.5% of highly hydrogenated cottonseed oil had a practically constant consistency over the temperature range of -15° to 49°C. (5° to 120°F.).

REFERENCES

1. Bailey, A. E., "Industrial Oil and Fat Products," 2nd ed., Interscience Publishers, New York, 1951, pp. 831-832.
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*, **21**, 78-84 (1944).
4. Feuge, R. O., and Bailey, A. E., *Oil & Soap*, **23**, 259-264 (1946).
5. Feuge, R. O., Vicknair, E. J., and Lovegren, N. V., *J. Am. Oil Chem. Soc.*, **29**, 11-14 (1952).
6. Feuge, R. O., Vicknair, E. J., and Lovegren, N. V., *J. Am. Oil Chem. Soc.* (in press).
7. Gros, A. T., and Feuge, R. O., *J. Am. Oil Chem. Soc.*, **26**, 704-709 (1949).
8. Handschumacher, H., and Linteris, L., *J. Am. Oil Chem. Soc.*, **24**, 143-145 (1947).
9. Jackson, F. L., and Lutton, E. S., Procter and Gamble Company, Cincinnati, O. (manuscript submitted for publication).
10. Jackson, F. L., Wille, R. L., and Lutton, E. S., *J. Am. Chem. Soc.*, **73**, 4280-4284 (1951).
11. Kuhrt, N. H., Welch, E. A., and Kovarik, F. J., *J. Am. Oil Chem. Soc.*, **27**, 310-313 (1950).
12. Ross, J. (to Colgate-Palmolive Peet Company), U. S. Pat. 2,567,404 (1951).
13. West, E. S., Hoagland, C. L., and Curtis, G. H., *J. Biol. Chem.*, **104**, 627-634 (1934).

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90% (86-87% in average including coconut oil from acidulated soapstocks). For this reason in times of high demand of glycerol (*i.e.*, before the World War in Europe) coconut oil was the main raw material for producing glycerol by the splitting of oils.

This correction, naturally, doesn't affect significantly this very interesting publication, the considerations of which (p. 248) are quite correct, in my opinion, because I obtained about the same results during my work in Europe (over 25 years).

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