peak area between 0.06 and 0.3 $R_f$ units. The peak area is essentially constant from an $R_f$ of about 0.3 to 0.8. The peak area-$R_f$ relationship is also somewhat dependent on sample size as shown in curves B–E. However, over an optimum range of $R_f$ and sample size, isomeric monostearins exhibit identical responses. Direct analysis of monoglycerides without standards can only be accurately made at $R_f$ values from about 0.3 to 0.8. A relationship similar to that shown by curve A was recently reported (28) for an unspecified weight of tripalmitin. Monoglycerides of other chain length and containing unsaturation would be expected to have a response in proportion to their carbon content as shown by Privett and Blank (24) for glycerides charred with chromic-sulfuric acids. Although at this time we do not have sufficient data to state the accuracy and precision of the method, one would expect absolute errors of about ±1.5% as previously reported (7) for the quantitative analysis of lipids by TLC and densitometry. There is some evidence which indicates that $R_f$ dependence may be related to light scattering effects as shown in Figure 6. Curves A and B represent the peak area-concn relationships for 2-monostearin and 1-monostearin having $R_f$ values of 0.12 and 0.06, respectively. The peak areas were obtained densitometrically as previously described. Curve C shows the peak area-concn relationship exhibited by monostearins on the same chromatoplate sprayed with mineral oil in ether to make the plate translucent and thus reduce light scattering. Linearity of the peak area-concn curves is considerably improved and both components exhibit a similar response over the range of sample size examined. However, the sensitivity of the measurement is considerably reduced. A more satisfactory method of eliminating the influence of refracted light without a corresponding decrease in sensitivity is to collimate the light beam by placing a narrow slit below as well as above the chromatoplate (7).

In view of the extreme ease with which monoglycerides isomerize, isolation and other handling prior to silica gel-boric acid chromatography must be carefully controlled. Procedures involving heat, acids or bases, and even chromatographic isolation in a noncomplexed form should be avoided.

## Summary

We have demonstrated that isomeric monoglycerides may be resolved by thin-layer adsorption chromatography on boric acid-impregnated silica gel, and that under the conditions described, no isomerization occurs. We have further demonstrated that monoglycerides may be isolated by preparative TLC or on columns without causing isomerization.

Finally, we have shown that monoglyceride isomers may be quantitated by the densitometric measurement of charred spots over an optimum range of $R_f$ and sample size.

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# Lubricants. I. Preparation and Properties of Benzyl and Substituted Benzyl Esters of Dilinoleic Acid

WINFRED E. PARKER, R. E. KOOS, H. B. KNIGHT and W. C. AULT, Eastern Regional Research Laboratory [1] Philadelphia, Pennsylvania

## Abstract

Benzyl and substituted benzyl esters of dilinoleic acid and of hydrogenated dilinoleic acid have been prepared in good yield. Some of the chemical characteristics and physical properties of the resulting products have been measured including a study of their thermal stability by thermogravimetry. Also, they have been examined by several of the bench tests used in laboratory evaluation of lubricants. Several of them compare favorably with control materials used in the study.

THE SILICONE, SILICATE, hydrocarbon, fluorocarbon, ether and ester fluids are among the important classes of compounds being prepared and evaluated in the search for new lubricants, lubricant additives, and hydraulic fluids to meet the needs of the future. Klaus, Tewksbury and Fenske have estimated that the upper useful limit for most of these classes is between 370–427 (15).

This paper is primarily concerned with the preparation and properties of long-chain esters derived from fatty materials and benzyl alcohol and its derivatives. These alcohols were selected because they lacked a *beta* hydrogen; therefore their esters could not decompose by the usual cyclic mechanism (6), but by a free radical mechanism (1,13), which insures higher thermal stabilities. Durr, Meador and Thompson used a sim-

TABLE I

Preparation of Dilinoleate Esters

| Sample | Acid [1] grams | Alcohol [1] grams | Catalyst [2] grams | Reflux time. hours | Yield [3] % | Molecular weight calculated |
|---|---|---|---|---|---|---|
| Bis(benzyl)- | 149.0 | 58.0 | 3.0 | 3 | 95 | 741.2(750)[4] |
| Hydrogenated [a] bis(benzyl)- | 151.0 | 58.0 | 3.0 | 4 | 90.4 | 745.2 |
| Bis(p-isopropylbenzyl)- | 282.5 | 150.2 | 5.65 | 5 | 99.0 | 825.3 |
| Bis(benzhydryl)-[b] | 28.3 | 18.3 | 0.65 | 8 | 89.6 | 893.4 |
| Bis(p-nitrobenzyl)- | 45.6 | 25.0 | 1.82[5] | 8 | 90.3 | 831.2 |
| Bis(anisyl)- | 10.2 | 5.0 | 0.4[6] | 6 | 80.0[7] | 801.2 |
| Dibenzyl sebacate [8] | 45.0 | 48.0 | 0.9 | 7 | 91.3 | 382.5 |

[1] Molar ratio, 2 moles alcohol: 1 mole acid.
[2] 2% Naphthalene-2-sulfonic acid based on weight of dimer acid.
[3] Yield of crude ester.
[4] Experimental mol wt.
[5] 4%, based on weight of dimer acid.
[6] 3%, based on weight of dimer acid.
[7] Reaction incomplete.
[8] Commercially available.
[a] Since acid portion is only partially hydrogenated, the above name is preferred.
[b] Can also be named bis(diphenylmethyl)dilinoleate.

ilar approach when they prepared a series of highly substituted neo-alkyl azelate esters (8). These proved to have better thermal stability than bis(2-ethylhexyl)-sebacate.

Although many esters and other derivatives of dimer acid (dilinoleic acid) have been made and tested as lubricants (19), lubricant additives (16), transmission fluid additives (12), and corrosion inhibitors (5), the benzyl esters have not been reported. Besides having good thermal stability such esters should have higher viscosities (hydrodynamic component) than the usual dibasic ester because of high molecular weight and the unique structure of the acid portion. Also the chemical properties (boundary component) should be the same or better than diesters which are considered to be good lubricants.

## Experimental

### Starting Materials

Dimer acid, Empol 1014, which contained 95% dilinoleic acid, 4% trimer acid, and 1% monobasic acid (acid number 191.2; neutralization equivalent, 293.4; molecular weight, 565) and hydrogenated dimer acid (acid number, 192.8; neutralization equivalent, 288.0; iodine number, 29.0) were contributed by Emery Industries, Inc. These were used as received. Benzhydrol and benzyl, p-isopropylbenzyl, p-nitrobenzyl, anisyl alcohols and naphthalene-2-sulfonic acid are commercially available and only anisyl alcohol was redistilled before use.

### Bis(benzyl)dilinoleate

The preparation and purification of this compound is typical for most esters (18). The exceptions are noted below and in Tables I and II. A 1:2 molar ratio of dimer acid (149.0 g) and benzyl alcohol (58.0 g) and naphthalene-2-sulfonic acid (2% based on the weight of dimer acid) were dissolved in 200 ml ACS

grade benzene in a one liter 3-neck flask. The flask was equipped with a thermometer, magnetic stirrer, and a Dean and Stark tube with a water-cooled condenser. The reaction mixture was heated at reflux temperature, 90C, until the calculated amount of water (9.5 ml) was separated in the Dean and Stark tube (3 hr). After cooling, the reaction mixture was water washed until acid-free. The benzene layer was dried over calcium sulfate and stripped under vacuum, using a rotating evaporator. The crude product, an amber fluid, weighed 189.0 g, Acid No. 0. The extent of reaction was confirmed by infrared spectra (absence of the broad acid band centered at 3000 cm$^{-1}$ and of the acid carbonyl band at 1700 cm$^{-1}$ and by the presence of the ester carbonyl band at 1735 cm$^{-1}$, the aromatic bands at 3030 cm$^{-1}$, 1600 cm$^{-1}$, and typical bands from 1225 cm$^{-1}$ to 650 cm$^{-1}$). The product was distilled through an A. F. Smith 2 in. molecular still, the main fraction coming over between 280–300C at 9–15$\mu$. The distilled amber liquid weighed 156.2 g and had a molecular weight of 750 which was determined by the method of Filipic et al. If a molar excess of the alcohol is used initial separation of the crude product is complicated by emulsion formation which results in a decrease in yield. Similar results are obtained if naphthalene-1-sulfonic acid is used.

### Bis(benzhydryl)-, bis(p-nitrobenzyl)-, and bis(anisyl) di-linoleates

Approximately twice as much catalyst was required to make these reactions yield the calculated amount of water, yet there was always unreacted dimer acid in the product (2–9%). Naphthalene-1-sulfonic acid, methanesulfonic acid and sulfuric acid gave poorer results than naphthalene-2-sulfonic acid.

### Kinematic Viscosity and Viscosity Index

The viscosity and viscosity index were determined according to the procedure given in ASTM D445-60

TABLE II

Preparation of Dilinoleate Esters

| Sample | B.P.[1] °C | Microns | N[30]D | Carbon, % Calcd[2] | Found | Hydrogen, % Calcd | Found | Saponification number Calcd | Found | Saponification equivalent Calcd | Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bis(benzyl)- | 280 | 9 | 1.5028 | 81.03 | 81.11 | 10.35 | 10.54 | 151.4 | 146.4 | 370.6 | 383.2 |
| Hydrogenated Bis(benzyl) | 275 | 10 | 1.5013 | 80.59 | 80.68 | 10.52 | 10.56 | 150.6 | 147.0 | 371.8 | 381.5 |
| Bis(p-isopropylbenzyl)- | 300 | 10 | 1.5020 | 81.50 | 80.95 | 10.74 | 10.84 | 136.0 | 138.3 | 412.7 | 406.0 |
| Bis(benzhydryl)- | —[3] | | 1.5295 | 83.36 | 82.72 | 9.48 | 9.53 | 125.6 | 126.2 | 446.8 | 444.6 |
| Bis(p-nitrobenzyl)[4] | >200 | 10 | 1.5177 | 72.25 | 72.33 | 8.98 | 9.32 | 135.0 | 139.5 | 415.6 | 403.0 |
| Bis(anisyl)- | >225 | 6 | 1.5230 | 77.95 | 77.80 | 10.06 | 9.60 | 140.1 | 143.5 | 400.6 | 391.0 |
| Dibenzyl sebacate [5] | 180 | 7 | 1.5162 (solid at room temp.) | 75.36 | 75.49 | 7.91 | 8.03 | | | | |

[1] Molecularly distilled.
[2] Based on calcd. mol wt of dilinoleic acid (mol wt 561), not on mol wt given for commercial dimer acid (mol wt 565).
[3] Alcohol insol. fraction.
[4] Nitrogen, % calcd. 3.37; found, 3.12.
[5] Control sample.

TABLE III

Viscosity Characteristics and Wear Scars of Dilinoleate Esters and Controls

| Sample | Kinematic viscosity, centistokes at °C | | | | Viscosity index | ASTM Slope | Wear scar Dia., mm |
|---|---|---|---|---|---|---|---|
| | 25.0 | 37.8 | 54.5 | 98.8 | | | |
| Bis(benzyl)- | 193.5 | 96.7 | 46.9 | 12.6 | 124.3 | 0.632 | 0.653 |
| Hydrogenated bis(benzyl)- | 215.4 | 109.1 | 52.1 | 14.0 | 126.0 | 0.600 | 0.748 |
| Bis(p-isopropylbenzyl)- | 412.8 | 192.8 | 82.5 | 18.3 | 110.2 | 0.634 | 0.843 |
| Bis(benzhydryl)- | 2606 | 858 | 270 | 36.8 | 78.4 | 0.684 | 0.829 |
| Bis(p-nitrobenzyl)- | 1522 | 553 | 199.5 | 32.3 | 95.4 | 0.651 | 0.863 |
| Bis(anisyl)- | Too viscous | | 401.5 | 49.34 | | 0.659 | 0.473 |
| Bis(2-ethylhexyl)sebacate | | 12.6 | | 3.26 | 148.8 | 0.710 | 0.830 |
| Dibenzyl sebacate | | | | | | | 0.950 |
| 100 Paraffin oil | | 45.7 | | 6.80 | 112.7 | 0.700 | 0.803 |
| **Oxidized samples (100C)** | | | | | | | |
| Bis(benzyl)dilinoleate + A[a] | 258.0 | 124.4 | 58.0 | 14.1 | 116.0 | 0.639 | |
| Hydrogenated bis(benzyl)dilinoleate + A | 271.2 | 131.6 | 61.6 | 15.0 | 118.2 | 0.629 | |
| 100 Paraffin oil | 104.1 | 50.5 | 23.8 | 6.25 | 70.6 | 0.798 | |
| 100 Paraffin oil + A | 114.9 | 54.2 | 24.8 | 6.48 | 68.8 | 0.795 | |
| Bis(2-ethylhexyl)sebacate | 19.6 | 12.6 | 8.00 | 3.4 | 165.6 | 0.687 | |
| Bis(2-ethylhexyl)sebacate + A | 23.3 | 14.4 | 8.80 | 3.70 | 167.0 | 0.677 | |

[a] A = 5% 4,4'-Methylene bis(2,6-di-tert-butylphenol) as inhibitor.

and ASTM D567-53, respectively, using Cannon-Manning semi-micro viscometers. The results are given in Table III.

### Precision Shell Four Ball Wear Test

The procedure is described in detail by Peale et al. (17). The samples were run at 120C under a 50 kg load. Rotation of the upper ball was 600 rpm. Bis(2-ethylhexyl)sebacate, dibenzyl sebacate, and 100 paraffin oil (Refined Pennsylvania oil with a viscosity of 100 Saybolt seconds at 100F.) were used as reference materials.

### Inhibited Oil Oxidation Test

The procedure followed is a modification of ASTM D943-54. The diameter of the bottom half of the sample tube was reduced from 41 mm to 23 mm so that smaller samples could be tested (75 ml sample and 15 ml water versus 300 ml sample and 60 ml water). Instead of using the recommended metal coils of wire, two each of highly polished aluminum, copper, and steel washers (22 mm outside diameter, 8 mm hole) separated by 0.25 in. glass tubing were used. The tests were run at 100C for 168 hr with pure oxygen being bubbled through at a rate of 3 liters per hour. Some samples were inhibited with 5% 4,4'-methylene bis(2,6-di-tert-butylphenol). The results are given in Table IV.

### Thermal Stability

An Aminco Thermo-Grav, Cat. No. 4-4430, was used. All components, except the sample holder, were manufactured by the American Instrument Co., Silver Spring, Md. The sample holder was made from 4 mm Pyrex glass tubing, 24 cm long. A small bulb (capacity—approximately 0.5 ml, 1.0 cm diameter) was formed at one end of the tube and a flared lip was formed at the other. The size of the bulb may be varied for the weight of the sample being used. The bulb, with the above dimensions, will accommodate a sample weighing 100 mg. We placed the sample in the holder with a long, thin dropper, being careful not to deposit liquid on the wall of the tube. The holder was then attached to the eyelet of the weighing mechanism (support rod) with a hook made from 22 gauge nichrome wire. Using this arrangement, the sample holder tube extends approximately 7.5 cm above the top of the furnace while the bulb is located approximately 6 mm above the sample thermocouple well. This distance can be adjusted by the wire hook.

The feasibility of this arrangement was tested with a 5 ml sample of bis(benzyl)dilinoleate placed in a 10 ml test tube with a ground glass joint. The test tube was equipped with an air condenser and a thermocouple which rested in the sample. The temperature of the sample was maintained at 382C, 2C under the indicated decomposition temperature determined by thermogravimetric (TGA) methods, for 16 hr. Little or no decomposition was detected. This was determined visually, by infrared spectra, and by chemical analysis. When the sample temperature was maintained above the indicated decomposition temperature, the sample decomposed slowly. The extent of decomposition was checked as above.

The samples were heated to 525–575C at a heating rate of 3C per minute in a dry air atmosphere which flowed at a rate of 10 ml per minute at atmospheric pressure. Decomposition took place at a maximum of one third of the distance up the sample holder tube as evidenced by observation of carbonaceous matter.

### Results and Discussion

All of the esters prepared for this study are liquids at room temperature, although they have relatively high molecular weights. The fact that these and other derivatives are not solids is probably due to the unique structure of dilinoleic acid, which was first described by Bradley (3). The resulting product may be considered to be a derivative of cyclohexene which has a half-chair conformation where four carbon atoms in the ring, including the double-bonded carbon atoms, are in the same plane. Four isomers are possible, depending on which of the double bonds of linoleic acid are involved in the reaction and whether the molecules are lined up in a head-to-head or head-to-tail fashion.

The viscosities of all the esters are higher than either bis(2-ethylhexyl)sebacate or 100 paraffin oil, which were used as reference standards. Bis(benzyl)dilinoleate had the lowest viscosity while bis(anisyl)dilinoleate had a viscosity so high that it was inconvenient to measure it at room temperature. The viscosity indices are not as good as bis(2-ethylhexyl)sebacate, however, most of them compare favorably to paraffin oil. The viscosities of the benzhydrol, p-nitrobenzyl, and anisyl esters suggest that they could be used to improve the high temperature viscosity in other base oils.

The effect of viscosity and/or viscosity index is not reflected in the lubricity of the esters, with the exception of bis(anisyl)dilinoleate, as measured by the wear scar diameter on the Shell four-ball wear tester. If it is assumed that the wear properties and the viscosities should increase in a parallel manner for a given class

TABLE IV

Oil Oxidation Tests of Dilinoleate Esters and Controls at 100C

| Sample | Weight loss, % of metal catalyst | | | Acid No.[a] | Iodine No. | Visual appearance | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Al | Cu | Steel | | | | | | |
| Bis(benzyl)- | | Before oxidation | | | 71.0 | Medium amber oil | | | |
| Bis(benzyl)- (no inhibitor) | 0.66 | 2.06 | 15.5 | 52.0 | 15.4 | Oil[1]; | Al[6]; | Cu[6]; | steel[8] |
| Bis(benzyl)- + A[b] | 0.09 | 1.10 | 0.58 | 16.9 | 43.0 | Oil[2]; | Al[6]; | Cu[6]; | steel[6] |
| Hydrogenated bis(benzyl)- | | Before oxidation | | | 24.6 | Yellow oil | | | |
| Hydrogenated bis(benzyl)- (no inhibitor) | 0.47 | 2.04 | 2.02 | 56.3 | 1.45 | Oil[3]; | Al[6]; | Cu[6]; | steel[7] |
| Hydrogenated bis(benzyl)- + A | 0.02 | 2.01 | 0.14 | 8.69 | 22.3 | Oil[1]; | Al[6]; | Cu[6]; | steel[5] |
| Bis(p-isopropylbenzyl)- | | Before oxidation | | | 67.9 | Dark brown oil | | | |
| Bis(p-isopropylbenzyl)- (no inhibitor) | 1.00 | 2.20 | 18.0 | 46.6 | 13.3 | Oil[3]; | Al[7]; | Cu[6]; | steel[8] |
| 100 Paraffin oil | | Before oxidation | | | 21.9 | Amber oil | | | |
| 100 Paraffin oil (no inhibitor) | 0.07 | 0.14 | 1.17 | 1.42 | 19.2 | Oil[4]; | Al[6]; | Cu[8]; | steel[7] |
| 100 Paraffin oil + A | 0.04 | 0.03 | 0.08 | 1.04 | 21.8 | Oil[5]; | Al[5]; | Cu[8]; | steel[6] |
| Bis(2-ethylhexyl)sebacate (no inhibitor) | 0.05 | 0.06 | 2.23 | 4.25 | | Oil—milky yellow; Al[6]; Cu[7]; steel[8] | | | |
| Bis(2-ethylhexyl)sebacate + A | +0.02 | 0.02 | 0.87 | 1.11 | 6.70 | Oil[1]; | Al[6]; | Cu[8]; | Steel[8] |

[a] Neutralization number.
[b] A = 5% 4,4'-Methylene bis(2,6-di-tert-butylphenol).
[1] Fluid.
[2] Sludge-fluid.
[3] Viscous-tarry.
[4] Tarry, semisolid.
[5] Clean.
[6] Light tarnish and/or light corrosion.
[7] Medium tarnish and/or medium corrosion.
[8] Heavy tarnish and/or heavy corrosion.

of compounds, it seems, therefore, that some unknown property is also essential to lubricity beside the hydrodynamic component (viscosity) and the boundary component (chemical) since the latter should be essentially the same for compounds studied.

Although the inhibited oil oxidation test was designed primarily for determining oxidation inhibitor life and not the stability characteristics of the base oil, it was informative to see how some of these compounds stood up under such rigorous conditions. Table IV lists the results of this test on uninhibited oils and oils with commercial additives present. In all cases, oils inhibited with a 4,4'-methylene-bis(2,6-di-tert-butylphenol) gave the best results in terms of the condition of the metal pieces and the oil, itself, after oxidation. The uninhibited oils, with the exception of the controls, became so viscous upon oxidation that the viscosity was not measured. In the presence of inhibitors, the viscosity characteristics were maintained for the most part (Table III).

The effect of oxidation is found when the esters are compared with bis(2-ethylhexyl)sebacate (no unsaturation) and paraffin oil (no ester group). In the benzyl esters, both reactive centers (double bond and carboxyl group) are effected by oxygen and water. This is shown by the increase in the acid number and the decrease in the iodine number. Paraffin oil, in the absence of an inhibitor gives a small acid number and a small decrease in iodine number, therefore, the carboxyl group was possibly formed by splitting at the double bonds. With the benzyl esters, however, most of the acid formed is possibly from hydrolysis.

The determination of thermal stability was not done by the procedure given by Klaus and Fenske (14), but by thermogravimetry (TGA). Thermogravimetry, the measurement of weight gain or loss with increasing temperature at a constant heating rate, was first put to extensive use by Duval (9). A more complete description than the one given here of this method is given by Coats and Redfern (4), and by Gordon (11). Coats and Redfern summarized the opinions of others in reference to the reliability of thermal stability (decomposition temperature) determined thermogravimetrically. It is pointed out that there is little agreement between values obtained from isothermal and nonisothermal methods. Variation in values obtained from TGA results because of a lack of uniformity in experimental procedure and because of a lack of an adequate definition for locating the decomposition temperature. Pellon defines the decomposition temperature as being that temperature where the cumulative weight change of the material is 10%. Dollimore, Griffiths and Nicholson defines the decomposition temperature as being the point at which the maximum rate of loss of material with a change in temperature $(dw/dT)$ occurs (7). As a result of the above, a number of temperatures have been listed in Table V for various degrees of decomposition. The "Onset of Decomposition" has been defined by the authors of this paper as the point where (a) the material shows the first detectable weight loss as determined by a deviation from a blank run and/or (b) the slope, $(dw/dT)$ shows a radical change from some minimum value.

The sample holder described in the experimental part is preferred over crucibles for high molecular weight organic materials because weight loss is only detected as a result of decomposition and not volatilization since the long tube which extends above the furnace acts as a condenser. This arrangement eliminates erroneous sample weights which occur when the sample recondenses on the crucible holder. Volatilization is usually detected 75–100C below the decomposition point.

The decomposition temperatures of bis(2-ethylhexyl)sebacate and dibenzyl sebacate were compared to those determined by Blake and co-workers who determined the thermal stability of over 100 organic compounds by measuring the rate of increase in vapor pressure with time $(dp/dt)$ as a result of decomposition (2). They defined the decomposition point $(T_d)$ as the temperature at which $dp/dt = 0.014$ mm Hg/

TABLE V

Thermal Stability of Dilinoleate Esters and Controls

| Sample | Onset of decomposition Temp,C[a] | Temp (C) where sample is decomposed approximately | | | |
|---|---|---|---|---|---|
| | | 1% | 2% | 5% | 10% |
| Bis(benzyl)- | 384 | 393 | 404 | 412 | 421 |
| Hydrogenated bis(benzyl)- | 392 | 402 | 407 | 416 | 427 |
| Bis(p-isopropyl-benzyl)- | 368 | 381 | 392 | 406 | 419 |
| Bis(benzhydryl)- | 306 | 325 | 338 | 358 | 364 |
| Bis(p-nitrobenzyl)- | 273 | 281 | 285 | 291 | 315 |
| Bis(anisyl)- | 345 | 360 | 377 | 402 | 418 |
| Bis(2-ethylhexyl)-sebacate | 289 | 325 | 349 | 374 | 387 |
| Dibenzyl sebacate | 300 | 344 | 365 | 390 | 403 |

[a] Temperatures determined on average of 3 runs. Accuracy, ±4C.

sec. According to their measurements, $T_d$ for bis(2-ethylhexyl)sebacate and dibenzyl sebacate was 284C and 296C, respectively. Our results are approximately 5 degrees higher.

The stability of the ester appears to depend upon the stability of the free radical formed in the intermediate state. The greater the stability of that radical the greater the chance for reaction. Since the radical formed by the unsubstituted benzyl ester would probably be the least stable (or the most difficult to produce), its ester is expected to be the most stable. In contrast, bis(p-nitrobenzyl)dilinoleate should produce the most stable radical; therefore, it should be the least stable ester. The stabilities of the other esters are in between these extremes, as expected. All of the benzyl dilinoleate esters are more stable than the control compounds except bis(p-nitrobenzyl)dilinoleate. Partial hydrogenation gives added stability to the benzyl esters, showing the effect of unsaturation far away from the active site of the molecule.

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# The Chemical and Physical Properties of Interesterified Milk Fat Fractions[1]

MOORE, J. L., T. RICHARDSON, and C. H. AMUNDSON, Department of Dairy and Food Industries, University of Wisconsin, Madison

## Abstract

Five fractions of anhydrous milk fat were obtained by fractional crystallization in the absence of solvent. The fractions were characterized, physically and chemically, before and after interesterification.

Cholesterol tended to fractionate into the lowest-melting fraction.

Slipping points of 38.5C, 32C, 28C, 22.5C, and 17C, respectively, were reflected in widely varying micropenetration curves, while differences in fatty acid composition were relatively small. The three higher-melting fractions, with very similar fatty acid compositions, had very similar physical properties after interesterification. Slipping points of 38C, 37C, 37C, 33C, and 32C, respectively, indicated that interesterification generally hardened the fractions. Interesterification altered the physical properties of lower-melting fractions more than the properties of higher-melting fractions.

Interesterification caused some triglyceride degradation and some butyrate loss, but these factors could not fully explain the unequal physical property changes induced in the different fractions.

Fractionation possibly tends to separate symmetrical triglycerides from their lower-melting, unsymmetrical isomers, yielding fractions with apparent differences in the degree of randomness of their triglyceride structure.

Positioning of fatty acids within the triglyceride molecule seems to be a principal determinant of the physical properties of milk fat fractions.

## Introduction

FULL UTILIZATION of milk fat in the future may depend upon the development of fractions having greatly modified properties, perhaps even "tailor-made" to specifications.

Fractional crystallization in the absence of solvent, interesterification, or combination of the two, might be used to produce milk fat fractions with widely varying physical properties. Interesterification is already industrially utilized and a recent patent (1) indicates that centrifugal fractionation of fat may also become commercially practical. Weihe (2) found that milk fat was hardened by interesterification. de Man (3) observed that the hardening of milk fat after interesterification was accompanied by an increased content of high-melting glycerides. Mickle, et al. (4) attributed the softening of butter-like products made from interesterified milk fat to triglyceride degradation.

Jack et al. (5,6) studied the composition of milk fat fractions derived by solvent fractionation. Physical properties of their fractions were not measured nor correlated with composition, and the fractions were not interesterified.

This study combined fractionation of milk fat with interesterification of the fractions to create physically modified fats. This paper attempts to correlate the differences in physical properties with composi-