TABLE II

The Hydrogenation of Three Samples of Soybean Methyl Ester with Each of Two Single 85 mg Samples of Metal-Polymer Catalyst in Methylene Chloride at 550 psi Hydrogen[a]

| Catalyst | Per cent composition of product | | | | |
|---|---|---|---|---|---|
| | Saturate | Monoene | Diene | Conjugated diene | Triene |
| $C_{48}H_{49}ClO_3P_2 \cdot (PtCl_2)_{0.505}$[b] | | | | | |
| First hydrogenation run | 14.5 | 37.8 | 28.3 | 20.1 | — |
| Second hydrogenation run | 14.9 | 26.8 | 38.3 | 18.5 | 1.6 |
| Third hydrogenation run | 13.8 | 26.6 | 39.2 | 18.4 | 2.0 |
| $C_{48}H_{49}ClO_3P_2 \cdot (PdCl_2)_{0.507}$[c] | | | | | |
| First hydrogenation run | 13.6 | 68.9 | 17.7 | — | — |
| Second hydrogenation run | 14.6 | 34.0 | 46.7 | — | 4.7 |
| Third hydrogenation run | 14.8 | 35.2 | 45.9 | — | 4.3 |

[a]Initial composition was 14.2% saturate, 22.3% monoene, 56.2% diene and 7.0% triene.

[b]Reactions at 150 C for 6 hr with 226 mg $SnCl_2 \cdot 2H_2O$.

[c]Reactions at 70 C for 3 hr.

and 600 psi of hydrogen. After 6 hr in methylene chloride, all of the triene fraction was reduced without the formation of saturate. The isomerization of the diene fraction to form conjugated diene was also observed under these conditions. The similar palladium-tin system decomposed below 150 C and was then catalytically inactive.

Both catalysts may be recovered by filtration and reused many times, although the platinum system requires the addition of fresh $SnCl_2 \cdot 2H_2O$ for each reaction. As shown in Table II, a slight loss of catalytic acitivity is observed after the first recovery of catalyst, but no further losses occur on subsequent reactions. The analytical data and IR spectrum of the palladium complex are unchanged after several catalytic reactions. The platinum compound is recovered considerably altered, but the data are not consistent with any structure analogous to known products of similar reactions between $SnCl_2 \cdot 2H_2O$ and platinum halide complexes.

HAROLD S. BRUNER
JOHN C. BAILAR, JR.
Department of Chemistry
University of Illinois
Urbana, Illinois 61801

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REFERENCES

1. Frankel, E., and H. Dutton, in "Topics in Lipid Chemistry," Vol. I, Logos Press, London, 1969, p. 161.
2. Heinemann, H., Chem. Tech. 1:286 (1971).
3. Bailar, J.C., Jr., JAOCS 47:475 (1970), and references therein.
4. Grubbs, R.H., and L.C. Kroll, J. Amer. Chem. Soc. 93:3062 (1971).
5. Collman, J.P., L.S. Hegedus, M.P. Cooke, J.P. Norton, G. Dolcetti and D.N. Marquardt, Ibid. 94:1789 (1972).
6. Capka, M., P. Svoboda, M. Cerny and J. Helfleji, Tetrahedron Lett. 1971:4787.
7. Haag, W.O., and D.D. Whitehurst, Belgian Patent Nos. 721 and 686, 1969.
8. Kharasch, M.S., R.C. Seyler and F.R. Mayo, J. Amer. Chem. Soc. 60:882 (1938).
9. Adams, D., "Metal-Ligand and Related Vibrations," First Edition, Edward Arnold Ltd., London, England, 1967, p. 74.

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# Alkali Isomerization of Linoleate Isomers: Characterization of Products

## ABSTRACT

Geometrical isomers of methyl linoleate were reacted with alakli, and the resulting conjugated isomers were separated into *trans,trans*; *cis,trans*; and *cis,cis* fractions. The position of double bonds in the various fractions was determined by reductive ozonolysis. *trans*-9,*trans*-12-Isomer of linoleate formed *trans,trans*- and *cis,trans*-conjugated dienes, whereas *cis*-9,*trans*-12- and *trans*-9,*cis*-12-isomers in addition formed *cis,cis*-conjugated dienes. The formation of the products is in accordance with the theoretical predictions. During conjugation *trans* double bonds shifted to form a *trans* bond preferentially. During conjugation of *cis*-9,*trans*-12- and *trans*-9,*cis*-12-linoleate isomers, the *cis* double bond shifted preferentially over the *trans* double bond. A small amount of diene not conjugated was probably a geometrical and positional isomer of the starting material.

Methylene-interrupted double bonds in polyunsaturated fatty acids undergo rearrangement to conjugated double bonds not only during hydrogenation and autoxidation, but also during treatment with alkali. Similar conjugated products might be produced by the three methods. Nichols et al. (1) characterized products from alkali-isomerized linoleic acid. On theoretical grounds they also formulated rules to predict products from geometrical isomers of linoleic acid; however these products have not been thoroughly characterized (2) to test the validity of these rules.

Methyl *trans*-9,*trans*-12-octadecadienoate (*t,t*-Lo) was prepared by the procedure of Harlow et al. (3). Final

TABLE I

Composition of Products from Alkali Isomerization of Linoleate Isomers

| Linoleate isomer | Weight % | | | |
|---|---|---|---|---|
| | Unconjugated diene | *trans, trans*-Conjugated diene | *cis trans*-Conjugated diene | *cis,cis*-Conjugated diene |
| *trans*-9,*trans*-12 | 5 | 56 | 39 | 0 |
| *cis*-9,*trans*-12 | 4 | 56 | 28 | 12 |
| *trans*-9,*cis*-12 | 4 | 55 | 29 | 12 |

purification was achieved by passage through a silver-exchanged resin column (4). Methyl *cis*-9,*trans*-12-octadecadienoate (*c,t*-Lo) and methyl *trans*-9,*cis*-12-octadecadienoate (*t,c*-Lo) were obtained from the methyl esters of dehydrated ricinoleic and ricinelaidic acids, respectively, by chromatography on a Ag-exchanged resin column. By capillary gas liquid chromatography (GLC) (5) and by ozonolysis (6), all isomers were better than 95% pure.

Alkali isomerization was carried out according to the official AOCS method (7), except the reaction time was 6 hr for *t,t*-Lo and 2.5 hr for *c,t*-Lo and *t,c*-Lo. Isomerized acids were converted into methyl esters with $BF_3$-MeOH reagent (8). The isomerized methyl esters were separated into *trans,trans*-; *cis,trans*-; and *cis,cis*- conjugated diene fractions by chromatography on a Ag-exchanged resin column. The *cis,trans*-conjugated diene includes all the isomers in which one double bond has *trans* configuration. Composition of the conjugated isomers shown in Table I was calculated from weight recovery and purity of the fractions. *cis,cis*-Conjugated diene fraction contained both unconjugated diene and *cis,cis*-conjugated diene. The latter was obtained by preparative GLC of the *cis,cis*-conjugated diene fraction. The position of double bonds in the various fractions as shown in Table II was determined by reductive ozonolysis (6).

Based on theoretical considerations, Nichols et al. (1) predicted that shifting of a *cis* double bond forms a new bond predominantly with a *trans* configuration, whereas shifting of a *trans* double bond forms a new bond with either *cis* or *trans* configuration. According to these rules *t,t*-Lo should conjugate to *trans,trans*- and *cis,trans*- conjugated dienes, while *c,t*-Lo and *t,c*-Lo should form all three isomers. The conjugated isomers formed from the three geometrical isomers of linoleate (Table I) are in accordance with these theoretical predictions.

*t,t*-Lo formed more *trans,trans*-conjugated diene (56%) than *cis,trans*-conjugated diene (39%). *c,t*-Lo and *t,c*-Lo formed more *cis,trans*-conjugated diene than *cis,cis*-conjugated diene. Apparently the *trans* double bonds shift to assume preferentially *trans* configuration. In *c,t*-Lo and *t,c*-Lo, if both double bonds shift at the same rate, equal amounts of *trans,trans*-conjugated diene and *cis,trans*-conjugated diene plus *cis,cis*-conjugated diene would be expected. Actually more *trans,trans*-conjugated diene formed than the other two isomers combined. Apparently *cis* double bonds move faster than *trans* double bonds during conjugation with alkali.

Conjugation of $\Delta^9$ and $\Delta^{12}$ double bonds in the geometrical isomers of linoleate should form $\Delta^{9,11}$ - and $\Delta^{10,12}$ -conjugated diene isomers. Presumably, the $\Delta^{8,10}$ - and $\Delta^{11,13}$ -isomers in the various fractions (Table II) are secondary reaction products, since they occur in larger quantities in alkali-isomerized *t,t*-Lo that was heated for 6 hr than in alkali-isomerized *c,t*-Lo and *t,c*-Lo that were heated for 2.5 hr. To test whether isomerization does indeed occur during prolonged heating, methyl esters of alkali-isomerized linoleate were heated at 180 C for 1 hr with ehtylene glycol-KOH reagent. Upon ozonolysis, methyl esters of the isolated fatty acids showed 8% of $\Delta^{8,10}$ - and $\Delta^{11,13}$ -conjugated isomers, whereas the original esters contained only 4%. From the ozonolysis data, it cannot be determined which double bond in the *cis,trans*-conjugated dienes had the *trans* configuration.

GLC analysis of alkali-isomerized esters showed that ca. 4-5% of the original diene esters did not conjugate (Table I) during treatment with alkali. The unconjugated dienes from c,t-Lo and *t,c*-Lo eluted with *cis,cis*-conjugated dienes during chromatography on a Ag-resin column, whereas the original esters eluted much later on the same column. Elution behavior of the unconjugated dienes was similar to *t,t*-Lo. To further characterize the nature of the unreacted dienes, a sample of methyl linoleate was alkali-isomerized

TABLE II

Distribution of Positional Isomers in Conjugated Diene Fractions

| Position of double bonds | *trans,trans*-Conjugated diene from | | | *cis,trans*-Conjugated diene[a] from | | | *cis,cis*-Conjugated diene from | |
|---|---|---|---|---|---|---|---|---|
| | *trans*-9,*trans*-12-Octadecadienoate | *cis*-9,*trans*-12-Octadecadienoate | *trans*-9,*cis*-12-Octadecadienoate | *trans*-9,*trans*-12-Octadecadienoate | *cis*-9,*trans*-12-Octadecadienoate | *trans*-9,*cis*-12-Octadecadienoate | *cis*-9,*trans*-12-Octadecadienoate | *trans*-9,*cis*-12-Octadecadienoate |
| 8,10 | 6 | 2 | 2 | 10 | 5 | 4 | 2 | 4 |
| 9,11 | 46 | 4 | 91 | 36 | 75 | 17 | 92 | 7 |
| 10,12 | 43 | 93 | 5 | 44 | 16 | 72 | 4 | 87 |
| 11,13 | 5 | 1 | 2 | 10 | 4 | 7 | 2 | 2 |

[a] *cis,trans*-Conjugated diene includes all the isomers in which one double bond has *trans* configuration.

for 25 min, and the unreacted diene was isolated by preparative GLC. IR analysis (9) showed 107% *trans*. Ozonolysis indicated that 44% of the first double bond moved equally in both directions. Aldehydes containing 5, 6 and 7 carbon atoms were present. Apparently during alkali-isomerization, a small amount of diene isomerizes to a nonconjugatable type of diene.

SAMBASIVARAO KORITALA
Northern Regional Research Laboratory,
ARS, USDA,
Peoria, Illinois 61604

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REFERENCES

1. Nichols, P.L., Jr., S.F. Herb and R.W. Riemenschneider, J. Amer. Chem. Soc. 73:247 (1951).
2. Jackson, J.E., R.F. Paschke, W. Tolberg, H.M. Boyd and D.H. Wheeler, JAOCS 29:229 (1952).
3. Harlow, R.D., C. Litchfield and R. Reiser, Ibid. 40:505 (1963).
4. Emken, E.A., C.R. Scholfield and H.J. Dutton, Ibid. 41:388 (1964).
5. Scholfield, C.R., and H.J. Dutton, Ibid. 48:228 (1971).
6. Stein, R.A., and N. Nicholaides, J. Lipid Res. 3:476 (1962).
7. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I, Third Edition, AOCS, Champaign, Ill., 1964, Method Cd-7-58.
8. Metcalfe, L.D., and A.A. Schmitz, Anal. Chem. 33:363 (1961).
9. Allen, R.R., JAOCS 46:552 (1969).

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# Thickening Action of Hydroxystearates in Peanut Butter

## ABSTRACT

When 0.5-1% of 12-hydroxystearic acid or the corresponding triglyceride is incorporated into unhardened peanut butter, the resulting product has stiff creamy consistency, and no oil separation takes place upon standing. Sensory evaluation of this peanut butter indicated that it was indistinguishable from typical commercial material in flavor and texture.

We wish to report that when either 12-hydroxystearic acid or tri-12-hydroxystearin (both derived from hydrogenated castor oil) is added at the level of 0.5-1.0% to unhardened peanut butter, the resulting product is indistinguishable from commercial, hardened peanut butter. Hydroxystearates increase the viscosity of hot aqueous starch and flour pastes (1), and it was of interest to examine a largely lipid-containing system for comparison. Thus we tested a number of derivatives of 12-hydroxystearic acid including the triglyceride, monoglyceride and the ethylene and propylene glycol monoesters. Thickening activity paralleled the melting point of the additivies, and this factor was confirmed by the ineffectiveness of the closely related ricinoleic (12-hydroxyoleic) acid, its triglyceride (castor oil) and monoglyceride, the first and second of which are liquid at room temperature with the third being a low melting solid. However these ricinoleates all behave much like the hydroxystearates in the aqueous starch systems mentioned above. Also examined were monostearin, stearic acid and tripalmitin. At the levels employed (0.5-1%) hardening action was minimal and oil separation occurred upon standing.

The solubility characteristics of the test compounds in vegetable oil were examined by dissolving the substances (1%) in hot oil and then permitting the mixtures to stand overnight at room temperature. The hydroxystearates formed gelatinous crystalline matrixes, in contrast to the nonhydroxy derivatives which either formed no crystals at all or the crystals of which were not held in suspension. The behavior of 9,10-dihydroxystearic acid and of 12-ketostearic acid was also examined in oil at the same concentration. Crystals which formed from these materials did not produce significant thickening, but rather settled out. Formation of satisfactory gels is restricted to the hydroxystearates, the most effective of which is the free acid.

Peanut butter samples for sensory evaluation were prepared from a brand of unhardened peanut butter containing salt only. Glucose, 1.5%, was added in finely powdered form to adjust the sweetness to that of the commercial hardened variety chosen for comparison.. The appropriate amount of 12-hydroxystearic acid or tri-12-hydroxystearin was added, and the mixture was warmed to ca. 90 C and blended with a household cycloidal mixer at ca. 50 cycles per minute for 5 min. The samples were stored overnight at 5 C before being warmed to room temperature and submitted to the evaluation panel. Experimental samples were compared against the commercial peanut butter as control, using the duo-trio test and a panel of 15 untrained judges who replicated each comparison twice giving a total of 30 judgements per comparison. The tests were conducted in a room with individual booths under subdued lighting to eliminate possible color differences between samples. Each judge received ca. 15 g of each sample for tasting as is. The results are shown in Table I.

TABLE I

Peanut Butter Test Results

| Comparison | Judgments | | |
|---|---|---|---|
| | Total | Correct | Preferring control |
| 0.5% 12-Hydroxystearic acid vs. control | 30 | 16 | 12 |
| 1.0% Tri-12-hydroxystearin vs. control | 30 | 15 | 17 |

[a] Twenty correct judgments needed for significance at P = 0.05.

From this test it is clear that the judges were unable to discriminate between peanut butter containing additive and the standard commercial control. This indicates that the additive did not cause significant alterations in flavor or texture of the product, at the level tested.

The hydroxystearates are nontoxic (2), as was demonstrated by Binder and coworkers in a series of rat-feeding studies. No adverse effects were noted, except for somewhat reduced growth in rats fed 10% of hydrogenated castor oil. Lower digestibility of this diet rather than chemical growth inhibition was cited as the cause of the lesser growth. No laxative activity is observed with derivatives of hydroxystearic acid (3). Castor oil itself has been used as a frying oil in China and also in India as an adulterant of various edible oils (4). Foods that contain other hydroxy fatty acids include milk (5) as well as such items as apples and pears (6). These facts suggest that 12-hydroxystearic acid and derivatives thereof should be