dition to dilinoleic and trilinoleic acids. Furthermore, the polymeric fat acid esters had acid numbers ranging from 2 to 32, and the free fatty acids would be expected to deactivate the catalysts used.

The esters of dilinoleic acid, except for the β-chlorallyl ester, were relatively pure substances, as shown by their saponification numbers and negligible acid values (below 2). Nevertheless, it is probable that, since purification was not accomplished, their rate of polymerization was decreased by the presence of unidentified impurities. In their study of the polymerization of styrene, Thompson and Burk (18) showed that even as little as 0.2% of an added substance produced a marked inhibiting effect.

It is probable that substantial improvement in the properties of both esters and polymers could be achieved if satisfactory methods of purification were found. Solvent extraction is being considered for this purpose.

Another factor which was believed to be partly responsible for the failure of the esters to polymerize readily is that the fat acid portions of the esters also contain unsaturation. If it participates in the polymerization, this unsaturation might interfere with smooth polymerization through the allyl groups. As a check on this, allyl ester of tetrahydrodilinoleic acid (5) was prepared, but it failed to show any superiority or inferiority in polymerization.

Utilization Studies. When the fusible polymers isolated by extraction were converted to the infusible form, the products appeared too weak to be of value as plastics, films, etc. However, if the fusible form was mixed with a catalyst and a filler, such as "Kalvan," and molded under heat and pressure, discs that were quite hard and strong could be obtained. Inspection of broken specimens showed a laminar structure, which caused the discs to fracture at right angles to the direction of the molding pressure. It is believed that a suitable choice of filler, catalyst, and molding conditions would produce a more nearly isotropic molded product. These factors were not investigated.

Suggested Uses for Polymers

The properties of these polymers suggest possible uses as modifiers and softening agents in the production of various other polymers, as tackifiers and softening agents for elastomers, and as components of surface coatings for special purposes. None of these possibilities were investigated.

Summary

1. Allyl, β-methallyl, and β-chlorallyl esters have been prepared from polymeric soybean fat acids by direct esterification and from dilinoleic acid by trans-esterification of methyl dilinoleate.

2. The method of polymerizing the esters and the properties of the polymers are described.

Acknowledgment

The authors express their indebtedness to R. W. Powers for his assistance in conducting the experimental work and to the Procter and Gamble Company, Cincinnati, Ohio, for its cooperation in supplying the methyl esters of polymeric fat acids used in this investigation.

REFERENCES

1. Bradley, T. F. and Johnston, W. B. Ind. Eng. Chem. *32*, 802-9 (1940).
2. *Ibid. 33, 86-9 (1941).*
3. Bradley, T. F. U. S. Patent 2,311,327, February 16, 1943.
4. Coleman, G. H. and Hadler, B. C. U. S. Patent 2,127,660, August 23, 1938.
5. *Ibid.*, 2,159,008, May 23, 1939.
6. Cowan, J. C. and Wheeler, D. H. J. Am. Chem. Soc. *66*, 84-88 (1944).
7. Falkenburg, L. B., Teeter, H. M., Skell, P. S., and Cowan, J. C. American Oil Chemists' Society Meeting, Chicago, Illinois, October, 1943. In press.
8. Groll, H. P. A. and Hearne, G. U. S. Patent 2,164,188, June 27, 1939.
9. Hearne, G., Tamele, N. and Converse, W. Ind. Eng. Chem. *33*, 805-9 (1941).
10. Hoffman, H. D. and Green, C. E. Oil and Soap *16*, 236 (1939).
11. Kass, J. P., Norris, F. A. and Burr, T. O. Cincinnati Meeting Am. Chem. Society, 1940.
12. Muskat, I. E. U. S. Patent 2,306,136, December 22, 1942.
13. Pollak, M. A. U. S. Patent 2,306,139, December 22, 1942.
14. Ryan, J. D. and Shaw, F. B., Jr. J. Am. Chem. Soc. *62*, 3469 (1940).
15. Staudinger, H. and Fleitmann, T. Ann. *480*, 92, (1930).
16. Tamele, M., Ott, C. J., Marple, K. E. and Hearne, G. Ind. Eng. Chem. *33, 115-20 (1941).*
17. Taylor, F. L. U. S. Patent 2,221,275, November 12, 1940.
18. Thompson, H. E. and Burk, R. E. J. Am. Chem. Soc. *57*, 711-13 (1935).

Spectrophotometric Analysis of Alkali-Isomerized Synthetic Glycerides[1]

A. R. BALDWIN[2] **and B. F. DAUBERT**
Department of Chemistry, University of Pittsburgh

THE application of the spectrophotometric method for the quantitative determination of linoleic and linolenic acids in fats and oils has been suggested by several investigators. Burr and Miller (1) found Moore's (2) reaction could be made reproducible with oils and thus an empirical quantitative measure of linoleic and linolenic acids could be obtained. These investigators subjected cottonseed, corn, almond, peanut, sunflower, castor, and olive oil to alkali isomerization and on the data obtained from spectral curves calculated the linoleic content of each oil. Similar analyses by Bradley and Richardson (3), Mitchell, Kraybill, and Zscheile (4), and Barnes, Rusoff, Miller, and Burr (5) have yielded data to support the fact that the quantitative estimation of the linoleic acid and linolenic acid content of fats can be placed on a satisfactory basis by spectrophotometric methods. Mitchell, Kraybill, and Zscheile (4) particularly, have shown that the percentages of linoleic and linolenic acids in soybean and linseed oils, calculated from spectral curves of the isomerized oils, were in good agreement with the percentages as obtained by the Kaufmann method on the mixed acids. This agreement between spectrophotometric and the Kaufmann methods is obtained only if empirical thiocyanogen values are used. Mitchell, *et al.* (4) have indicated that the amounts of linoleic, linolenic, oleic, and saturated acids may be determined in an oil simply and accurately when the iodine value of the oil is known, par-

---

[1] The generous assistance of the Buhl Foundation and the Nutrition Foundation, Inc. is acknowledged; Contribution No. 559 from the Department of Chemistry, University of Pittsburgh.

[2] Present address: Corn Products Refining Company, Argo, Illinois.

ticularly when other acids of two or more double bonds are not present.

Since several synthetic glycerides containing linoleic and linolenic acids were available in our laboratory, in a high degree of purity as determined by chemical methods, they were subjected to alkali isomerization. The percentages of the unsaturated acids in the glycerides calculated from the extinction coefficient at 234 mμ and 270 mμ support the conclusion of others that the amounts of these acids can be determined by spectrophotometric analysis with a reasonable degree of accuracy.

All of the synthetic glycerides were examined, before alkali isomerization, for preformed conjugation of two and three double bonds by measuring the absorption of the glycerides in iso-octane solution. The linoleic and linolenic acids which were used as the starting materials in the syntheses were prepared by debromination of the corresponding bromostearic acids in ether solution. This procedure has been reported (6) to cause increased conjugation of double bonds. The actual amounts of conjugated diene and triene material in our acids prepared by this method were relatively small and were somewhat lower than reported by Brode, *et al.* (6). It may be apropos, however, to point out that when either fatty acid is heated in the presence of air during the removal of ether following debromination or at any subsequent time, the conjugation increases materially. In general, our experience has indicated that manipulation of glycerides containing these unsaturated acids in the presence of air tends to increase the conjugated double bond material. It has been found that although the preparation and purification of simple and mixed triglycerides containing linoleic and linolenic acids resulted in increased conjugation, the amount was small and may be considered almost insignificant. The preformed conjugation in the glycerides containing only linolenic acid amounted to less than 1% diene and 0.15% triene as maximum values. In the simple and mixed triglycerides containing linoleic acid the percentage of diene conjugation was less than 1.5% and that for triene conjugation less than 0.2%. Complete spectrophotometric data on the preformed conjugation in these and other synthetic glycerides have been reported in previous publications (7, 8).

Experimental

Preparation of Synthetic Glycerides. The linoleic acid and linolenic acid were prepared from tetrabromostearic acid (m.p. 115°) and hexabromostearic acid (m.p. 186°), respectively, by the method of Frankel and Brown (9).

The fatty acid chlorides and the synthetic glycerides were prepared by methods described in previous publications (10, 7, 8). The methyl linoleate and methyl linolenate used as standards were prepared from the same debromination acids as the fatty acid chlorides and synthetic glycerides. The highly purified glycerides after preparation were vacuum sealed in pyrex tubes and stored at —30°.

Spectrophotometric Analysis for Preformed Conjugation. Approximately 0.1 g. of glyceride was dissolved in iso-octane and proper dilutions made to obtain appropriate density readings in the Beckman Spectrophotometer.

As indicated in the introduction, the amount of preformed diene and triene conjugation was small and therefore was not considered in the final calculations of the alkali isomerized products.

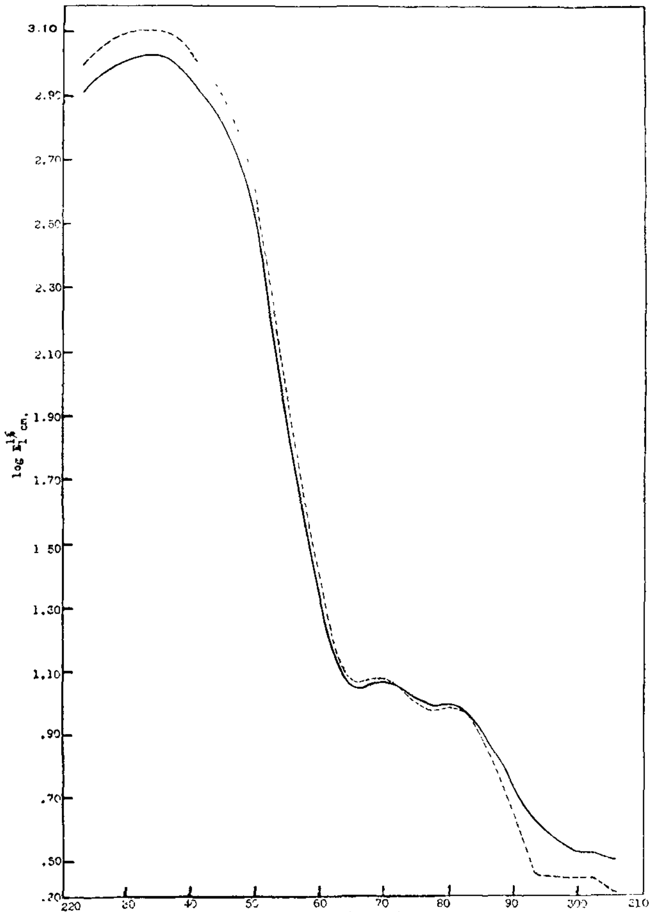

FIG. 1. Absorption curves of alkali isomerized glycerides, ——— 1-monolinolein, – – – – – trilinolein.

Alkali Isomerization of the Synthetic Glycerides. Isomerization of approximately 0.1 g. samples was carried out by a modification (11) of the method of Mitchell, Kraybill and Zscheile (4).

$E^{1\%}_{1\ cm.}$ values were calculated by the relationship, $E^{1\%}_{1\ cm.} = \frac{d}{cl.}$, where d is the optical density, c is the concentration (gm./100 cc.) of fat in the dilution measured, and l is the length of the absorption cell in centimeters. All optical density measurements were made in the Beckman Spectrophotometer.

The $E^{1\%}_{1\ cm.}$ values for the isomerized purified methyl esters were lower than those calculated from the standard acid values of Mitchell, Kraybill, and Zscheile (4). The average $E^{1\%}_{1\ cm.}$ value for isomerized methyl linoleate was 802 at 234 mμ and for methyl linolenate 529 at 234 mμ and 453 at 270 mμ. Because we have consistently obtained these values by the method of isomerization used, we feel justified in using them as standard $E^{1\%}_{1\ cm.}$ values for calculation of the linoleic acid and linolenic acid present in the glycerides in preference to those of Mitchell, *et al.*

Discussion

IN Table I are listed the $E^{1\%}_{1\ cm.}$ values obtained from optical density measurements at 234 mμ for methyl linoleate, 1-monolinolein, trilinolein, and 1-linoleyl-2,3-

dipalmitin. Typical absorption curves for 1-monolinolein and trilinolein are shown in Figure 1. It will be observed in the curves that the absorption peaks at 270 mμ indicate the presence of conjugated triene material. Since little or no absorption at this wavelength was evident for the original isomerized methyl linoleate, this absorption at 270 mμ represents an increase over and above that observed as preformed conjugated triene. This increase was evident for all the glycerides containing linoleic acid that were subjected to alkali isomerization. Because of the absence of conjugated triene in the original methyl ester and the small percentage of preformed conjugation in the unisomerized glycerides, no correction at 234 mμ was made for the absorption at 270 mμ. The $E^{1\%}_{1\text{ cm.}}$ values given in Table I are those calculated from the optical density measurements at 234 mμ. Since we are not prepared at this time to offer an explanation for the apparent increase in triene absorption at 270 mμ, a correction for the absorption at 234 mμ is, in our opinion, unjustifiable. In any case, the corrections are small and would have little effect on the final $E^{1\%}_{1\text{ cm.}}$ values at 234 mμ.

TABLE I

Experimental and Calculated $E^{1\%}_{1\text{ cm.}}$ Values at 234 mμ for Alkali Isomerized Synthetic Glycerides of Linoleic Acid.

	$E^{1\%}_{1\text{ cm.}}$	
	Found	Calculated
Methyl Linoleate	802	......
1-Monolinolein	663	666
Trilinolein	797	805
1-Linoleyl-2,3-dipalmitin	275	284

The calculated and found percentages for the linoleic content of the glycerides calculated as methyl linoleate are listed in Table II. It may be seen that a comparison of the found and calculated percentages indicate very good agreement.

TABLE II

Percentages of Linoleic and Linolenic Acids Calculated as the Methyl Esters in the Synthetic Glycerides.

	Found	Calculated
1-Monolinolein	82.7	83.0
Trilinolein	99.4	100.4
1-Linoleyl-2,3-dipalmitin	34.3	35.4
1-Monolinolenin	80.1	82.9
Trilinolenin*	94.7	100.5

*The trilinolenin which was subjected to alkali isomerization was stored at —30° in vacuum. Even with these precautions, the triglyceride developed a slight yellow color. This may in part account for the difference in the found and calculated values. Iodine value (Wijs) of the freshly prepared trilinolenin was 261.4 (theory 261.6).

Typical absorption curves for 1-monolinolenin and trilinolenin are shown in Figure 2, and in Table III are given the $E^{1\%}_{1\text{ cm.}}$ values at 234 and 270 mμ. In the curves in Figure 2 it may be observed that inflection points present at 301 mμ and the absorption peak at 316 mμ represent conjugated tetraene material. The found percentages of linolenic acid, as methyl linolenate, in the glycerides and those calculated from the $E^{1\%}_{1\text{ cm.}}$ values (Table III) are listed in Table II. Although the calculated and found percentages are not in as good agreement as expected from the high degree of purity of the compounds as indicated by chemical methods, the results are adequate, particularly when the susceptibility of these glycerides to chemical change during manipulation is taken into consideration.

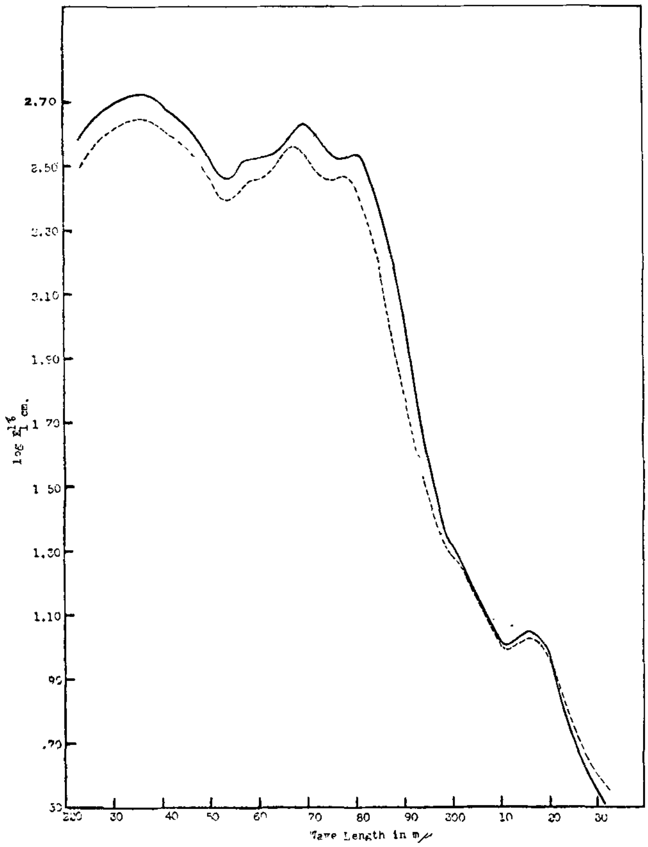

FIG. 2. Absorption curves of alkali isomerized glycerides, ----- 1-monolinolenin, ———— trilinolenin.

TABLE III

Experimental and Calculated $E^{1\%}_{1\text{ cm.}}$ Values at 234 and 270 mμ for Alkali Isomerized Synthetic Glycerides of Linolenic Acid.

	$E^{1\%}_{1\text{ cm.}}$ 234 mμ		$E^{1\%}_{1\text{ cm.}}$ 270 mμ	
	Found	Calculated	Found	Calculated
Methyl Linolenate	529	......	453	......
1-Monolinolenin	447	439	363	376
Trilinolenin	537	532	429	455

It seems, therefore, that the estimation of the linoleic and linolenic acid content of glycerides can be placed on a quantitative spectrophotometric basis, and the method should be adaptable to oils and fats containing glycerides of these acids.

Summary

Spectrophotometric data for several synthetic glycerides containing linoleic and linolenic acids are reported.

BIBLIOGRAPHY

1. Burr, G. O., and Miller, E. D., Chem. Rev., *29*, 419 (1941).
2. Moore, T., Biochem. J., *31*, 138 (1937).
3. Bradley, T. F., and Richardson, D., Ind. Eng. Chem. *34*, 237 (1942).
4. Mitchell, J. H., Jr., Kraybill, H. R., and Zscheile, F. P., Ind. Eng. Chem., Anal Ed., *15*, 1 (1943).
5. Barnes, R. H., Rusoff, I. I., Miller, E. S., and Burr, G. O., Ind. Eng. Chem., Anal. Ed. *16*, 385 (1944).
6. Brode, W. R., Patterson, J. W., Brown, J. B., and Frankel, J., Ind. Eng. Chem., Anal. Ed., *16*, 77 (1944).
7. Daubert, B. F., and Baldwin, A. R., J. Am. Chem. Soc., *66*, 997 (1944).
8. Daubert, B. F., and Baldwin, A. R., J. Am. Chem. Soc., *66*, 1507 (1944).
9. Frankel, J., and Brown, J. B., J. Am. Chem. Soc. *65*, 415 (1943).
10. Wood, T. R., Jackson, F. L., Baldwin, A. R., and Longenecker, H. E., J. Am. Chem. Soc., *66*, 287 (1944).
11. Baldwin, A. R., and Longenecker, H. E., Oil and Soap, in press, (1945).