9. Koritala, S., J.P. Friedrich and T.L. Mounts, Ibid. 57:1 (1980).
10. Johansson, L.E., and S.T. Lundin, Ibid. 56:981 (1979).
11. Koritala, S., and E. Selke, Ibid. 48:222 (1971).
12. Adkins, H., E.E. Burgoyne and H. Schneider, J. Am. Chem. Soc. 72:2626 (1950).
13. Miya, B., F. Hoshino and I. Iwasa, J. Catalysis 5:401 (1966).
14. Johansson, L.E., and S.T. Lundin, JAOCS 56:974 (1979).
15. Stroupe, J.D., J. Am. Chem. Soc. 71:569 (1949).
16. Konetzke, G., H. Aring, P.E. Nau, G. Kunicke and J. Hille, Chem. Technol. 25:40 (1973).
17. D'Huysser, A., A. Lucchetti, G. Wrobel and J.P. Bonelle, J. Microsc. Spectrosc. Electron. 2:609 (1977).
18. Schreifels, L.A., A. Rodero and W.E. Swartz, Jr., J. Appl. Spectrosc. 33:380 (1979).
19. Moulton, K.J., D.J. Moore and R.E. Beal, JAOCS 46:662 (1969).
20. Koritala, S., and C.R. Scholfield, Ibid. 47:262 (1970).
21. Kirschner, E., and E.R. Lowrey, Ibid. 47:237 (1970).
22. Gargano, M., P. Giannoccaro and M. Rossi, J. Organomet. Chem. 84:389 (1975).
23. Fragale, C., M. Gargano and M. Rossi, JAOCS 56:498 (1979).
24. Cocks, L.V., and C. Van Rede, Laboratory Handbook for Oil and Fat Analysts, Academic Press, London, 1966, pp. 152-156.
25. Briggs, D., Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy, Heyden, London, 1977, chap. 1, 3, 5, and 7.
26. Di Castro, V., C. Fragale, C. Furlani, M. Gargano, G. Mattogno and M. Rossi, XIII Congr. Naz. Chim. Inorg. C22:237 (1980).
27. Capece, F.M., V. Di Castro, C. Fragale, C. Furlani, M. Gargano, G. Mattogno and M. Rossi, J. Spectrosc. (in press).
28. Capece, F.M., V. Di Castro, C. Fragale, C. Furlani, M. Gargano, G. Mattogno and M. Rossi, XIV Congr. Naz. Chim. Inorg. D8: 234 (1981).
29. Van Den Bosh, G., JAOCS 50:421 (1973).

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cis-trans Isomerization of Unsaturated Fatty Acids with *p*-Toluenesulfinic Acid

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ABSTRACT

Elaidination of unsaturated fatty acids using *p*-toluenesulfinic acid yielded 77-80% total *trans* unsaturation in the products. Results from reactions with monoene, diene, and triene isomers indicated that only geometric isomerization takes place. Each double bond isomerized randomly and independently in the polyunsaturated fatty acids. Reactions proceeded quickly, and the method proved convenient and reliable.

INTRODUCTION

Much research has been done to find a convenient method for *cis-trans* isomerization of long-chain fatty acids. Nitrous acid and selenium, although mild reagents, produce byproducts difficult to remove; side reactions and impurities occur more readily with polyunsaturates than with monounsaturates during isomerization (1). Recently, Gibson and Strassburger reported *p*-toleuensulfinic acid as a good reagent to accomplish the geometric isomerization of methyl oleate (2). We have extended the study to include polyunsaturated methyl esters.

EXPERIMENTAL

Pure methyl esters were prepared using counter double current distribution (3). Methyl *cis*-9,*cis*-15 octadecadienoate was prepared by argentation countercurrent distribution of hydrazine-reduced linolenic acid (4). *p*-Toluenesulfinic acid was prepared by acidification of the sodium salts (5).

In the elaidination experiments, which were carried out in a manner similar to those of Gibson and Strassburger (2), 250-mg methyl ester in 10-ml dioxane was added to 20-mg *p*-toluenesulfinic acid and refluxed 15 min. The cooled mixture was diluted with 25-ml 1N NaOH solution, extracted with petroleum ether, and washed twice with saturated NaCl solution, dried, and evaporated. The overall recovery of methyl ester was 88-93%.

Analyses of the elaidinized mixtures were performed on a Perkin Elmer 3920 Gas Chromatograph using a 50 m × 0.25 mm id Silar 10-C glass capillary column. Column temperature was 170 C; the flow rate was 1.06 mL/min through the column and 175 mL/min through the splitter for a split ratio of 165. The amount of *trans* bonds in the isomerized samples was calculated from the capillary gas chromatograph (GC) data and also was determined by AOCS infrared (IR) spectrometric methods (6). Double bond distribution was determined from the sodium borohydride reduced ozonides (7).

RESULTS AND DISCUSSION

Litchfield et al. indicated an equilibrium mixture containing about 75% *trans* isomer was attained with oleic, linoleic, and linolenic acids were elaidinized with nitrous acid or selenium (1). Results in Table I show that *p*-toluenesulfinic acid-catalyzed isomerizations of these fatty acid methyl esters gave approximately the same 75-25 equilibrium mixture.

In agreement with Gibson and Strassburger (2), isomerization of *cis*-9-octadecenoate yielded 79% *trans*. Analysis of both the *trans* and *cis* monoene fractions for positional isomerization showed 100% of the double bond is located at the $\Delta 9$ position.

Two different diene isomers were evaluated, *cis*-9,*cis*-12-octadecadienoate with one methylene group between the double bonds and *cis*-9,*cis*-15-octadecadienoate with 4 methylene groups between the double bonds. Geometric isomers formed during each reaction were identified by comparing equivalent chain length data to values published by Scholfield (8). Total *trans* calculated from GC data is 78% for the 9,12 diene mixture and 79% for the 9,15 diene mixture (Table I). From IR data, the value for the 9,12 diene isomerized mixture was 132% compared to methyl elaidate. A pure sample of methyl *trans*-9,*trans*-12-octa-

TABLE I

cis-trans Isomerization with *p*-Toluenesulfinic Acid

Initial isomer	Final isomer composition[a] (%)				Total *trans* double bonds (GC)	Total *trans* double bonds (IR)
18:1 *c*-9	79.0 *t*[b]	21.0 *c*[c]			79%	79%
18:2 *c*-9,*c*-12	61.7 *t,t*	16.3 *t,c*	16.7 *c,t*	5.3 *c,c*	78%	77%
18:2 *c*-9,*c*-15	61.6 *t,t*	18.8 *t,c*	15.5 *c,t*	4.1 *c,c*	79%	80%
18:3 *c*-9,*c*-12,*c*-15	47.6 *t,t,t*	41.1 *t,t,c*[d]	10.3 *t,c,c*[e]	1.0 *c,c,c*	79%	79%

[a] Determined from capillary GC data.

[b] *t* = *trans*.

[c] *c* = *cis*.

[d] Total amount of 3 di-*trans* isomers.

[e] Total amount of 3 mono-*trans* isomers.

decadienoate gave a value of 169%, which agrees with 166% reported by Scholfield et al. in 1963 (9). By comparison with the pure *trans*-9,*trans*-12-diene, the isomerized 9,12 diene mixture contained 77% *trans* double bond as shown in Table I. The value for the 9,15 diene mixture was 160% compared to elaidate. Each *trans* double bond in methyl *trans*-9,*trans*-15-octadecadienoate being equivalent to the single bond in elaidate, the value for pure *trans*-9,*trans*-15 was 199%. The isomerized 9,15 mixture therefore contained 80% *trans* double bond when compared to *trans*-9, *trans*-15 diene.

Identification of the elaidinized triene samples was made using equivalent chain lengths from GC data, as determined by Rakoff and Emken (10). The gas chromatogram of the isomerized sample (Fig. 1) showed 6 peaks. The tri-*trans* fraction in peak 1 equaled 47.6%; peak 2 (27.4%) consisted of 2 isomers, *t,c,t* and *c,t,t*; peak 3 (17.2%) was comprised of *t,t,c* and *c,c,t*; peak 4 (3.1%) *t,c,c*-triene; peak 5 (3.9%) *c,t,c*; and all *cis*-isomer remained in peak 6 (1%). Random distribution in the diene fraction yielded approximately equal amounts of *c,t* and *t,c* isomers (Table I). Assuming this randomization with triene isomers, then peak 2 was composed of equal amounts of di-*trans* isomers calculated at 13.7%. Peak 3 comprised of a di-*trans* and a mono-*trans* isomer partitioned into 13.7% *t,t,c*- and 3.5% *c,c,t*-trienes; the latter corresponded to 3.1% and 3.7% mono-*trans*-isomers. The sums of the values of the mono-*trans*- and di-*trans*-isomers are included in Table I. Total *trans* for the triene isomers determined from GC composition was 78%. Total *trans* for the triene mixture was determined by IR in a similar manner as the diene mixtures. The value for the 9,12,15 elaidinized triene mixture was 198% compared to methyl elaite. This result was compared to 258% *trans* value reported for methyl *trans*-9,*trans*-12,*trans*-15-octadecatrienoate (10); thus the total *trans* double bond was 79%. The percentages of all the diene and triene isomers agreed with those expected if the double bonds isomerize randomly and independently.

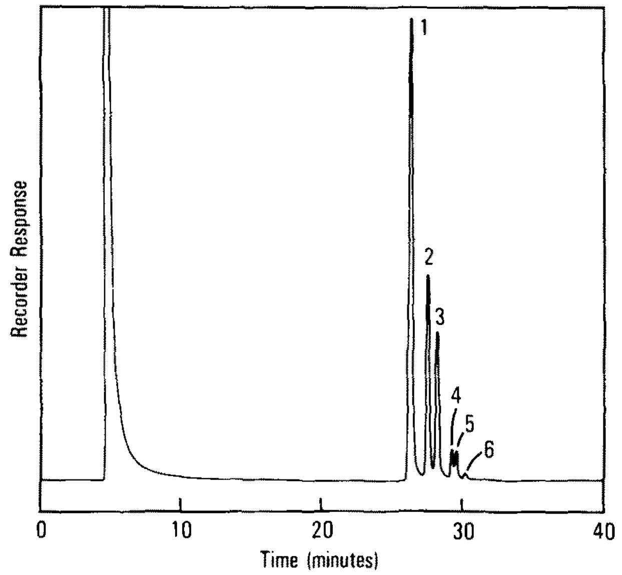

FIG. 1. Gas chromatogram of methyl octadecatrienoate mixture on a 50 m × 0.25 mm id Silar 10C glass capillary column. 1-*t,t,t*; 2-*t,c,t* and *c,t,t*; 3-*t,t,c* and *c,c,t*; 4-*t,c,c*; 5-*c,t,c*; 6-*c,c,c*.

Reductive ozonolysis of the diene and triene isomers indicated there was no positional isomerization. GLC data of the reduced ozonides from the starting samples and the final elaidinized mixtures were identical.

We have shown that impurities are not detected and a purification step is not necessary when unsaturated esters are elaidinized with *p*-toluenesulfinic acid. This reagent is especially useful for polyunsaturates and for precious samples available in limited amounts.

REFERENCES

1. Litchfield, C., J.E. Lord, A.F. Isbell and R. Reiser, JAOCS 40:553 (1963).
2. Gibson, T.W., and P. Strassburger, J. Org. Chem. 41:791 (1976).
3. Scholfield, C.R., R.O. Butterfield and H.J. Dutton, Lipids 1:163 (1965).
4. Butterfield, R.O., C.R. Scholfield and H.J. Dutton, JAOCS 41:397 (1964).
5. Kice, J.L., G. Guaraldi and C.G. Venier, J. Org. Chem. 31:3561 (1966).
6. Official and Tentative Methods of the American Oil Chemists' Society, 3rd edn., AOCS, Champaign, IL, 1974.
7. Johnston, A.E., H.J. Dutton, C.R. Scholfield and R.O. Butterfield, JAOCS 55:486 (1978).
8. Scholfield, C.R., Ibid. 58:662 (1981).
9. Scholfield, C.R., E.P. Jones, R.O. Butterfield and H.J. Dutton, Anal. Chem. 35:1588 (1963).
10. Rakoff, H., and E.A. Emken, accepted by Chem. Phys. Lipids.

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