Methods for the Determination of Cyclopropenoid Fatty Acids. II. A Stepwise Hydrogen Bromide Titration Method for Cyclopropenoid and Epoxy Derivatives

J. A. HARRIS, F. C. MAGNE, and E. L. SKAU, Southern Regional Research Laboratory,[1] New Orleans, Louisiana

Abstract

A rapid titration method is described for the quantitative determination of both cyclopropenoid and epoxy fatty acid derivatives in mixtures. It was found that epoxy compounds can be titrated selectively with Durbetaki reagent at 3C without interference from cyclopropenoid derivatives. Cyclopropenoid derivatives can be titrated much more rapidly to a much sharper end point at 55C than at room temperature. Thus mixtures can be analyzed by first titrating at 3C to determine the epoxy compounds and then continuing the titration at 55C to determine the cyclopropenoid components.

Introduction

A SIMPLE RAPID TITRATION METHOD is presented for the determination of both cyclopropenoid and epoxy fatty acid derivatives in their mixtures. The cyclopropenoid acids, of general formula

$$CH_3(CH_2)_m - \overset{CH_2}{\overset{/\quad\backslash}{C = C}} - (CH_2)_n - COOH,$$

occur as a minor constituent in the fatty acids of cottonseed oil and constitute about 50% of the fatty acids of *Sterculia foetida* oil.

Smith and coworkers (1) found that cyclopropenoid acids interfere with the Durbetaki (2) titration method for epoxides and consume a mole of hydrogen bromide sufficiently rapidly to be mistaken for epoxides. They overcame this interference by eliminating the epoxy compounds either by lithium aluminum hydride reduction (1) or by acetolysis (3). From the Durbetaki titrations before and after such pretreatment the percentage of cyclopropenoid moiety and, by difference, the percentage of oxirane oxygen can be calculated. These titrations are time-consuming and unsatisfactory because of the extreme slowness of the reaction of hydrogen bromide with the cyclopropene ring and the resultant difficult and indefinite end point. The change in sample weight resulting from the pretreatments necessitates corrections which are subject to question of either degree (4) or kind unless complete recovery of the sample is achieved.

The method described below is based upon the findings (A) that epoxy compounds can be titrated with Durbetaki reagent at 3C without interference from cyclopropenoid acid derivatives, and (B) that cyclopropenoid derivatives can be titrated rapidly to a sharp, definite end point at an elevated temperature. Thus a mixture containing both epoxy and cyclopropenoid compounds can be analyzed by a simple stepwise titration with Durbetaki reagent; i.e., by titrating at 3C to determine the epoxy compounds and then continuing the titration at 55C to determine the cyclopropenoid acids.

[1] A laboratory of the So. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.

Procedure

Materials

The *Sterculia foetida* oil employed in this investigation was obtained by petroleum ether extraction of the meats of *Sterculia foetida* seed in a Waring blender. The oil was recovered from the extract by the conventional steps of filtration and stripping at temperatures not exceeding 60C. The oil was kept refrigerated in evacuated glass ampoules. These storage conditions were apparently quite adequate since no change in the hydrogen bromide equivalent was ever observed even after several months.

The corn and cottonseed oils used were commercial salad oils. Two epoxy-containing materials were used: a commercial epoxidized linseed oil containing 1.79% oxirane oxygen, and 1,2-epoxydecane containing 10.16% oxirane oxygen. The 0.1N Durbetaki reagent was prepared from the concentrated solution of HBr in glacial acetic acid obtained from Eastman Kodak Co. It was standardized daily against anhydrous sodium carbonate.

Results and Discussion

It was observed that the rate of the titration of the cyclopropenoid moiety of *Sterculia foetida* oil, which was prohibitively slow at room temperature, decreased as the temperature was lowered until at 3C no titration took place, and that conversely, it increased as the temperature was raised. At the same time, the titration value increased asymptotically up to 50C, remained constant between 50 and 60C, and then increased again because of an obvious loss of hydrogen bromide to the gas phase. On the basis of these observations a titration temperature of 55C was selected. At this temperature a reproducible titration to a sharp end point could be completed within 15–20 min and the resulting cyclopropenoid analysis, 45.58% calculated as sterculic acid, was in good agreement with the value 45.75% obtained by the hydrochloric acid method (5) for the same sample of *Sterculia foetida* oil.

The precision of the 55C titration method for cyclopropenoid fatty derivatives was tested by applying it to a graded series of *Sterculia foetida*-corn oil mixtures covering the whole compositional range and also to an overlapping series with a cottonseed oil instead of corn oil as the diluent. The sample size was varied from 0.5–7.0 g with decreasing *Sterculia foetida* oil concentration. The results obtained, calculated as % sterculic acid, are listed in Table I. The calculated values (column 4) were based upon the experimental value for the *Sterculia foetida* oil, i.e., the 100% value in the table. The corn oil, though cyclopropenoid-free, and the cottonseed oil gave titration values equivalent to 0.38 and 0.13% of sterculic acid, respectively. The values in column 3 have been corrected accordingly to eliminate the contribution of these diluent oils. The average deviation of the observed from the calculated

values for the entire series is only 0.15% and for sterculic acid concentrations below 0.5% it is only 0.03%.

An investigation of the effect of temperature on the Durbetaki titration of epoxides, using epoxidized linseed oil and 1,2-epoxydecane as model compounds, showed that a complete and rapid titration could be achieved at 3C.

On the basis of these observations, it appeared reasonable to assume that both epoxy and cyclopropenoid acids could be determined in mixtures containing both components by resorting to successive titrations on the same sample at 3C and 55C.

Stepwise Titration Procedure. A 0.5- to 7.0-g sample, depending upon the anticipated epoxy and cyclopropenoid content of the oil, is accurately weighed into a 50 ml Erlenmeyer flask and dissolved in 5 ml of benzene and 15 ml of acetic acid. After adding the crystal violet indicator, the flask is attached to the titration burette graduated in 0.05 ml, the magnetic stirrer is turned on, and the solution cooled to 3C by a surrounding ice bath. At this point, it is titrated with Durbetaki reagent to a blue-green end point of at least 30 sec duration. The ice bath is then replaced with a water bath maintained at 55C by a thermostatically controlled hot-plate equipped for magnetic stirring and the solution is titrated again to the same blue-green end point. The two titrations corrected for the solvent blank titration are recorded separately, that at 3C representing the epoxide and that at 55C representing the cyclopropenoid acid.

Analysis of Mixtures. This procedure was tested on a series of known mixtures of epoxidized linseed oil and *Sterculia foetida* oil covering the range from 0–100% of each component. The resulting data are reported in Table II. The calculated percentages in the various mixtures, reported as epoxyoleic and sterculic acids in columns 3 and 6, were calculated from the observed values for the 100% epoxidized linseed oil and *Sterculia foetida* oil samples, respectively. The parenthetical values in columns 2 and 5 are analyses based upon a 55C titration before and after the elimination of the epoxide by the acetolysis procedure of Wilson et al. (3).

Inspection of the data in Table II shows that in the absence of interfering substances oil containing epoxy or cyclopropenoid moieties or both, can be analyzed with a high degree of accuracy by the 3–55C stepwise titration technique. The average deviation of the observed from the calculated values over the entire composition range was 0.17% for the epoxide moiety and 0.15% for the cyclopropenoid moiety. On the other hand, when the acetolysis pretreatment procedure was used, the average deviations on the same compositions were 0.75% and 0.66%.

TABLE I
Analysis of Mixtures of *Sterculia foetida* Oil with Corn Oil by Titration at 55C

% *Sterculia foetida* oil	% Cyclopropenoid acid (as sterculic acid)			
	Observed (uncorr.)[a]	Observed (corr.)[b]	Calculated[c]	Deviation
100.00	49.56	49.56	49.56	.....
72.10	35.70	35.59	35.73	−0.14
75.46	37.35	37.25	37.40	−0.15
34.18	16.94	16.68	16.94	−0.26
34.30	17.20	16.95	17.00	−0.05
10.01	5.08	4.74	4.96	−0.22
9.94	5.24	4.90	4.93	−0.03
8.02[e]	3.85	3.73	3.98	−0.25
5.31	2.73	2.37	2.63	−0.25
5.06	2.61	2.25	2.51	−0.26
4.01[d]	1.94	1.80	1.99	−0.19
2.08	1.27	0.90	1.03	−0.13
2.01[d]	0.99	0.85	1.00	−0.15
1.98	1.23	0.86	0.98	−0.12
1.00[d]	0.59	0.46	0.50	−0.04
0.50[d]	0.36	0.22	0.25	−0.03
0.20[d]	0.22	0.08	0.10	−0.02
0.00	0.38	0.00	0.00	.....
0.00[d]	0.13	0.00	0.00	.....
				avg −0.15

[a] Average of duplicate determinations.
[b] Corrected for contribution of the corn oil or cottonseed oil used as diluent.
[c] Based on value for *Sterculia foetida* oil, 49.56%.
[d] Cottonseed oil instead of corn oil used as diluent.

The results in Table I indicate that so far as precision is concerned the method is adequate for the analysis of oils such as cottonseed oil which have cyclopropenoid-moiety contents corresponding to less than 1% of sterculic acid. However, experiments on a number of refined noncyclopropenoid vegetable oils revealed that in general they contain traces of interfering substances, evidently autoxidation products, which result in small Durbetaki titrations at both 3 and 55C. The stepwise titration method would therefore tend to give results which are a few tenths of a percentage

TABLE II
Analysis of Mixtures of *Sterculia foetida* Oil and Epoxidized Linseed Oil by 3–55C Stepwise Titration Method

% *Sterculia foetida* oil in mixture	% Epoxy acid (as epoxyoleic acid)			% Cyclopropenoid acid (as sterculic acid)		
	Observed[a, b]	Calculated[c]	Deviation	Observed[a, d]	Calculated[e]	Deviation
100.00	0.11	0.00	+0.11	49.39	49.39	0.00
88.33	4.18	3.86	+0.32	43.61	43.63	−0.02
80.23	6.78	6.53	+0.24	39.67	39.62	+0.05
71.24	9.68	9.51	+0.17	35.17	35.18	−0.01
49.98	16.72	16.54	+0.18	24.59	24.68	−0.09
49.98	(16.08)	16.54	(−0.46)	(25.19)	24.68	(+0.51)
49.98	(15.17)	16.54	(−1.37)	(25.98)	24.68	(+1.30)
49.99	16.80	16.53	+0.27	24.59	24.69	−0.10
49.99	(16.18)	16.53	(−0.35)	(25.21)	24.69	(+0.52)
49.99	(17.20)	16.53	(+0.67)	(24.19)	24.69	(−0.50)
48.40	17.20	17.05	+0.14	23.45	23.90	−0.45
33.21	22.30	22.08	+0.22	16.25	16.40	−0.15
33.21	(22.61)	22.08	(+0.53)	(15.96)	16.40	(−0.44)
33.21	(23.24)	22.08	(+1.16)	(15.33)	16.40	(−1.07)
25.06	24.79	24.77	+0.02	12.06	12.38	−0.32
25.06	(24.20)	24.77	(−0.57)	(12.67)	12.38	(+0.29)
25.06	(23.88)	24.77	(−0.89)	(12.99)	12.38	(+0.61)
15.20	28.09	28.03	±0.06	7.34	7.50	−0.16
0.00	33.06	33.06	±0.00	0.13	0.00	+0.13
			avg 0.17			avg 0.15
			(0.75)			(0.66)

[a] Average of duplicate titrations.
[b] Values in parentheses based upon difference between 55C titration values before and after acetolysis.
[c] Based on value for epoxidized linseed oil: 33.06%.
[d] Values in parentheses based upon 55C titration value after acetolysis.
[e] Based on value for *Sterculia foetida* oil: 49.39%.

unit too high. While this error may be considered negligible for high concentrations of epoxy and cyclopropenoid materials, it assumes major significance at low concentrations. Further investigation is being directed toward the elimination of the effect of these trace interfering substances so that the stepwise titration method may be applied to the accurate determination of the cyclopropenoid constituents in cottonseed oils.

REFERENCES

1. Smith, C. R., Jr., M. C. Burnett, T. L. Wilson, R. L. Lohmar, and I. A. Wolff, JAOCS, *37*, 320–323 (1960).
2. Durbetaki, A. J., Anal. Chem., *28*, 2000–2001 (1956).
3. Wilson, T. L., C. R. Smith, Jr., K. L. Mikolajczak, JAOCS, *38*, 696–699 (1961).
4. Gaylord, N. G., Reduction with Complex Metal Hydrides, Interscience Publishers, New York, N. Y. (1956).
5. Magne, F. C., J. A. Harris, and E. L. Skau, JAOCS *40*, 716–717 (1963).
6. King, G., J. Chem. Soc., *1951*, 1980–1984.

[Received December 13, 1962—Accepted April 26, 1963]

Methyl Azelaaldehydate Purification Via the Bisulfite Compound

W. R. MILLER, D. J. MOORE, and J. G. FULLINGTON, Northern Regional Research Laboratory,[1] Peoria, Illinois

Abstract

Methyl azelaaldehydate was obtained at 99.8% purity with 82.5% recovery from the ozonolysis products of commercial methyl oleate by separation as the sodium bisulfite addition compound, regeneration with 10% NaOH, and distillation.

Introduction

PREVIOUS PAPERS from this laboratory (2) have reported the ozonolysis of unsaturated fatty acid derivatives. Separation and purification of individual aldehydic ozonolysis products from certain impurities have presented difficulties because of similarity in physical properties, particularly boiling points. Methyl azelaaldehydate (MAZ) can be obtained in high yield and is an especially versatile intermediate (3). It was sought in a high state of purity for certain studies now under way in this laboratory. Purification of aldehydes through their sodium bisulfite addition compounds is a useful procedure (1) because of the ease of separation of the derivative and of subsequent regeneration of the aldehyde. This paper reports the application of this method to the purification of MAZ from the complex mixture obtained by the ozonolysis of commercial methyl oleate.

Experimental

Reductive decomposition of the ozonolysis product from pure methyl oleate gives two compounds, MAZ and pelargonaldehyde. These compounds are easily separable by simple distillation because the difference in boiling points is about 50°. However, commercial methyl oleate contains a number of other components (Table I), so that the ozonolysis mixture contains saturated esters—methyl laurate, myristate, palmitate, and stearate—as well as aldehydes and aldehyde esters derived from the unsaturated esters. Positional isomers of the unsaturated esters like palmitoleic, give rise to homologs of the desired products. In addition,

TABLE I

Typical Analysis of Commercial Methyl Oleate [a]

Methyl ester	Percentage
Laurate	Trace
Myristate	2.5
Palmitate	5.0
Palmitoleate	3.5
Stearate	1.0
Oleate	79.0
Linoleate	8.0
Linolenate	1.0

[a] Swift and Company, Technical Products Department, Hammond, Ind.

[1] No. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.

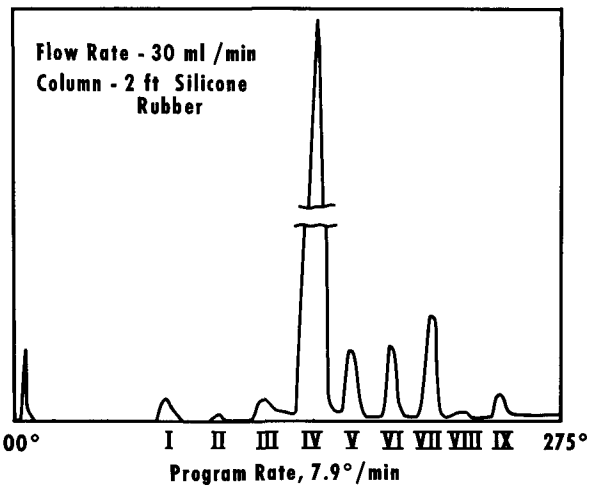

FIG. 1. GLC of Fraction 2, crude methyl azelaaldehydate.

there are present acetals, condensation and oxidation products, and esters like dimethyl azelate, which are formed by decomposition of methoxy hydroperoxides over certain hydrogenation catalysts (2c).

Distillation through a simple Vigreux column of the products obtained from commercial methyl oleate gave three fractions. Fraction 1 consisted of pelargonaldehyde, homologous aldehydes, their acetals, and lower esters. Fraction 2 contained crude MAZ, some homologous aldehyde esters, dimethyl azelate and some of its homologs, acetals, and esters of myristic and palmitic acids. The residue contained esters of higher fatty acids and condensation products. A typical GLC analysis is shown in Figure 1. The identity of the main peaks and the relative quantities are shown in Table II. Fraction 2 contained 79% MAZ and its dimethyl acetal, 4.4% dimethyl azelate and C_{10} aldehyde ester, 4.7% C_{11} aldehyde ester, 6.9% methyl myristate, and lesser quantities of other compounds.

Isolation of MAZ was effected by treatment of Fraction 2 with an aqueous-methanolic saturated solution of sodium bisulfite. The crude crystalline addition compound was removed by filtration and washed with ether to remove C_{14} and C_{16} fatty acid methyl esters, diesters, and acetals. Ether was more effective than ethanol, pentane-hexane, or methylene chloride for washing the adduct. The purified adduct was treated with 10% NaOH solution and the regenerated aldehyde ester distilled. Figure 2 depicts the GLC of the regenerated MAZ. The analyses of regenerated MAZ and of distilled product, 99.8% pure, are