Evaluation of a Gas Chromatogram of a Mixture Containing Aldehydes and Aldehydic Esters Obtained by Oxidative Degradation of the Positional Isomers of Methyl Octadecenoate

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ABSTRACT

A simple method is described to evaluate gas chromatograms of mixtures containing aldehydes and aldehydic esters obtained by ozonolysis of mixtures of positional isomers of methyl octadecenoate. The evaluation is based on the assumption that the process of ozonolysis and the subsequent reduction of the ozonides is independent of the double bond position. This implies the formation of equivalent amounts of aldehydes and aldehydic esters, which results in certain ratios between the values of gas chromatographic peak areas of degradation products from the same molecule. These ratios can be calculated for a flame-ionization detector. Peak area values of partly or completely fused peaks can then easily be corrected.

INTRODUCTION

During the catalytic hydrogenation of methyl oleate with a metal catalyst, isomerization phenomena occur which lead to change of position as well as configuration of the double bond. Several reviews (1-3) have been written about the methods that can be used for the analysis of these reaction mixtures. In general the double bond distribution (DBD) in the mixtures is determined by an oxidative degradation method such as ozonolysis. Very good results are claimed by Privett and Nickel (4), who calculated the composition of isomeric mixtures from the total chromatographic peak area of the two degradation products sprung from the same molecule. These degradation products were obtained after ozonolysis and subsequent reduction of the ozonides. However, when the process of double bond migration proceeds very fast compared with the hydrogenation reaction, many positional isomers are formed, and analysis of the isolated unsaturated fractions via ozonolysis will result in a complicated mixture of aldehydes and aldehydic esters. The gas chromatogram of this mixture will contain some unidentified peaks of artifacts in addition to the peaks of the aldehydic products. Overlapping of one or more peaks is, in general, unavoidable. However the fused peaks can be corrected in a simple manner assuming that ozonolysis and subsequent reduction of the ozonides proceed via a mechanism that is independent of the location of the double bond, so that the total amount of aldehydes and aldehydic esters formed is representative of the original mixture of positional isomers.

The correction method described is based on a certain ratio between the value of a chromatographic peak area of an aldehyde and that of its ester. The theoretical value of this ratio can easily be calculated for a flame-ionization detector (FID).

ANALYSIS

Two samples have been analyzed. One sample (A) originates from the *cis* fraction of partly hydrogenated methyl oleate, while the other sample (B) was obtained from the isolated *cis*-monoene fraction of partly hydrogenated glyceryl trilinoleate. In the latter case the mixture of triglycerides was converted into their methyl esters before separation into *cis*- and *trans*-monoene, diene, etc., was achieved by a method described by de Vries and Jurriens (5).

First 5-10 mg of the sample to be analyzed was dissolved in carbon disulfide. After ozonolysis at -80 C, the ozonides formed were reduced with triphenylphosphine at 40 C for 30 min. The mixture of aldehydes and aldehydic esters was analyzed by single column gas chromatography under the following conditions: column, glass; length, 200 cm; ID, 4 mm; packing, mixture of 5% Carbowax and 5% Apiezon on Diatoport S (80-100 mesh); temperature, programed from 50-200 C (6 C/min); carrier gas, N_2 40 ml/min; detector, FID; H_2, 30 ml/min; air, 200 ml/min; injection, 150 C.

The peak areas were integrated by means of a digital computer via an on-line DATA-acquisition system. Figures 1

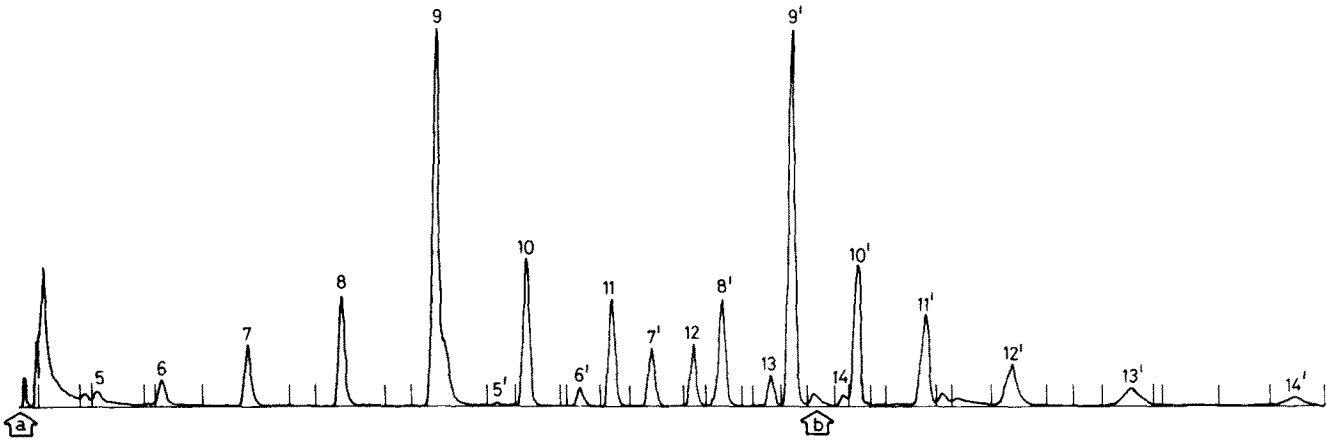

FIG. 1. Gas chromatogram of a mixture of aldehydes and aldehydic esters from the *cis* fraction isolated from partially hydrogenated methyl oleate (sample A). a = moment of injection, temperature, 50 C; b = 25 min after injection, temperature, 200 C; 5-14 are aldehydes; 5'-14' are aldehydic esters.

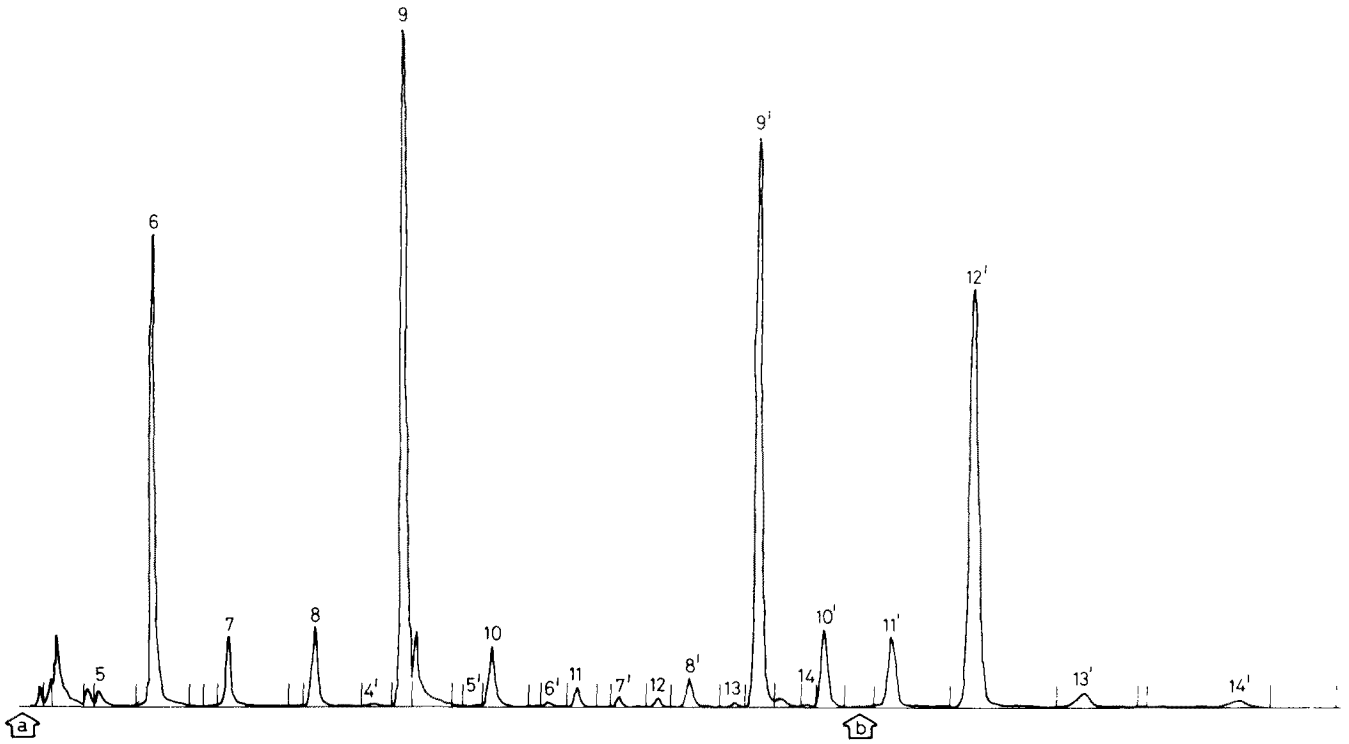

FIG. 2. Gas chromatogram of a mixture of aldehydes and aldehydic esters from the *cis*-monoene fraction isolated from partially hydrogenated and subsequently methylated glyceryl trilinoleate (sample B). a = moment of injection, temperature, 50 C; b = 25 min after injection, temperature, 200 C; 5-14 are aldehydes; 4'-14' are aldehydic esters.

and 2 show the computer plots of the gas chromatograms of samples A and B, respectively. The peak areas were integrated between two minima in the gas liquid chromatography curve and the base line; the position of a minimum is indicated by a vertical line.

As the large excess of triphenylphosphine required for the reduction of the ozonides cannot be removed easily and disturbs a second analysis, the gas chromatograph is operated in single column mode, using the second column of the chromatograph after the first one. Subsequently both columns are stabilized by heating at 200 C for a couple of hours. This procedure is justified by the behavior of the base line, which does not necessitate dual column operation.

METHOD OF EVALUATION

According to Perkins et al. (6), the molar sensitivity factor of a FID is proportional to the effective number of available carbon atoms in such compounds as $C_nH_{2n+1}X$, $C_nH_{2n}X_2$, etc. The effective number of carbon atoms of an aldehyde is equal to m-1, where m represents the total number of carbon atoms. The molar sensitivity factor is then equal to K(m-1) and the sensitivity factor per unit of weight, S_a^m, is:

$$S_a^m = A_a^m/W_a^m = K(m\text{-}1)/M_a^m \quad [1]$$

where A_a^m denotes the peak area, W_a^m the weight and M_a^m the molecular weight of the aldehyde.

The gas chromatograms were evaluated by the normalization method, which was applied separately to the aldehydes and the aldehydic esters. This makes it unnecessary to know the absolute values of the sensitivity factors as defined by equation 1, because the mutual ratios of these factors contain sufficient information. Relating the sensitivity factor of an aldehyde to that of the C_9-aldehyde, we can define the relative sensitivity factor, C_a^m, by:

$$C_a^m = S_a^9/S_a^m = 8 \cdot M_a^m/(m\text{-}1)M_a^9 \quad [2]$$

The relative weight of an aldehyde with m carbon atoms with respect to the total weight of aldehydes present in the injected sample can be calculated from the peak area values and the corresponding relative sensitivity factors:

$$W_a^m/\sum_i W_a^i = \left(A_a^m/S_a^m\right)\Big/\left(\sum_i A_a^i/S_a^i\right) = A_a^m \cdot C_a^m/\sum_i \left(A_a^i \cdot C_a^i\right) \quad [3]$$

The same definitions are valid for the aldehydic esters. Thus the sensitivity factor of an aldehydic ester with n carbon atoms in the chain is:

$$S_e^n = A_e^n/W_e^n = K'(n\text{-}1)/M_e^n \quad [4]$$

where e stands for aldehydic ester. The mutual ratios of the sensitivity factors of the aldehydic esters are now related to the sensitivity factor of the methyl ester of the C_9-aldehydic carboxylic acid. The relative sensitivity factor and the relative weight of an aldehydic ester with n carbon atoms in the carbon chain thus are:

$$C_e^n = S_e^9/S_e^n = 8 \cdot M_e^n/(n\text{-}1)M_e^9 \quad [5]$$

and

TABLE I

Theoretical Relative Sensitivity Factors of Aldehydes (C_a^m) and Aldehydic Esters (C_e^n)

m or n	Relative sensitivity factors	
	C_a^m	C_e^n
4	1.35	1.66
5	1.21	1.40
6	1.13	1.24
7	1.07	1.13
8	1.03	1.06
9	1.00	1.00
10	0.97	0.95
11	0.96	0.92
12	0.94	0.89
13	0.93	0.87
14	0.92	0.85

TABLE II

Double Bond Distribution (DBD) in Samples A and B, Derived from Uncorrected Gas Chromatographic Peak Area Values of Aldehydes and Aldehydic Esters Together with Experimental (R_n) and Theoretical (R'_n) Peak Area Ratios

Sample	Position of double bond	Uncorrected peak area values		DBD (%) based on		R_n	$\frac{m\text{-}1}{n\text{-}1}$	K''	R'_n
		Aldehydes	Aldehydic esters	Aldehydes	Aldehydic esters				
	4	6,805	—	0.5	—	—	3.7	—	3.74
	5	23,160	7,135	1.9	1.9	3.25	3.0	1.08	3.03
	6	48,131	19,212	4.2	4.2	2.51	2.20	1.14	2.22
	7	84,180	50,271	8.2	9.2	1.67	1.67	1.00[a]	1.69
	8	117,721	91,232	12.7	14.3	1.29	1.29	1.00[a]	1.30
A	9	344,373	284,456	41.8	38.9	1.21	1.00	1.21	1.01
	10	85,146	106,275	11.8	12.8	0.80	0.78	1.03[a]	0.79
	11	50,325	84,778	8.2	9.3	0.59	0.60	0.98[a]	0.61
	12	24,845	53,230	4.8	5.3	0.47	0.45	1.04[a]	0.45
	13	24,126	28,396	5.9	2.6	0.85	0.33	2.58	0.33
	14	—	17,855	—	1.5	—	0.23	—	0.23
	4	1,040	2,152	0.06	0.7	0.48	3.7	0.13	4.85
	5	4,003	3,413	0.3	0.8	1.17	3.0	0.39	3.93
	6	6,805	4,397	0.5	0.8	1.55	2.20	0.70	2.88
	7	13,832	8,032	1.1	1.2	1.72	1.67	1.03	2.19
	8	42,781	25,563	3.7	3.4	1.67	1.29	1.29[a]	1.69
B	9	425,497	391,905	41.1	44.7	1.09	1.00	1.09	1.31
	10	52,509	52,677	5.8	5.3	1.00	0.78	1.28[a]	1.02
	11	44,279	54,656	5.7	5.0	0.81	0.60	1.35[a]	0.79
	12	258,011	431,160	40.0	35.7	0.60	0.45	1.33[a]	0.59
	13	9,851	20,348	1.9	1.6	0.48	0.33	1.45	0.43
	14	—	12,082	—	0.9	—	0.23	—	0.30

[a]These values have been selected on the basis of fully resolved peaks to calculate a mean value of K'' with equation 8. Values of 1.01 and 1.31 were found, so $R'_n = 1.01\ (m\text{-}1)/(n\text{-}1)$ and $1.31\ (m\text{-}1)/(n\text{-}1)$ for samples A and B, respectively.

$$W_e^n / \sum_i W_e^i = A_e^n \cdot C_e^n / \sum_i \left(A_e^i \cdot C_e^i \right) \qquad [6]$$

$$R_n = A_a^m / A_e^n = W_a^m \cdot K(m\text{-}1)\, M_e^n / \left\{ M_a^m \cdot K'(n\text{-}1)\, W_e^n \right\} \qquad [7]$$

The relative sensitivity factors calculated with equations 2 and 5 are given in Table I.

The ratio R_n between the peak area values of the degradation products of a positional isomer of methyl octadecenoate, Δ_n, with the double bond located in the n position, is:

bearing in mind that in this equation $m + n = 18$. If we assume that the mechanism of ozonolysis and subsequent reduction of the ozonides is independent of the location of the double bond, yielding aldehydes and aldehydic esters in equivalent amounts, so that both series of degradation products are representative of the DBD in the mixture of

TABLE III

Corrected Double Bond Distributions (DBD) in Samples A and B, Derived from Corrected Peak Area Values of Aldehydes and Aldehydic Esters

Sample	Position of double bond	Corrected peak area values		Corrected DBD (%) based on	
		Aldehydes	Aldehydic esters	Aldehydes	Aldehydic esters
	4	6,805	1,820[a]	0.57	0.66
	5	21,619[a]	7,135	1.95	1.93
	6	42,651[a]	19,212	4.17	4.18
	7	84,180	50,271	9.11	9.10
	8	117,721	91,232	14.02	14.20
A	9	287,301[a]	284,456	38.68	38.61
	10	85,146	106,275	13.11	12.76
	11	50,325	84,778	9.04	9.24
	12	24,845	53,230	5.36	5.25
	13	9,371[a]	28,396	2.52	2.58
	14	4,107[a]	17,855	1.47	1.50
	4	1,040	214[a]	0.06	0.07
	5	4,003	1,019[a]	0.24	0.24
	6	6,805	2,363[a]	0.44	0.44
	7	13,832	6,316[a]	0.98	0.98
	8	42,781	25,563	3.35	3.41
B	9	513,396[a]	391,905	45.40	45.53
	10	52,509	52,677	5.31	5.41
	11	44,279	54,656	5.23	5.10
	12	258,011	431,160	36.58	36.38
	13	8,750[a]	20,348	1.55	1.58
	14	3,624[a]	12,082	0.85	0.87

[a]The magnitudes of these peak areas have been adapted in such a way that the ratio between the peak area value of the aldehyde and that of the corresponding ester is equal to R'_n.

TABLE IV

Analysis of Two Mixtures of Known Composition, Containing Some Positional Isomers of *cis*-Methyl Octadecenoate, Using Two Identical Columns

Mixture	Position of double bond	Composition, %			
		Column I	Column II	Mean	Real
A	6	23.2	22.5	22.8	23.5
	8	30.3	30.5	30.4	29.6
	9	23.1	23.6	23.3	23.2
	10	22.6	22.9	22.8	23.1
	11	0.7	0.6	0.7	0.6
B	6	18.5	18.4	18.4	18.9
	8	24.3	24.5	24.4	23.9
	9	37.7	37.6	37.7	37.5
	10	18.4	18.4	18.4	18.6
	11	1.1	1.1	1.1	1.0

positional isomers, R_n may be written as:

$$R_n = K''(m\text{-}1)/(n\text{-}1) \quad [8]$$

where

$$K'' = W_a^m \cdot M_e^n \cdot K/W_e^n \cdot M_a^m \cdot K' = K/K' \quad [9]$$

RESULTS AND DISCUSSION

The computer-calculated magnitudes of the peak areas of the aldehydes and aldehydic esters are given in Table II. The uncorrected computer data have been used to calculate the uncorrected DBD with the aid of the theoretical relative sensitivity factors mentioned in Table I. For example, A_a^{12}, from Δ_6 in sample A, is equal to 48131. This corresponds with a relative amount of 48131 x 0.94 weight units of the C_{12}-aldehyde. As the molar weight of this aldehyde is 184, a relative amount of 48131 x 0.94/184 = 245.9 moles is present. The total relative molar amount of aldehydes, calculated in this way, is 5789.2, which means that 245.9/57.892 = 4.2% C_{12}-aldehyde moles were present. So we can conclude that 4.2% of Δ_6 was present in the original mixture of positional isomers in sample A. A similar exercise can be performed with the aldehydic esters.

Taking the other degradation product of Δ_6, the C_6-aldehydic ester, we find A_e^6 = 19212. As C_e^6 = 1.24 and M_e^6 = 144, this peak area value corresponds with a relative amount of 19212 x 1.24/144 = 165.4 moles. The total relative amount of aldehydic ester moles is 3930.5, so 4.2 mole% of the C_5-aldehydic ester is present, based on the total amount of these esters, implying that also along this route 4.2% of Δ_6 is found.

Except for some isomers, the percentages agree rather well. An exception, for example, is shown in Table II, where in sample A, a higher Δ_9 content, 41.8%, is found on the basis of the aldehydes than on that of the corresponding ester, 38.9%. However Figure 1, from which these results are derived, shows that the C_9-aldehyde peak is fused with an unidentified peak, so that too large a peak area is registered by the computer.

Peaks not too badly fused can be resolved mathematically. In our case, however, equation 8 can be used as a simple tool to correct unreliable values of peak areas. We first select a number of peaks which are not fused and which are integrated properly. For sample A, the degradation products of Δ_7, Δ_8, Δ_{10}, Δ_{11} and Δ_{12} have been selected and the R_n values of these products are calculated. For example, R_7 = 84180/50271 = 1.67; applying equation 8 (m = 11 and n = 7), we find that K'' = 1.00.

On an average, we derive a value of 1.01 for K'', as can be concluded from Table II. This value is used to calculate, again with equation 8, R'_n-values, which are also given in Table II. R'_n stands for the theoretical value of the ratio between corresponding peak area values. So A_a^9/A_e^9 should be 1.01 instead of 1.21. Taking R'_9 and A_e^9 as a basis for calculating the theoretical magnitude of the peak area, we find 284456 x 1.01 = 287301 (Table III).

A very clear example is provided by the large difference between R_{13} = 0.85 and R'_{13} = 0.33 in sample A. It means that A_a^5 is ca. 2.5 times too large, which can easily be verified from Figure 1. Applying the correction method described above, we obtain a value of 28396 x 0.33 = 9371 for this peak area (Table III).

It is not always clear which of the two corresponding peaks belonging to deviating R_n values must be corrected, e.g., what to say of the difference of ca. 10% between R_6 and R'_6 in sample A, in view of the fact that the C_{12}-aldehyde peak and the C_6-aldehyde ester peak hardly show any irregularities. In cases like this we generally make one of the peak area values smaller, so that the new ratio between the values is equal to R'_n. Here we adapted A_a^{12}, resulting in a new value of 42651.

The same procedure was applied to sample B, which has completely different DBDs in the mixture of positional isomers. The chromatographic analysis of the degradation products was carried out on another, identical column. However on this column the C_9-aldehyde peak and the artifact near this peak were partly resolved, and too small a value for A_a^9 was obtained by the integration method, as can be seen from Figure 2. This is reflected in the R_9 value which is smaller than R'_9, which is in contrast to the results obtained with sample A. A_a^9, together with some other peak area values, have been corrected with R'_n values derived from K'' = 1.31. Most of these corrections can be provided with good arguments, as can be concluded from Figure 2. (Too large area values for A_e^4, A_e^5 and A_a^5.) Only the corrections of A_e^6 and A_e^7 are somewhat arbitrary. However it is striking that the corrected area values result in DBDs which agree very well, as can be seen in Table III. This implies that K'', derived from completely resolved peak areas, can indeed be regarded as a constant which is independent of the chain length of the corresponding degradation products and, moreover, that the theoretical relative sensitivity factors mentioned in Table I are quite reliable.

Finally we applied the evaluation procedure to two mixtures of known composition, that were analyzed on two identical chromatographic columns. The mean percentages, based on aldehydes and aldehydic esters, as listed in Table IV, show that good agreement was obtained between the calculated and the real composition.

Hainová et al. (7) have demonstrated that the relative molar sensitivity factor for a FID depends on such parameters as the flow of carrier and hydrogen gas and the structure of the compounds to be analyzed. As aldehydes and aldehydic esters have different structures, it is to be expected that the ratio between the molar relative sensitivities of two corresponding degradation products varies and that the mutual ratio among the relative sensitivities of aldehydes and that among the aldehydic esters is constant.

According to equation 9, K'' relates the molar sensitivities of aldehydes and aldehydic esters. K'' is constant during the length of an analysis, but it may vary when the chromatographic operating conditions are changed, as is suggested by the experiments of Hainová et al. (7). It is possible that the difference found between K'' values (1.01 and 1.31) should be interpreted on the basis of similar phenomena.

So far we have not paid any attention to these differences, but it may be worthwhile for theoretical reasons to investigate the underlying causes. Nevertheless the constant K'' appears to be an important tool to quantify the theoretical ratio between peak area values of corresponding degradation products obtained from methyl

octadecenoates via ozonolysis. This at last ensures a more reliable calculation of the DBD in a mixture of positional isomers.

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[Received July 30, 1971]