Conclusions

The present pyrolysis-gas chromatographic method does not furnish a single analytical scheme for all conceivable surfactant mixtures. As formulations become more complicated and the number of components increases, interpretation of the experimental data becomes more difficult. However, when used in conjunction with other analytical procedures, such as ultraviolet, infrared, nuclear magnetic resonance, mass spectrometry, phosphoric acid decomposition (12), ion exchange, and quaternary titration (11), this technique can be of significant value in the analysis of surfactants.

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Gas-Liquid Chromatography of the Positional Isomers of Methyl Nonynoate[1]

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Abstract

A mixture of all the positional isomers of methyl nonynoate is poorly resolved by gas-liquid chromatography on packed polar (diethylene glycol succinate) and packed nonpolar (Apiezon L) columns. Better resolution is obtained on capillary columns, with the polar liquid phase giving baseline separations between all the isomers except 9:T4 and 9:T5. The nonynoic esters are eluted later than methyl nonanoate on either liquid phase. The isomers with the triple bond near the center of the molecule come off first, and the elution time increases as the triple bond moves toward either end of the chain. Methyl 8-nonynoate, the only isomer with a terminal triple bond, does not follow this pattern.

Introduction

ONLY ISOLATED EXAMPLES appear in the literature on the gas-liquid chromatographic (GLC) separation of mixtures of acetylenic esters; what has appeared has been confined to a few naturally occurring or easily prepared compounds. Zeman (1) determined the elution times for saturated, monoenoic, and monoynoic esters and found that on polyethylene glycol adipate the elution order was 18:0[3] (methyl stearate), 18:Δ9 (methyl oleate) and 18:T9 (methyl stearolate), while on Apiezon L it was 18:Δ9, 18:T9, and 18:0. Analogous results were obtained on both liquid phases with 22:0 (methyl behenate), 22:Δ13 (methyl erucate) and 22:T13 (methyl behenolate). The equivalent chain lengths for 18:T9 and 18:T6 (methyl tarirate) were found by Miwa et al. (2) to be identical on packed columns of either Apiezon L or of diethylene glycol pentaerythritol adipate, and thus the esters were not separable. Lefort et al. (3) found the equivalent chain lengths for 18:T6 and 18:T9 to be identical on diethylene glycol succinate (DEGS) and also on Apiezon M. They found an elution order identical to that of Zeman for 18:0, 18:Δ9, and 18:T9 on the polar and nonpolar phases. Achaya et al. (4) made an extensive study of the separation of fatty acetylenic, ethylenic, and saturated compounds by thin-layer chromatography. They were unable to separate positional isomers, either acetylenic or ethylenic, as esters, acids, or alcohols by any of the systems tried. For example, they could not separate 18:T9 from 18:T6.

To our knowledge, no separation of a series of isomeric acetylenic esters has been reported. This paper describes the behavior of the isomeric methyl nonynoates on both packed and capillary columns of DEGS and Apiezon L.

Experimental

3-Nonynoic acid was prepared by a method similar to that of Knight and Diamond (5) for the preparation of 3-octynoic acid. The other nonynoic acids were prepared by the method of Wotiz and Hudak (6) with minor modifications. Nonanoic acid, used as the reference for calculation of relative retention times, was prepared by hydrogenation of 9:T7. Methyl esters were prepared with diazomethane (7).

The esters were assayed by analytical GLC and found to be about 99% pure, except for 9:T3, which contained a small amount of an unknown contaminant. To establish the identities of the peaks in the mixture, each individual acetylenic ester was chromatographed with methyl nonanoate (9:0).

Four columns were used in this study: a) 6 ft × ¼ in. 15% DEGS on 60–80 mesh Gas-Chrom RZ (Applied Science Laboratories, State College, Pa.), b) 3 ft × ¼ in. 10% Apiezon L on 60–80 mesh Gas-Chrom RZ, c) 85 ft × 0.01 in. I.D. DEGS capillary, and d) 100 ft Apiezon L capillary. The capillary

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[3] Abbreviations used in the text and graphs are interpreted as follows: The number before the colon specifies the chain length, zero after the colon indicates a saturated compound, Δ (delta) indicates an ethylenic ester, and T (tau) an acetylenic ester. Numbers following Δ or T specify the position of the unsaturation.

DEGS column was coated with 18% DEGS in chloroform. The preparation and conditioning of these capillary columns has been described (8). A Barber-Coleman Model 20 Gas Chromatograph equipped with an argon ionization detector was used for the capillary column analyses and a Research Specialties Model 600 Gas Chromatograph, equipped with either an argon ionization detector or a hydrogen flame detector, was used for the packed column analyses.

Results

Figure 1 illustrates the behavior of the seven isomeric esters on packed DEGS and packed Apiezon L columns. The first peak in each chromatogram corresponds to methyl nonanoate. The separation on the Apiezon L column was very poor and no attempt was made to determine which esters appeared in each peak. A better separation was achieved on the packed DEGS column and the peaks are labeled according to the isomers they represent. No baseline separations were obtained among the acetylenic esters on either of the packed columns; manipulations of column temperature and inlet pressure did not increase the number of peaks or improve the separations.

The behavior of the nonynoic esters on the 100 ft Apiezon L capillary column is shown in Figure 2. Separation was considerably better than on the packed column, but baseline separation was obtained only between 9:T6-9:T3 and 9:T7. From the data in Table I it can be seen that 9:T4, 9:T5, and 9:T8 have similar relative retention times (1.11–1.12) with respect to 9:0, and thus they are eluted as a single peak. It is indeed surprising that 9:T3 ($R_t = 1.22$) even shows as a shoulder on 9:T6 ($R_t = 1.20$). The 9:T2 and 9:T7 are well removed from the other esters.

The elution pattern of the nonynoic esters from the 85 ft DEGS capillary column is shown in Figure 3. Baseline separations are obtained between all of the esters except 9:T4 and 9:T5. The order of elution is similar to that from the Apiezon L, but the resolution is much better.

The relative retention times for the esters from both DEGS and Apiezon L capillary columns are listed in Table I.

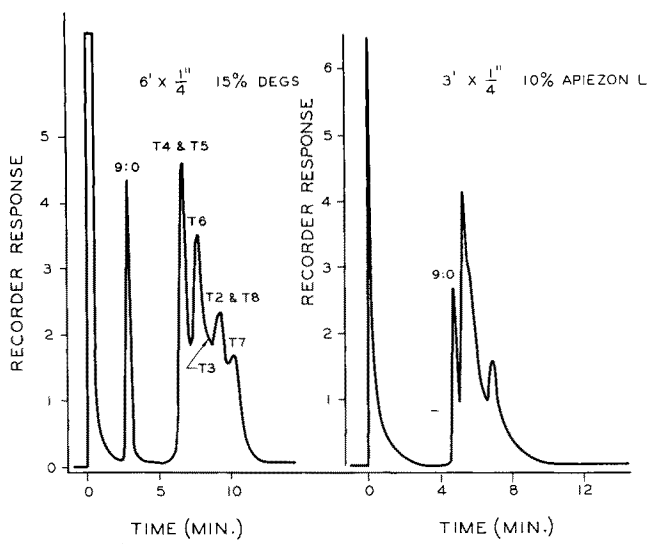

FIG. 1. Analysis of a mixture of seven isomeric nonynoic esters on (a) 6 ft × ¼ in. 15% DEGS on 60–80 Mesh Gas Chrom RZ at 160C and (b) 3 ft × ¼ in. 10% Apiezon L on 60–80 mesh Gas Chrom RZ at 152C. Reference compound is methyl nonanoate.

TABLE I

Retention Times on Capillary Columns of Methyl Nonynoates Relative to Methyl Nonanoate

Acid	Relative retention time	
	Apiezon L	DEGS
9:0	1.00	1.00
9:T2[a]	1.62	3.51
9:T3	1.22	3.31
9:T4	1.11	2.52
9:T5	1.11	2.59
9:T6	1.20	2.99
9:T7	1.50	4.13
9:T8	1.12	3.74

[a] 9 = carbon chain length; T2 = triple bond at position 2.

Discussion

It is apparent from Figure 1 that packed Apiezen L and packed DEGS columns, which effect good separation of long chain saturated and ethylenic esters, are not useful for the separation of positional isomers of the nonynoic esters. Much better separations are achieved on the capillary columns than on the packed columns.

From Figures 2 and 3 it can be seen that the esters which contain the triple bond near the middle of the molecule (9:T4 and 9:T5) are eluted first and that the relative retention times increase for those molecules which have the triple bond closer to either end, i.e., the T4 and T5 esters are followed by the T6 and T3, which are followed by the T7 and T2. The behavior of 9:T8 is probably due to the presence of the terminal alkyne group.

The good separations obtained in the present study may be due partially to the short chain lengths of the esters studied. In view of the poor resolution of 9:T4 and 9:T5, it is likely that long chain acetylenic

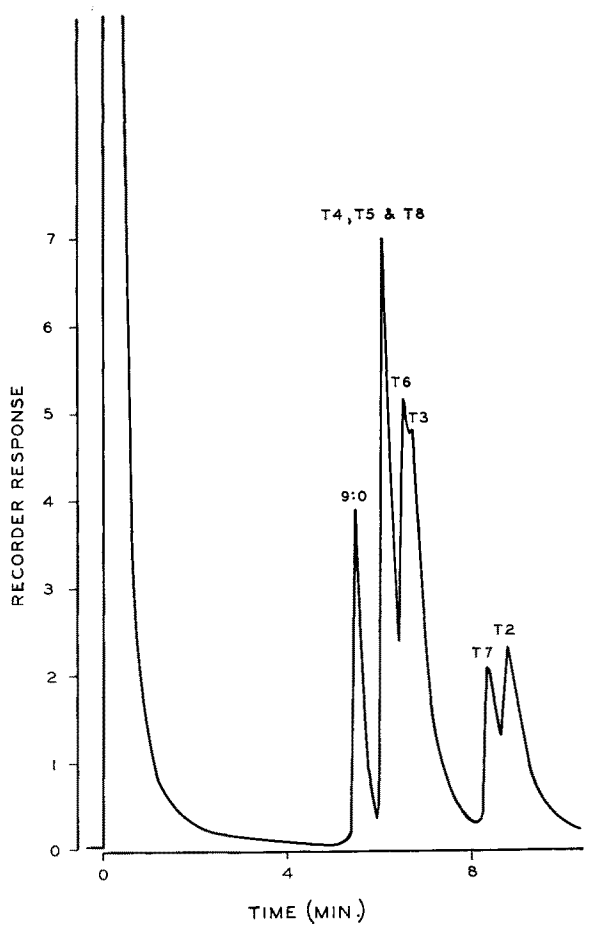

FIG. 2. Analysis of a mixture of seven isomeric nonynoic esters on a 100 ft Apiezon L capillary column at 126C. Reference compound is methyl nonanoate.

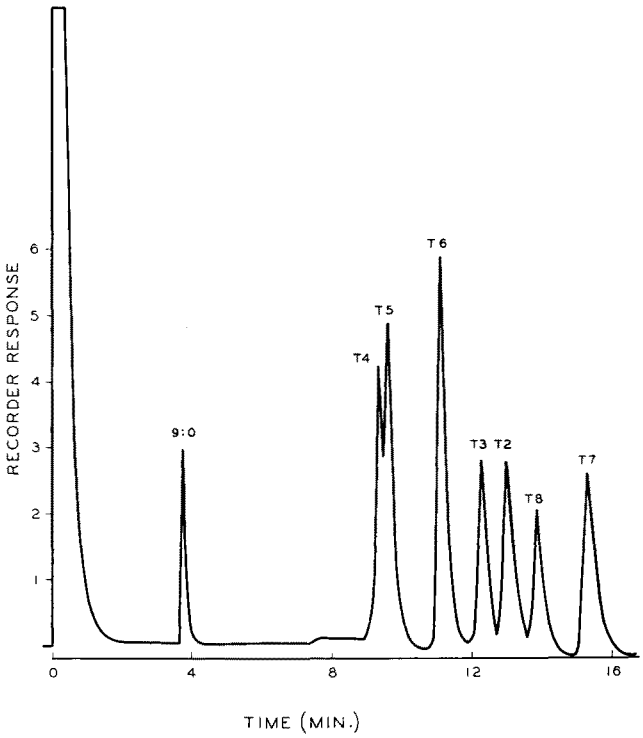

FIG. 3. Analysis of a mixture of seven isomeric nonynoic esters on an 85 ft DEGS capillary column at 136C. Reference compound is methyl nonanoate.

esters containing triple bonds at some distance from either end of the chain would be resolved only with great difficulty. This could account for the inability of Miwa et al. and Lefort et al. to resolve 18:T6 and 18:T9. The reported inability to resolve monoenoic positional isomers by GLC may be due to the fact that the compounds studied most thoroughly have also been of long chain length with the double bond near the middle of the molecule. Preliminary studies by us with the positionally isomeric *cis*-nonenoic esters have shown that they too are resolvable by GLC.

It has been reported (1–3) that 18:0 precedes 18:T9 on the polar DEGS column, but follows it on the nonpolar Apiezon L column. In the present study, the nine carbon acetylenic esters were eluted from both the DEGS and Apiezon L columns after their saturated counterpart. The observation (1–3) that the relative retention times of the acetylenic esters are greater on the polar column than on the nonpolar column was confirmed, however.

By plotting the log retention time versus carbon number of 18:T9 and 22:T13, Zeman obtained a line parallel to those for the saturated and monoenoic esters. From this he concluded that the behavior of the triple bond esters was similar to that of the other classes of esters and that log plots could be used to easily identify acetylenic esters. The two esters he chromatographed had their triple bond near the center of the molecule. From the results of the present study, it is unlikely that long chain acetylenic esters with their triple bond near either end of the molecule would fall on this line.

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Preparation of Some Linseed Esters of Methyl *a*-D-Glucopyranoside Using the Methoxycarbonyl Blocking Group[1]

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Abstract

The three possible methoxycarbonyl derivatives of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside have been prepared. The methoxycarbonyl at the C_2 position in the 2,3-di-*O*-methoxycarbonyl derivative is removed selectively in anhydrous ammonia. The ability of the methoxycarbonyl group to block selectively the C_2 hydroxyl in methyl glucoside has been utilized to synthesize some mono-, di-, and tri-linseed esters of methyl glucoside. The use of this new blocking group has permitted the first synthesis of some unsaturated esters of methyl glucoside.

RECENT WORK at the Northern Laboratory necessitated the use of some positionally distinct linseed acid esters of methyl α-D-glucopyranoside. Preparation of the tetralinseed ester is straightforward and unequivocal. Preparation of partial esters, such as the 2,3-di-*O*-linseed and 2,3,4-tri-*O*-linseed acyl esters, requires use of the 4,6-benzylidene and the 6-trityl groups as acid-removable blocking groups as is done in making certain acetates. Preparation of partial esters requiring blocking groups at the 2 and 3 positions or both, as well as at the 4 and 6 positions, is more difficult. Methyl 2- or 3-*O*-linseed acyl-α-D-glucopyranosides are examples. Blocking groups used in the 2 and 3 positions are the tosylate (10), trifluoroacetate (2,3), trichloroacetate (8), benzyl ether (5), and the benzylthiocarbonyl group (14).

The use of these groups was not feasible in this work. For example, because the tosylate group is removed by hydrogenation or alkali, it is not suitable with linseed esters. Trifluoroacetate and trichloroacetate groups are subject to migration; neither is trifluoracetate stable to aqueous acid. The benzyl

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