ranged from 6.3 to 27.9 p.s.i., ultimate elongation from 27 to 121%, and 50% compression modulus from 0.5 to 10.4 p.s.i. Neither modification of the unsaturation of castor oil, as by hydrogenation, elaidinization, or partial epoxidation, nor aging at elevated temperature and humidity greatly affected the density, tensile strength, or elongation, but water resistance and shrinkage of the foams were improved by such modification.

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Gas-Liquid Chromatography of Fatty Derivatives. I. Separation of Homologous Series of a-Olefins, n-Hydrocarbons, n-Nitriles, and n-Alcohols[1,2]

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SINCE THE FIRST application of gas-liquid chromatography by James and Martin (3) to the separation of long-chain fatty acids, the technique has been extended by other investigators (8) to fatty acids through C_{22}, as their methyl esters, and to the fatty alcohols (1, 6) up to C_{18}. James and Martin and their co-workers have shown that gas-liquid chromatography can be applied to the separation of the methyl esters of saturated and unsaturated fatty acids (2, 4) and have studied the structure of unsaturated fatty acids (5) through chromatography of their oxidation products. Very recently Orr and Callen (7), screening various partitioning agents, have found that polyester columns will resolve unsaturated acids, giving good, quantitative separations in reasonable times.

In this laboratory conditions have been established for the separation and identification of *alpha*-olefins from C_8 to C_{24}, saturated n-hydrocarbons from C_8 to C_{24}, and fatty nitriles from C_6 to C_{20}. The separation of the saturated higher fatty methyl esters and fatty alcohols has been improved so that the useful range has been extended through ricinoleic for the fatty acids and through behenyl for the fatty alcohols. Through the use of pure standards the accuracy has been established for the olefin and nitrile separations and subsequent analyses.

Experimental

Gas Chromatography. The chromatographic separations were carried out on a Beckman GC-2 gas chromatograph. The columns had as the stationary phase, Apiezon L (Burrell No. 341-117) for hydrocarbons, Carbowax 4000 monostearate (Beckman No. 70006), and Carbowax (Wilkens No. 3),[3] for alcohols and

nitriles, and silicone (Wilkens No. 1)[3] for alcohols and castor derivatives. The support for the stationary phase was 30–60 mesh C-22 firebrick (Johns-Manville). The column packing contained 31–38% by weight of the partitioning agent. Packing of the columns was done as previously described (3). Columns were prepared from stainless steel tubing 0.25 in. o.d. by 0.020 in. wall thickness.

Helium was used as the carrier gas. The column and detector were operated at the same temperature in the range of 220–260°C. The detector was maintained at atmospheric pressure. The recorder was a strip-chart type with a 1-mv. full-scale deflection. Other variables are defined in the results following. Samples were injected with a Beckman liquid sampler, a precision hypodermic syringe. Solid samples were easily handled by their previous melting. This required heating the barrel and the needle of the sampler with an infrared lamp. Peaks were identified by their retention volumes and by the method of internal standards; peaks areas were measured with a compensating planimeter.

1-Olefins. Through the chromatography of standard samples of 1-decene, 1-dodecene, 1-tetradecene, and 1-hexadecene, obtained from the American Petroleum Institute, the relationship between chain length and retention time was established for three sets of operating conditions. The results shown in Figure 1 were obtained by chromatographing these pure olefins and a commercial olefin containing both odd and even chain lengths from C_{10} to C_{18}. A typical curve, Figure 2, and the data derived from the curve, Table I, revealed that the method was suitable for the quantitative analysis of long chain *alpha*-olefin mixtures since peak areas were directly proportional to weight percentage. A statistical evaluation of a limited set of data shows that the standard deviation for this analysis is 0.47.
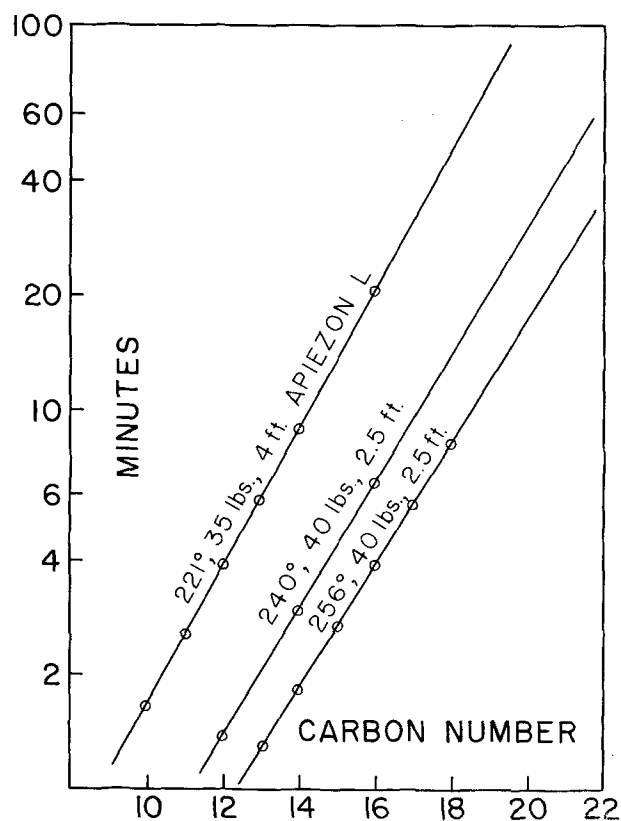
FIG. 1. Plot of log retention time *versus* carbon number for 1-olefins. Helium pressure at inlet measured in p.s.i.g.; pressure at outlet, atmospheric. Flow rate at 221°C., 77 ml./min.; 240°C., 95 ml./min.; 256°C., 88 ml./min.

At that time it was not possible to distinguish between positional isomers of the olefins. Consequently, to calculate the percentage of *alpha*-olefin in a mixture, it was necessary to measure the area under each peak, divide the area fraction of each component by the respective molecular weight, add the mole fractions, and divide the total number of moles into actual
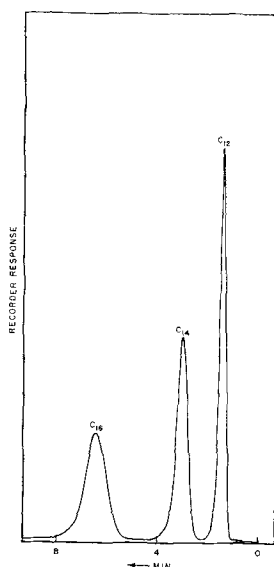

FIG. 2. Separation of 1-olefins from C_{12} to C_{16} on a 2.5-ft. column with Apiezon L (31.5% by wt.) at 240°C. Pressure 40 p.s.i.g., current 250 ma., sample 0.010 ml., helium flow, 95 ml./min.

TABLE I

Gas Chromatographic Analysis of 1-olefins

Mixture	Component	Calculated composition % by wt.	Analyzed area %[b]
1[a]	1-Dodecene	32.3	32.1
	1-Tetradecene	32.9	33.0
	1-Hexadecene	34.8	34.9
2	1-Decene	0.0	0.4
	1-Dodecene	18.1	18.3
	1-Tetradecene	4.1	4.1
	1-Hexadecene	77.8	77.2
3	1-Decene	23.1	23.7
	1-Dodecene	34.9	35.5
	1-Tetradecene	11.0	10.1
	1-Hexadecene	31.0	30.7

[a] From Figure 2.
[b] Standard deviation—0.47.

moles of *alpha*-olefin as determined by infrared spectroscopy.

In Figure 3 the curve shows a separation of *alpha*-olefins from C_{12} to C_{22}, on an Apiezon L column operated at 256°C. This is approximately the limiting temperature for Apiezon L. The peaks between the even-numbered components are probably odd-numbered olefins for a plot of the log of the retention time *versus* carbon number for the chromatogram gives a straight line.
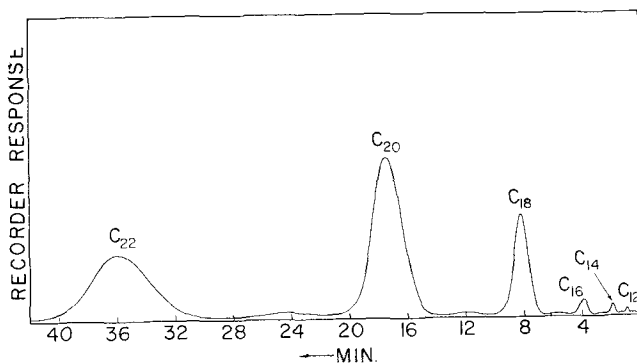

FIG. 3. Separation of 1-olefins from C_{12} to C_{22} on a 2.5-ft. column with Apiezon L at 256°C. Pressure 40 p.s.i.g., current 250 ma., sample 0.015 ml., helium flow, 88 ml./min.

Hydrocarbons. The n-hydrocarbons were prepared by hydrogenation of the corresponding terminally unsaturated olefins, using 5% palladium on carbon as the catalyst and a pressure of 50 p.s.i.g. The chromatographic characteristics of these hydrocarbons were established by a procedure similar to that used for the *alpha*-olefins.

Figure 4 compares the curves obtained from the parent 1-olefin and the n-hydrocarbon. The difference in retention time between the saturated and unsaturated hydrocarbon is negligible through a chain length of 14, but beyond 14 the slower movement of the hydrocarbon is noted. Absolutely no separation of saturated from unsaturated components was observed when a mixture of equal parts of the *alpha*-olefin and n-hydrocarbon was run under conditions described in Figure 4.

Nitriles. Fatty nitriles, containing even-numbered carbon atoms from C_8 to C_{20}, have been successfully resolved by employing 18-in. Carbowax columns. The operating temperature was 220-235°C., depending on chain length; the higher temperature was employed when C_{20} was involved. A nitrile derived from coconut oil was distilled to obtain chromatographically
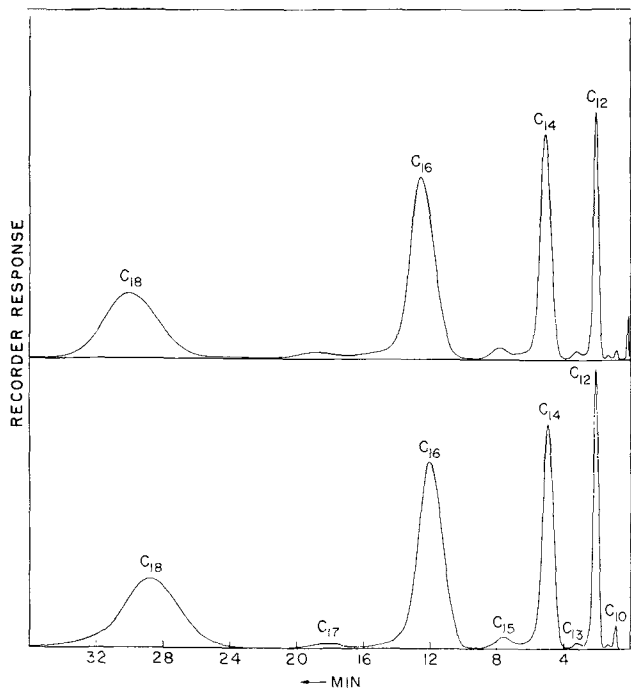
FIG. 4. Separation of 1-olefins and corresponding hydrocarbons on a 2.5-ft. column with Apiezon L at 214°C. Pressure 40 p.s.i.g., current 250 ma., sample 0.015 ml., helium flow, 105 ml./min. Upper curve, hydrocarbon; lower curve, *alpha*-olefin.

pure fractions; these were then used to identify peaks in chromatograms of unknown mixtures.

Figure 5 shows the chromatograms of a known mixture of pure nitriles and of a coconut nitrile under the conditions indicated. These chromatograms fulfill the requirements of an ideal chromatographic separation, namely, high resolution, relatively short retention time, good symmetry, and almost quantitative separation. A statistical analysis of the data in Table II reveals there is no significant difference in the actual percentage by weight and the percentage by gas chromatography at the 95% level.

Fatty Alcohols. Fatty alcohols have previously been separated (1, 6), but the resolution has not been completely satisfactory. By using Carbowax 4000 monostearate on C-22 firebrick at column temperatures up to 230°C., it is possible to achieve good separations. Stearyl alcohol in an alcohol derived from coconut oil was eluted under these conditions in 16 min. (Figure 6).
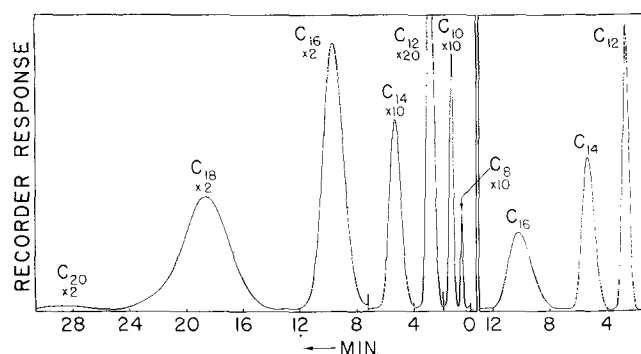

FIG. 5. Separation of mixtures of pure nitriles and of coconut nitriles on a 1.5-ft. column with Carbowax 4000 monostearate at 226°C. Pressure 25 p.s.i.g., current 250 ma., sample 0.015 ml., attenuation as noted, helium flow, 52 ml./min. Curve on left, coconut nitrile.

TABLE II
Gas Chromatographic Analysis of Nitriles

Mixture	Component	Calculated composition % by wt.	Analyzed area %[a]		
I	C_{12}	33.6	33.4		
	C_{14}	33.3	33.5		
	C_{16}	33.1	33.1		
II	C_{12}	28.4	28.7	29.2	30.1	29.1
	C_{14}	38.5	37.4	37.1	37.5	37.4
	C_{16}	33.1	33.9	33.7	32.4	33.5
III	C_{12}	37.4	38.2		
	C_{14}	37.0	37.1		
	C_{16}	25.6	24.7		

[a] Standard deviation—0.84.

The arachidyl and behenyl peaks are so broad when these higher alcohols are run on Carbowax 4000 monostearate that area measurements are difficult. A silicone column gives a better resolution and a better background at the temperature required for the elution of these alcohols in a reasonable time. Behenyl alcohol may be eluted in 80 min. on a 1.5-ft. silicone
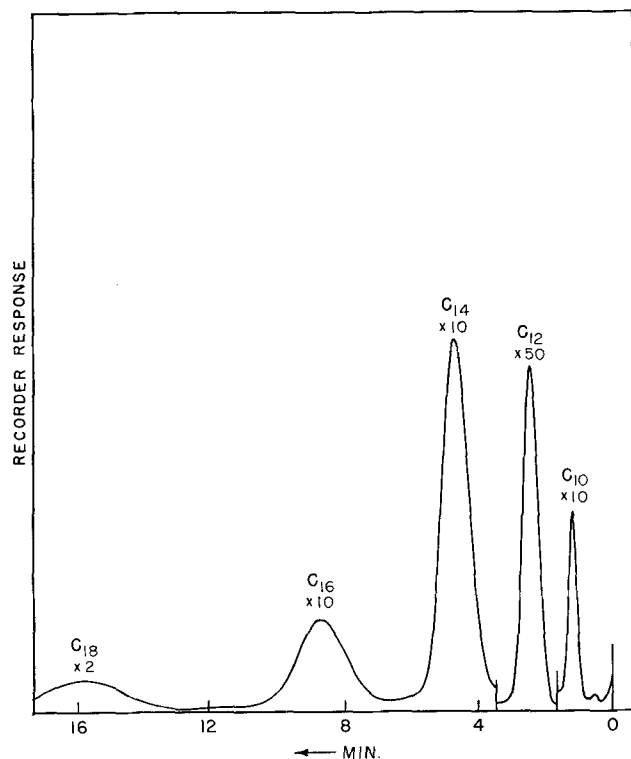

FIG. 6. Separation of coconut alcohols on a 1.5-ft. column with Carbowax 4000 monostearate at 225°C. Pressure 30 p.s.i.g., current 250 ma., sample 0.015 ml., attentuation as noted, helium flow, 67 ml./min.

column, employing 31.6% by weight of silicon grease on 30–60 mesh C-22 firebrick, at 230°C., with a helium flow of 85 ml./min. and a 0.010-ml. sample.

Attempts to resolve alcohol mixtures with similar chain lengths but varying degrees of unsaturation have met with only limited success. An alcohol derived from soybean oil shows only five peaks when run on a 15-in. Carbowax column at 232°C. At 217°C. (Figure 7) the main C_{18} alcohol peak is partially resolved into three peaks, presumably stearyl and oleyl, linoleyl, and linolenyl. Apparently the less unsaturated alcohols are retained more strongly.
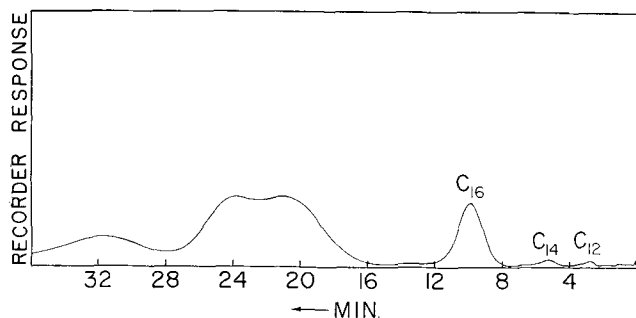
The peak areas have been used in an attempt to

FIG. 7. Separation of soy alcohols on a 15-in. Carbowax column (37.6% by wt., Wilkens No. 3) at 217°C. Pressure 35 p.s.i.g., current 200 ma., sample 0.005 ml., helium flow, 87 ml./min.

establish the composition of the alcohol mixture, but the method is not applicable in a quantitative sense. Better resolution will certainly be possible through a study of other partitioning agents. Under similar conditions the C_{18} peak of linseed alcohol was partially resolved into four peaks. Only a tentative assignment can be made to these C_{18} peaks, stearyl, oleyl, linoleyl, and linolenyl alcohol, respectively.

Castor Derivatives. The determination of ricinoleic acid and ricinoleyl alcohol in their parent mixtures has presented the analyst with a difficult problem. Efficient distillation invariably produces pyrolysis; fractional crystallization is tedious and inefficient. To follow either process requires a hydroxyl value determination. Gas-liquid chromatography affords a method of analysis independent of hydroxyl values. Figure 8 shows the curve obtained by chromatographing the mixed castor alcohols, from sodium reduction, on a 15-in. silicone column. Ricinoleyl alcohol appears in the chromatogram in approximately the position of the C_{20} alcohol. No pyrolysis is apparent. The composition may be easily determined by measuring the peak areas.

Figure 9 shows the composition of the mixed methyl esters of hydrogenated castor fatty acids. The large
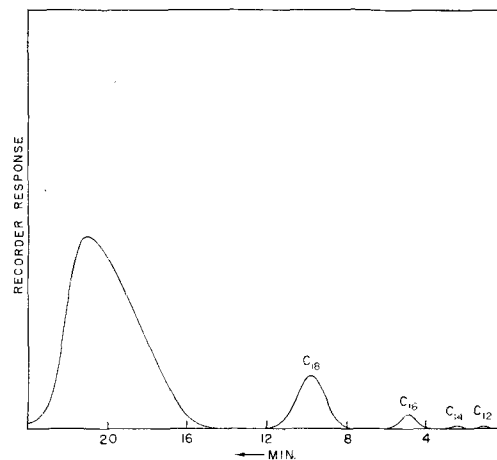
FIG. 9. Separation of mixed methyl esters of hydrogenated castor fatty acids on a 15-in. silicone column (Wilkens No. 1) at 222°C. Pressure 40 p.s.i.g., current 200 ma., sample 0.005 ml., helium flow, 98 ml./min.

peak is methyl ricinoleate. The additive effect on the retention time on a silicone column of the hydroxyl group is approximately that of two additional carbon atoms.

Summary

Gas-liquid chromatography has been shown to be applicable to the analysis of several fatty derivatives. The difficulties inherent in conventional separation schemes such as liquid-liquid chromatography, fractional distillation, and crystallization can be overcome through the use of gas-liquid chromatography. It becomes the preferred procedure for several reasons: a) fractions are more nearly pure, b) analysis time is a fraction of the time required for conventional separations, c) operational procedures are simple and highly reproducible, d) sample size requirements are low, e) the cost per unit analysis is low.

These factors suggest that gas-liquid chromatography is highly useful as an analytical tool in fat research. In many cases the determination of chain-length distribution has already become a routine function.

There remain areas in which gas-liquid chromatography has not been completely successful. Until very recently the separation of fatty methyl esters of similar chain length and varying degrees of unsaturation has been time-consuming and tedious. Several new partitioning agents hold out great promise in the separation of the isomeric C_{18} fatty acids. More selective partitioning agents and refined techniques undoubtedly will equally improve the resolution of unsaturated alcohols and other unsaturated fatty derivatives.

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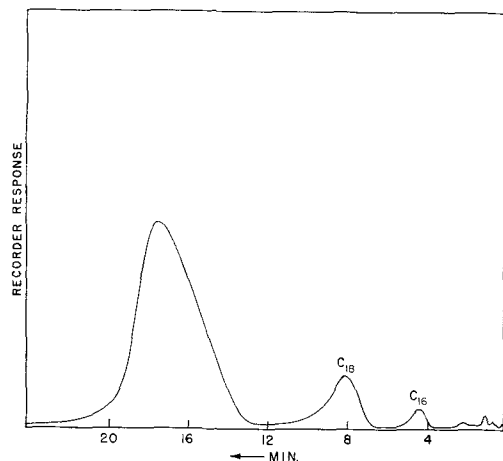8. Podbielniak, W. J., and Seaton, S. T., Pet. Ref., *35*, 215 (1956).

FIG. 8. Separation of castor alcohols from reduction on a 15-in. silicone column (31.6% by wt., Wilkens No. 1) at 222°C. Pressure 40 p.s.i.g., current 200 ma., sample 0.005 ml., helium flow, 98 ml./min.