indicated in Figure 1. The overlap between the sensitive and resistant species is readily apparent but it is also of interest to observe that the distribution between the saturated and unsaturated fatty acids of these species occur at the critical composition where a small increment of added unsaturated fatty acid has a marked effect on the freezing point of that mixture. Freezing points were not determined for 3 or 4 component mixtures to evaluate the influence of oleic acid on mixtures of palmitic, linoleic, and linolenic. Oleic acid would certainly raise the freezing point of a mixture in proportion to the amount present, however, it occurs in relatively small amounts in the membrane and phospholipid fractions.

Several hypotheses have been presented to explain the mechanism of injury to chilling-sensitive plants including disorganization of protein molecules, disruption of enzymatic activity, accumulation of toxins, altered membrane permeability, and physical changes in lipids (1,4). None of these hypotheses has been proven or disproven, but with increased knowledge on composition and function of subcellular membranes additional support is placed on the hypotheses relating to physical changes in lipids. Luzzati and Husson (5) indicated that the physical condition of a lipoprotein complex such as a cell membrane is on the borderline of a phase transition from a liquid-crystalline structure to a coagel. When one of the parameters is altered (such as temperature), the hydrocarbon chains crystallize, thus blocking some physiological activity of the lipid. Similarly, Byrne and Chapman (3) reported that when temperature is increased from a low temperature, the hydrocarbon moiety of a phospholipid begins to twist and flex until finally the melting of the chain occurs. In his discussion on the thermostability of proteins, Ushakov (11) points out that cellular proteins are complexed with other protoplasmic substances, such as lipids, and thermostability of these proteins is a function of the properties of the complexing substances as well as their own properties.

The phase diagrams presented here indicate that differences of less than 5 mole % in the amount of unsaturated fatty acid in a fatty acid mixture have a marked effect on the solidifaction of these mixtures. This effect could be of significance in determining the sensitivity to chilling of a given plant species.

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[Received April 9, 1965—Accepted September 2, 1965]

Gas-Solid Chromatography of Hydrocarbons on Activated Alumina[1]

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Abstract

Volatile hydrocarbons representative of those in autoxidizing fats were analyzed on a single column of activated alumina by gas-solid adsorption chromatography (GSC). Mixtures of C_1 to C_8 paraffins and α-olefins were readily separated from one another, and from several branched hydrocarbons in less than 40 min. Semilog plots of carbon number versus log retention time for these individual mixtures indicate that good separations may be expected when all components are present simultaneously. Alumina is a unique chromatographic substrate for these separations. Since no liquid phase is employed, wide temperature ranges may be applied, column bleeding is eliminated and the system becomes ideal for temperature programming even on single column instruments. This system of GSC offers a convenient and direct method for hydrocarbon analysis since more polar materials such as aldehydes, ketones and esters are irreversibly adsorbed on alumina. It shows promise not only for the analysis of volatiles in the flavor evaluation of edible oils, but also as an aid in solving many other food and biological problems.

[1]Presented at AOCS meeting in Houston, Texas, 1965.
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Introduction

ALIPHATIC HYDROCARBONS are becoming important factors in everwidening areas of biological and medical research. The need for their detection and identification is no longer limited to the field of synthetic chemicals. Pertinent areas of investigation are smog and air pollution studies (7), ripening and aging of fruit (4,5), fat autoxidation (8), enzyme and microbiological studies (17) and food storage and stability (6). In all these investigations trace amounts of hydrocarbons present must be rapidly identified and their concentrations determined. Other areas of application would be synthetic and structure investigations where high-temperature hydrogenation is used to obtain complete reduction and splitting of the compound to yield hydrocarbon fragments that are charactertistic of the original compound (1–3).

Alumina has been previously employed in gas chromatography as a support for liquid phase. McKenna and Idleman (16) have reported complete resolution of C_1 to C_4 paraffins and olefins on alumina coated with propylene carbonate. Early work by Greene et al. (9–10) showed that alumina, silica gel or a mixture of the two was effective for gas-solid adsorption chromatography (GSC) of atmospheric gases and light hydrocarbons. They reported good separation of homologues up to butadiene by temperature programming from +5 to 170C with an analysis time of approximately 1 hr. Investigations

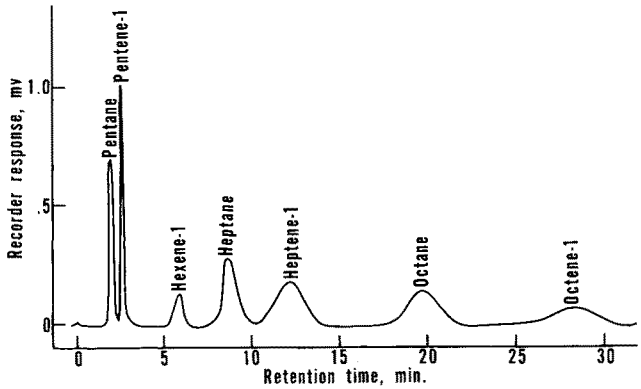

FIG. 1. Chromatogram of paraffins and olefins. Isothermal, 200C; 4 ft × ¼ in. aluminum column packed with 60/80 mesh alumina.

(14) have shown that in addition, higher molecular weight hydrocarbons up to C_8 may be separated in less than 30 min without the use of refrigerated columns.

Experimental

A flame ionization gas chromatograph, F & M Model 1609 (18), was used in conjunction with a Model 40 linear temperature programmer. The chromatographic columns were 4-ft and 8-ft by ¼-in. aluminum tubes packed with 60/80 mesh activated alumina (F-20) obtained from the Microtek Company of Baton Rouge, Louisiana. Hydrocarbon samples were purchased commercially, except the ethane was synthesized by the hydrolysis of ethyl magnesium bromide. Hydrocarbons were taken from a gas-sampling bulb that had been evacuated and manometrically filled except where indicated.

Results and Discussion

Figure 1 shows an isothermal (200C) alumina adsorption chromatogram of C_5 to C_8 paraffins and α-olefins. Baseline separation of the mixture was achieved with an analysis time of less than 30 min. Although the longer chain C_8 hydrocarbons are eluted as flat peaks because of their increased retention times, peak shapes are improved with temperature programming. Figure 2 shows a semilog

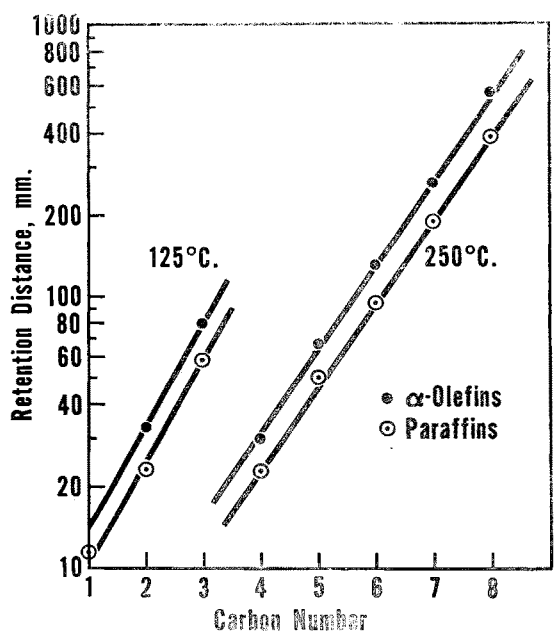

FIG. 2. Semilog plot of hydrocarbon retention time versus carbon number. Isothermal conditions, 250C.

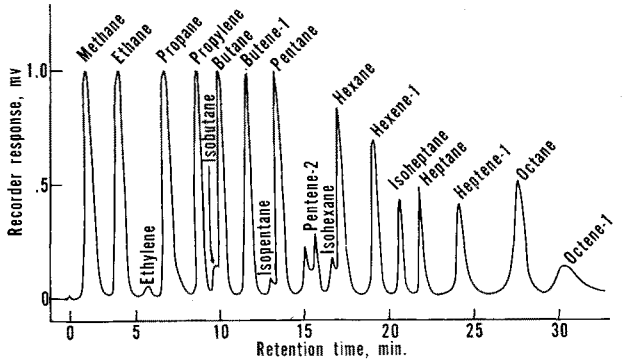

FIG. 3. Chromatogram of hydrocarbons with a boiling point range of −162C to 121C. Temperature programmed from 75–300C at 21C/min in an 8 ft × ¼ in. column.

plot of carbon number versus log retention time for a homologous series of n-paraffins and α-olefins chromatographed isothermally at 250C. Graphic representation of such data shows a good linear relationship between log retention time and carbon number. Only the lower members of a homologous series would show slight deviation from the plot.

Figure 3 is a chromatogram programmed at 21C/min from 75 to 300C composed of a complete homologous series of C_1 to C_8 *N*-paraffins and α-olefins. Sample introduction was accomplished by simultaneous injection of gaseous and liquid component mixtures into the chromatographic column by using two syringes. At this rate of temperature programming there is no drift in the baseline. However, branched members, present as impurities, are not completely resolved from the straight-chain members.

Figure 4 illustrates the separation obtained when branched and straight-chain hydrocarbons are present in the same gaseous mixture. This gas sample was drawn from an upright cylinder of compressed hydrocarbons and the concentration of each component depends on their partial pressures. Branched hydrocarbons exhibit shorter retention times because of their lower boiling points; consequently, they can be separated from an unbranched hydrocarbon of equivalent carbon number.

Although the polar carbonyl-containing fragments arising from fat autoxidation have received considerable attention (11–13), little is known about hydrocarbons present in the vapors of autoxidizing fats. Figure 5 shows a chromatogram of volatiles taken from the headspace of a home kitchen-type potato chip fryer containing soybean oil heated to 180C. The chromatogram was obtained by tempera-

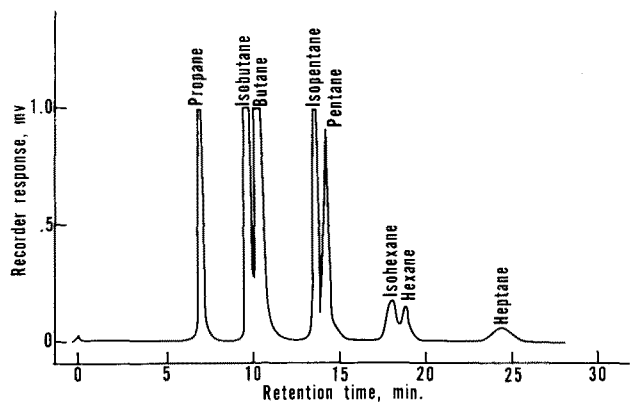

FIG. 4. Temperature programmed chromatogram showing separations obtained for branched and straight-chain hydrocarbons; 8 ft × ¼ in. column.

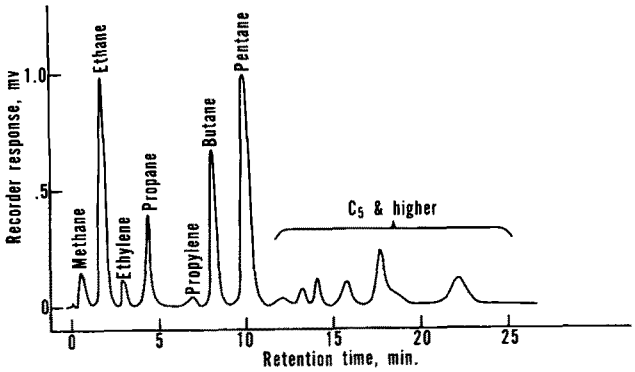

FIG. 5. Saturated and unsaturated hydrocarbons taken from the headspace gas of a home kitchen-type potato chip fryer. Temperature programmed from 75–300C at 21C/min in a 4 ft × ¼ in. column. Sample size 2.5 ml.

ture programming (21C/min from 75–300C) a headspace gas sample of 2.5 ml. Only the saturated and unsaturated hydrocarbons appear in the chromatogram. Polar oxygen-containing components in the sample are irreversibly adsorbed on the active sites of the alumina and have no effect on the hydrocarbon separations. Alumina GSC offers a direct and quantitative method for hydrocarbon analysis in fat autoxidation systems without prior removal of more polar materials which would complicate the interpretation of the chromatogram and identification of the component peaks. A limited number of injections may be made of samples dissolved in polar solvents (diethyl ether, methanol) before the adsorptive capacity of the column is exceeded. These columns can be regenerated to their original activity by a short baking period at 350C.

Gas-chromatographic analysis of low-boiling mixtures frequently requires refrigerated columns. Alumina adsorption gas chromatography is ideal for low molecular-weight hydrocarbons, whose boiling points vary over a wide range, because the troublesome use of refrigerated columns is avoided. Alumina is a unique substrate for these separations because it is stable even at elevated temperatures, and since no liquid phase is employed, column bleeding is eliminated making an ideal system for temperature programming. Separations are achieved at conditions well within the range of commercial gas chromatographs.

Chromatographic studies of aromatic hydrocarbons on alumina by Klemm et al. (15) are useful for interpretation of our results even though their investigations dealt with liquid-solid adsorption phenomena. Solute adsorption increased with the number of double bonds present, molecular approach to coplanarity, symmetry number, extent of conjugation and the number of sterically unhindered methyl or alkylene groups. In GSC systems of activated alumina the saturated hydrocarbons are eluted before olefins of equivalent carbon number because the electron-rich unsaturated bonds of the olefin are more firmly bound to the electropositive sites of the alumina lattice. Separation of branched-chain from straight-chain compounds is possible because of differences in individual vapor pressures. Behavior of diene, cyclic and isomeric hydrocarbons in GSC will be treated in a separate publication.

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[Received July 14, 1965—Accepted September 15, 1965]

Preparation of Linseed Acid Chlorides[1]

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Abstract

A method is described for the preparation of linseed acid chlorides in excellent yields and functional purity. After linseed acids are reacted with phosphorus trichloride, the mixture is briefly heated in vacuo, cooled, and decanted. The linseed acid chlorides were also distilled in a specially modified molecular still to obtain a nearly colorless product.

RECENT WORK at this laboratory required the use of linseed acid chlorides (LAC). Various chlorinating agents such as oxalyl and thionyl chloride or phosphorus tri- and pentachloride have been used to prepare the acyl chlorides of long-chain fatty acids. Bauer (1) studied the use of various chlorinating agents in the preparation of saturated and unsaturated C_{18}-acyl chlorides. Yields reported by Bauer for linoleoyl chloride were 26.6 and 89.9%, using phosphorus trichloride and oxalyl chloride, respectively. Craig et al. (2) used an improved vacuum-distillation technique to eliminate resinification and decomposition of the product and increase the yields of palmitoyl, stearoyl, and oleoyl chlorides. Ralston et al. (3) eliminated the distillation procedure for purification of the long-chain acyl chlorides by washing the reaction mixture with water to remove the various phosphorus byproducts. Youngs, Epp, Craig, and Sallans (4) obtained excellent results by carrying out the washing procedure in an inert solvent to minimize the hydrolysis of the acyl chloride.

Numerous attempts to purify LAC by washing with water as described by Youngs et al. gave products that analyzed 75 to 94% pure. However, when the chlorination mixture was heated rapidly to 150C in vacuo, LAC were obtained in nearly quantitative yields and with almost 100% purity.

[1] Presented at AOCS meeting in Cincinnati, Ohio, 1965.
[2] A laboratory of the No. Util. Res. and Dev. Div., ARS, USDA.