Gas Chromatographic Separation of *cis* and *trans* Isomers of Long Chain Amines

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ABSTRACT

There are important differences in the physical properties of the *cis* and *trans* isomers of unsaturated long chain amines. Because of these differences, it is desirable to know the ratio of the *cis* and *trans* isomers. This separation can be accomplished by capillary column gas chromatography of the amine derivatives; however, the use of capillary columns is too slow for routine analysis. It was found that the *cis* and *trans* isomers of unsaturated amines can be rapidly separated on packed columns containing cyanopropylphenylsilicone liquid phases (Apolar 10C). The primary amines are converted to the trifluoroacetamides and separated on 6- to 10-ft columns containing 10% Apolar 10C at 180 C. The technique has been applied to unsaturated long chain primary amines and diamines. Useful information on the isomerization of these compounds during their synthesis can be obtained.

INTRODUCTION

The *cis* and *trans* isomers of long chain unsaturated amines have considerable differences in physical properties. The *cis* isomer of octadecenylamine is liquid at room temperature and the *trans* isomer is a solid. The *trans* isomers will precipitate under certain conditions, along with the saturated amines. The amount of *trans* isomer present also appears to have some effect on end uses of these amines. Under some manufacturing conditions, considerable *trans* isomer may be formed. For these reasons, it was of considerable interest for us to find a rapid means of determining the *cis* and *trans* isomers present in long chain amines.

A great deal of work has been reported on the gas chromatographic (GC) separation of *cis* and *trans* fatty acid methyl esters. Most of the reports have involved the use of capillary columns. Both nonpolar (1-3) and polar liquids have been used in this separation (4-8). Recently, the use of cyanopropylphenyl silicones has been reported to give relatively good separation of the *cis* and *trans* isomers of the unsaturated fatty acid methyl esters (8).

The separation of *cis* and *trans* monoene fatty esters has also been accomplished by the GC of the epoxide derivatives (9). Argentation column chromatography has also been used to obtain this separation (10,11). However, in this study, we were concerned only with GC separation techniques.

No literature reports have been made on the separation of the *cis* and *trans* isomers of unsaturated long chain amines. The separation of positional isomers of long chain amines and heterocyclic amines using capillary columns has been reported (12-13).

In our laboratory, occasional analyses of the *trans* unsaturation in amines have been made using infrared (IR) techniques. When these analyses were made, the AOCS methyl ester standards for *trans* unsaturation were used as a basis for quantitation. We have also used capillary GC to obtain the *cis* and *trans* isomer ratio. It was observed that the IR analysis did not always agree with the chromatographic results. This variation probably was due to the fact that the methyl ester standards were not appropriate for this analysis.

Capillary column GC of amines gives results that are adequate for determining *cis* and *trans* ratios. However, this technique is very time-consuming, taking up to 3-5 hr for a single analysis. There are occasions when it is desirable to determine a large number of *cis* and *trans* ratios in amines for process studies and other research work. For this reason, we began to search for a more rapid method to accomplish this analysis.

Eventually, it was found that the fatty amine *cis* and *trans* isomers could be separated as trifluoroacetamides, on cyanopropylphenylsilicone columns. (Silar 10C and Silar 5C). The parameters for this separation were explored and a rapid analytical method was developed. The method has been applied to long chain primary amines, diamines, and other fatty nitrogen compounds.

EXPERIMENTAL

Instruments

Hewlett Packard Models 5750 and 7620 gas chromatographs were used for the packed column work. These instruments had dual flame ionization detectors. The capillary GC was performed with a Barber Colman Model 20 gas chromatograph equipped with an Argon ionization detector. The packed columns were made with 6-10 ft of 1/8-in. stainless steel tubing packed with 10% Silar 10C (Apolar 10C, Applied Science) on 100-120 mesh Chromosorb G. The open tubular column was a 200-ft 0.02-in. stainless steel capillary coated with SF-96 silicone oil modified with trioctadecylmethylammonium bromide (14).

Instrument Conditions

When packed columns were used, helium was the carrier gas at 30 mL/min, a temperature of 240 C for the column oven, 280 C for the injector and 300 C for the flame ionization detector.

When the capillary column was used, the Argon gas flow was 8 mL/min. A 60-mL/min scavenger gas flow was used with the Argon detector. A temperature of 190 C was used for the column oven, 265 C for the inlet and 210 C for the detector.

Procedure

The trifluoroacetamides of the primary amines were prepared by a modified version of the Morrissette and Link method (15). About 100 mg of amine was placed in a vial and dissolved in 1 mL of petroleum ether. About 10 drops of trifluoroacetic anhydride were added to the vial. The vial was shaken and allowed to stand for several minutes. One μL of this solution was normally injected into the gas chromatograph.

RESULTS AND DISCUSSION

The separation of *cis* and *trans* isomers of the trifluoroacetamide (TFA) derivatives of the long chain primary amines can be made on capillary columns. A typical capillary separation is shown in Figure 1. This separation was done on a 200-ft stainless steel capillary coated with SF-96

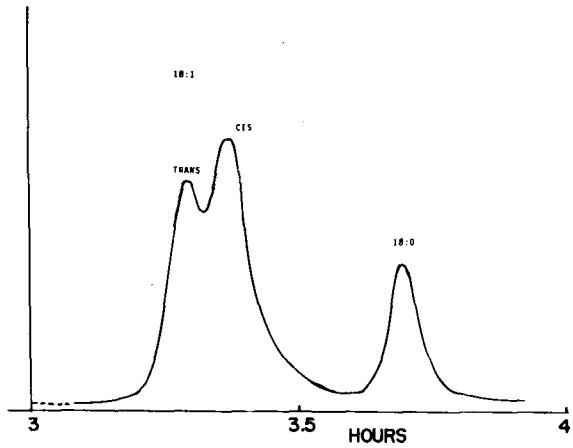

FIG. 1. A commercial oleylamine containing high *trans* isomer chromatographed as the trifluoroacetyl (TFA) derivative on a 200-ft capillary column coated with SF-96.

silicone oil at 190 C. In this chromatogram, only the C-18 amine derivatives are shown. The octadecenylamine derivatives emerged in just under 4 hr. Attempts to speed up the separation by using higher column temperatures only resulted in less resolution of the *cis-trans* isomers. Lower column temperatures gave slightly better separations but resulted in even longer emergence times. Capillary column GC analysis would certainly not readily lend itself to a routine or quality control analytical situation.

Figure 2A shows a chromatogram of the TFA derivative of an abnormal commercial oleylamine. The separation was made on a 10-ft, 10% Silar 10C column. The order of separation is similar to that which would be obtained with methyl esters on a polyester column. The saturated compounds emerge before the unsaturated compounds of the same carbon number. There is one interesting difference evident using these Silar columns that is not seen using polyester columns. The octadecenylamine peak splits into two peaks. The first peak is the *trans* isomer and the second is the *cis* isomer. This is analogous to what had been observed with methyl esters. This particular sample was analyzed because it had considerable amounts of solid material present at room temperature. Normally, an oleylamine should be a liquid at room temperature. Even though the separation of the two peaks is incomplete, the ratio of the two isomers can easily be determined by peak height measurements. In this analysis, it should be noted that a relatively large amount of stearylamine was formed in the reduction.

Figure 2B shows a normal commercial oleylamine sample chromatographed under similar conditions. The 18:1 *trans* isomer is considerably smaller and shows up as a shoulder in this chromatogram. The chromatogram of a tallow amine is shown in Figure 2C. In this sample, more than 50% of the 18:1 amine exists as the *trans* isomer.

It was decided to apply the method to long chain diamines. A 6-ft column was employed to achieve reasonable resolution between *cis*- and *trans*- isomers. We had some indications that as the temperature was raised, the separation of the *cis* and *trans* monoamines became worse. Nevertheless, it was found that at 240 C, a relatively good separation could be made of the *cis* and *trans* diamine isomers. Figures 3A and B are the chromatograms of N-alkyl 1,3 propane diamines with different *cis*- and *trans*- isomer ratio for the C-18 monoenes. The alkyl group in these amines was derived from tallow.

It was reasoned that, if the trifluoroacetamides could be used for the separation of the *cis-trans* monoene isomers, then could this separation be done with underivatized primary amines or dimethylalkylamines? Though primary amines will not emerge from polyester columns, perhaps they would emerge from Silar columns. Our attempts to separate the primary amines on Silar columns met with failure. We routinely separate dimethylalkylamines on polyester columns in order to determine the unsaturated amines. The dimethylalkylamines are easily prepared from primary amines using the Leukart reaction. It was found that the dimethylamines would emerge readily, but that the *cis* and *trans* separation was not accomplished. Not only did the *cis-trans* separation not occur, but the injection of the amines had an obvious deleterious effect on the Silar column.

After amines were injected on a Silar column, the *cis-trans* separation could no longer be accomplished on that

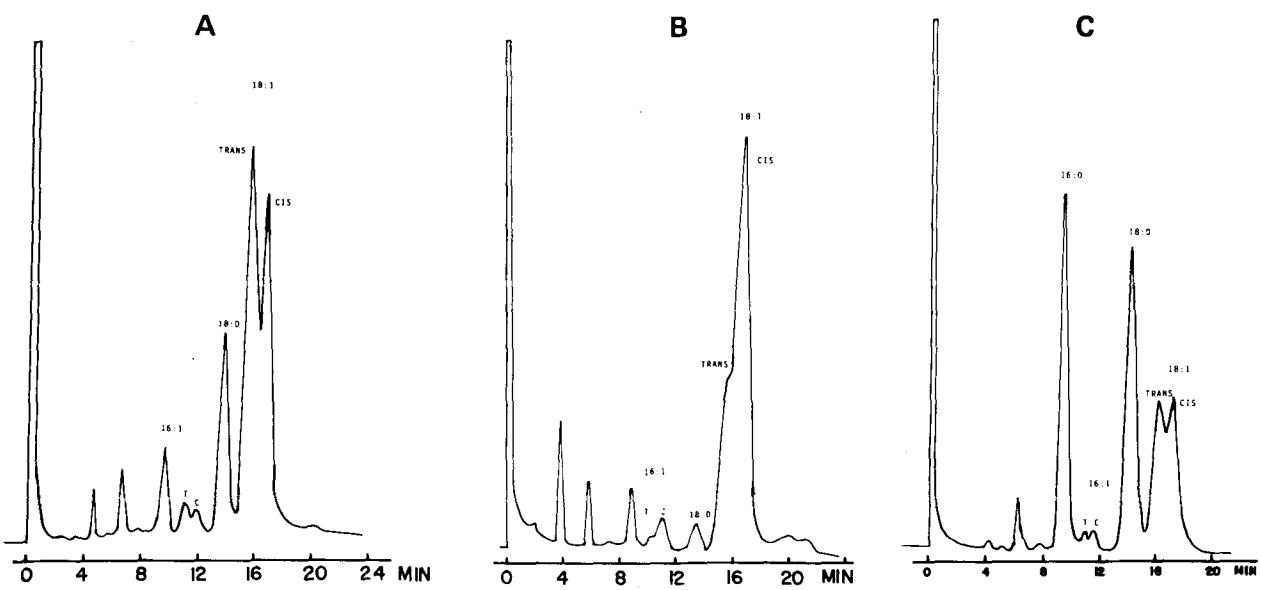

FIG. 2. (A) A commercial oleylamine (high *trans* isomer), chromatographed as the TFA derivative on a 10-ft 10% Apolar 10C column at 250 C. (B) A low *trans* isomer oleylamine as the TFA derivative chromatographed on a 10-ft Apolar 10C column. (C) A tallow amine chromatographed as the TFA derivative on an Apolar 10C column.

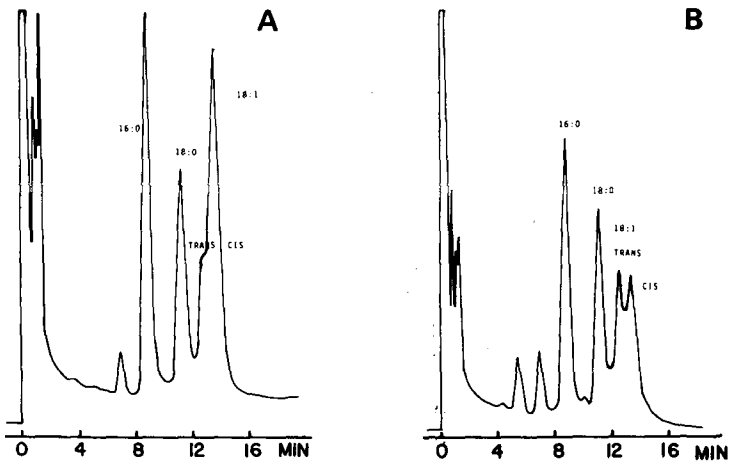

FIG. 3. (A) Chromatogram of N-alkyl 1,3 propane diamine containing high amounts of C-18 *cis* isomer. (B) Chromatogram of N-alkyl 1,3 propane diamine containing low amounts of C-18 *cis* isomer.

column, even when TFA derivatives were used. For some reason which was not readily apparent to us, the amines reacted with the liquid phase and destroyed the column's ability to separate these isomers.

Primary amines are often separated on GC columns containing potassium hydroxide or other bases on the support. Liquid phases used for this separation are the Apiezon greases, silicones and carbowaxes. Polyester columns with their unique separations of the saturates and unsaturates have never been able to be used in this manner. It occurred to us that the Silar columns could be treated with KOH to give the separation we desired with primary amines. We made a Silar column containing 1% KOH on the support. The column failed completely. The primary amines did not emerge and the *cis/trans* separation of the TFA derivatives could not be accomplished on this column. The experiment added credence to the theory that basic substances are detrimental to the cyanopropyl silicone liquid phases.

Quantitation of samples has been made using peak area normalization. Further work along this line will be needed using pure standards to get absolute numbers. There have been some differences between GC and IR analyses of *trans* isomers. Further study will be required to resolve these differences.

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