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Note

The separation and identification of some isomeric alkylamines as their trifluoroacetyl derivatives

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The inherent problems associated with the analysis of free amines by gas chromatography are well known and the use of trifluoroacetyl (TFA) derivatives to overcome these difficulties has been described previously[1]. Although excellent resolution of free amines may be obtained on surface-coated capillary columns containing a stationary phase which has been alkali-treated, the associated low flow-rates of the carrier gas and low capacity often make these columns inconvenient for connection to a mass spectrometer. Support-coated open tubular (SCOT) columns, however, are capable of being operated at a helium flow-rate of up to 15 ml/min without undue loss of resolution, but nevertheless suffer from the disadvantage that preparation of a column by deposition of caustic alkali on the finely divided support material might lead to decomposition.

The present communication describes the application of TFA derivatives for the analysis of some aliphatic amines by coupled gas chromatography (GC) and mass spectrometry (MS), employing commercially available SCOT columns.

EXPERIMENTAL

The amines were obtained from commercial suppliers and other sources, but when this was not possible the secondary amines were synthesised by treatment of the appropriate benzylidene alkylamine with an alkyl bromide[2]. The TFA derivatives were formed with trifluoroacetic anhydride.

Gas chromatography

All investigations were carried out on a Perkin-Elmer F-11 gas chromatograph fitted with a flame ionization detector. Nitrogen was used as a carrier gas, except during GC–MS studies, when helium was employed.

Separations were carried out on a SCOT column containing DEGS and operated in an oven which was temperature-programmed from 50° to 180° at 5° per min.

Mass spectrometry

Mass spectra were recorded on a Perkin-Elmer-Hitachi RMU 7L spectrometer coupled to a gas chromatograph through a Watson-Biemann separator operating

at 200°. Spectra were obtained at an ionising voltage of 75 eV and a source temperature of 250°. Each component was scanned several times across the GLC peak in order to avoid the production of distorted spectra. High resolution determinations were made at a resolution of 10,000.

RESULTS AND DISCUSSION

A comparison of the results given in Tables I and II indicates that the retention time is dependent upon three factors, *viz.* carbon number, degree of branching and

TABLE I

GC DATA ON C_4 AMINES

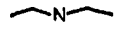
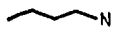
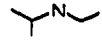
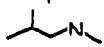
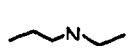
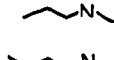
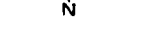
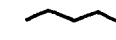
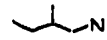
Compound No.	*TFA derivative of*	*Schematic structure of amine*	*Retention time (min)*
1	N-Methylisopropylamine		6.2
2	Diethylamine		6.4
3	*tert.*-Butylamine		6.4
4	N-Methyl-*n*-propylamine		7.2
5	1-Methylpropylamine		10.2
6	2-Methylpropylamine		11.6
7	*n*-Butylamine		12.5

TABLE II

GC DATA ON C_5 AMINES

Compound No.	*TFA derivative of*	*Schematic structure of amine*	*Retention time (min)*
8	N-Ethylisopropylamine		6.9
9	N-Methyl-*sec.*-butylamine		7.9
10	N-Methylisobutylamine		7.9
11	N-Ethyl-*n*-propylamine		7.9
12	N-Methyl-*n*-butylamine		9.3
13	3-Aminopentane		11.6
14	2-Aminopentane		12.0
15	*n*-Pentylamine		13.8
16	2-Methylbutylamine		13.8
17	Isopentylamine		14.4

position of the nitrogen atom in the molecule. Comparison of compound 7 with 15, and 6 with 17 clearly shows that a simple increase in chain-length causes an increase in retention time. The effect of branching in the carbon chain generally causes a decrease in retention time, and this phenomenon is demonstrated by comparison of compounds 3, 5 and 7 in the C_4-series, and compounds 9, 10 and 12 in the C_5-series However, an exception to this rule can be seen in compounds 15, 16 and 17, where the reverse is true.

Within a given series, the retention time is increased as the nitrogen atom is positioned nearer the end of an unbranched chain. This effect is clearly demonstrated in the following series of compounds: 11, 12 and 15; 8, 10 and 17; 9 and 16; 2, 4 and 7; 1 and 6.

In a series of primary amines, in which the nitrogen atom is positioned on different carbon atoms along the chain, those derivatives with a short retention time tend to have the nitrogen atom attached to a carbon near the centre of the chain. This effect is demonstrated in compounds 5 and 7, and in compounds 13, 14 and 15.

In all the derivatives studied the molecular ion (M^+), the $(CF_3)^+$ ion and the $(M-CF_3)^+$ ion are visible, although their intensities are variable. In nearly all cases the base peak in the spectrum represents the loss of an alkyl fragment from the molecular ion, although the nature of the moiety depends upon the substitution and degree of branching in the carbon chains.

The TFA derivatives of diethylamine (compound 2) and *tert.*-butylamine (compound 3) have similar retention times, but may be distinguished by mass spectrometry. Diethylamine-TFA possesses a strong ion at *m/e* 154, due to the loss of a methyl radical from the molecular ion. This ion is absent in *tert.*-butylamine-TFA.

TABLE III

MASS SPECTRA OF TFA ALKYLAMINES

Compound No.	*Ten principal ions in mass spectrum (in order of intensity)*
1	154, 140, 169, 110, 69, 155, 100, 92, 114, 141
2	126, 69, 154, 72, 70, 100, 140, 169, 78, 56
3	154, 56, 114, 41, 57, 69, 42, 84, 155, 94
4	140, 69, 100, 42, 78, 112, 60, 43, 40, 154
5	140, 43, 69, 154, 41, 56, 57, 70, 141, 126
6	56, 41, 58, 127, 69, 126, 42, 57, 114
7	126, 127, 56, 69, 41, 100, 140, 114, 57, 78
8	43, 168, 140, 41, 126, 42, 183, 69, 70, 72
9	154, 110, 183, 114, 69, 128, 126, 56, 41, 140
10	140, 128, 183, 141, 69, 114, 110, 168, 90, 97
11	154, 126, 140, 43, 114, 69, 41, 183, 56, 78
12	140, 114, 141, 112, 69, 126, 154, 90, 78, 42
13	41, 154, 43, 69, 126, 140, 70, 55, 71, 114
14	140, 55, 69, 114, 70, 41, 126, 42, 43, 168
15	126, 127, 114, 42, 140, 70, 41, 69, 51, 97
16	127, 41, 57, 70, 126, 58, 55, 69, 114, 71
17	126, 127, 55, 114, 70, 72, 41, 57, 69, 43

Similarly, the latter derivative possesses an ion at *m/e* 84 absent in the diethylamine-TFA[3].

The derivatives numbered 9 and 10 in Table II may be distinguished by the presence of an ion at *m/e* 154 in the latter which is absent in the former. Similarly compound 10 contains an *m/e* 140 ion, which is only of low intensity in compound 9. These ions are formed by loss of an ethyl and an isopropyl fragment from the molecular ion, respectively.

The derivative from N-methylisobutylamine possesses a large *m/e* 110 ion. A high resolution determination on this ion yielded on exact mass value of 110.0216 (calc. for $C_3H_3NF_3$: 110.0217) and is formed from the *m/e* 154 ion (confirmed by the appropriate metastable ion) by loss of the elements of acetaldehyde. In contrast, the TFA derivative of N-ethyl-*n*-propylamine exhibits only a very small *m/e* 110 ion.

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