CHROM. 6113

## Gas chromatography and mass spectrometry of some isomeric cyclic amines as their trifluoroacetyl derivatives

During an investigation into some constituents of cheese and chocolate by gas chromatography (GC) and mass spectrometry (MS), a number of amines were detected which were found to be components common to the two foodstuffs. Amines were isolated by a newly developed procedure[1] and then converted to trifluoroacetyl (TFA) derivatives by treatment of the extract with trifluoroacetic anhydride. The TFA derivatives were analysed by GC and MS.

The mass spectrum of the TFA derivative of one common constituent of the two food products exhibited a mass spectrum with a molecular ion at *m/e* 243 and fragments which were consistent with the presence in the original foodstuff of a bicyclic amine with a mol. wt. of 147. An examination of published work on the separation and identification of the TFA derivatives of tetrahydro-naphthylamines, -methylquinolines and -methylisoquinolines indicated that this field of work was largely unexplored, though the separation and mass spectra of several simple amine TFA derivatives have been published[2-4].

The TFA derivatives of a number of isomeric amines with a mol. wt. of 147 have been synthesised. The separation of these derivatives was carried out by GLC on a capillary column, whilst mass spectra were recorded on a portion of the column effluent.

*Experimental*

The four possible tetrahydronaphthylamines were obtained by reduction of the appropriate naphthylamine[5] or tetralone oxime with sodium and ethanol, or by high-temperature sulphonation of tetralin, followed by fusion with sodamide. An authentic sample of 5,6,7,8-tetrahydro-1-naphthylamine was also available from a commercial supplier. The tetrahydroquinolines and isoquinolines were synthesised by sodium–ethanol reduction of the corresponding methyl substituted aromatic amines, which were in turn either obtained from a number of sources or synthesised by the Pomeranz–Fritsch reaction[6]. Trifluoroacetyl derivatives were prepared as previously described[2].

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

Separations were carried out on a support-coated open tubular column containing Carbowax 20M and operated in an oven which was temperature-programmed from 50° to 180° at 5° per minute.

*Mass spectrometry.* Mass spectra were recorded on a Perkin-Elmer–Hitachi RMU6 spectrometer coupled to a gas chromatograph through a Watson–Biemann separator operating at 200°. Spectra were obtained with 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.

*Results and discussion*

The separation of a selection of methyltetrahydroquinolines, methyl tetrahydroisoquinolines and tetrahydronaphthylamines as TFA derivatives is shown in Fig. 1. Although the tetrahydronaphthylamines are clearly separated as a group from the heterocylic derivatives, no such clear separation occurs between the two groups containing the cyclic nitrogen in the 1 and 2 positions. In fact, it has not been possible to effect any separation between the derivatives of 7-methyltetrahydroquinoline and 1-methyltetrahydroisoquinoline. In the naphthylamine series, there is similarly no separation between 5,6,7,8-tetrahydro-1-naphthylamine TFA and 1,2,3,4-tetrahydro-2-naphthylamine TFA.

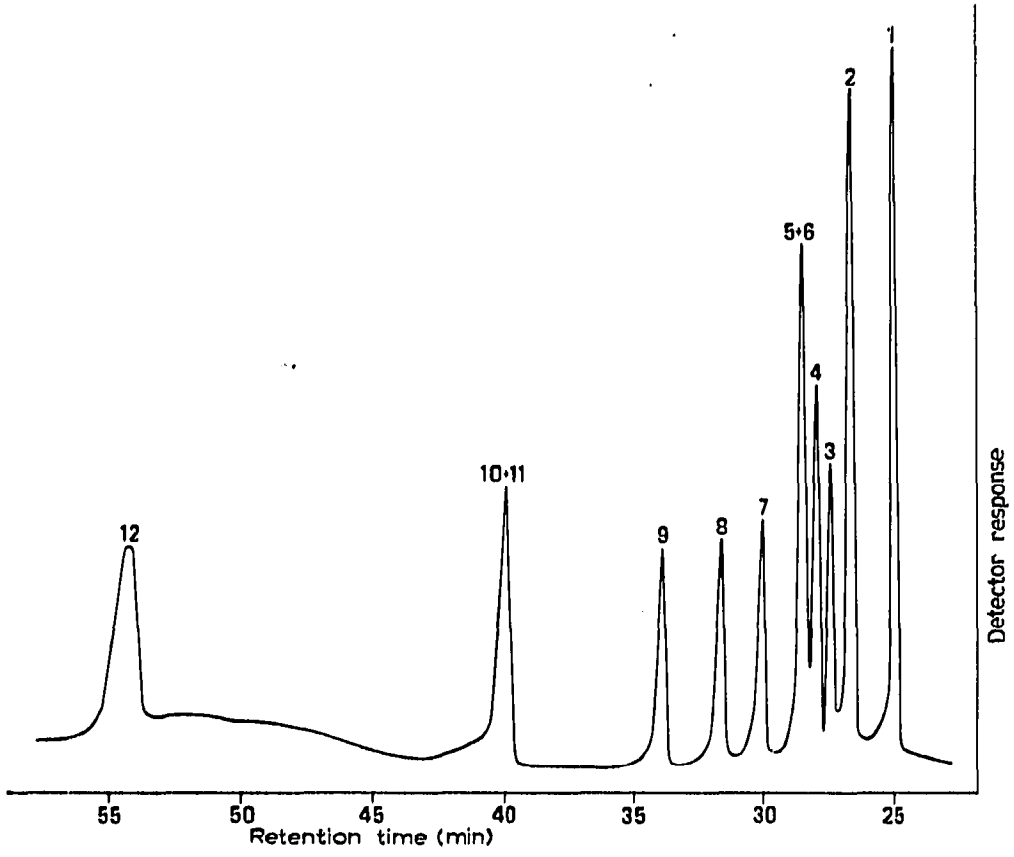


Fig. 1. GC separation of the N-TFA derivatives of (1) 2-methyl-1,2,3,4-tetrahydroquinoline; (2) 8-methyl-1,2,3,4-tetrahydroquinoline; (3) 4-methyl-1,2,3,4-tetrahydroquinoline; (4) 3-methyl-1,2,3,4-tetrahydroisoquinoline; (5) 7-methyl-1,2,3,4-tetrahydroquinoline; (6) 1-methyl-1,2,3,4-tetrahydroisoquinoline; (7) 6-methyl-1,2,3,4-tetrahydroquinoline; (8) 5-methyl-1,2,3,4-tetrahydroquinoline; (9) 1,2,3,4-tetrahydro-1-naphthylamine; (10) 5,6,7,8-tetrahydro-1-naphthylamine; (11) 1,2,3,4-tetrahydro-2-naphthylamine; (12) 5,6,7,8-tetrahydro-2-naphthylamine.

Although it is very difficult to account for all the differences in retention times between closely similar compounds, molecular models of the foregoing TFA derivatives suggest that those in which the trifluoroacetyl group stands away from the remainder of the molecule tend to have relatively long retention times. In the molecule of the TFA derivative of 2-methyltetrahydroquinoline, there is a considerable interaction between the carbonyl group and a number of surrounding protons, whereas

the complete reverse is found in the model of 5,6,7,8-tetrahydro-2-naphthylamine TFA, and these properties may account for the considerable disparity in retention times between these two derivatives.

The mass spectra of the two 1,2,3,4-tetrahydronaphthylamine derivatives (Fig. 2) are devoid of molecular ions but they both show intense peaks at *m/e* 130 and these ions clearly distinguish the compounds from the isomeric 5,6,7,8-tetrahydro derivatives, which only exhibit the *m/e* 130 in low intensity. The most significant dissimilarity between the two 5,6,7,8-tetrahydro derivatives is the difference in the relative intensity of the $[M-CF_3]^+$ and $[M-COCF_3]^+$ ions at *m/e* 174 and 146, respectively.

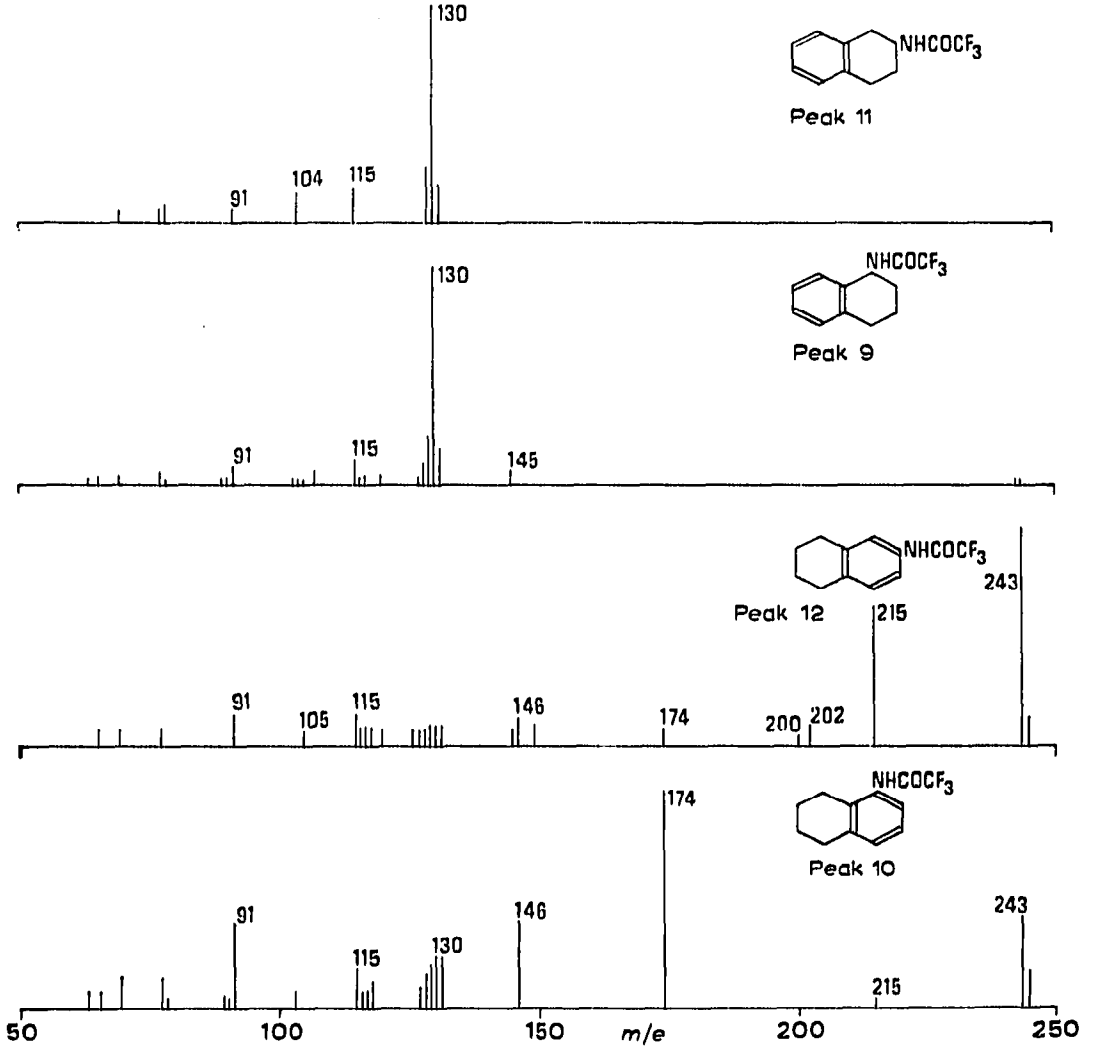


Fig. 2. Mass spectra of N-TFA-tetrahydronaphthylamines.

The spectra of all the methyltetrahydroquinoline derivatives (Fig. 3) exhibit strong molecular ions, which are often also base peaks, together with ions at *m/e* 174 and 146 due to the $[M-CF_3]^+$ and $[M-COCF_3]^+$ species, respectively. A peak at *m/e* 228 may be attributed to the loss of methyl radical from the molecular ion and this transition is confirmed by a metastable peak in the spectrum of the 4-methyl derivative, where the *m/e* 228 ion is particularly intense. The TFA derivatives of the methyl-

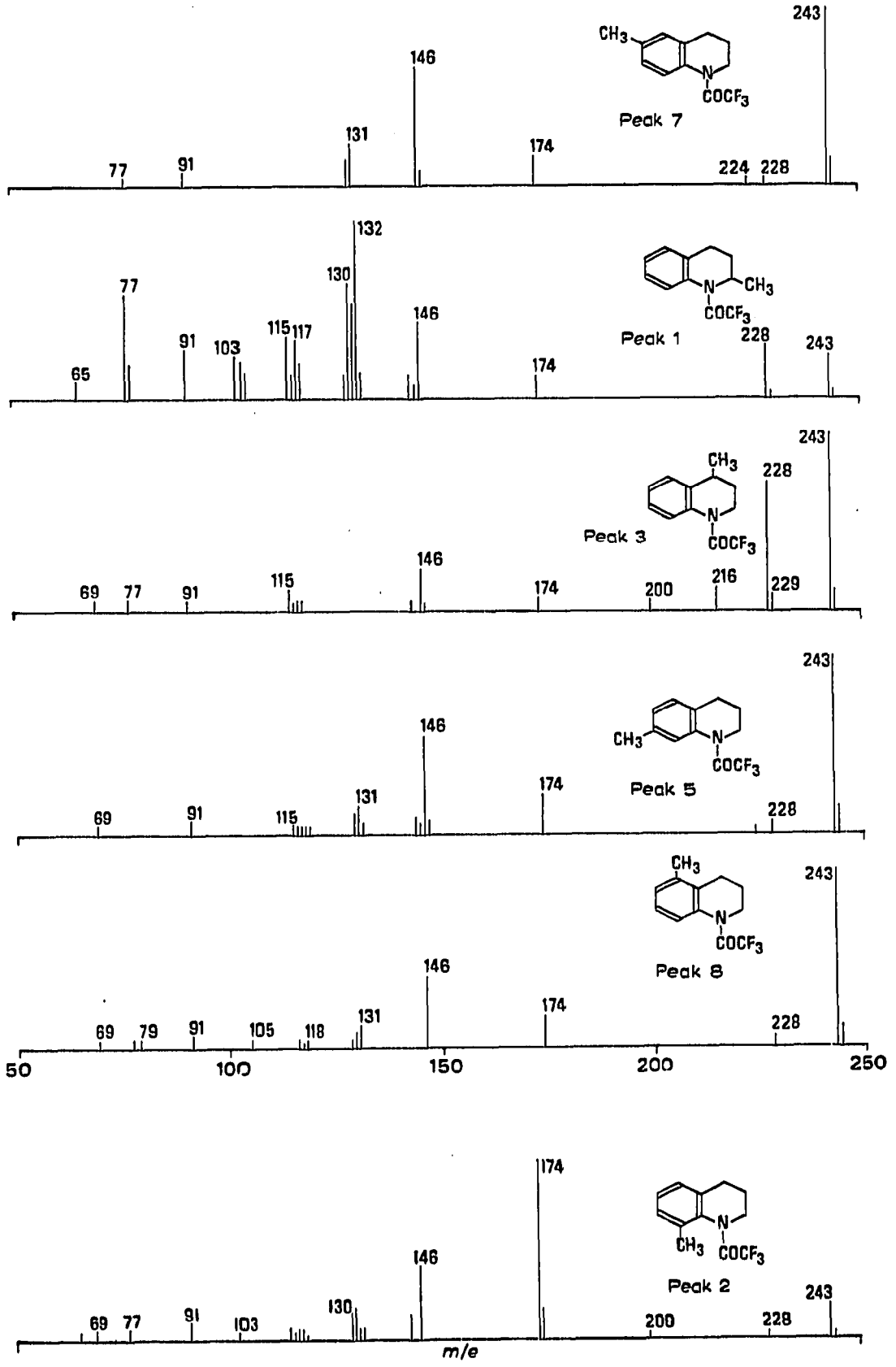


Fig. 3. Mass spectra of N-TFA-methyl-1,2,3,4-tetrahydroquinolines.

tetrahydroisoquinolines exhibit spectra which show similarities with the corresponding quinolines, though greater differences occur between individual members of the groups. Thus, the *m/e* 174 ion is absent from the spectrum of the 4-methyl derivative and the *m/e* 228 ion is the base peak in the spectrum of the 1-methyl derivative. The compound derived from 3-methyltetrahydroisoquinoline also exhibits unusual characteristics owing to the presence of ions at *m/e* 215 and 214, and at *m/e* 104 (ref. 7).

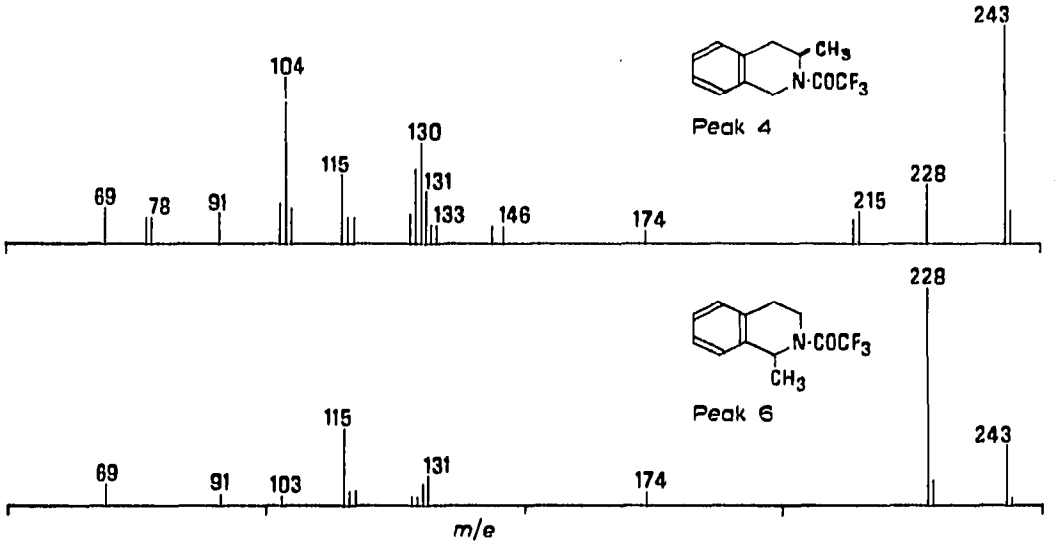


Fig. 4. Mass spectra of N-TFA-methyl-1,2,3,4-tetrahydroisoquinolines.

Although the TFA derivatives from 7-methyltetrahydroisoquinoline and 1-methyltetrahydroquinoline (Fig. 4) possess almost identical retention times on the chromatograms, they are readily distinguished, even in mixtures of the two, by the presence of an *m/e* 103 ion and an *m/e* 146 in the two derivatives, respectively, which do not appear in the spectrum of the other component.

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