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Fragmentation of the Chain in the Mass Spectra of the Pyrrolidides of Alkylcyclohexanecarboxylic Acids

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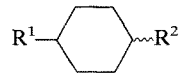
The electron impact mass spectra of the pyrrolidides of both the *cis*- and *trans*-octylcyclohexanecarboxylic acids show the structure of the aliphatic chain, despite the steric hindrance of a direct H transfer from the chain to the functional group.

INTRODUCTION

The positions of the branchings and double bonds in the chain are much more clearly revealed by the electron impact (EI) mass spectra of the pyrrolidides of fatty acids than by the spectra of the acids themselves or their alkyl or trimethylsilyl esters.[1–3] This property of the mass spectra of pyrrolidides is the result of a particularly favourable fragmentation mechanism, which is initiated by the ionized functional group.[1,4,5] The mechanism starts with the abstraction by the pyrrolidide group of a hydrogen atom from the aliphatic chain, whereby a radical is created somewhere along the chain. The radical subsequently causes the rupture of the chain, giving rise to even-electron fragments of every possible length. Since the charge is localized in the protonated pyrrolidide group in all these fragments, there is no easy path for further fragmentation, and therefore the mass spectrum gives a quite clear picture of the chain structure.

A comparable effect on the mass spectra of long chains is exerted by the pyridine nucleus attached in various ways to the chain, as for example in the nicotinate of an alcohol[6] or the 3-pyridylmethyl ester of an acid.[7]

It seemed interesting to investigate whether the chain structure is also expressed in the mass spectrum of the pyrrolidide of an acid, in which the direct attack of the functional group on the chain is sterically hindered.



R^1	R^2	*trans*	*cis*
CO_2H	n-C_8H_{17}	**1**	**2**
$CON(CH_2)_4$	n-C_8H_{17}	**3**	**4**
$CON(CH_2)_4$	$CH_2CH(CH_3)C_2H_5$	**5**	
CH_2OCO–(N)	n-C_8H_{17}	**6**	**7**
CH_2OH	n-C_8H_{17}	**8**	**9**

trans-4-Octylcyclohexanecarboxylic acid (**1**) was available to us for this experiment. By comparing the mass spectrum of the pyrrolidide of **1** with that of the corresponding *cis* isomer (**2**), the additional question as to whether mass spectrometry would be capable of distinguishing between such geometrical isomers could also be answered.

EXPERIMENTAL

cis-4-Octylcyclohexanecarboxylic acid (**1**) was obtained by hydrogenation of 4-octylbenzoic acid with H_2/PtO_2 in acetic acid. Methyl *trans*-4-octylcyclohexanecarboxylate was obtained by treating the corresponding *cis* compound with a catalytic amount of $NaOCH_3$ in DMSO at 110 °C for 6 h as the major component of the *cis*/*trans* mixture. The pyrrolidides **3** and **4** were obtained by heating the methyl esters in excess pyrrolidine and a drop of acetic acid in a sealed ampoule at 110 °C for 3 h.[1] The alcohols **8** and **9** were produced by treating the mixture of acids **1** and **2** with excess $LiAlH_4$ in ether at room temperature overnight. The nicotinates **6** and **7** were obtained by treating the mixture of alcohols with an excess of nicotinoyl chloride HCl in dry pyridine for 1 h at 100 °C.[7]

All mixtures of stereoisomers could be separated for mass spectroscopic analysis by capillary gas chromatography using a gas chromatographic/mass spectral combination. Gas chromatograph: Varian 2700 (column: SE 52), mass spectrometer: VG 7070-F (VG Analytical Wythenshawe UK). The mass spectra were run at 70 eV and an ion source temperature of approx. 230 °C.

RESULTS AND DISCUSSION

The mass spectra of the pyrrolidides **3** and **4** are shown in Figs 1 and 2. It can be seen that the whole 8-carbon chain is clearly exhibited in the mass spectra of both isomers, thus allowing structure elucidation of

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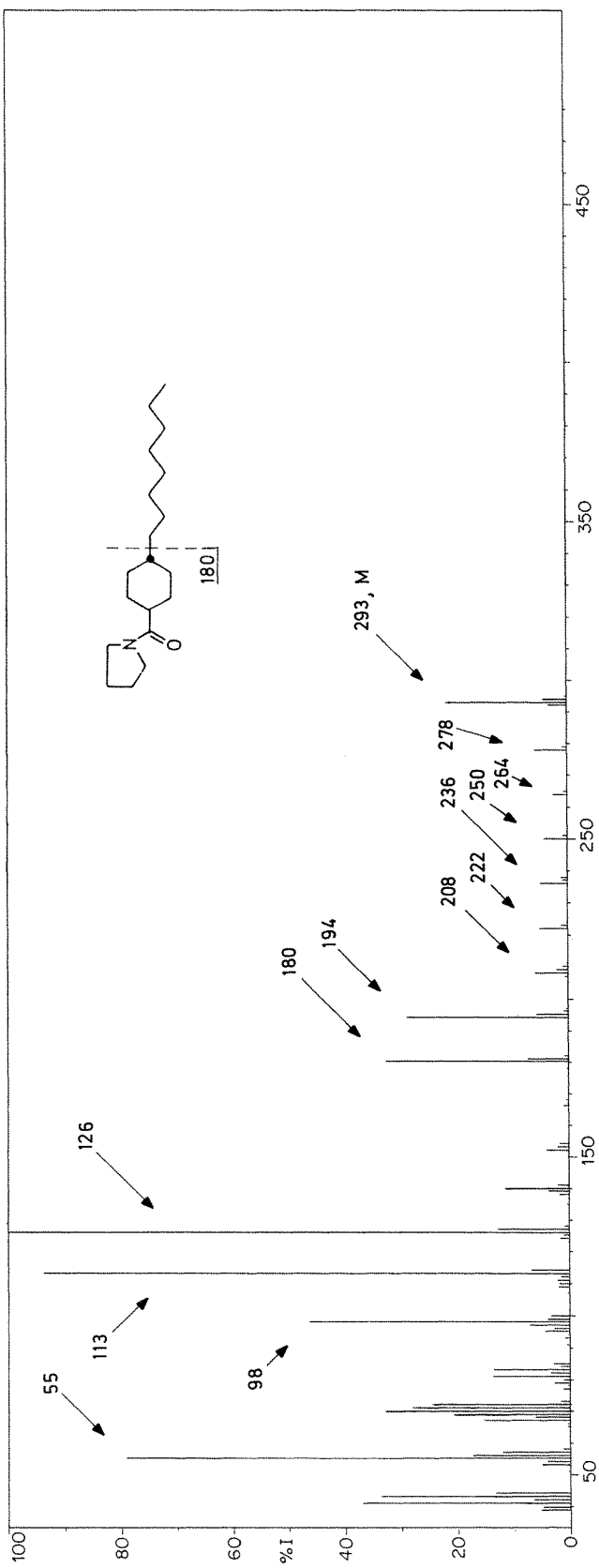

Figure 1. Mass spectrum of *trans*-4-octylcyclohexanecarbonylpyrrolidine (**3**).

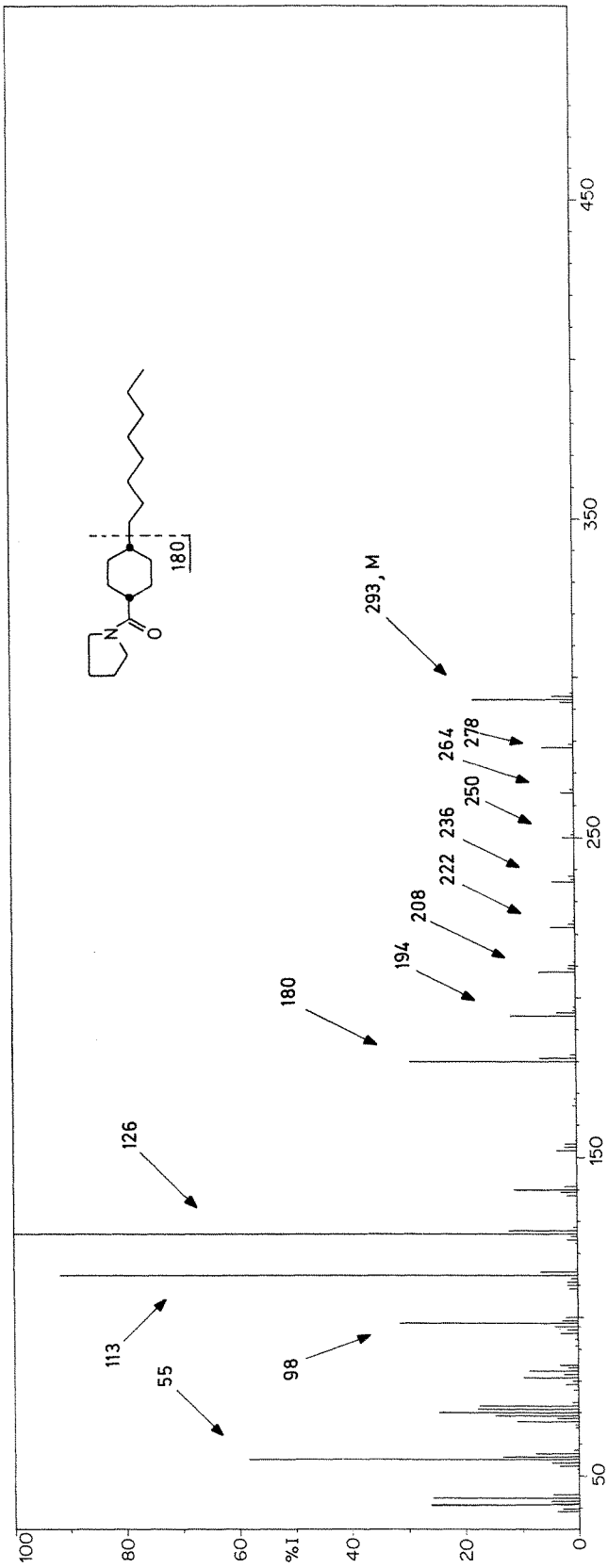

Figure 2. Mass spectrum of *cis*-4-octylcyclohexanecarbonylpyrrolidine (**4**).

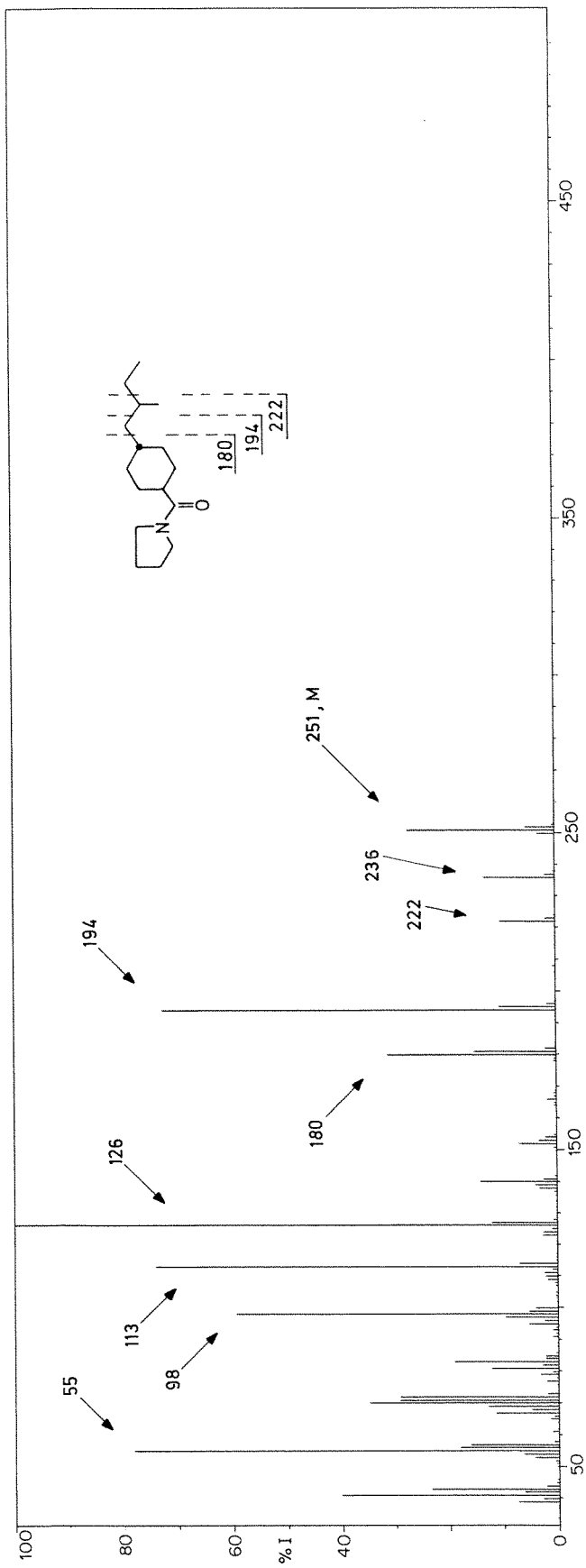

Figure 3. Mass spectrum of *trans*-4-(2-methyl)butylcyclohexanepyrrolidine (**5**).

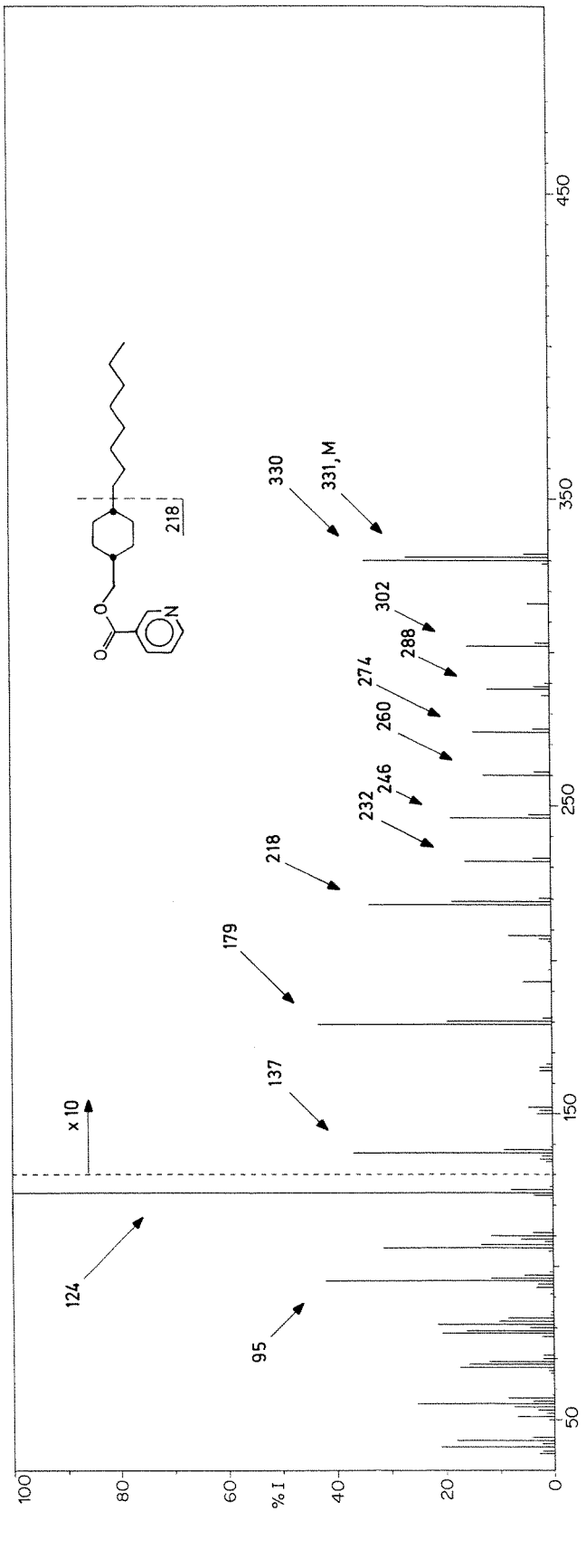

Figure 4. Mass spectrum of *cis*-4-octylcyclohexylmethyl nicotinate (**7**).

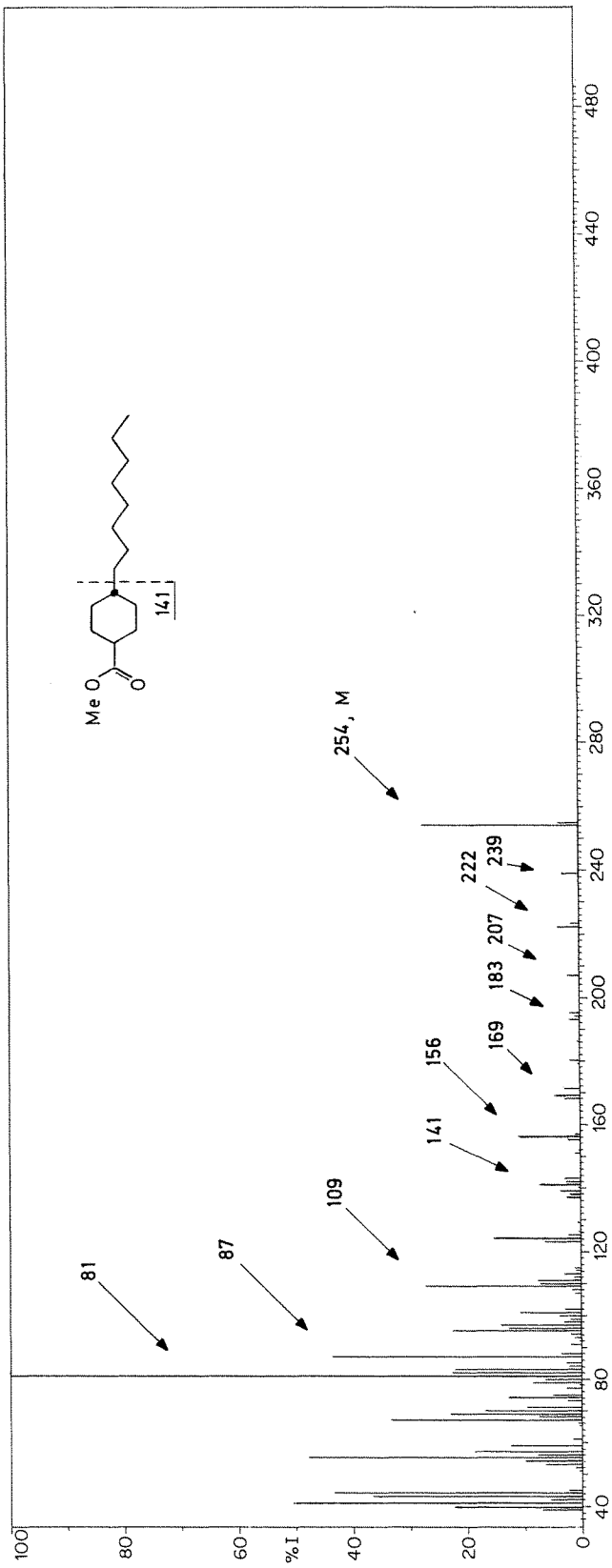

Figure 5. Mass spectrum of methyl *trans*-4-octylcyclohexanecarboxylate.

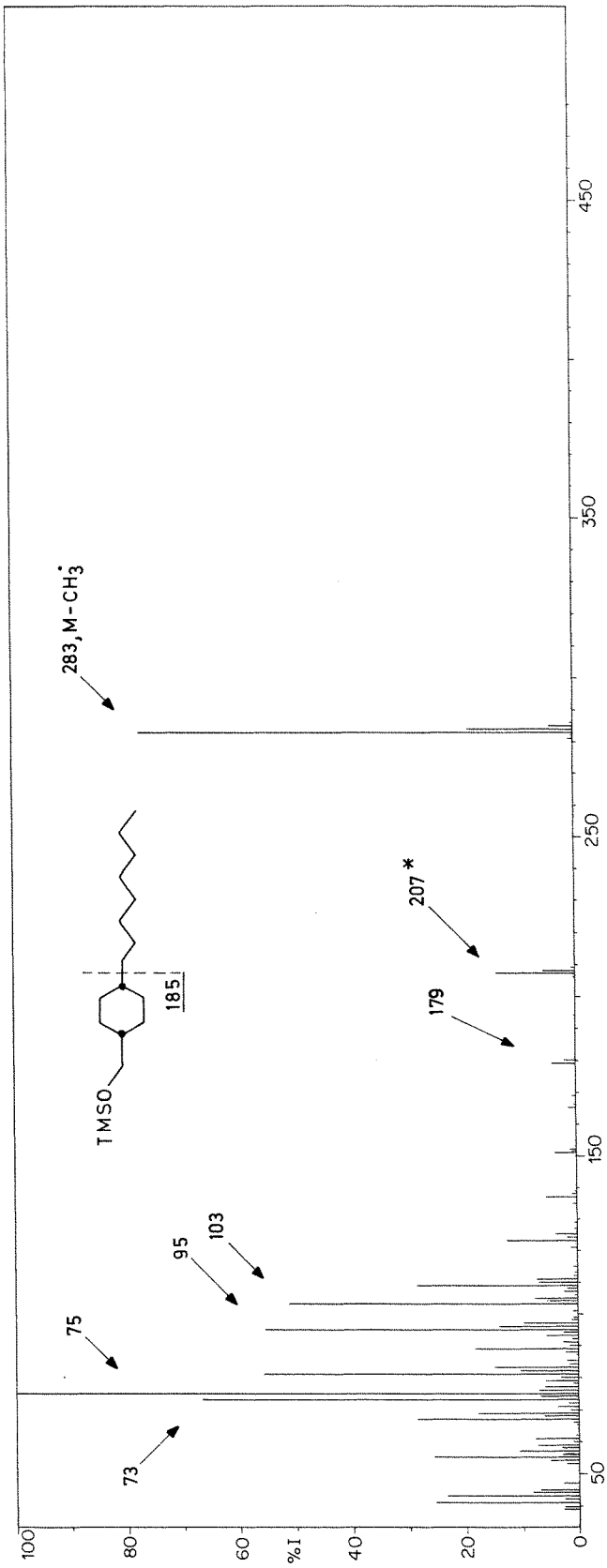

Figure 6. Mass spectrum of *trans*-4-octylcyclohexylmethanol trimethylsilyl ether. (* From gas chromatographic column.)

the chain in such compounds just as well as in unhindered cases. This conclusion is confirmed by the mass spectrum of an analogous pyrrolidide **5**, which carries a methyl branch on the chain (Fig. 3).

The differentiation of geometrical isomers appears to be very difficult by this method, however, if only one of the isomers is available. The similarity of the spectra of the two isomers, despite the great difference in the steric hindrance of the direct attack of the pyrrolidide on the chain in the two structures, suggests that such a direct attack is not required to produce fragmentation of the chain. Probably the first step in the mechanism consists of the transfer of a hydrogen atom from the cyclohexyl residue to the pyrrolidide group, whereby a radical is created somewhere on the ring. This radical then triggers fragmentation along three lines: (i) cleavage of the ring near the functional group, leading eventually to the peaks m/z 113 and 126 in mechanisms not yet elucidated and of no particular interest in the present context, (ii) breaking away of the whole chain and (iii) displacement of the radical to a carbon atom within the chain by a second H transfer, followed by radical-triggered cleavage of the chain.

An analogous result is obtained with the nicotinates **6** and **7** of the corresponding octylcyclohexylcarbinols **8** and **9**.[7] The mass spectrum of the *cis* derivative is shown in Fig. 4. The spectrum of the *trans* isomer is again very similar and therefore is not shown.

For comparison the spectra of the methyl ester of the acid **1** and the trimethylsilyl ether of the alcohol **8** are shown in Figs 5 and 6. As was expected, these spectra contain very little information on the aliphatic portion of the molecules.

CONCLUSION

The EI mass spectra of the pyrrolidides of cyclohexanecarboxylic acids substituted in the 4-position by an aliphatic chain show the positions of branchings in the chain. The spectra of the *cis* and *trans* isomers are very similar, in spite of the fact that a direct H transfer from the chain to the functional group is sterically hindered in the latter case.

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