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MASS SPECTRA OF ALDITOL TRIFLUOROACETATES

O. S. CHIZHOV, B. A. DMITRIEV, B. M. ZOLOTAREV, A. YA. CHERNYAK
and N. K. KOCHETKOV
N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences
of the USSR, Moscow, USSR

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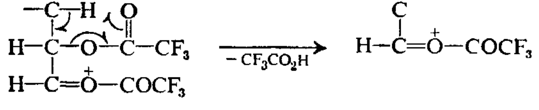
Abstract—The trifluoroacetyl derivatives of alditols are convenient compounds for mass spectrometric investigation as they are easily obtainable and highly volatile. They show simple fragmentation patterns with intensive peaks in the high mass range. Trifluoroacetates of alditols may be used for detection and location of deoxy groups in the molecule.

THE SUCCESSFUL development of mass spectrometry[1] and mass spectrometry combined with gas liquid chromatography[2,3] (g.l.c.) in carbohydrate field emphasises the need for highly volatile and easily available sugar derivatives with simple fragmentation patterns. Trifluoroacetyl (TFA) derivatives of sugars described by Tatlow[4] seemed attractive from this point of view and their mass spectra should be *a priori* simpler than those of acetates[5,6] and trimethyl silyl ethers.[7]

We started our investigation with TFA derivatives of alditols. Our preliminary data as well as the paper[8] published recently showed that alditol trifluoroacetates could be readily separated by g.l.c. techniques and hence may be of value for examination by g.l.c./mass spectrometry. We measured the mass spectra of TFA derivatives of glycerol, erythritol, arabinitol, ribitol, xylitol, glucitol, mannitol, galactitol, 1-deoxy-L-mannitol and 2-deoxy-D-arabinohexitol. All the mass spectra except those of glycerol and deoxyhexitol show a molecular peak intense enough for direct molecular weight determination in contrast to the mass spectra of acetates[6] and methyl ethers[9] of alditols. The mass spectra of TFA derivatives of the diastereomeric alditols are all very similar and coincide within the limits of error. The electron-impact fragmentation of alditol trifluoroacetates resemble that of other esters of polyols. The fragmentation of the molecular ion starts from the splitting of the trifluoroacetyl radical and then of molecules of trifluoroacetic acid to give fragments of the C_n series (where n is the number of carbon atoms in the original alditol molecule) or from the rupture of one of carbon-carbon bonds to give the primary fragments ($C_{n-1} - C_1$). These primary fragments split off sequentially the molecules of trifluoroacetic acid. Thus, the mechanism of fragmentation of trifluoroacetates is analogous to that of esters of other carboxylic acids and can be considered as an example of a McLafferty rearrangement.



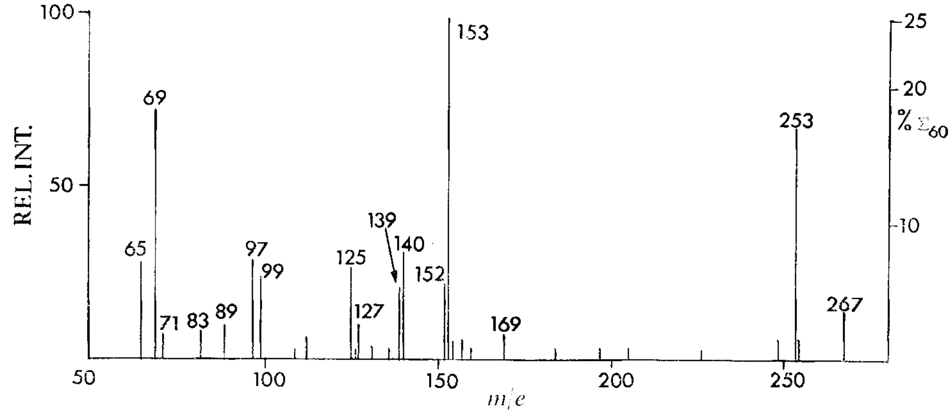


Fig. 1. Mass spectrum of TFA derivative of glycerol.

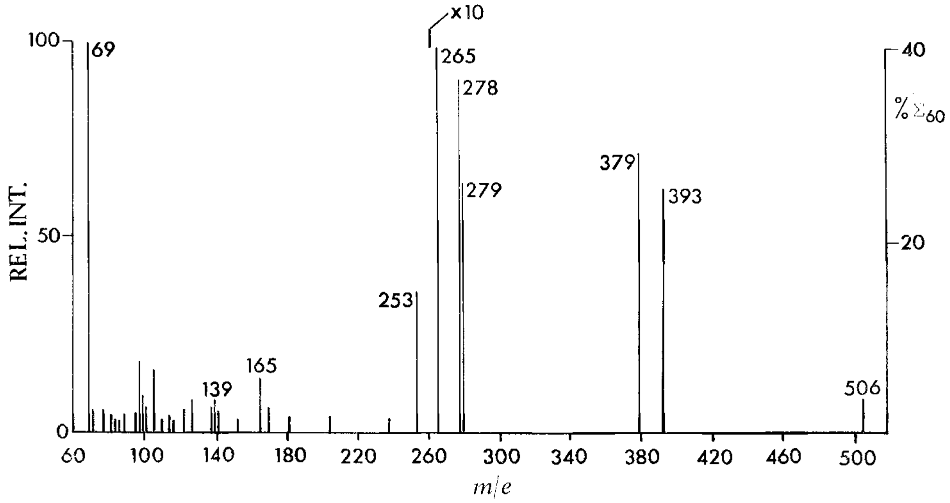


Fig. 2. Mass spectrum of TFA derivative of erythritol.

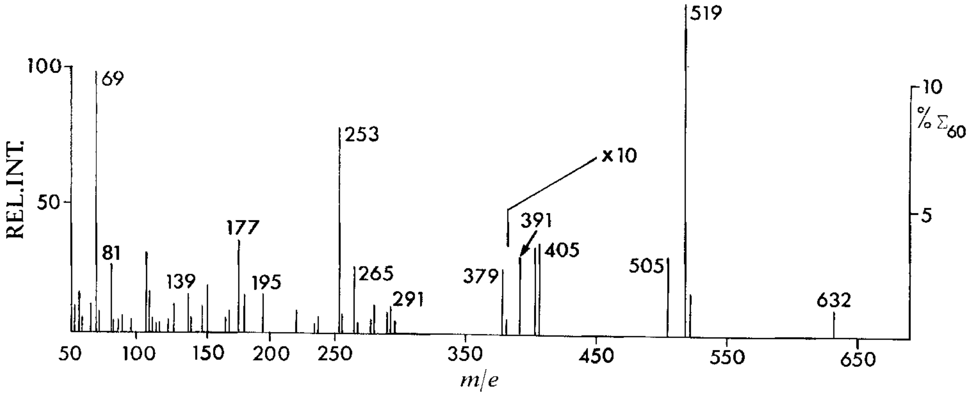


Fig. 3. Mass spectra of TFA derivatives of pentitols: arabinitol, ribitol and xylitol.

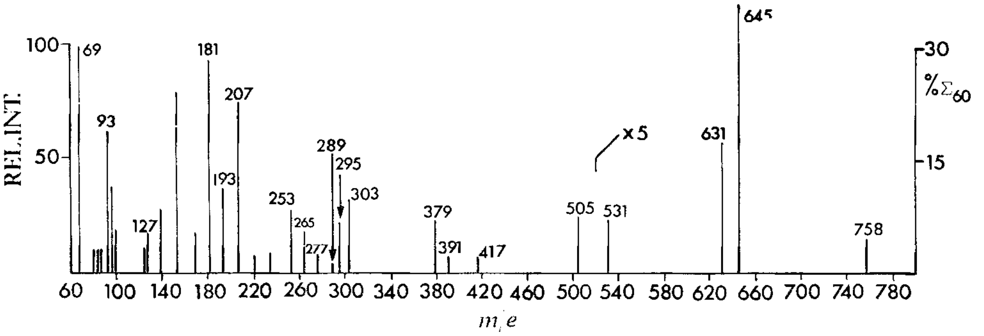


FIG. 4. Mass spectra of TFA derivatives of hexitols: glucitol, mannitol and galactitol.

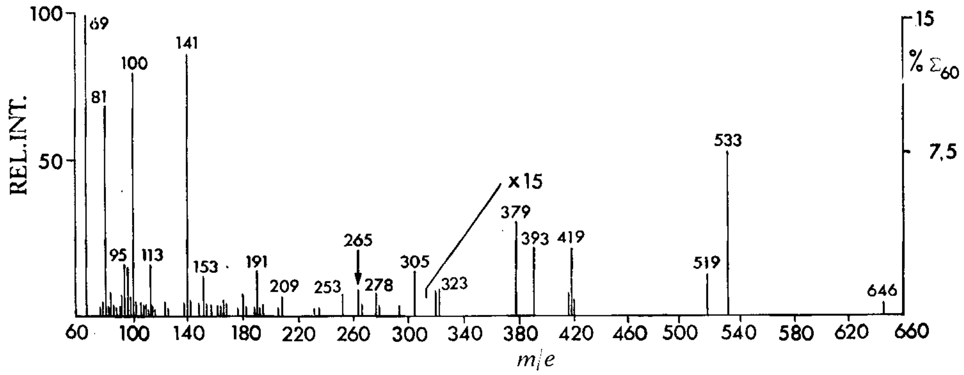
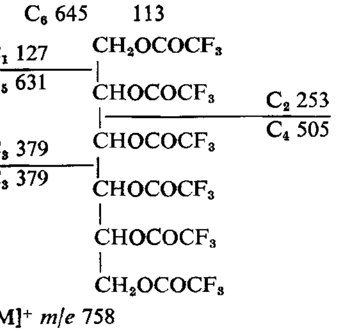


FIG. 5. Mass spectrum of TFA derivative of 1-deoxy-mannitol.

It is interesting to note that the C_5 series in the mass spectra of TFA derivatives of hexitols (see Fig. 4) and deoxy hexitols (see Figs. 5 and 6) consist of only the primary fragments containing the maximum number of TFA groups. The major suggested amount fragmentation pathways of hexitols are presented in Scheme 1.

SCHEME 1



C_6 645 113

C_1 127 | C_5 631

CH_2OCOCF_3 — $CHOCOCF_3$ — $CHOCOCF_3$ — $CHOCOCF_3$ — $CHOCOCF_3$ — CH_2OCOCF_3

C_2 253 | C_4 505

C_3 379 | C_3 379

$[M]^+$ m/e 758

C_6 $[M]^+$ m/e 758-645-531-417-303

C_5 m/e 631-517*-403*-289*

C_4 m/e 505-391-277

C_3 m/e 379-265

C_2 m/e 253-139

*

The fragmentations of the molecular ions of TFA derivatives of glycerol, erythritol and pentitols proceed analogously. It is evident that in these cases the series of fragments with the same number of carbon atoms as in the molecular ion are shifted 2

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* These fragments and related ones of C_5 series of deoxy hexitols are absent in mass spectra.

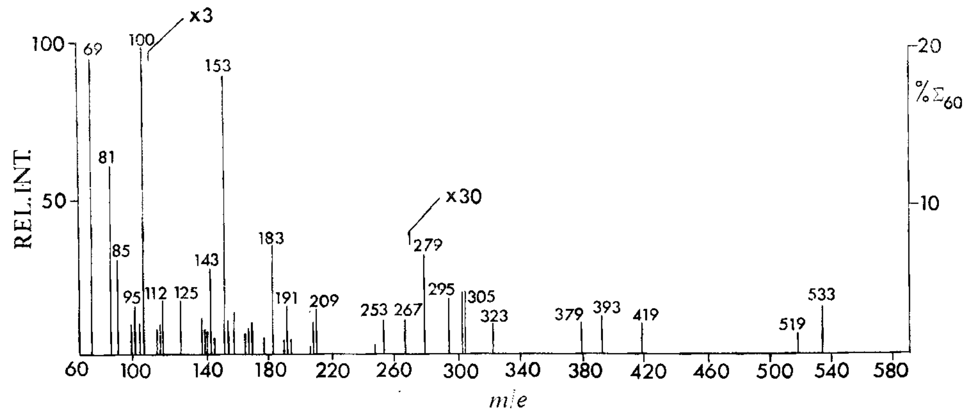
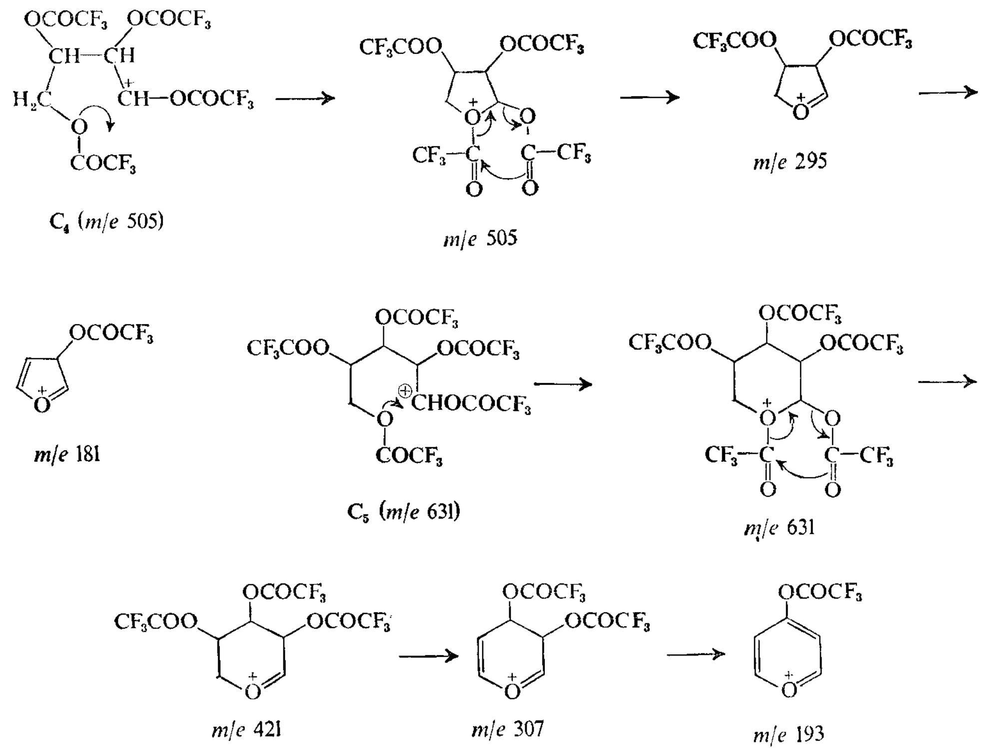


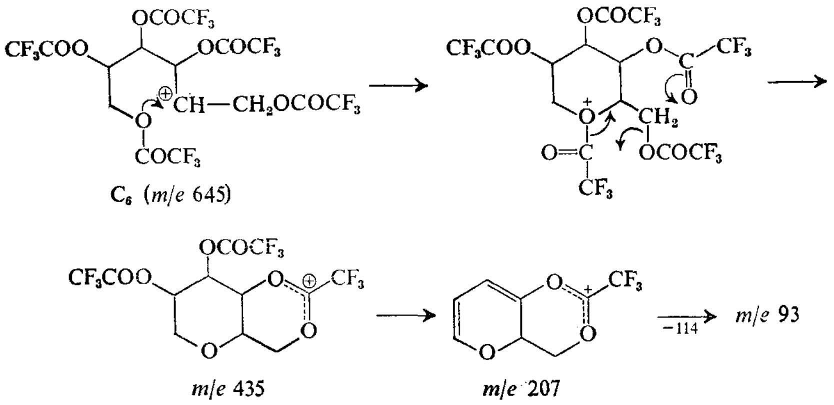
FIG. 6. Mass spectrum of TFA derivative of 2-deoxy-D-arabino-hexitol.

mass units to higher masses in comparison with the corresponding C_n fragments in the mass spectra of hexitols. The fragmentation of ions of the C_4, C_5 and C_6 series proceeds not only with the splitting off of trifluoroacetic acid molecules but accompanied by the loss of trifluoroacetic anhydride as well, leading apparently to the cyclic ions (Scheme 2). The most abundant peaks of this type are observed in the mass spectra of hexitol trifluoroacetates. The last members of each of these series

SCHEME 2

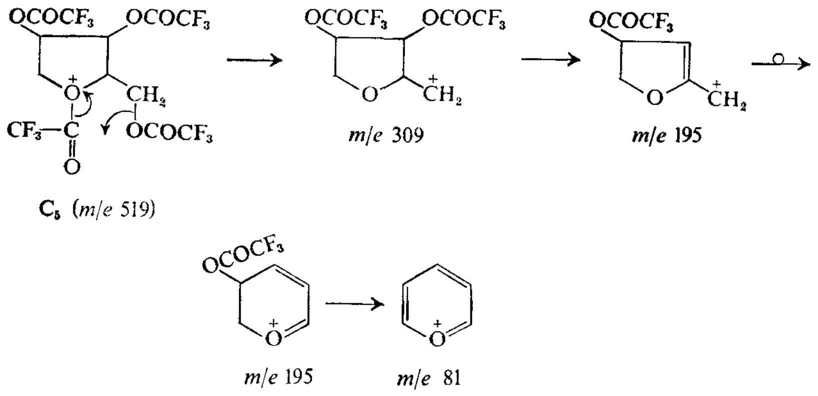


Scheme 2 (*cont.*)

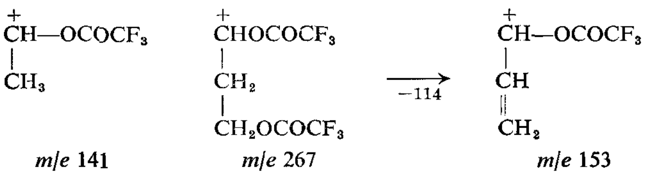


containing the least number of trifluoroacetyl groups give the most intense peaks. The fragmentation of the C_5 series of pentitols with the loss of trifluoroacetic anhydride leads to two peaks at *m/e* 195 and 81 with the possible structures shown below (Scheme 3). The splitting of trifluoroacetic anhydride for pentitol derivatives is less pronounced than for hexitols, however, and leads only to peaks of moderate intensity.

Scheme 3



As follows from the mass spectra of the trifluoroacetyl derivatives of 1-deoxy-mannitol and 2-deoxy-arabino-hexitol the most characteristic feature is the high abundance of the ions formed by cleavage of the carbon-carbon bond in β-position to the deoxy group and low abundance of all the others. Thus, the mass spectrum of TFA derivatives of 1-deoxy-mannitol (see Fig. 5) reveals the very abundant peak at *m/e* 141 and that of TFA derivatives of 2-deoxy-arabino-hexitol (see Fig. 6) contains an abundant peak at *m/e* 153. At the same time the peak at *m/e* 631 and peaks at *m/e*



$$\overset{+}{C}H{-}OCOCF_3{-}CH_3 \qquad \overset{+}{C}HOCOCF_3{-}CH_2{-}CH_2OCOCF_3 \xrightarrow[-114]{} \overset{+}{C}H{-}OCOCF_3{-}CH{=}CH_2$$

m/e 141 *m/e* 267 *m/e* 153

141 and 505 are absent from the mass spectra of TFA derivatives of 1-deoxy-mannitol and 2-deoxy-arabino-hexitol respectively, thus indicating the absence of carbon-carbon bond rupture in α-position to the deoxy-group.

Hence the determination of the molecular weight, and the presence and position of the deoxy-group may be accomplished by the mass spectroscopy of the trifluoroacetates of alditols as in the case of acetates of alditols and methyl ethers. The TFA derivatives of alditols may be preferred from the practical point of view, however, since they are readily available, highly volatile and exhibit rather simple spectra with the abundant peaks in the high mass range $[M - 113]^+$ and $[M - 127]^+$. These peaks together with the occasional molecular peaks provide a definitive molecular weight determination. The satisfactory resolution of TFA derivatives of alditols by g.l.c. makes them suitable for examination by the coupled g.l.c./mass spectrometry technique.

EXPERIMENTAL

The TFA derivatives of alditols are prepared as follows:[10] 1 to 3 mg of the corresponding alditol was dissolved in 0·1 ml of 10% solution of sodium trifluoroacetate in acetonitrile and 0·1 ml of trifluoroacetic anhydride was added. The mixture was heated in sealed tube for 10 to 15 min. at the 60° and then taken to dryness. Mass spectra were measured with an MX-1303 instrument at 70 eV. Temperature of the inlet system was maintained at about 150°.

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