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Note

^{13}C-Enrichment as an aid in the analysis of mass-spectral fragmentation patterns*

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Deuterium is used widely in mass spectrometry as an isotopic marker to facilitate the interpretation of fragmentation patterns. The ^{13}C nucleus, although relatively rarely employed in this context[1], may be a more reliable label in certain applications because it is less likely to be involved in intramolecular migration. The mass spectra of some *O*-isopropylidene derivatives illustrate the usefulness of ^{13}C-enrichment.

Major peaks in the spectrum (Fig. 1A) of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) are found[2] at *m/e* 245, 187, 159, 131, 129, 127, 101, 59, and 43. According to DeJongh and Biemann[2], the peak at *m/e* 245 represents the loss of a methyl group, whereas that at *m/e* 187 is due to the further loss of an *O*-isopropylidene group, as acetone. The peak at *m/e* 127 corresponds to a loss of CH_3 + $CH_3COCH_3 + CH_3COOH$, whereas those at *m/e* 59 and 43 are attributed to fragments from the *O*-isopropylidene moiety, corresponding to C_3H_7O and C_2H_3O, respectively.

Figs. 1B and 1C, which illustrate the mass spectra of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose-*1*-^{13}C (80% enriched) (**2**) and -*6*-^{13}C (60% enriched) (**3**), respectively, confirm the above assignments. In both the 1-^{13}C and 6-^{13}C derivatives, the peaks at *m/e* 245, 187, and 127 shift to 246, 188, and 128 (commensurate with the degree of enrichment), whereas the peaks at *m/e* 43 and 59 are unaffected. Cleavage of the C-4–C-5 bond is thought[2] to give rise to the peaks at *m/e* 101 and 159 (**4**). Accordingly, in the spectrum of the 6-^{13}C compound, the corresponding peak is at *m/e* 102, whereas the *m/e* 159 peak remains; by contrast, the spectrum of the 1-^{13}C compound shows a shift from *m/e* 159 to 160, and no effect on the peak at 101.

Peaks of *m/e* 129 and 131 most likely represent a fragmentation by cleavage of the C-1–O-5 and C-3–C-4 bonds with either loss, or addition, of a hydrogen, depending on the pathway[2]. With the aid of Figs. 1B and 1C, these peaks can now be assigned. In the spectrum of the 6-^{13}C compound (Fig. 1B), the peak at *m/e* 129 remain unaffected, whereas there is now a peak at *m/e* 132 rather than at 131. In

*Dedicated to the memory of Dr. Hewitt G. Fletcher, Jr.

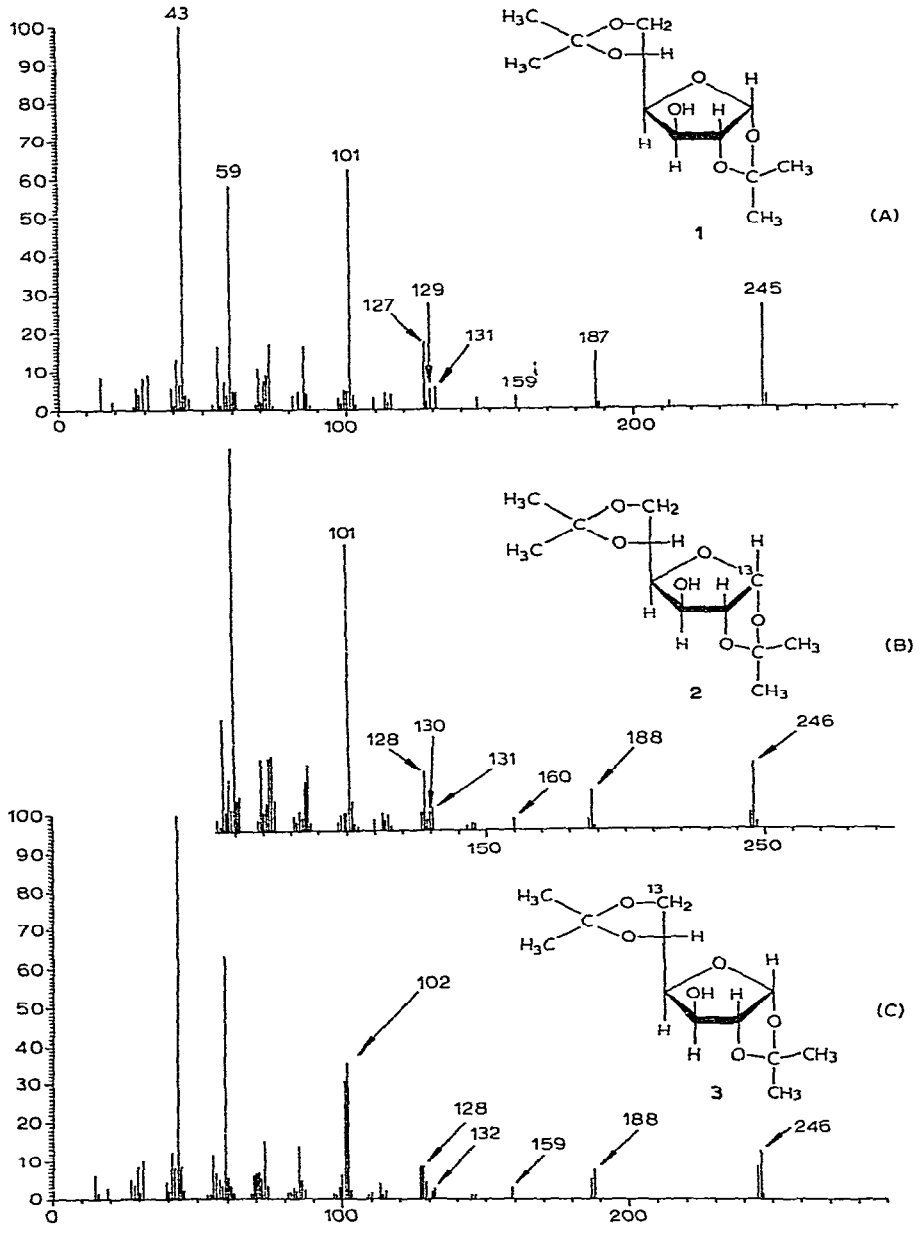
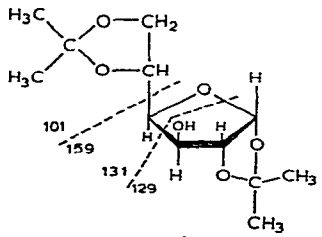


Fig. 1. Mass spectra of (A) 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**), (B) its 1-^{13}C analog (**2**), and (C) its 6-^{13}C analog (**3**).

Fig. 1C, the opposite is noted, *i.e.*, the *m/e* 129 peaks is replaced by one at *m/e* 130, and the *m/e* 131 peak is unaffected. This means that the *m/e* 129 peak can now be assigned with confidence to the fragment containing C-1, C-2, and C-3, and the *m/e* 131 peak to the fragment containing C-4, C-5, and C-6 (**4**).

The fragmentation pattern for 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**5**) is very similar to that observed for **1**, except for the relative intensity of the peaks at *m/e* 129 and *m/e* 131; *i.e.*, the latter peak is relatively less intense than found for the *gluco* derivative. In the spectrum of the 1-^{13}C analog of **5**, the fragment of *m/e* 129 is replaced by a peak at *m/e* 130, indicating that it incorporates C-1, C-2, and C-3, as noted above for **2**.



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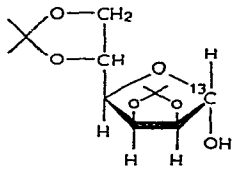

5

EXPERIMENTAL

Mass spectra were recorded with an LKB gas chromatograph–mass spectrometer operating at 70 eV.

1,2:5,6-Di-O-isopropylidene-α-D-glucofuranose-1-^{13}C (**2**) *and -6-*^{13}C (**3**). — The synthesis of these compounds has been described elsewhere[3].

2,3:5,6-Di-O-isopropylidene-α-D-mannofuranose-1-^{13}C (**5**). — D-Mannono-1,4-lactone-*1-*^{13}*C*[3] was reduced with diborane(6) in tetrahydrofuran, as recently described[4], affording D-mannose-*1-*^{13}*C*. The latter sugar (100 mg), anhydrous acetone (50 ml), and conc. sulfuric acid (20 drops) were shaken together for 18 h, excess of anhydrous sodium carbonate was then added, the suspension was filtered, and the filtrate concentrated to a thin syrup. Column-chromatographic purification of the syrup was carried out with silica gel (MN, grain size 0.08 mm), using 6:2 toluene–ether as the eluant. This afforded 65 mg of crystalline **5**, m.p. 116–119° (the non-enriched compound[5] had m.p. 122–123°).

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REFERENCES

1 M. F. Grostic and K. C. Rinehart, in G. W. A. Milne (Ed.), *Mass spectrometry: Techniques and applications*, Wiley–Interscience, New York, 1971, pp. 261–270.
2 D. C. DeJongh and K. Biemann, *J. Am. Chem. Soc.*, 86 (1964) 67–74.
3 J. A. Schwarcz and A. S. Perlin, *Can. J. Chem.*, 50 (1972) 3667–3676.
4 S. S. Bhattacherjee, J. A. Schwarcz, and A. S. Perlin, *Carbohydr. Res.* 41 (1975) 259–266.
5 K. Freudenberg and R. M. Hixon, *Ber.*, 56 (1923) 2119–2123.