Tetrahedron Letters No.32, pp. 3545-3548, 1968. Pergamon Press. Printed in Great Britain.

AN APPROACH TO THE SEQUENTIAL ANALYSIS OF DISACCHARIDES BY MASS SPECTROMETRY

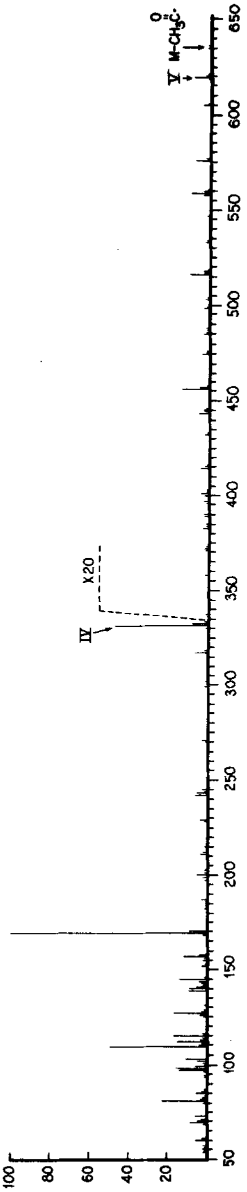
Jerrold Karliner

Lederle Laboratories Division, American Cyanamid Company
Pearl River, New York 10965

(Received in USA 3 April 1968; received in UK for publication 13 May 1968)

Although the mass spectral properties of various monosaccharides have been investigated in considerable detail (1), the electron-impact induced fragmentation of disaccharides has received little attention and has been limited in its applications to structure elucidation. The mass spectra of permethylated disaccharides have furnished complicated data due to competing fragmentation of both sugar moieties and formation of many isomeric fragment ions (2). While recent studies on the electron-impact induced fragmentation patterns of aminocyclitols have demonstrated that the trimethylsilyl ether derivatives of these compounds are amenable to mass spectral characterization (3), the mass spectra of trimethylsilyl ethers of disaccharides do not afford molecular ions and show only very weak M-15 peaks (4).

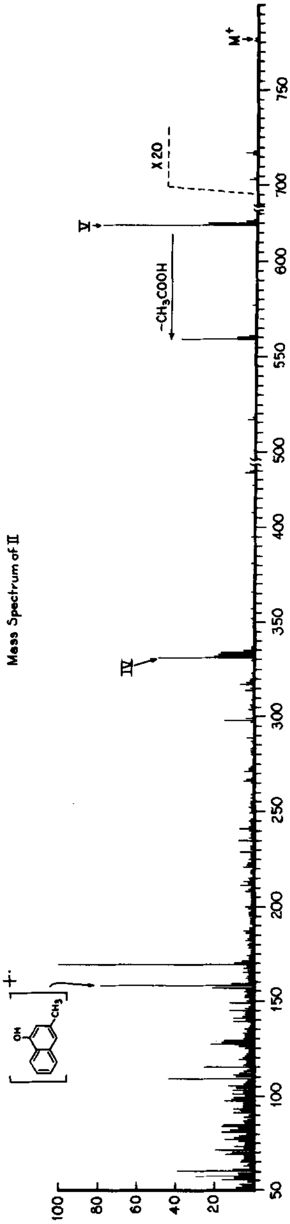
In an attempt to provide suitable disaccharide derivatives which would afford diagnostic fragmentation patterns, we decided to focus our attention on the 1⟶4 linked sugars and used maltose (I) for our initial studies. The mass spectrum (5) of maltose octaacetate (II), reproduced in Figure 1, does not exhibit a molecular ion or abundant peaks in the high mass region, but instead is dominated by cleavage along the glycosidic bond to give IV, the latter fragmenting as previously described (6,7). It appears that expulsion of the acetoxyl radical from C-1 cannot compete effectively with α-cleavage to afford IV. Hence we searched for a substituent which when attached to C-1 would stabilize the molecular ion and would cause fragmentation to occur initially at the reducing end of



m/e

FIG. 1

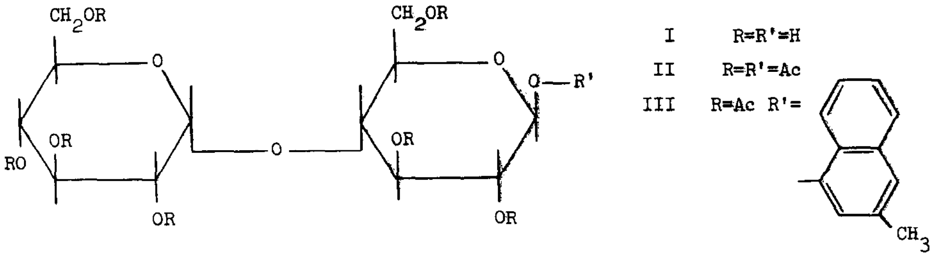
Mass Spectrum of II



m/e

FIG. 2

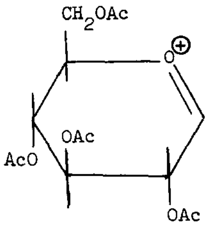
Mass Spectrum of III



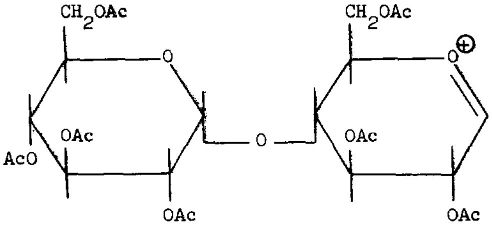
I R=R'=H

II R=R'=Ac

III R=Ac R'=



IV, m/e 331



V, m/e 619

the molecule. One such substituent is the aryl group since expulsion of a stable aryloxy radical would be a preferred mode of scission and could be expected to provide a suitable M-OR' ion. Indeed, the mass spectrum of the 3-methyl-1-naphthyl derivative III (8) shown in Figure 2 exhibits the M-OR' peak (m/e 619, V) as the most intense ion and the fragment ion IV as the next most intense ion above m/e 170. Thus, it appears that mass spectrometry can be used to determine the molecular weight (from the M-OR' peak) and the sequential arrangement of suitably derivatized disaccharides.

Work is currently in progress to determine the utility of this approach in other di- and trisaccharide derivatives and also to ascertain the effects on the overall fragmentation pattern of other aryl groups.

References

1. For a recent review see N. K. Kochetkov and O. S. Chizhov, Advan. Carbohyd. Chem., **21**, 39 (1966).
2. N. K. Kochetkov, N. S. Wulfson, O. S. Chizhov and B. M. Zolotarev, Tetrahedron, **19**, 2209 (1963).
3. D. C. DeJongh, J. D. Hribar, S. Hanessian and P. W. K. Woo, J. Amer. Chem. Soc., **89**, 3364 (1967).
4. O. S. Chizhov, N. V. Molodtsov and N. K. Kochetkov, Carbohyd. Res., **4**, 273 (1967).
5. The mass spectra were determined with an A.E.I. MS-9 high resolution mass spectrometer. Samples were introduced into the ion source via the direct insertion probe.
6. K. Biemann, D. C. DeJongh and H. K. Schnoes, J. Amer. Chem. Soc., **85**, 1763 (1963).
7. K. Heyns and H. Scharmann, Liebigs Ann. Chem., **667**, 183 (1963).
8. Synthesized by B. R. Baker.