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Note

Application of field-desorption mass spectrometry in carbohydrate chemistry: Two lactones, xylitol, and L-sorbose

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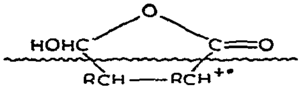
The new technique of field desorption (f.d.) has greatly increased the practical applicability of mass spectrometry (m.s.) to molecules that tend to undergo pyrolysis in the source of a mass spectrometer. In f.d.–m.s. the method of forming gaseous ions is entirely different from conventional mass-spectrometric methods, in which evaporation followed by electron impact (e.i.) is employed. The new technique consists of coating carbon microneedles, grown on a 10-μm tungsten wire[1,2] by dipping the assembly (called an emitter) into a solution or suspension of the sample in a volatile solvent, and inserting it through a vacuum lock into the source of a mass spectrometer[3]. It is positioned a few mm from a cathode plate, and a potential in excess of 10 kV is applied between the two units. Under these conditions, the electric field-gradient near the microneedles is a few volts per Å; the potential field of an adsorbed molecule is distorted, and an electron is removed by tunneling through the distorted molecular-potential wall to the anode on which the molecule is adsorbed. This process results in a positively charged ion having little internal energy, adjacent to a positively charged surface. Coulombic repulsion between the ion and the surface leads to desorption of the ion from the surface. In practice, the desorption process is frequently aided by heating the emitter through application of a small direct current. The ion is then mass analyzed by any one of several conventional arrangements.

Biochemical applications of this technique are obvious and exciting. Among the compounds from which useful information can be obtained are the carbohydrates and their derivatives. Only a few such compounds have been studied: several mono-[3,4] and di-saccharides[4–6], deoxyfluoroglucose phosphate salts[7], several glycosides[4,8,9] nucleosides[4,10], and ascorbic acid[4,11]. Few generalities have been drawn from published spectra, except that the molecular weight can be determined for such compounds without use of trimethylsilylation to increase volatility. We have examined other carbohydrate compounds by f.d.–m.s. and illustrate here their satisfactory behavior as a guide to others contemplating use of this technique. The previous study of some vitamins[12] has been extended to several compounds related to the synthesis of Vitamin C; these compounds were D-glucurono-6,3-lactone, L-gulono-1,4-lactone, xylitol, and L-sorbose.

The f.d. mass spectra of the two lactones were recorded with an emitter heating-current near 20 mA, and are very simple. That of the former showed an M+1 peak at *m/e* 177 as the base peak, and the peak corresponding to the molecular weight M was about 90% as intense. A small peak (10%) corresponding to the loss of OH (perhaps H_2O from M+1), and another fragment at *m/e* 102 (10%) were found. The spectrum of L-gulono-1,4-lactone under similar conditions displayed similar information: the base peak was the M+1 ion, *m/e* 179; a small peak (6%) at *m/e* 147 corresponds to the loss of $-CH_2OH$, and there was a peak (60%) at *m/e* 104. This fragmentation, and that giving the *m/e* 102 peak for D-glucurono-6,3-lactone, are consonant with the illustrated cleavage of the lactone ring as an important process in the f.d. mass spectra of these lactones. This fragmentation is reminiscent of lactone cleavage in the e.i. mass spectrum of glucofurano-6,3-lactone[13], which is complicated by a rearrangement*. Characteristic fragmentations in f.d. mass spectra useful for structural analysis of carbohydrate structures have been suggested only once before[7].



The spectrum of xylitol was also determined without derivatization. At a low heater-current, the dominant peak was the M+1 ion at *m/e* 153. Other important peaks (10% to 20%) were observed at *m/e* 31, 61, and 91. These correspond to cleavage of the skeleton to yield $HOCH_2^+$, $HOCH_2CHOH^+$, and $HOCH_2CHOHCHOH^+$ ions, respectively. No f.d.–m.s. studies of alditols have yet been reported; their simple fragmentation appears to make their identification as a class straightforward.

L-Sorbose was also examined. At a heater current of 25 mA, the M+1 ion (25%) was observed. Ions at *m/e* 163 (100%) and *m/e* 149 (75%) point to losses of OH and CH_2OH from the molecular ion; again, the former may actually arise by loss of H_2O from the M+1 ion. A small peak at *m/e* 127 corresponds to loss of three H_2O molecules from the M+1 ion. Similar peaks appear in the f.d. mass spectrum of its diastereoisomer, D-fructose[4].

Because the effects of heating have not been thoroughly explored in f.d.–m.s.[4,5], we examined the effect of increasing the emitter current. The spectra reported above are typical examples of the effect of heating to intermediate temperatures. In general, at low temperature (very low emitter-current) only the M+1 ion is observed. At very high emitter-current, pyrolysis of the compound occurs and clusters of molecules appear to be desorbed from the surface, producing ions of mass 2M+1, 2M, $2M+1-H_2O$, and so forth, the mechanism of this last reaction may involve a surface reaction between two molecules with elimination of water. The formation of these clusters is reminiscent of cluster formation even in ionic species[14–16] upon

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*This compound does show a weak molecular-ion in its e.i. spectrum[13].

desorption. In any event, the result clearly indicates that experimental conditions for f.d.–m.s. must be carefully controlled. Although there is a reasonably wide operating-range of heating current within which cluster formation does not occur with these four carbohydrates, only spectra obtained near the minimum heating-temperature needed to observe the M+1 peak should safely be considered reliable for determination of molecular weight.

EXPERIMENTAL

Materials. — D-Glucurono-6,3-lactone, D-gulono-1,4-lactone, xylitol, and L-sorbose (Nutritional Biochemicals Corporation, Cleveland, Ohio) had acceptable melting points, and there was no indication of impurities in their f.d. mass spectra.

Spectra. — The f.d. mass spectra were recorded with a Varian MAT CH5-DF mass spectrometer fitted with a field-ionization (f.i.)/f.d. source designed according to Schulten and Beckey[10]. The instrument was tuned on the *m/e* 58 peak produced by f.i. of acetone, and the mass scale was calibrated against the known f.i. mass spectrum of perfluorotributylamine. Samples were adsorbed onto emitters from concentrated aqueous solutions. The spectra were recorded at various heating currents between 10 and 35 mA.

The minimum amount of sample capable of giving a spectrum was not studied in these experiments; the source was not a commercially available one, and the emitters were not reactivated between use, as should be done to achieve high sensitivity. Nevertheless, about 15 spectra were obtained under various heating conditions from about 2 μg of material. In Professor Beckey's laboratory, where this problem has been investigated, spectra have been obtained from 50 ng of sample coated onto an emitter[17]. The problem of sensitivity is being jointly studied in several laboratories.

For comparison with the e.i.–m.s. technique, the length of time required to perform an analysis was noted. Removal, dipping, and reinsertion of the emitter probe, pumping out of the solvent, tuning the source on the molecular ion of field-ionized acetone, recording of 15 spectra with manual adjustment of the emitter current between runs, and computer print-out time, took 25 min. Considering the wide range of temperatures scanned, this time is similar to that required for a direct-probe temperature scan with print-out of several spectra.

CONCLUSIONS

The e.i.–m.s. technique requires less sample than was used in these experiments with f.d.–m.s. although this point was not thoroughly investigated. There is no obvious advantage in operating time for either technique. The information obtained from e.i.–m.s. and f.d.–m.s. is complementary, as e.i.–m.s. frequently does not give the molecular weight for carbohydrates directly but does produce many fragment-ions useful in structural assignment. Derivatization does extend the utility of e.i.–m.s. enormously, although rearrangements involving trimethylsilyl groups may be misleading if the recent literature[18,19] is not consulted. At low emitter temperatures, identification of the M+1 peak as the sole peak in the f.d.–m.s. spectrum has obvious advantages. In general, the f.d.–m.s. technique is a useful extension of current, generally available, instrumentation, although it will not replace it.

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