



Fig. 1. Curve of  $s + s^{1/2}$  against reciprocal dose for rubber at 25°C. ○, Dose-rate,  $5.5 \times 10^4$  rads/hr.; ●, dose rate =  $5.1 \times 10^4$  rads/hr.

from the slope of the straight line in Fig. 1 and the osmotic molecular weight of the rubber (683,000), is 0.83 at 25°C.

The ratio of the rate of dislinking to cross-linking ( $p/q$ ), determined from the intercept, is 0.05 at 25°C., in fair agreement with estimations by alternative methods<sup>3</sup>.

Infra-red spectroscopic analysis revealed a marked increase in the absorption near  $1,639 \text{ cm.}^{-1}$ , identified as terminal unsaturation, presumably arising from the dislinking reaction. There was also evidence of the formation of *trans*-vinylene unsaturation during irradiation, manifested by the appearance of an absorption band at  $980 \text{ cm.}^{-1}$ , similar to that observed on sulphur-vulcanization of rubber<sup>4</sup>.

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### Application of the Mass Spectrometer to Polysaccharide Chemistry

DURING work on the dissociation of certain classes of organic molecules induced by electron-impact<sup>1</sup>, the field has been extended to some members of the carbohydrate series<sup>2</sup>. Using a newer technique<sup>3</sup> we have obtained a spectrum of a polysaccharide derivative. A methylated polysaccharide—methylated laminarin—was chosen for this study, since previous experience<sup>4</sup> has shown that methylated derivatives of carbohydrates are most suitable for this type of work.

<i>m/e</i>	27	28	29	31	32	39	40	41	42	43	44
rating	w	vs	m	m	s	w	vw	m	w	s	m
	45	55	56	57	60	67	68	69	70	71	82
	vw	m	w	m	w	w	vw	m	vw	w	w
	83	84	85	86	95	97	99	107	108	110	111
	vw	w	vw	w	vw	vw	vw	w	w	m	vw
	112	124	129	131	143	144	145				
	m	w	m	w	w	vw	w				
	156		188		230	268	296				
	m		m		m	w	w				
	364	367	395	397	434	490	493	500	515	532	550
	m	w	m	m	s	w	w	w	w	w	w
	566		595		635	644	656				
	w		s		s	s	s				

vw. very weak, w. weak, m. medium, s. strong, vs. very strong.

As can be seen from Table 1, the spectrum obtained can be considered to consist of two main parts: (a) a series of peaks of medium to strong intensity corresponding to fragment ions having  $m/e$  ranging from 28 to 156; and (b) a series of rather widely spaced peaks of weak to medium intensity which extend from  $m/e$  152 up to 700. In this experiment scanning above 700 was not attempted. From work<sup>4</sup> already carried out on the 'cracking patterns' of methylated monosaccharide derivatives, part (a) of the spectrum is recognizably associated with the decomposition induced by electron impact of individual methylated sugar units; it will not be discussed further here.

Part (b) of the spectrum gives a picture of the fragmentation of the polymer. There appears to be a number of series of fragment ions being produced, but on examination of the  $m/e$  values, patterns can be distinguished for two main series (188, 395 and 595; 230, 434 and 635). These two series have an approximate mean difference of 204, and a third though weaker set of peaks in the spectrum (156, 364 and 566) can also be considered as having the same separation. It appears significant that this mass factor of 204 is the same as the mass of a 2:4:6-tri-O-methyl glucose residue of which methylated laminarin<sup>5</sup> is mainly (at least 85 per cent) composed. These observations are consistent with the view that stepwise fragmentation of the polymer is taking place.

The ions ( $m/e$  156, 188 and 230) corresponding to the first members of the three fragmentation patterns mentioned probably arise from the end-groups of the methylated laminarin. For example, it is not unreasonable to suggest that the ion of  $m/e$  230 comes from the tetra-O-methyl glucose residue (molecular weight 235) at the non-reducing end of the polymer. This aspect of the problem, together with further extensions of this work, will be discussed more fully at a later date.

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