

380. *Random Depolymerisations of Partly Substituted Linear Polysaccharides in which Unsubstituted Fragments are Resistant to Further Cleavage.*

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A theoretical treatment is described of the random depolymerisation of partly substituted linear polysaccharides, in which unsubstituted fragments, once liberated, are resistant to further cleavage.

The behaviour of both uniformly and randomly substituted polysaccharides is considered, and in each instance an equation is derived relating the final yield of an unsubstituted fragment to the degree of substitution of the starting material.

The results show that, with a uniformly substituted polysaccharide, the maximum yield of unsubstituted oligosaccharides is higher, and the reaction product for a given degree of substitution is less highly polydisperse, than with a randomly substituted polysaccharide.

WHEN starch is partly substituted with diethylaminoethyl ether groups, and then heated in aqueous solution with polystyrenesulphonic acid, hydrolysis of the starting material and of all substituted fragments is rapid, whereas unsubstituted fragments, once liberated, are hydrolysed relatively slowly.^{1,2} If the reaction mixture is sufficiently dilute, the selectivity of the polymeric acid for the hydrolysis of substituted fragments is so great that the unsubstituted fragments are virtually resistant to further hydrolysis.²

In connection with this work, it is of interest² to determine the effect upon the final yield of any unsubstituted fragment of the way in which the substituents are distributed in the molecule of the parent polysaccharide. To this end, a simple theoretical model for this type of depolymerisation is now considered, and, for both uniformly and randomly substituted polysaccharides, an equation is derived relating the final yield of an unsubstituted fragment to the degree of substitution of the starting material.

In the theoretical model, it is assumed that (a) the polysaccharide chains are unbranched, and of infinite length; (b) all the monosaccharide residues have the same molecular weight, and are unable to carry more than one substituent; (c) all glycosidic linkages in substituted fragments are hydrolysed at the same rate; and (d) all unsubstituted fragments, once liberated, are completely resistant to further cleavage.

The mathematical principles are similar to those originally applied to the hydrolysis of unsubstituted polysaccharides by Kuhn,³ and subsequently extended by the present author.^{4,5} The figures given for yields of unsubstituted fragments are not corrected for the addition of the elements of water to each fragment that occurs during hydrolysis.

THEORY

If a section of a polymer chain, consisting of N contiguous unsubstituted monomer units lying between two substituted units, is subjected to random depolymerisation, the probability that a particular unsubstituted n -membered fragment (*i.e.*, an n -mer) exists for a degree of scission α is $\alpha^2(1 - \alpha)^{n-1}$. Since there are $(N - n + 1)$ ways of choosing such an n -mer from the section, the total probability of an n -mer's existing is $(N - n + 1)\alpha^2(1 - \alpha)^{n-1}$, and hence the yield (Y_n) of n -mer, expressed as a fraction of the total weight of unsubstituted monomer units in the section, is given by:

$$Y_n = (n/N)(N - n + 1)\alpha^2(1 - \alpha)^{n-1}. \quad (1)$$

¹ Painter and Morgan, *Chem. and Ind.*, 1961, 437.

² Painter, *J.*, 1962, 3932.

³ Kuhn, *Ber.*, 1930, **63**, 1503.

⁴ Painter, *J.*, 1963, 779.

⁵ Painter, preceding paper.

Differentiation of equation (1) with respect to α , followed by integration of the positive term in the first derivative between the limits $\alpha = 0$ and $\alpha = 1$, shows³⁻⁵ that, if the n -mer, but no larger oligomer, is resistant to further cleavage, the final yield of the n -mer, expressed as a fraction of the original unsubstituted monomer units in the section, is:

$$2(N - n + 1)/N(n + 1). \quad (2)$$

Since all unsubstituted fragments are resistant to further cleavage, the final yield of the largest possible fragment, the N -mer, is $2/N(N + 1)$, that is, expression (2) when $n = N$. The final yield of the $(N - 1)$ -mer is obtained by putting $n = (N - 1)$ in expression (2), and subtracting from the resultant expression the amount of $(N - 1)$ -mer that would have been obtained by further cleavage of the N -mer, had the N -mer not been resistant. As shown elsewhere,⁴ the amount to be subtracted is obtained by multiplying the yield of the N -mer by $2/(n + 1)$, where $n = (N - 1)$. The final yield of the $(N - 1)$ -mer is then:

$$4/N^2 - (2/N)[2/N(N + 1)] = 4/N(N + 1).$$

The final yield of the $(N - 2)$ -mer is obtained by putting $n = (N - 2)$ in expression (2), and subtracting that fraction of the combined yields of N -mer and $(N - 1)$ -mer that would have yielded $(N - 2)$ -mer if these oligomers had not been resistant to further cleavage. The amount to be subtracted in this case is therefore obtained by multiplying the combined yield of N -mer and $(N - 1)$ -mer by $2/(n + 1)$, where $n = (N - 2)$. The final yield of the $(N - 2)$ -mer is therefore:

$$6/N(N - 1) - 2/(N - 1)[2/N(N + 1) + 4/N(N + 1)] = 6/N(N + 1).$$

Further calculation shows that, in general, the fraction of the N unsubstituted monomer units in the section that finally exists as n -mer is:

$$2(N - n + 1)/N(N + 1). \quad (3)$$

Depolymerisation of a Uniformly Substituted Polysaccharide.—In this type of polymer, all groups of contiguous unsubstituted monomer units are of the same size, so that, for a degree of substitution s , the value of N is $(1 - s)/s$. By substitution for N in expression (3), it is found that the final yield of an unsubstituted n -mer, expressed as a fraction of the total weight of unsubstituted monomer units in the polymer, is $2s(1 - ns)/(1 - s)$. The corresponding yield (Y_n), expressed as a fraction of all the monomer units, is therefore given by:

$$Y_n = 2s(1 - ns). \quad (4)$$

Application of the calculus to equation (4) shows that the maximum possible yield of the n -mer occurs when $s = 1/2n$, and amounts to $1/2n$.

Depolymerisation of a Randomly Substituted Polysaccharide.—It is shown elsewhere² that, when a linear polymer of infinite length is randomly substituted to a degree of substitution s , the fraction of the total monomer units which exist as discrete groups of N contiguous unsubstituted monomer units is $Ns^2(1 - s)^N$. Expression (3) provides that, when the polymer is depolymerised in the prescribed manner, the fraction of every such group that finally exists as n -mer is given by $2(N - n + 1)/N(N + 1)$. Therefore, the yield of n -mer from all groups of this particular size, expressed as a fraction of the total weight of monomer units in the starting material, is $2(N - n + 1)s^2(1 - s)^N/(N + 1)$. The total yield (Y_n) of n -mer from groups of all sizes is therefore given by:

$$Y_n = 2s^2 \sum_{N=n}^{\infty} \frac{N - n + 1}{N + 1} (1 - s)^N. \quad (5)$$

The right-hand side of equation (5) can be evaluated by making use of the following relationships:

$$(a) \quad \sum_{N=n}^{\infty} \frac{N-n+1}{N+1} x^N = \sum_{N=n}^{\infty} \left(x^N - \frac{n}{N+1} x^N \right) \\ = \frac{x^n}{1-x} - n \sum_{N=n}^{\infty} \frac{1}{N+1} x^N = \frac{x^n}{1-x} - \frac{n}{x} \sum_{N=n}^{\infty} \frac{x^{N+1}}{N+1}$$

$$(b) \quad \sum_{N=n}^{\infty} \frac{x^{N+1}}{N+1} = \sum_{N=0}^{\infty} \frac{x^{N+1}}{N+1} - \sum_{N=0}^{n-1} \frac{x^{N+1}}{N+1} \\ = -\log_e(1-x) - (x + x^2/2 + x^3/3 + \dots + x^n/n) \\ = -\log_e(1-x) - \int (1+x+x^2+\dots+x^{n-1}) dx \\ = -\log_e(1-x) - \int (1-x^n)/(1-x) dx$$

Equation (5) can now be written:

$$Y_n = 2s(1-s)^n + \frac{2s^2n}{1-s} \left[\log_e s - \int \frac{1-(1-s)^n}{s} ds \right] \\ = 2s(1-s)^n + \frac{2s^2n}{1-s} \left[\int \frac{(1-s)^n}{s} ds + C \right] \\ = 2s(1-s)^n + \frac{2s^2n}{1-s} \left[C' + \log_e s + \sum_{i=1}^n \frac{n!}{i!(n-i)!} \frac{(-s)^i}{i} \right]$$

By putting $Y_n = 0$ when $s = 1$, the integration constant (C') is found to be:

$$-\sum_{i=1}^n \frac{n!}{i!(n-i)!} \frac{(-1)^i}{i},$$

so that

$$Y_n = 2s(1-s)^n + \frac{2s^2n}{1-s} \left[\log_e s + \sum_{i=1}^n \frac{n!}{i!(n-i)!} \frac{(-s)^i - (-1)^i}{i} \right] \quad (6)$$

From equation (6), the maximum possible yields of several unsubstituted fragments, and the values of s required to obtain them, were computed graphically (Table 1).

TABLE 1.

Maximum possible yields of unsubstituted fragments, and the corresponding values of s .							
n	1	2	3	4	5	6	7
Optimum s	0.435	0.259	0.182	0.144	0.118	0.099	0.086
Y_n (max.) (%)	31.24	16.30	10.97	8.25	6.61	5.51	4.72

RESULTS

For both uniformly and randomly substituted polysaccharides, the maximum possible yields of several homologous series of unsubstituted oligosaccharides, and the values of s required to obtain them, were calculated (Table 2). For the randomly substituted polysaccharide, the optimum values of s were computed graphically.

To compare the polydispersity of the hydrolysis products of the two types of substituted polysaccharide, the yields from each of various unsubstituted fragments for given degrees of substitution were calculated (Table 3).

TABLE 2.

Maximum possible yields of unsubstituted oligosaccharides, and the corresponding values of s .

	Substitution	For all oligomers up to and including:				
		trimer	tetramer	pentamer	hexamer	heptamer
Maximum combined yield (%)	U	40.00	50.00	57.14	62.49	66.67
	R	26.84	34.44	40.25	44.88	48.70
Optimum s	U	0.200	0.167	0.143	0.125	0.111
	R	0.221	0.197	0.179	0.162	0.150

(U = uniform; R = random.)

TABLE 3.

Yields (%) from unsubstituted fragments for different degrees of substitution.

s	Substitution	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n > 7$
0.025	U	4.88	4.75	4.63	4.50	4.38	4.25	4.13	65.98
0.025	R	4.52	4.17	3.90	3.65	3.42	3.22	3.05	71.57
0.050	U	9.50	9.00	8.50	8.00	7.50	7.00	6.50	39.00
0.050	R	8.42	7.35	6.50	5.82	5.24	4.73	4.30	52.64
0.100	U	18.00	16.00	14.00	12.00	10.00	8.00	6.00	6.00
0.100	R	14.89	11.77	9.55	7.87	6.56	5.51	4.66	29.19
0.125	U	21.88	18.75	15.63	12.50	9.38	6.25	3.13	—
0.125	R	17.57	13.27	10.34	8.19	6.54	5.25	4.20	22.14
0.143	U	24.50	20.40	16.32	12.25	8.17	4.08	—	—
0.143	R	19.31	14.13	10.69	8.25	6.46	5.06	3.95	17.85
0.167	U	27.79	22.22	16.67	11.11	5.56	—	—	—
0.167	R	21.42	15.01	10.93	8.14	6.15	4.70	3.64	13.31
0.200	U	32.00	24.00	16.00	8.00	—	—	—	—
0.200	R	23.90	15.80	10.91	7.71	5.55	4.03	2.95	9.15
0.250	U	37.50	25.00	12.50	—	—	—	—	—
0.250	R	26.90	16.29	10.37	6.80	4.54	3.08	2.09	4.93
0.333	U	44.44	22.22	—	—	—	—	—	—
0.333	R	30.04	15.65	8.67	4.97	2.91	1.69	0.69	2.08
0.500	U	50.00	—	—	—	—	—	—	—
0.500	R	30.68	11.36	4.55	1.89	0.83	0.36	0.16	0.17

DISCUSSION

In an earlier paper,² it was suggested that, in the hydrolysis of diethylaminoethyl ethers of polysaccharides by polystyrenesulphonic acid, the yield of oligosaccharides in any given range of molecular weights would depend upon the way in which the substituents were distributed in the polymer molecule. The foregoing calculations show that this is correct for the special case in which all glycosidic linkages in substituted fragments are hydrolysed at the same rate. It is noteworthy that, although only two kinds of substitution are considered here, expression (3) can be used to calculate the final yield of n -mer obtained by random depolymerisation of any substituted linear polymer, provided that the distribution of the substituents is known.

The results calculated here, when compared with those obtained experimentally, should indicate how, in practice, the rate of hydrolysis of a glycosidic linkage varies with distance from a substituted sugar residue. If, for example, glycosidic linkages close to substituted sugar residues are hydrolysed more rapidly than more distant ones, the yields of the larger unsubstituted fragments should be higher, and those of the smaller ones lower, than the yields shown in Table 3. Completely selective cleavage of the glycosidic linkages next to substituted sugar residues should give, from uniformly and randomly substituted polysaccharides, respectively, (a) a single oligomer, $(1 - s)/s$ units in length, in a yield of $(1 - s)$, and (b) a polydisperse reaction product in which the yield of any n -mer is given by $ns^2(1 - s)^n$.

The better understanding so obtained of the selective catalytic properties of polymeric

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acids may suggest new or improved methods for the structural analysis of mucopolysaccharides,^{1,2} glycoproteins,⁵ and many other natural polymers.

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