

## The Influence of Reducing Substances on the Rate of Degradation of Alginates

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In the preceding note\* the rate of degradation of alginate prepared from *L. digitata* was reported at different values of pH. A similar investigation was carried out for alginate prepared from *Ascophyllum nodosum*. It was observed that the rate of degradation was considerably higher for alginate prepared from this species in the pH region between 4 and 11. If, however, the algae had been treated with formaldehyde prior to the pre-extraction with acid, the rate of degradation was approximately the same as for *L. digitata* alginate. The degradation at two different values of pH is shown in Fig. 1.

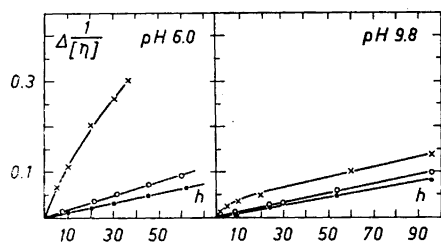


Fig. 1. Rate of degradation of alginates from different species at 68°.

- Alginate from *L. digitata*, Tarva, 29/8,  $[\eta]_0 = 30$ .
- × » » *A. nodosum*, Være, 31/8,  $[\eta]_0 = 13$ .
- » » *A. nodosum*, Være, 31/8, algae pre-treated with formaldehyde,  $[\eta]_0 = 31$ .

It is known that most brown algae contain varying amounts of phenolic compounds<sup>1,2</sup> ("fucosan") which is responsible for the brown colouration of alkali extracts and alginates. *Laminaria digitata* does not contain significant amounts of these phenolic compounds, while *Ascophyllum nodosum* contains considerable amounts.

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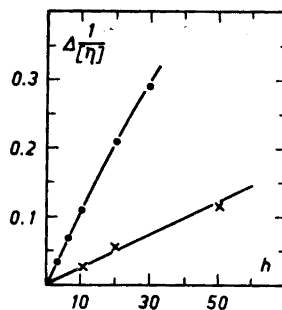


Fig. 2. Rate of degradation of alginates after addition or removal of phenolic compounds. 68°, pH 6.

- Alginate from *L. digitata*, phenolic compounds added.
- × » » *A. nodosum*, phenolic compounds removed.

It is further known that formaldehyde reacts with the phenolic compounds, making them insoluble in acid and alkali. The difference between the three samples shown in Fig. 1 could thus be explained if the presence of phenolic compounds increased the rate of degradation of alginate.

A solution of alginate (0.6%) from *L. digitata* was mixed with equal volumes of a dilute, neutralized acid extract of *Ascophyllum nodosum*, containing reducing phenolic compounds (0.0006 mequiv/ml). A solution of alginate from *A. nodosum* was shaken with perlon powder to absorb and remove phenolic compounds. The two samples were then subjected to degradation at pH 6. Results are shown in Fig. 2. It is observed that the addition of phenolic compounds to the *L. digitata* alginate markedly increased the degradation rate, while the removal of most of the phenols from the *A. nodosum* alginate led to a significant stabilization of the alginate solution. Thus it seems safe to conclude that the difference in the stability of alginate from the two species is due to the presence of phenolic compounds in *Ascophyllum nodosum*. The low intrinsic viscosity of alginates prepared from *A. nodosum* compared with alginates from *L. digitata*<sup>3</sup> may also be explained as a difference in degradation during the preparation. This is supported by the observation that treatment of *Ascophyllum nodosum* with formal

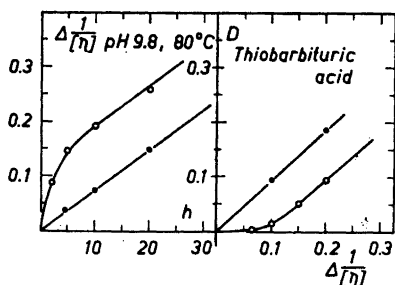


Fig. 3. Influence of phloroglucinol on the rate of degradation. Correlation between decrease of viscosity and thiobarbituric acid reaction.

Alginate from *L. digitata*, Espevær, 10/6. pH 9.8, 80°.

● Without addition.

○ 0.001 M phloroglucinol added.

dehyde prior to alginate preparation gives rise to alginates with values of intrinsic viscosity of the same magnitude as for *L. digitata* alginates ( $[\eta] = 25-35$  dl/g).

In the preceding note a method was described by which it is possible to detect to what extent  $\beta$ -elimination is responsible for the degradation reaction. This method was applied to a solution of alginate from *L. digitata* containing 0.001 M phloroglucinol at pH 9.8 and 80°. The rate of degradation and the correlation between the decrease in viscosity and the formation of colour with thiobarbituric acid is given in Fig. 3. For comparison, the results without phloroglucinol are also given. Addition of phloroglucinol leads to a rapid degradation during the first 5 h, and the degradation is not accompanied by the formation of unsaturated uronic acid derivatives, as shown by the thiobarbituric acid reaction. All phloroglucinol was destroyed by oxidation or polymerization after approximately 5 h, and the rate of degradation and formation of derivatives giving colour by thiobarbituric acid became normal. The mechanism of the rapid degradation in the presence of phenols is thus different from the usual mechanism of thermal degradation in the slightly alkaline medium.

We have found that a number of reducing substances, such as hydroquinone, sodium sulphite, sodium hydrogen sul-

phide, cystein, ascorbic acid, hydrazine sulphate and leuco-methylene blue have the effect of increasing the rate of degradation of the alginate. We have also observed that the presence of ascorbic acid increases the degradation of pectin and carrageenin. In a patent concerned with the use of alginate in well-drilling<sup>4</sup>, the use of hydrazine sulphate to reduce the viscosity of the alginate solution is described. Recently, ascorbic acid has been shown to degrade deoxyribonucleic acid<sup>5</sup>. Work is in progress in this laboratory to further elucidate the influence of reducing substances on the degradation of polysaccharides.

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### On the Solubility of Sulfated Galactosaminoglycans (Chondroitinsulfates)

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As shown by Scott<sup>1</sup> and Stacey and Baker<sup>2</sup> acidic polysaccharides form insoluble complexes with quaternary ammonium ions. Scott showed that these complexes are soluble in salt solutions and that different salt concentrations were required to dissolve different complexes. Several approaches for the separation of polysaccharides based on these circumstances have been published (for references see Scott<sup>3</sup>). These complexes are also soluble in organic solvents<sup>4-5</sup>.