CXVII. THE OCCURRENCE OF SUGAR ALCOHOLS IN MARINE ALGAE.

II. SORBITOL.

By PAUL HAAS AND THOMAS GEORGE HILL.

From the Botanical Department, University College, London.

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SOME time ago we reported the occurrence of dulcitol in the red seaweed, *Bostrychia scorpioides* [1931]; at that time there was no reason to suspect the presence of any other similar substance, and the detection of a second sugar alcohol, sorbitol, as set forth in this communication, was more or less accidental. The syrupy mother-liquor "S" from which the dulcitol had been precipitated was treated with benzaldehyde in the presence of fuming hydrochloric acid with a view to preparing the benzylidene derivative of dulcitol, it being suspected that the precipitation of the dulcitol had not been complete. To this end 2 g. of the syrup "S" were dissolved in 7 cc. of ice-cold fuming hydrochloric acid and shaken up with 3.5 g. of benzaldehyde; the mixture was left in an ice-chest for 6 hours and then transferred to a glass dish and placed in a vacuum desiccator over caustic potash for 4 days; it was then washed with water until free from acid when 0.6 g. of a buff-coloured solid remained; this was boiled with several successive quantities of alcohol, after which treatment there was obtained 0.2 g. of a white solid. This substance was only sparingly soluble in boiling absolute alcohol but dissolved readily in hot benzene or acetone. Repeated attempts to crystallise it were unsuccessful, and the addition of light petroleum or alcohol to an acetone or alcohol solution invariably led to the formation of an amorphous precipitate the melting-point of which could not be raised above 180–182°. The melting-point quoted in the literature for the tribenzylidene derivative of dulcitol is 215–220°, while that of the corresponding derivative of sorbitol, which is described as amorphous, is variously given as 172–175° [Meunier, 1891] and 179–184° [Davis, Slater and Smith, 1926]. The former author regarded the product as a mixture of the mono- and di-benzylidene derivatives as evidenced by his combustion figures which were consistently about 2 % low for the carbon. Analysis of our material, however, gave figures suggesting rather that it was a mixture of a tribenzylidene derivative with some of the di-derivative:

	C %	H %
Found	71.37	5.88
Calc. for $C_{27}H_{26}O_6$	72.65	5.83
„ $C_{26}H_{22}O_6$	67.04	6.14

As some further evidence for the identification of sorbitol seemed necessary, 7 g. of the syrup "S" were heated with 10 g. of acetic anhydride and 1 g. of pyridine for one hour over a sand-bath [Tutin, 1925]; after removal of the excess of acetic anhydride and washing there remained a light yellow syrup which rapidly set to a mass of crystals which, after pressing on a porous tile, weighed 0.5 g.; they were recrystallised from a mixture of ethyl acetate and light petroleum from which they separated in well-formed, flat, elongated prisms melting at 98–99°, the melting-point given for hexa-acetylsorbitol by Tutin being 99°, while that of hexa-acetyldulcitol is 171°. Furthermore the substance when mixed with an authentic sample of hexa-acetylsorbitol still melted at 98–99°.

From these data there could no longer be any doubt that the syrup "S" actually contained sorbitol.

As a further confirmation, however, some of the benzylidene derivative above described was hydrolysed with dilute sulphuric acid and steam-distilled to remove benzaldehyde; after neutralising the sulphuric acid with baryta and evaporating there remained a syrup which, treated with alcohol, gave, after some time, crystals of sorbitol.

Whilst no claim to an accurate estimation can be made, the evidence from the amount of crude material obtained from the syrup of *Bostrychia* indicates that this material contained approximately 8.3 % of dulcitol and 13.6 % of sorbitol.

Comment has already been made on the fact that the only sugar alcohol previously recorded as occurring in marine algae was mannitol [Haas and Hill, 1931]. With the establishment of the presence of both dulcitol and sorbitol in *Bostrychia*, all three alcohols are now known to occur in this group of plants, but we have found no evidence of the presence of dulcitol or sorbitol in any other of the Rhodophyceae of which we have examined the following: *Batrachospermum moniliforme*, *Chylocladia articulata*¹, *Corallina officinalis*, *Cystoclonium purpureum*, *Gigartina stellata*, *Laurencia pinnatifida*, *Polysiphonia fastigiata*, *Rhodymenia palmata*.

It is moreover worthy of note that outside the family of the Rosaceae only very few occurrences of sorbitol have been recorded.

The reaction between sugar alcohols and benzaldehyde.

The problem here presented of detecting both dulcitol and sorbitol in the same mixture was made the occasion for an investigation of the relative ease with which the three sugar alcohols react with benzaldehyde. For this purpose three equal quantities of mannitol, sorbitol and dulcitol were treated simultaneously with quantities of fuming hydrochloric acid and benzaldehyde; on shaking the resulting mixtures mannitol and sorbitol set almost immediately to a solid mass while the solution containing the dulcitol remained liquid. After

¹ Kindly supplied by Miss M. Parke of Liverpool University.

standing for five hours in the ice-chest the products were washed under identical conditions; the weights of crude material obtained from the three experiments corresponded to approximately 100 and 95.6 % yields from mannitol and sorbitol respectively, and only 38 % from dulcitol.

As an extension of this observation a mixture of equal parts of dulcitol and sorbitol was treated with fuming hydrochloric acid and benzaldehyde as above: it was found that the weight of crude product corresponded to a yield of about 60 % of the amount which should have been produced on the assumption that both alcohols had been converted into tribenzylidene derivatives, but the product consisted for the most part of the sorbitol derivative since approximately 50 % of the dulcitol was recovered unchanged.

From the experience gained by the above experiment it is clear that where dulcitol and sorbitol occur together in the same solution they can be reasonably well separated by precipitating the dulcitol in crystalline form by the addition of alcohol and by recovering the sorbitol from the mother-liquor by conversion into its benzylidene derivative.

The adsorption of sugar alcohols by basic lead acetate.

It is an established fact that soluble carbohydrates tend to be removed from solution by adsorption upon basic lead acetate precipitates if the latter are left in contact with the solution for some hours. Evidence has now been obtained that the same holds for dulcitol and sorbitol.

A 60 % alcoholic extract of *Bostrychia scorpioides*, after distilling off the alcohol under reduced pressure, was precipitated with excess of basic lead acetate and set aside overnight. Next morning the precipitate was filtered and washed very thoroughly by repeated grinding under hot water and filtering. The resulting precipitate was decomposed with hydrogen sulphide and the filtrate from the lead sulphide neutralised with baryta and evaporated to small bulk under reduced pressure; it was then treated with twice its volume of alcohol, filtered and evaporated to a syrup; on cooling typical crystals of dulcitol separated (m.p. after recrystallisation 185–186°), showing that, in spite of the thorough washing to which the lead precipitate had been subjected, some of the dulcitol had adhered to it.

The filtrate from the dulcitol crystals was shown to contain sorbitol by conversion into the benzylidene derivative. In addition this same solution was shown to contain an ethereal sulphate since, on hydrolysis with hydrochloric acid, it gave a heavy precipitate of barium sulphate due to the interaction between the barium acetate present in the solution with sulphuric acid liberated as a result of the hydrolysis. In this respect, therefore, *Bostrychia* resembles other red algae.

SUMMARY.

1. *Bostrychia scorpioides* contains the sugar alcohol sorbitol as well as dulcitol.
2. In common with other Rhodophyceae, it also contains an ethereal sulphate complex.
3. The reaction between sugar alcohols and benzaldehyde is commented on.
4. The marked adsorption of dulcitol and sorbitol upon precipitates with basic lead acetate is noted.

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