CIX. *On the occurrence of Mannite in the Laminaria saccharina and other Sea-weeds.* By JOHN STENHOUSE, Ph.D.

MORE than thirty years ago the *Laminaria saccharina*, with some others of our commonest sea-weeds, were examined by Vauquelin, who detected in several of them a sweet-tasted crystalline substance. Subsequently, in 1815, the *L. saccharina* and five other fuci were again subjected to analysis by M. Gaultier de Claubry, who also detected in the *L. saccharina* and in the *Halydris siliquosa* the same saccharine substance, which he called manna.

From the imperfect state of organic chemistry at these early periods, neither of these eminent chemists were enabled to subject this saccharine substance to analysis; and so little reliance has been placed upon their statements, that for some years past they have been generally discredited both by che-

mists and botanists; Berzelius, for instance, has not once mentioned sea-weeds as a source of mannite, though he has enumerated all the other known sources; and Dr. Greville, in his *Algæ Britannicæ*, regards the crystalline incrustations which usually appear on the *L. saccharina* and the *Halydris siliquosa* when dried, as nothing else than common salt. Under these circumstances I was lately induced to subject the *L. saccharina* and some other sea-weeds to examination.

A quantity of the dried *L. saccharina* was repeatedly digested with hot water, which formed with it a mucilaginous solution of a brownish red colour, and of a sweetish but at the same time of a very disagreeable taste. When evaporated to dryness on the water-bath, it left a considerable quantity of a saline semi-crystalline mass. This was reduced to powder and treated with boiling alcohol, by which a considerable portion of it was dissolved. The alcoholic solution on cooling became nearly solid, from the quantity of long transparent prismatic crystals with which it was filled. When purified by a second crystallization, these were deposited in large hard prisms of a fine silky lustre, and possessing all the external characters of mannite. When dried at 212° F., they were subjected to analysis.

I. 0.4334 grm. of substance gave 0.6235 of carbonic acid and 0.2995 of water.

II. 0.4215 grm. gave 0.6058 carbonic acid and 0.294 water.

		Calculated Numbers.	
		At.	Per cent.
Carbon	I. 39.78	II. 39.74	6 Carbon . 40.02
Hydrogen	7.67	7.74	7 Hydrogen . 7.62
Oxygen	52.25	52.52	6 Oxygen . 52.36
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

It is evident from the result of these analyses, that the sweet crystalline substance in the *L. saccharina* is nothing else than mannite. The quantity of mannite contained in it is very considerable. One thousand grains of the dried sea-weed, when treated in the way already described, first with water and then with alcohol, gave 121.5 grains = 12.15 per cent. The specimen operated on had been kept for six months, and was covered with an incrustation in long slender needles. I also examined a quantity of the fresh sea-weed, and found it to contain as much mannite as the older specimen. It appears, therefore, that the epithet *saccharina*, as applied to this species of *Laminaria*, is not so inappropriate as has been often supposed.

Mannite may be easily distinguished from cane-sugar by the following test. If a little strong sulphuric acid is poured

upon the mannite and a gentle heat is applied, the mannite dissolves without being in the least discoloured, and gives a transparent solution. If the heat is much increased the liquid becomes of a deep brown colour, but does not lose its transparency. When cane-sugar, on the contrary, is gently heated with sulphuric acid, it is, as is well known, immediately charred with evolution of sulphurous acid gas. From grape-sugar mannite may be likewise easily distinguished. If mannite is boiled with a strong solution of potash or soda, it dissolves without any change of colour, while grape-sugar when similarly treated acquires a deep brown colour. When heated with a solution of potash and some sulphate of copper, mannite completely prevents the precipitation of the oxide of copper, while grape-sugar causes the immediate precipitation of the red oxide of copper.

Besides mannite, the *L. saccharina*, in common with most of the other sea-weeds, contains a great deal of a peculiar mucilage, which when dried has a deep reddish colour. It differs however from ordinary gum, for when digested with nitric acid it yields oxalic, but neither mucic or saccharic acids. I intend subjecting this substance to more minute examination.

L. digitata.—Besides the *L. saccharina* I have also examined some of the other sea-weeds for mannite, and among others the *L. digitata* or common tangle. The aqueous solution of this sea-weed is also reddish brown, and when evaporated it yields a similar mucilage with the *L. saccharina*, but in much smaller quantity. The *L. digitata* also contains a considerable quantity of mannite, though I should think scarcely half as much as what exists in the *L. saccharina*.

Halydris siliquosa.—The next sea-weed examined was the *Halydris siliquosa*. With hot water it forms a very dark-coloured solution of a bitter and slightly astringent taste. The quantity of mannite contained in it is very great, amounting I should think to between 5 and 6 per cent. As already mentioned, mannite forms a great part of the white incrustations which appear on the surface of this sea-weed when dried.

Alaria esculenta.—This beautiful sea-weed, which is by no means uncommon on the coasts of Scotland, where, as its name imports, it often serves as an article of food, also contains mannite in considerable abundance.

Rhodomenia palmata.—*Rhodomenia palmata*, or common dulce, contains a good deal of a sweet-tasted greenish-coloured mucilage. It also yields a considerable quantity of mannite, amounting probably to 2 or 3 per cent.

Fucus vesiculosus.—The *Fucus vesiculosus*, the most common perhaps of British Algæ, contains I should think from 1 to 2

per cent. of mannite, and the *Fucus nodosus*, also a very common sea-weed, likewise yields a small but very appreciable quantity of the same principle.

Fucus serratus.—This sea-weed also contains a considerable quantity of mannite, less perhaps than the *L. digitata*, but more than the *Rhodomenia palmata*. The mannite which the *Fucus serratus* yields is much freer from colouring matter than that from any of the other Algæ, being nearly colourless from the first.

I could not detect any mannite in the *Ulva latissima* or Laver. The experiment was made on a very small scale, and will be repeated on the first opportunity. The Laver contains a good deal of a sweet-tasted green-coloured mucilage, similar to that of the *Rhodomenia palmata*.

As mannite has occurred in eight out of nine of the sea-weeds which I have happened to examine, it probably exists in larger or smaller quantity in most sea-weeds, in which it appears to replace the cane- and grape-sugar so abundant in many of our land-plants. It is evident also that mannite occurs much more plentifully in nature than has been hitherto imagined. The following is a list of the Algæ just described, arranged in order according to the quantity of mannite which they severally contain :—

1. <i>Laminaria saccharina</i> .	5. <i>Alaria esculenta</i> .
2. <i>Halydris siliquosa</i> .	6. <i>Rhodomenia palmata</i> .
3. <i>Laminaria digitata</i> .	7. <i>Fucus vesiculosus</i> .
4. <i>Fucus serratus</i> .	8. <i>Fucus nodosus</i> .

The quantity of mannite in the *L. saccharina* is such that I think mannite might be more œconomically procured from this sea-weed than from the usual source, manna.

Supposed existence of Mannite in the Roots of Triticum repens, or Couch-grass.

In a note on the article Mannite, in the eighth volume of the last German edition of Berzelius's *Lehrbuch*, it is stated that Professor Pfaff had succeeded in obtaining mannite from the roots of *Triticum repens*, or couch-grass. M. Pfaff says that he treated the extract of the couch-grass roots with boiling alcohol, which on cooling deposited a number of long needle-shaped crystals, which he believed to be a new species of sugar, but which Berzelius is rather disposed to regard as more probably mannite. I have twice repeated M. Pfaff's experiment on two different quantities of couch-grass roots, but with very opposite results. The alcoholic solution on standing deposited it is true a quantity of long slender cry-

140 Mr. Denham Smith *on the Composition of*

stalline needles. These, however, had not a sweet taste, and when thrown into hot sulphuric acid they dissolved with effervescence without blackening the solution. When heated on platinum foil they melted, and left a white fusible alkaline residue, which, when neutralized with muriatic acid, produced a yellow crystalline precipitate in an alcoholic solution of platinum. I have every reason to believe, therefore, that these acicular crystals were merely binoxalate of potash. The grass roots certainly contained a great deal of an uncrystallizable sugar which readily fermented.