



Fig. 3. Abhängigkeit der Protonenübergangswärme vom Lösungsmittel. Protonenspender: Essigsäure.

Unterschiede lange nicht so gross, dass sie das Gesamtbild veränderten.

Es ist auffallend, dass der Protonenübergang an das Alkoxy-Ion in alkoholischer Lösung viel weniger Wärme befreit als derjenige an das Hydroxyl-Ion in wässriger Lösung.

1. Day, J. N. E. und Ingold, C. K. *Trans. Faraday Soc.* **37** (1941) 686; Bender, M. L. *J. Am. Chem. Soc.* **73** (1951) 1626.
2. Siehe Literaturverzeichnis: Dippy, J. F. J. *J. Chem. Soc.* **1941** 550; *Chem. Revs.* **25** (1939) 151.
3. Siehe auch Wolfenden, J. H., Jackson, W. und Hartley, H. B. *J. Phys. Chem.* **31** (1927) 850.

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Low-molecular Carbohydrates in Algae

VII*. Investigation of *Fucus spiralis* and *Desmarestia aculeata*

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In Parts I¹, IV² and V³ of this series, studies on the brown algae *Fucus vesiculosus*, *Pelvetia canaliculata* and *Laminaria*

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cloustoni were reported. These algae all contained mannitol, 1-mannitol β -glucoside and 1,6-mannitol di-(β -glucoside). 1-Mannitol acetate was isolated from *F. vesiculosus* and *L. cloustoni*, volemitol and its mono- and di-glucosides from *P. canaliculata* and a substance, laminitol, later proved to be a C-methyl inositol (Part VI) from *L. cloustoni*. It was therefore of interest to investigate other brown algae to see if some of these substances were characteristic for the whole group, and in the present communication the investigation of *Fucus spiralis* and *Desmarestia aculeata* is reported. Mannitol, 1-mannitol β -glucoside and laminitol were isolated from both and the presence of 1,6-mannitol diglucoside was demonstrated by paper chromatography. It is most probable that laminitol was overlooked in *F. vesiculosus* and *P. canaliculata* and that this substance, as well as mannitol and its glucosides, is characteristic for brown algae in general. 1-Mannitol acetate was isolated from *F. spiralis* but not from *D. aculeata* and it seems significant that this substance has been obtained in a good yield only from the *Fucus* species. Volemitol was not found in either of the two algae now investigated. It has thus so far only been found in *P. canaliculata* but it is intended to investigate its possible occurrence in other brown algae.

The algae, *Fucus spiralis* (740 g) and *Desmarestia aculeata* (240 g) were kindly supplied by Institut for Tang- og Tareforskning, Trondheim. They were extracted and the extracts worked up as described in previous communications¹. After fractionation on carbon columns and, when necessary, further separation on thick filter paper, the following substances were isolated:

Fucus spiralis. Laminitol, 0.18 g (0.025 %). M. p. 245–247° (slight decomp.).

Mannitol, 23 g (3.1 %). M. p. 160–162°.

1-Mannitol acetate, 0.70 g (0.1 %). M. p. 121–122°.

1-Mannitol β -glucoside, 0.30 g (0.04 %). M. p. 141–142°.

1,6-Mannitol di-(β -glucoside), about 0.03 g (0.004 %). Amorphous, chromatographically indistinguishable from authentic material.

Desmarestia aculeata. The crude laminitol was purified as acetate. Yield 20 mg (0.004 %, calculated as laminitol). M. p. 147–148°.

Mannitol, 13.5 g (5.6 %). M. p. 162–163°.

1-Mannitol β -glucoside 0.11 g (0.045 %). M. p. 138–139°.

1,6-Mannitol di-(β -glucoside), about 5 mg (0.002 %). Amorphous, chromatographically indistinguishable from authentic material.

The melting points of all the crystalline compounds were undepressed on admixture with authentic specimens.

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1. Lindberg, B. *Acta Chem. Scand.* **7** (1953) 1119.
2. Lindberg, B. and Paju, J. *Acta Chem. Scand.* **8** (1954) 817.
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Low-molecular Carbohydrates in Algae

VIII*. Investigation of Two Green Algae

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Two green algae, one marine, *Enteromorpha compressa*, and one fresh water alga, *Chlorella*, strain Tx 14–10, have been investigated, using the same technique previously applied to brown algae (Part V¹).

Sucrose was isolated in good yield from both algae and evidence for the occurrence of *meso*-inositol in the two algae was also obtained. A small amount of mannitol was isolated from *E. compressa*, but this might have come from contaminating brown algae. From the *Chlorella* maltose and maltotriose were isolated. These substances certainly have some connection with starch, either as precursors in its

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biosynthesis or as products of a post-mortal, enzymatic hydrolysis. In addition, the presence of several unidentified substances, occurring in small amounts, was demonstrated by paper chromatography.

Enteromorpha compressa (250 g), kindly supplied by Marinbotaniska Institutionen, Göteborg, was extracted and worked up as previously described for the brown algae¹. The carbohydrate fraction was separated on a carbon column, using the gradient elution technique. Mannitol (90 mg), m. p. 158–162° and sucrose (1.4 g), m. p. 178–179° were isolated, and the presence of *meso*-inositol demonstrated by paper chromatography.

Chlorella, strain Tx 14–10, (160 g), kindly supplied by Docent L. E. Enebo, Kungl. Tekniska Högskolan, Stockholm, was refluxed for 4 hours with 75 % ethanol (2 000 ml), the extract separated by centrifugation and the residue re-extracted and treated in the same manner. The combined extracts were worked up as above, separated on a carbon column and further fractionated on thick filter paper. The following substances were isolated:

meso-Inositol (0.22 g), m. p. 216–217°. Acetate, m. p. 209–211°. Sucrose (3.8 g), m. p. 182–183°.

Maltose (80 mg) was isolated by further separation of a fraction from the carbon column on thick filter paper. It was amorphous and not quite pure, $[\alpha]_D^{20} + 110^\circ$ (c, 2.0 in water), but was chromatographically indistinguishable from authentic maltose and on hydrolysis yielded glucose only.

Maltotriose (270 mg) was isolated from another fraction in the same manner. It was also amorphous and not quite pure, $[\alpha]_D^{20} + 139^\circ$ (c, 2.0 in water), but chromatographically indistinguishable from authentic maltotriose and on partial hydrolysis yielded glucose and maltose (identified by paper chromatography).

The melting points of all the crystalline compounds were undepressed on admixture with authentic materials.

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1. Lindberg, B. and McPherson, J. *Acta Chem. Scand.* **8** (1954) 1547.

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