

Low-molecular Carbohydrates in Algae

VI*. Laminitol, a New C-Methyl Inositol from *Laminaria cloustoni*

BENGT LINDBERG and JOHN McPHERSON**

Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

A C-methylinositol, laminitol, has been isolated from the brown alga *Laminaria cloustoni*. It is isomeric but not identical with mytilitol, another C-methylinositol, obtained from the mussel *Mytilus edulis*.

An investigation of the low-molecular carbohydrates of *Laminaria cloustoni* was reported in Part V of this series. One of the substances isolated was not identified. It was fast on the carbon column but had a low R_F -value, only slightly higher than that of *d*-inositol with the ethylacetate-acetic acid-water (3 : 1 : 1) mixture. Finally it reduced the silver nitrate-sodium ethoxide reagent¹ strongly, though not spontaneously like the reducing sugars. We suggested that the substance might be a cyclitol, and it has now been subject to further investigations.

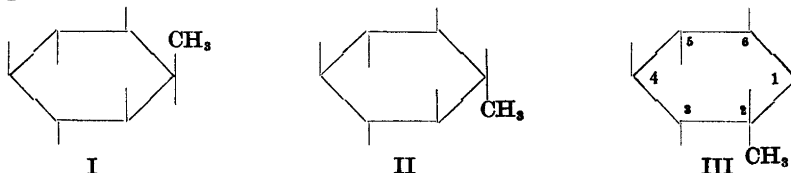
The analysis of the substance, after drying, was consistent with the formula $C_7H_{14}O_6$. When the substance was dried, water, corresponding to two moles of water of crystallization, was lost. It consumed 6.5 moles of periodic acid with formation of 5.2 moles of acid. Its acetate was shown by analysis to be a hexaacetate. Finally, the presence of a C-methyl group was demonstrated by analysis according to Kuhn-Roth². The only formula in agreement with these analyses is that of a C-methylinositol.

Two C-methylinositols have been described previously. One, mytilitol (I) has been isolated from the mussel *Mytilus edulis*³ and the configuration has been determined by Posternak⁴. The other, *isomytilitol* (II) is a synthetic product, prepared by Posternak⁴. From the melting points of our substance, mytilitol, *isomytilitol* and their hexaacetates, 266—269°, 266—268°, 225—226°, and 151—152°, 181°, 188—189°, respectively, it is evident that our substance is not identical with either of these, but is a new natural product, for which we suggest the name laminitol. Further, laminitol is much faster than mytilitol on the paper chromatogram and the m.p. of its hexaacetate was not raised on recrystallisation and seeding with mytilitol hexaacetate.

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** Present address: C.S.I.R.O. Div. For. Prod., Melbourne, Australia.

Four of the nine possible *cyclohexanehexols* are naturally occurring, *d*- and *l*-inositol, *meso*-inositol and scyllitol. Of these *meso*-inositol is the most widespread. It seems reasonable to assume



that laminitol should have the same configuration as one of these. It is optically active, $[\alpha]_D -3^\circ$, but the low value for the rotation agrees better with an unsymmetrically substituted *meso*-inositol (2-methyl *meso*-inositol, III, or the corresponding 3-methyl derivative, IV) than with a *d*- or *l*-inositol derivative. This possibility is especially attractive, because it provides us with a potential biochemical relationship between laminitol and mytilitol. The hydroxyl group at C_1 is axial and known to be oxidized under biochemical conditions (*Cf. e.g. Ref.*⁵) and the carbonyl derivative formed could give a mixture of mytilitol (I) and III or IV, resp., on subsequent reduction.

The configuration of laminitol and its potential occurrence in other algae is under investigation. Provided that laminitol is a constituent of microscopic algae serving as food for *Mytilus* there may be a direct casual relation between laminitol and mytilitol.

EXPERIMENTAL

(Melting points uncorrected.)

Pure laminitol was prepared by deacetylation of the acetate. Paper chromatograms and m. p. determinations showed that the substance was not affected by the acetylation-deacetylation. It was recrystallised from aqueous ethanol. M. p. 266–269° (Slight decomp.) $[\alpha]_D^{20} -3^\circ$ (water, $c = 2$). On drying at 110° 15.9 % water was lost. Calc. for $C_7H_{14}O_6 \cdot 2H_2O$ (230.2) 15.6 %. (Found: C 42.9; H 7.27; C–CH₃ 4.92. Calc. for $C_7H_{14}O_6$ (194.2): C 43.3; H 7.27; C–CH₃ 7.73).

By analysis of lauric acid, under identical conditions⁶ 4.52 % C-methyl was obtained, compared to the calculated value, 7.52 %. On periodate oxidation with 0.1 *M* solution, buffered with acetate to pH 4.0, at room temperature and over-night, the substance consumed 6.5 ± 0.1 moles periodate. By oxidation with sodium metaperiodate under similar conditions, 5.2 ± 0.1 moles acids were formed.

Laminitol hexaacetate. By acetylation of laminitol with acetic anhydride, using either pyridine (equal part) or conc. sulphuric acid (1 %) as catalyst, the same acetate was obtained in good yield. It was purified by recrystallisation from ethanol. M. p. 151–152° $[\alpha]_D^{20} -19^\circ$ (chloroform, $c = 2$). (Found: C 51.1; H 5.70; COCH₃ 59.0. Calc. for $C_7H_8O_6$ (OCCH₃)₆ (446.4): C 51.1; H 5.87; COCH₃ 57.8).

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