CCXCIX. THE MOLECULAR STRUCTURE OF GLYCOGEN FROM THE WHOLE TISSUES OF *MYTILUS EDULIS*.

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THE investigation, by Haworth's "end-group assay" method, of glycogen obtained by the alkaline disintegration of the whole tissues of *Mytilus edulis* is described below. Employing the author's technique [Bell, 1935; 1936] the chemical basic molecule of this glycogen is shown to be derived from 18 glucose units. The compositions of glycogens already investigated in this way are listed in Table I.

Table I.

Source of glycogen	No. of glucose units	Reference
Rabbit liver	12	Haworth & Percival [1932]
Rabbit liver	12	Bell [1935]
Rabbit liver (commercial)	18	Haworth [1935]
Rabbit liver, after galactose feeding	18	Bell [1936]
Fish liver	12	Bell [1935]

The *Mytilus* glycogen, examined according to Bell & Young [1934] and Bell & Kosterlitz [1935], showed no significant differences from the other glycogens described by these authors. Similarly the methylated and acetylated derivatives differed in no apparent manner from the corresponding substances prepared from glycogens from other sources (see Table I).

Hydrolysis of the methylated glycogen, followed by separation and identification of the cleavage products, yielded tetramethylglucose amounting to 6% of the starting material, corresponding to a mean "chain-length" of 18 glucose units for the glycogen molecule. This chain length is further confirmed by the relative amounts of the different cleavage products, isolated in over 90% yield, viz.:

1 mol.	...	...	2:3:4:6-tetramethylglucose.
15 mols.	...	...	2:3:6-trimethylglucose.
2 mols.	...	...	dimethylglucoses.

It is noteworthy that here, and in the investigations cited above, glycogen appears to occur solely in one or other of the two known forms, 12-unit or 18-unit, and that we have as yet no evidence for the occurrence of mixtures of these.

EXPERIMENTAL.

The crude glycogen was prepared by the Pflüger method by Dr F. G. Young, to whom the author is indebted for the material used in this investigation. Purified by the procedure of Bell & Young [1934], the glycogen showed a rate of hydrolysis with aqueous acid identical with that of previously examined specimens. With iodine, the colour was identical with that developed by fish liver glycogen.

Mytilus glycogen had the following other properties: $[\alpha]_D^{25}$ in water, $+195.4^\circ$ ($l=2$, $c=0.5$); reducing power (Macleod-Robison, glucose = 100), 1.3; phosphate, inorganic—nil, organic—nil.

Acetylation. By the method of Haworth & Percival [1932] 30 g. of glycogen gave 48 g. acetate (90 % of theory); $[\alpha]_D^{25}$ in CHCl_3 , $+172^\circ$. (Found, COCH_3 : 44.5 %.)

Methylation. 37 g. of the acetate simultaneously deacetylated and methylated by the procedure of the above authors, yielded, after 12 treatments, 24.0 g. (90 %) of methylated glycogen. (Found, OMe: 45.1 %.) $[\alpha]_D^{20}$ in CHCl_3 , $+211^\circ$ ($l=2$, $c=4.5$).

Hydrolysis by aqueous acid and separation of cleavage products.

The procedure was exactly as described by the author [Bell, 1935; 1936] (Table II).

Table II.

OMe % of methylated glycogen	45.1
Amount hydrolysed (g.)	22.95
2:3:4:6-Tetramethylglucose found (g.)	1.359
2:3:4:6-Tetramethylglucose as % of starting material	6
2:3:4:6-Tetramethylglucose m.p. drained on tile	87°
2:3:4:6-Tetramethylglucose $[\alpha]_D$ in water ($c=5$)	$+82.0^\circ$
2:3:4:6-Tetramethylglucose n_D^{17}	1.4585
2:3:4:6-Tetramethylglucose OMe %	52.4
2:3:6-Trimethylglucose found (g.)	18.79
2:3:6-Trimethylglucose m.p. drained on tile	115°
2:3:6-Trimethylglucose $[\alpha]_D$ in water ($c=4.5$)	$+70.3^\circ$
Dimethylglucose found (g.)	2.19

The trimethylglucose fraction consisted entirely of the 2:3:6-derivative, and no evidence of monomethyl- or unmethylated glucose was found in the hydrolysate of the methylated glycogen.

The methyl content and the ratios of the different fractions to one another correspond well with the methylated glycogen being an octadecasaccharide in which 54 of the 56 free OH groups are methylated [cf. Bell, 1936].

Table III.

Ratios	Found	Calculated
Trimethylglucose Tetramethylglucose	13.8	13.1
Trimethylglucose Dimethylglucose	8.6	7.4

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