Structure of the Agarose Constituent of Agar-agar

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The latest communication[1] together with the previous ones contributed from this laboratory has enabled me to come to the following conclusion concerning the composition and the structure of agar.

Agar is composed of two polysaccharides, agarose and agaropectin, a composition similar to starch, which is composed of amylose and amylopectin. Agarose, a main constituent of agar, exhibits a composition $[C_{12}H_{14}O_5(OH)_4]_n$; whereas agaropectin is a more complicated polysaccharide with sulfuric and uronic acid residues. This view is supported by the actual separation of the acetylated agar into two different constituents; agarose acetate and agaropectin acetate, most of the sulfuric acid and uronic acid present in agar being accumulated in the latter constituent[2]. The former constituent, having the formula $[C_{12}H_{14}O_5(OCOCH_3)_4]_n$, is converted into the corresponding methyl ether $[C_{12}H_{14}O_5(OCH_3)_4]_n$ being treated with dimethylsulfate and sodium hydroxide[3].

Now, it is possible to propose that agarose consists of alternatively repeated residues of 1, 3-linked β-D-galactopyranose and 1, 4-linked 3, 6-anhydro-α-L-galactopyranose as shown in Fig. 1, the chain being terminated by D-galactose and 3, 6-anhydro-L-galactose residues at the reducing and non-reducing ends, respectively.

The above structure, which is in agreement with the composition $[C_{12}H_{14}O_5(OH)_4]_n$, accounts for all the experimental facts reported previously. Since the 3, 6-anhydro-L-galactoside linkages appearing every second unit in the molecule are extremely susceptible to acid-cleavage, even very mild methano

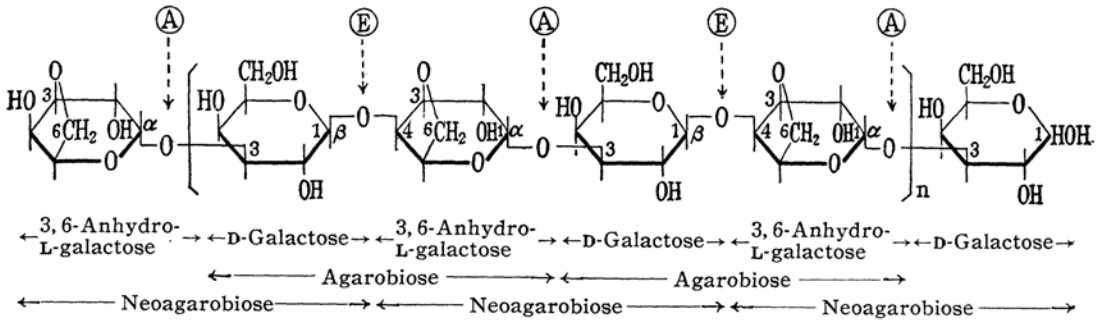

Fig. 1. Possible structure of agarose.
Ⓐ: the position cleaved by acid.
Ⓔ: the position cleaved by enzymes.

lysis led to the isolation of agarobiose dimethylacetal in an excellent yield, together with small amounts of methyl D-galactoside and 3, 6-anhydro-L-galactose dimethylacetal[4]. The last two products are inferred to have arisen chiefly from the reducing and nonreducing ends of the molecule, respectively. The partial acid-hydrolysis[5] and mercaptolysis[6] also afforded agarobiose (4-*O*-*β*-D-galactopyranosyl-3, 6-anhydro-L-galactose) and its diethylmercaptal, respectively, supporting the structure proposed. On the other hand, when agar was subjected to the enzymatic hydrolysis[1], neither D-galactose nor 3, 6-anhydro-L-galactose was detected in the hydrolysate, but neoagarobiose (3-*O*-3, 6-anhydro-*α*-L-galactopyranosyl-D-galactose) was isolated as the lowest cleavage fragment. This fact is also explained by the structure, if the enzymes are capable of splitting only the *β*-D-galactoside linkages. Moreover, the structure is in accordance with the fact that scission of the methylated agarose yielded 2, 4, 6-tri-*O*-methyl-D-galactose[7], 2-*O*-methyl-3, 6-anhydro-L-galactose[8], and none of tetra-*O*-methyl-D-galactose. In addition, the absence of adjacent hydroxyl groups in the molecule of the polysaccharide is corroborated by the observation of Barry and Dillon[9] that agar consumed no periodate at all.

In conclusion, all the experimental results are compatible with only one structure (Fig. 1) for agarose, which constitutes the greatest part of agar. The sole problem to be solved is whether it is a linear polysaccharide or a branched one.

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