Isolation of 6-O-Methyl-D-galactose from the Agar of Ceramium Boydenii

By Susumu HIRASE and Choji ARAKI

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The chemical structure of agar has been extensively investigated in this Institute[1]. One of the present writers has assigned the linear structure consisting of D-galactose and 3, 6-anhydro-L-galactose to agarose, which is the main polysaccharide of the agar of *Gelidium amansii*[2]. Besides these two sugars, there are also contained L-galactose, xylose, D-glucuronic acid, pyruvic acid and sulfuric acid in the agar[1]. The present communication reports the isolation of 6-*O*-methyl-D-galactose in 12% yield from the hydrolysis products of the agar of *Ceramium boydenii.* This is the first reported instance of 6-*O*-methyl-D-galactose as far as agar is concerned. The synthesis of the sugar has been reported on several occasions[3-5]. It has also been isolated from the non-gelling polysaccharide of the red seaweed *Porphyra capensis*[6].

Experimental

Preparation of Agar.—Agar was extracted from dry *Ceramium boydenii* with hot water and purified by freezing and thawing in the usual way. It contains 2.81% of ash and 1.18% of sulfate on the dry basis.

Hydrolysis of the Agar.—The agar (15 g. on the dry basis) was hydrolyzed with N-sulfuric acid (200 ml.) in a boiling water bath for 15 hr. After filtration followed by neutralization with barium carbonate and subsequent refiltration, the solution was allowed to pass through columns of Amberlite IR-120 (100 ml.) and Amberlite IR-4B (100 ml.) in succession. The resins were then washed with water (1500 ml.). All the effluents were combined and evaporated under reduced pressure to a sirup (7.5 g.). Paper chromatographic examination using *n*-butanol-ethanol-water (4 : 1 : 2 v/v) as a developing solvent and aniline hydrogen phthalate as a sprayer indicated the prensence of galactose, xylose, 6-*O*-methyl-galactose and 5-hydroxymethylfuraldehyde. The last compound would arise from 3, 6-anhydrogalactose which would have been decomposed during the hydrolysis[7].

Isolation of 6-*O*-Methyl-D-galactose.—The sirup obtained above afforded D-galactose on crystallization from a mixture of methanol (25 ml.) and ethanol (35 ml.); yield 2.6 g., m. p. 160~165°C; $[\alpha]_{\mathrm{D}}^{24}+78.0^\circ$ (*c* 0.80 in water). The mother liquor (4.7 g.) was then chromatographed on a charcoal-Celite column, from which a mixture (2.9 g.) of galactose and xylose was eluted with first 2 l. of water. Further elution with additional 5 l. of the same solvent afforded chromatographically pure 6-*O*-methyl-D-galactose; yield 1.8 g. (12% of the agar). The sugar was purified by recrystallization twice from absolute ethanol; m. p. 122~124°C; $[\alpha]_{\mathrm{D}}^{20}+135^\circ\rightarrow+77.0^\circ$ (*c* 1.0 in water) (Found: C, 43.15; H, 7.11; OCH_3, 16.15. Calcd. for $C_7H_{14}O_6$: C, 43.29; H, 7.27; OCH_3, 15.98%). The melting point and optical rotation reported for 6-*O*-methyl-D-galactose are: m. p. 128°C, $[\alpha]_{578}^{20}+114^\circ\rightarrow+77^\circ$[3]; m. p. 118°C, $[\alpha]_{\mathrm{D}}^{20}+120^\circ\rightarrow+70^\circ$[4]; m. p. 122~123°C, $[\alpha]_{\mathrm{D}}^{18}+112^\circ\rightarrow+66^\circ$[4]; m. p. 113~114°C, $[\alpha]_{\mathrm{D}}^{18}+137^\circ\rightarrow+77^\circ$[5]; m. p. 122~123°C, $[\alpha]_{\mathrm{D}}^{17}+117^\circ\rightarrow+77.3^\circ$[6]. For comparison, 6-*O*-methyl-D-galactose was prepared by the method of Freudenberg and Smeykal[3] and purified on a charcoal-Celite column. It had the same melting point and mixed melting point as that isolated above.

The sugar was also identified as its phenylosazone[3-6]: m. p. and mixed m. p. 200~201°C; $[\alpha]_{\mathrm{D}}^{20}+140^\circ$ (*c* 0.40 in pyridine) (Found: N, 14.98; OCH_3, 8.19. Calcd. for $C_{19}H_{24}O_4N_4$: N, 15.05; OCH_3, 8.33%).

Institute of Chemistry
Faculty of Industrial Arts
Kyoto Technical University
Matsugasaki, Kyoto

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