Communications to the Editor

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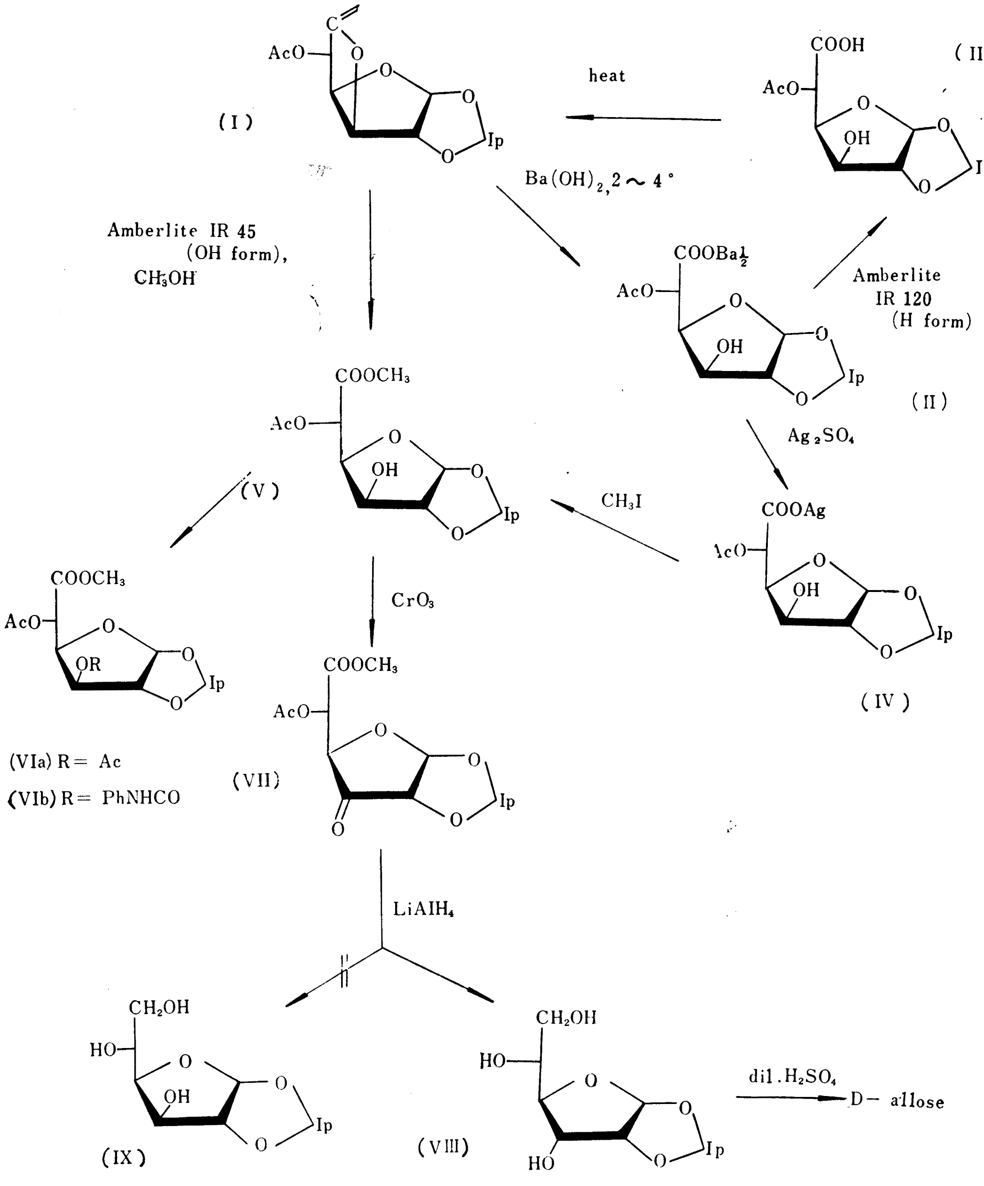
Synthesis of Methyl 1,2-O-Isopropylidene-3-oxo-5-O-acetyl-D-glucofuranuronate

In the studies on oxidized starch, an oxidation product of starch with fuming nitric acid, the presence of 3-oxoglucuronic acid residue in the molecule was suggested by Imai *et al.*,1) and its chemical behavior appeared to be of particular interest. In this connection, in the course of synthesizing 3-oxoglucuronic acid, methyl 1,2-O-isopropyli-



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1) Y. Imai: Yakugaku Zasshi, 81, 1115 (1961); Y. Imai, Y. Hirasaka: *ibid.*, 81, 1362 (1961).

dene-3-oxo-5-O-acetyl-D-glucofuranuronate (VII) was obtained as an intermediate substance and its structure was established by the authors.

Treatment of 1,2-O-isopropylidene-5-O-acetyl-D-glucofuranurono-γ-lactone (I)[2] with barium hydroxide solution at 2 to 4° gave, in almost quantitative yield, barium 1,2-O-isopropylidene-5-O-acetyl-D-glucofuranuronate (II) as an amorphous powder (corresponding S-benzylthiuronium salt : m.p. 183~184° (*Anal.* Calcd. for $C_{19}H_{26}O_8N_2S$: C, 51.58; H, 5.92; N, 6.33. Found : C, 51.54; H, 5.71; N, 6.81). The structure of (II) was supported by the fact that it was converted by Amberite IR 120 (H form) into a free acid (III) which readily lactonized to regenerate (I). The silver salt (IV) was obtained, from (II) by the action of silver sulfate, and treatment of (IV) with methyl iodide gave methyl 1,2-O-isopropylidene-5-O-acetyl-D-glucofuranuronate (V) m.p. 105~106° (*Anal.* Calcd. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found : C, 49.85; H, 6.59. IR : ν_{O-H} 3400~3600 cm^{-1} ($CHCl_3$). Moreover, (V) was directly obtained from (I) in excellent yield by stirring with Amberlite IR 45 (OH form) in methanol. 3-O-Acetate (VIa) and 3-O-carbanilate (VIb) were prepared from (V) (VIa) : m.p. 80° (*Anal.* Calcd. for $C_{14}H_{20}O_9$: 50.60; H, 6.07. Found: C, 50.63; H, 6.08). (VIb) : m.p. 183°. (*Anal.* Calcd. for $C_{19}H_{23}O_9N$: C, 55.74; H, 5.66; N, 3.42. Found : C, 55.87; H, 5.30; N, 3.45)).

Oxidation of (V) with chromium trioxide led to methyl 1,2-O-isopropylidene-3-oxo-5-O-acetyl-D-glucofuranuronate (VII), m.p. 102~103° (*Anal.* Calcd. for $C_{12}H_{16}O_8$: C, 50.00; H, 5.60. Found : C, 50.02; H, 5.86. IR : $\nu_{C=O}$ 1783 cm^{-1} ($CHCl_3$)). So far as we examined, acetic acid and acetone were suitable media for the oxidation while pyridine and *tert*-butanol brought about unsatisfactory results.

Reduction of (VII) by the use of lithium aluminum hydride gave crystalline 1,2-O-isopropylidene-D-allofuranose (VIII) as a sole product, m.p. 133° (*Anal.* Calcd. for $C_9H_{16}O_6$: C, 49.08; H, 7.32. Found : C, 48.43; H, 7.23). No other product was detected in the mother liquor by means of paper chromatography. The structure of (VIII) was confirmed, by the fact that it was obviously distinguished from another possible isomer, 1,2-O-isopropylidene-D-glucofuranose (IX), by mixed melting point and paper chromatography and that the hydrolytic product of (VIII) was identified with D-allose by paper electrophoresis. The result is of interest in that the reduction proceeded along the stereo-specific course to afford a single product. Details of this work will be published in the near future.

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Faculty of Pharmaceutical Sciences,
University of Tokyo.
Hongo, Tokyo, Japan.

Morizo Ishidate (石舘守三)
Zenzo Tamura (田村善蔵)
Toshio Kinoshita (木下俊夫)

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[2] Y. Nitta, J. Ide, A. Momose, M. Kawada : *Ibid.*, 82, 790 (1962).