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著者	ADACHI Susumu
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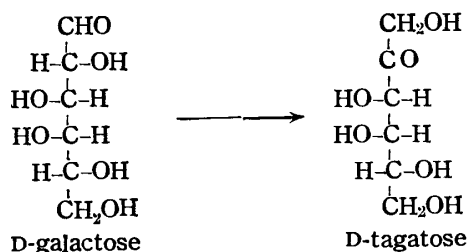
Susumu ADACHI

*Department of Animal Husbandry, Faculty of Agriculture,
Tohoku University, Sendai, Japan*

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Since it has been shown that the ketose formed newly in highly heated milk is identical with tagatose from the results of paper chromatography, it is necessary for the authentic sample to synthesis the tagatose (1).

Although the literature contains several references to the chemical synthesis of tagatose (2), the typical methods are the procedures of Totton and Lardy (3), Reichstein and Bosshard (4). These methods are based on the Lobry de Bruyn and van Ekenstein transformation of galactose that is converted to tagatose with mild action of pyridine solution at high temperature.



However, these methods, while moderately satisfactory, are rather tedious and time consuming for the following reason: the strain of galactose fermenting yeast have been used in removing the galactose from the mixture of isomerized galactose.

Recently it was reported by Samuelson and Sjoström that the ion exchange resin 'Amberlite IRA-400' in HSO_3 form is used for the isolation of ketose from aldose in their mixture. (5) The principle of this method is based on the observation that the ketose passed unchanged through the exchanger but the aldose absorbed on the resin. This method has been applied to the isolation work of lactulose from the highly heated milk by the author (6). Therefore, interest in these works has led to the suggestion that the chromatographic method may be adopted to the purification of tagatose for the removing galactose. The present investigation was undertaken to obtain simply the tagatose by the essentially same manner of Samuelson and Sjoström.

As the result, it was found that the time consumed for the synthesis of tagatose may be reduced and its yield increased by the use of ion exchange of 'Amberlite IRA-410' in HSO_3 form. The melting point of tagatose prepared by this method corresponded well to those reported for the substance prepared by an entirely different method. It gave a spot on the paper chromatograms by using the several developing solvents, and showed the specific reaction for the ketose.

Experimental

Materials: The anion exchange resin 'Amberlite IRA-410' was allowed to stand overnight in water and, after several washes by decantation using pure water, the column was packed by sedimentation. The packed column was treated once with 10 per cent sodium hydroxide followed by water and then with *N* sodium sulfite followed by water until the effluent was free from HSO_3 ion.

Paper chromatography: Paper chromatography was carried out in the usual way with Toyo No. 50 filter paper. The chromatograms were developed by the ascending technique with the mixture of isopropanol: pyridine: acetic acid: water (8:8:1:4) (7), ethylacetate: pyridine: water (2:1:2) (8), and water saturated phenol in 1 per cent w/v ammonia (9), ketose was located with a solution consisting of 10 ml of 1 per cent (w/v) resorcin in ethanol and 90 ml of 2 *N* hydrochloric acid solution.

Synthesis: Twenty-five grams of dry D-galactose was refluxed for five hours in 250 ml of dry pyridine, protecting from moisture. After removal of most of the pyridine by a reduced pressure distillation, the residual traces of it were removed by two times evaporation with 100 ml of water under a reduced pressure. The solution was concentrated to the syrup. To the resultant syrup was added 50 ml of heated absolute ethanol, and allowed to stand in an ice box for a day. The galactose crystallized was filtered and washed with 50 ml of methanol. The filtrate and washings were combined and then evaporated to remove the methanol under a reduced pressure to syrup. The residual portion dissolved in 50 ml of water was washed into the column (5.0 × 40 cm) of resin 'Amberlite IRA-410' (HSO_3 form) and 500 ml of water were passed through at a rate of 150 ml per hour. The effluent was decolorized, filtered and concentrated to syrup by the flash evaporator modified from the apparatus of Aso (10), Beeby and Mantle (11). The hot absolute ethanol was added to the syrup until the solution became turbid and allowed to remain in an ice box for a day. The precipitate was collected on a filter and subjected to recrystallization from hot ethanolic solution. A small portion of the products was submitted to paper chromatography. In each paper chromatograms there

were obtained no spots reacting with the resorcin spray reagent as shown in Table 1. 3.6 Grams, M. P. 183~184, $[\alpha]_D^{20} - 2.8$ (c 2.5 in water) of white crystalline product was obtained and the product was Seliwanoff reaction positive, and cysteine-carbazol-sulfuric acid reaction positive. The phenyl osazone prepared according to the direction of Miyake and Hayashi (12) was melted at 186~187°. These properties correspond well with those reported for the D-tagatose by some workers (2).

Table 1. *R_f* values of D-tagatose and related ketoses

ketoses	Solvents	<i>R_f</i>				
		<i>iso</i> Propanol Pyridine Acetic acid Water	8 8 1 4	Ethylacetate Pyridine Water	2 1 2	Phenol saturated with water
Tagatose		0.58		0.67		0.45
Fructose		0.54		0.62		0.52
Sorbose		0.54		0.64		0.41
Lactulose		0.44		0.55		0.53

Summary

The preparation method of D-tagatose from galactose according to the Lobry de Bruyn and van Ekenstein transformation in pyridine solution has been modified by the use of ion exchange resin 'Amberlite IRA-410' in HSO₃ form to remove directly the remaining galactose.

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