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[1] Preparation of D-Arabinose-5-C^{14} From D-Glucose-6-C^{14}

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D-Arabinose-5-C^{14} has been prepared from D-glucose-6-C^{14} by bromine oxidation to D-gluconic-6-C^{14} acid, followed by a Ruff degradation of the calcium salt. The over-all yield, 58 percent, was obtained without the separation of any intermediate products.

1. Introduction

Improved methods for the synthesis of D-glucose-6-C^{14} [1, 2, 3] [2] have now made this radioactive sugar available as a starting material for conversion to other sugars and related products. A previous report from the Bureau [4] described the preparation of D-arabinose-5-C^{14} from D-fructose-1,6-C^{14}. The method involved oxidation of D-mannitol-1-C^{14} by *Acetobacter suboxydans* to D-fructose-1,6-C^{14}, alkaline oxidation of the fructose to D-arabonic-5-C^{14} acid, and sodium amalgam reduction of the corresponding lactone to D-arabinose-5-C^{14}. Because the alkaline oxidation removed 50 percent of the activity, the over-all radiochemical yield from the D-mannitol-1-C^{14} was low (about 30 percent).

2. Discussion

D-Arabinose-5-C^{14} has now been prepared from D-glucose-6-C^{14} by bromine oxidation to D-gluconic-6-C^{14} acid [5], followed by degradation of the corresponding calcium salt to the lower sugar, D-arabinose-5-C^{14} by the method of Ruff [6, 7]. The method involves the separation of no crystalline intermediates, is less complicated than that previously reported, and gives a higher radiochemical yield (58 percent of the D-glucose-6-C^{14}).

3. Experimental Details

One millimole (180 mg) of D-glucose-6-C^{14}, having an activity of 230 μc, and 600 mg of barium benzoate were added to 7.5 ml of water contained in a test tube equipped with a glass-covered magnetic stirrer. In order to obtain a saturated solution with respect to barium benzoate, the mixture was warmed slightly, and then cooled in ice water. By means of a micropipet, 0.1 ml of bromine was added; the tube was stoppered, and the mixture, protected from light, was stirred for 1 hr and stored at room temperature for 24 hr. Water and excess bromine were then evaporated in the dark under a gentle stream of dry air. The residue was dissolved in 10 ml of water, and the solution was treated with approximately 2 millimoles of freshly prepared silver carbonate.[3] The mixture was stirred vigorously for 15 min, the silver bromide and excess silver carbonate were removed by filtration, and the combined filtrate and washings were passed through a column containing 15 ml of cation exchange resin.[4] The acid effluent and an excess of calcium carbonate were heated in a boiling water bath for 30 min. After removal of excess carbonate by filtration, the solution of the calcium salts was concentrated under an air stream, and finally adjusted to a volume of 5 ml.[5] Two-tenths milliliter each of barium acetate (9 g/100 ml) and ferrous sulfate (9.2 g/100 ml) were added, and finally 0.1 ml of 30-percent hydrogen peroxide. The mixture was kept at 45° C for 1½ hr, treated again with 0.1 ml of hydrogen peroxide, and allowed to stand at room temperature over night. The dark brown solution was filtered with a small amount of decolorizing carbon, and the filtrate was passed through 50 ml of mixed cation and anion [6] exchange resins. The effluent contained chromatographically pure D-arabinose having an activity of 135 μc. This is a yield of 58 percent of the parent sugar, D-glucose-6-C^{14}. After lyophilization, D-arabinose-5-C^{14} crystallized readily on addition of a few drops of 1:1 methanol-ethanol.

4. References

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[7] R. C. Hockett and C. S. Hudson, J. Am. Chem. Soc. **56,** 1632 (1934).

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[2] Figures in brackets indicate the literature references at the end of the paper.

[3] A solution of 680 mg of silver nitrate in 20 ml of water was added, with stirring, to 20 ml of water containing 360 mg of sodium bicarbonate. After effervescence had ceased, the precipitate was collected on a filter, thoroughly washed with hot water, and transferred, while moist, to the sugar preparation.
[4] Amberlite IR-120, Rohm & Haas Co., Philadelphia, Pa.
[5] In a separate preparation, benzoic acid was removed at this point by extraction with chloroform, and the subsequent oxidation was carried out in a volume of 2 ml. However, the radiochemical yield was not improved, and hence the removal of benzoic acid is unnecessary.
[6] Duolite A-4, Chemical Process Co., Redwood City, Calif.

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