

# Reactions of saccharides catalyzed by molybdate ions. XXVIII.\*

## Preparation of D-[U-<sup>14</sup>C]arabinose from D-[U-<sup>14</sup>C]glucose

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D-Glucose 4-nitrophenylhydrazone is degraded to D-arabinose in a reaction affected by hydrogen peroxide. By this simple procedure D-[U-<sup>14</sup>C]arabinose can be obtained from D-[U-<sup>14</sup>C]glucose in 53% yield.

Отщеплением с перекисью водорода из 4-нитрофенилгидразона D-глюкозы получается D-арабиноза. Метод является простым и из D-[U-<sup>14</sup>C] глюкозы образуется D-[U-<sup>14</sup>C]арабиноза с выходом 53%.

Treatment of per-*O*-acetyl-D-galactose phenylhydrazone with oxygen affords the corresponding 1-hydroperoxy compound, 60% of which is decomposed in alkaline medium to D-lyxose [1]. Analogously, L-rhamnose phenylhydrazone is converted to 5-deoxy-L-arabinose [1]. In alkaline solution of hydrogen peroxide molybdate ions catalyze conversion of D-galactose phenylhydrazone to D-lyxose and D-galactose in the ratio 1:1. The ratio of aldoses formed during oxidative decomposition of phenylhydrazone derivatives of D-galactose (2-nitrophenyl-, 4-nitrophenyl-, 2,4-dinitrophenyl-, 2,5-dichlorophenylhydrazone) is influenced by the substituent [2].

The present work is concerned with the preparation of <sup>14</sup>C-labelled D-arabinose from easily available D-[U-<sup>14</sup>C]glucose [3] employing the oxidative degradation of D-[U-<sup>14</sup>C]glucose 4-nitrophenylhydrazone.

Reaction of D-glucose with 4-nitrophenylhydrazine in methanolic solution (3 h, 60°C) gives D-glucose 4-nitrophenylhydrazone in 86.5% yield. Without isolation from the reaction mixture D-glucose 4-nitrophenylhydrazone is further degraded to D-arabinose in ammoniacal solution of hydrogen peroxide under catalytic action of molybdate ions. Saccharides are isolated from the reaction mixture by paper chromatography. In experiments with D-[U-<sup>14</sup>C]glucose, distribution of radioactivity on chromatograms was determined to obtain the ratio

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of components in the reaction mixtures. It was found that of the original radioactivity of starting D-[U-<sup>14</sup>C]glucose, 10% correspond to D-glucose, 27% to aldonic acids, and 44% to D-arabinose, *i. e.* 53% conversion of starting D-[U-<sup>14</sup>C]glucose to D-[U-<sup>14</sup>C]arabinose was achieved.

Under the same conditions as those of oxidative degradation of D-glucose 4-nitrophenylhydrazone to D-arabinose, D-glucose, D-gluconic acid, and *N'*-(4-nitrophenyl)-D-gluconohydrazide are degraded to D-arabinose in trace amounts only. According to these findings, the above-tested compounds which can be formed in the reaction medium parallelly with D-glucose 4-nitrophenylhydrazone, do not serve as precursors of D-arabinose. Under conditions of oxidative degradation, D-gluconic acid is considerably resistant, D-arabinose and D-glucose are partially oxidized to the corresponding aldonic acids and *N'*-(4-nitrophenyl)-D-gluconohydrazide is quantitatively decomposed to D-gluconic acid. Oxidative degradation of D-glucose 4-nitrophenylhydrazone does not proceed significantly to D-arabinose in the absence of molybdate ions (in the course of 4–6 h).

The described method is very simple and suitable for preparation of D-[U-<sup>14</sup>C]arabinose from milligram and even less quantities of starting D-[U-<sup>14</sup>C]glucose. In the previous work [4] we have reported that epimerization of arbitrary D-[U-<sup>14</sup>C]aldopentose under increased concentration of molybdic acid leads to an equilibrium mixture of all four D-[U-<sup>14</sup>C]aldopentoses (34% of xylose, 29% of arabinose, 24% of lyxose, 13% of ribose). This epimerization reaction offers a possibility to prepare from D-[U-<sup>14</sup>C]arabinose all three complementary D-[U-<sup>14</sup>C]aldopentoses.

## Experimental

D-[U-<sup>14</sup>C]Glucose (specific radioactivity 180 Ci mol<sup>-1</sup>) was obtained from Institute for Development, Production and Use of Radioisotopes (ÚVVR), Prague.

Composition of reaction mixtures was followed by chromatography on Whatman No. 1 paper eluted with 1-butanol—ethanol—water (5:1:4) for 20 or 120 h at 20–23°C. The same technique was used for isolation of individual saccharides. The mobilities of compounds related to that of D-arabinose (1.00) were for D-glucose 0.83, D-glucose 4-nitrophenylhydrazone 2.85, and 4-nitrophenylhydrazine 4.62. Ammonium salts of aldonic acids moved only slightly beyond the origin.

Relative proportions of saccharides in reaction mixtures were determined on the basis of radioactivity distribution on chromatograms. Radioactivity of 1 cm strips of cut paper was measured on a Tri-Carb Scintillation Spectrometer, Packard, model 3330, using a toluene scintillation liquid (5 g of 2-phenyl-5-biphenyl-1,3,4-oxadiazole and 0.3 g of 1,4-bis[2-(4-methyl-5-phenyloxazolyl)]benzene in 1 l of toluene).

### Preparation of D-[U-<sup>14</sup>C]arabinose

A solution of D-glucose (10 mg) and D-[U-<sup>14</sup>C]glucose (10  $\mu$ Ci) in water (1 ml) was mixed with 2% solution of 4-nitrophenylhydrazine in methanol (2 ml) and heated at 60°C for 3 h. After cooling, 2.8% aqueous solution of ammonia (2 ml), 0.5% solution of sodium molybdate (1 ml), and 15% hydrogen peroxide (2 ml) were added. The resulting mixture was left to stand at room temperature for 20 h, then concentrated *in vacuo* (at 30°C) to above one third of the original volume and chromatographed on Whatman No. 1 paper.

After reaction of D-glucose with 4-nitrophenylhydrazine 86.4% of the original radioactivity of starting D-[U-<sup>14</sup>C]glucose was found in the zone of 4-nitrophenylhydrazone and 4.3% in the zone of D-glucose. After oxidative decomposition 27.2% of the original radioactivity was found in the zone of ammonium aldonates (the slowest radioactive zone), 10% in the zone of D-glucose, and 44.2% in the zone of D-arabinose.

The same reaction carried out on a larger scale gave from D-glucose D-arabinose which after crystallization from methanol showed m. p. 154—158°C and  $[\alpha]_D^{23} = -103 \pm 1^\circ$  (equil., c 1.5, water). Ref. [5] gives for  $\beta$ -D-arabinose m. p. 159—160°C and  $[\alpha]_D = -105^\circ$  (water).

### References

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