

# Isolation of arabinose from a mixture of arabinose and xylose via their *N-p*-nitrophenylglycosylamines

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Reaction of *p*-nitroaniline with a mixture of arabinose and xylose leads to isolation of crystalline *N-p*-nitrophenylarabinosylamine which on hydrolysis gives arabinose of high purity. This simple procedure was applied for a large-scale isolation of L-arabinose from a mixture with D-xylose obtained by hydrolysis of beech bark.

После воздействия *p*-нитроанилина на смесь арабинозы и ксилозы выделен в кристаллическом виде *N-p*-нитрофениларабинозиламин, из которого гидролизом получается высоко чистая арабиноза. Метод очень простой и был применен для изолирования L-арабинозы из смеси L-арабинозы и D-ксилозы в гидролизате буковой коры в препаративном масштабе.

*N*-Arylglycosylamines of aldoses are generally known as well crystallizing compounds [1]. The differences in their ability to crystallize were in several instances employed for separation of aldoses or aldoses from ketoses. Of all aldopentoses, aldohexoses, and aldoheptoses an exceptional ability to crystallize exhibit *N*-phenylglycosylamines of ribose, lyxose, mannose, and mannoheptose. These four aldoses when present in mixtures with other aldoses or ketoses at sufficiently high concentration, can be isolated in the form of crystalline *N*-phenylglycosylamines (ribose [2, 3], lyxose [3], mannose [4, 5], mannoheptose [6]). Separation of aldoses via their *N*-nitrophenylglycosylamines is considerably limited since these derivatives crystallize much easier than *N*-phenylglycosylamines. Glucose present in the hydrolysate of saccharose and mannose in mannan hydrolysate were separated in the form of their *N-p*-nitrophenylglycosylamines [7]. From *N*-phenylglycosylamines aldoses can be liberated by hydrolysis with formic, sulfuric [8] or acetic acid [7], and occasionally, by steam distillation [3, 5, 6]. Liberation of aldoses from *N*-phenylglycosylamines can be achieved also by formaldehyde [4] and, more commonly, by benzaldehyde treatment [2].

The reaction of aldoses with aniline is used for separation of ribose from arabinose or xylose from xylose [3]. *N*-Phenylglycosylamines of ribose and xylose are isolated as crystalline products while *N*-phenylglycosylamines of arabinose and xylose remain quantitatively in the mother liquors. *N*-*p*-Nitrophenylarabinosylamine crystallizes much easier than the corresponding derivative of xylose known to crystallize only from very pure and concentrated solutions. Reaction of *p*-nitroaniline with *D*-xylose gave two different *N*-*p*-nitrophenylglycosylamines (m.p. 109°C,  $[\alpha]_D = -96.5^\circ$  (pyridine) and m.p. 192°C,  $[\alpha]_D = +292.5^\circ$ ) which are supposed to possess pyranoid and furanoid structure [7]. The presence of two components in alcohol solutions of *N*-*p*-nitrophenylxylosylamine was also shown by paper chromatography (solvent system 1-butanol—ethanol—water). Reaction of *p*-nitroaniline with a mixture arabinose—xylose leads to isolation of crystalline *N*-*p*-nitrophenylarabinosylamine, the yield of which is dependent on the relative proportion of the aldoses in the mixture

Table 1

Isolation of *D*-arabinose via *N*-*p*-nitrophenyl-*D*-arabinosylamine from a mixture of *D*-arabinose and *D*-xylose

<i>D</i> -Arabinose g	<i>D</i> -Xylose g	Crystalline <i>N</i> - <i>p</i> -nitrophenyl- - <i>D</i> -arabinosylamine g	Conversion of <i>D</i> -arabinose to <i>N</i> -glycoside %
4.5	—	6.9	85.2
3.0	1.5	4.35	80.4
2.25	2.25	3.0	74.7
1.5	3.0	1.65	61.1

(Table 1). Hydrolysis of *N*-*p*-nitrophenylarabinosylamine in aqueous solution of acetic acid results in liberation of arabinose and almost quantitative recovery of crystalline *p*-nitroaniline ready for further use without special purification. This simple procedure for separation of arabinose from xylose affords arabinose of high purity.

Barks of deciduous trees contain about 17% of hemicelluloses [9] from which aldopentoses are released under mild conditions of acid hydrolysis. Hydrolysis of beech bark, depending on the concentration of sulfuric acid (1—2%), temperature (100—120°C), and duration (2—6 h) liberates a mixture of *L*-arabinose and *D*-xylose in weight ratios ranging from 2.6 : 0.2 to 3.0 : 13.1 in overall yield 2.8—16% referred to dry beech bark [10]. From such a hydrolysate, separation of *L*-arabinose or *D*-xylose by direct crystallization is not possible since only a small part of these aldoses can be obtained in crystalline form, and always as their

mixture. After hydrolysis of a beech bark (2% H<sub>2</sub>SO<sub>4</sub>, 100°C, 4 h) and further processing of the hydrolysate we have obtained a mixture of L-arabinose and D-xylose in the ratio 1 : 1, from which L-arabinose was isolated via *N-p*-nitrophenylglycosylamine. The elaborated procedure enables to obtain L-arabinose from dry beech bark in 1.9% yield.

### Experimental

Composition of reaction mixtures and purity of aldopentoses was examined by chromatography on Whatman No. 1 paper in 1-butanol—ethanol—water (5 : 1 : 4). Mobility of compounds in relation to that of D-arabinose (1.00) was for xylose 1.14, *N-p*-nitrophenylarabinosylamine 2.97, *N-p*-nitrophenylxylosylamine 3.22 and 3.59, *p*-nitroaniline 4.23.

#### *Isolation of D-arabinose from a mixture of D-arabinose and D-xylose*

A mixture of aldopentoses (4.5 g), *p*-nitroaniline (4.2 g), methanol (20 ml), and acetic acid (1 ml) was heated at 65°C for 3 h. After standing at room temperature for 20 h crystalline *N-p*-nitrophenyl-D-arabinosylamine was filtered off and washed with methanol (Table 1).

Isolated *N-p*-nitrophenyl-D-arabinosylamine (15.9 g) was suspended in water (80 ml) and, after addition of acetic acid (8 ml), the mixture was heated at 90°C for 4 h. The separated *p*-nitroaniline was removed by filtration and the filtrate was evaporated to dryness. The distillation residue was dissolved in water (50 ml), purified with activated charcoal and evaporated again to give chromatographically homogeneous D-arabinose (in 100% yield referred to *N-p*-nitrophenyl-D-arabinosylamine).

#### *Isolation of L-arabinose from beech bark hydrolysates*

A beech bark (1 kg, milled to 1.5 mm particles of 93% dry weight) was suspended in 2% sulfuric acid (8 l) and kept at 100°C for 4 h. After filtration, the solution was neutralized with saturated aqueous solution of calcium hydroxide, purified with charcoal and deionized on ion exchangers (Wofatit KPS in H<sup>+</sup> form, Wofatit SBW in acetate form). The deionized solution was evaporated to sirup containing neutral saccharides (59 g; arabinose, xylose, and small amounts of galactose, mannose, glucose, and rhamnose) which were dissolved in tap water (1 l) and treated with baker's yeast (10 g) until complete removal of D-galactose. After filtration, the solution was evaporated and the distillation residue was dissolved in methanol, filtered and evaporated to dryness to give a mixture of L-arabinose and D-xylose (52 g) in the ratio ca. 1 : 1. This residue (52 g) was dissolved in methanol (250 ml) and, after addition of *p*-nitroaniline (40 g) and acetic acid (10 ml), heated at 65°C for 3 h and then left to stand at room temperature for 20 h. Crystalline portion of *N-p*-nitrophenyl-L-arabinosylamine (35 g) was filtered off, washed with methanol and suspended in water

(175 ml). The suspension was mixed with acetic acid (17 ml) and heated at 90°C for 4 h. Insoluble *p*-nitroaniline (18 g) was removed by filtration and the filtrate evaporated to dryness. The residue was dissolved in water (100 ml), treated with activated charcoal and evaporated again to give L-arabinose (18 g) free of D-xylose.

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