SHORT COMMUNICATIONS

Studies on Amino-hexoses. V. An Improved Preparation of D-Arabinose via Oxidation of D-Glucosamine

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The Ruff degradation of calcium D-gluconate, a practicable method of preparing D-arabinose, was much improved and 41 to 46 % theoretical yield was secured in obtaining a practically pure specimen[1]. One of the present authors reported previously that the hypochlorite oxidation of D-glucosamine resulted in the formation of D-arabinose, ammonia and formic acid and the conditions suitable for preparing crystalline specimen were recorded[2]. The main cause of the difficulty was contamination of a large amount of inorganic salts in the reaction mixture. The introduction of ion-exchangers now available has enabled the authors to overcome the difficulty and a good yield of practically pure D-arabinose has been obtained. The ion-exchangers remove inorganic salts, residual glucosamine and colored impurities, and the concentration of the aqueous solution affords immediately raw crystals. Paper chromatography reveals no formation of sugars other than D-arabinose.

Experimental

A mixture of 21.6 g. of D-glucosamine hydrochloride, 100 ml. of water and some 200 g. of cracked ice is placed in a beaker surrounded by ice and salt. Under mechanical stirring a solution of 4 g. of sodium hydroxide in 20 ml. of water is added and sodium hypochlorite solution equivalent to 7.1 g. of chlorine is dropped in. After consumption of the oxidant the reaction mixture is neutralized to pH 3 with 6 N hydrochloric acid and is concentrated in vacuo as far as possible. The resulting mixture of salts and colored syrup is mixed with 50 ml. of ethanol, filtered and washed thoroughly with 70 % ethanol. The ethanolic solution is diluted with water to about 300 ml. and passed alternately through the columns of Amberlite IR-120 and Dowex-2. The combined solution and washings give, after concentration in vacuo, crystals melting at 153° (uncorr.) when once recrystallized from aqueous methanol. $[\alpha]_D$ (final) $-104.6°$ (c, 3.26; water). The yield reaches 45 to 48 % of theory.

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1) H. G. Fletcher, Jr., H. W. Diehl and C. S. Hudson, *J. Am. Chem. Soc.*, **72**, 4546 (1950).
2) Y. Matsushima, This Bulletin, **24**, 17 (1951).