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Improvements in the Preparation of D-Arabinose from Calcium D-Gluconate and of D-Lyxose from Calcium D-Galactonate

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The technique of degrading salts of aldonic acids to lower-carbon sugars by oxidation with hydrogen peroxide in the presence of a ferric acetate catalyst was originally introduced by Ruff[1] and has more recently received much study, particularly in connection with the preparation of D-arabinose from calcium D-gluconate[2] and of D-lyxose from calcium D-galactonate.[2,3] However, although this reaction at present constitutes the only source of consequence for these two important sugars, the yields of them obtainable by the recorded procedures leave something to be desired. Thus Hockett and Hudson[2] reported the preparation of D-arabinose in 34 to 40% yield and of D-lyxose in 17% yield while a yield of 14% of the latter sugar has been attained by Bates and his co-workers.[3]

One of the chief sources of difficulty in the Ruff degradation lies in the separation of the sugar from the gross quantities of organic and inorganic materials which are found dissolved in the final reaction mixture. Since these contaminating materials are predominantly if not exclusively ionic, it appeared obvious that ion-exchange resins (which had not, of course, been available at the time of the earlier work) offered a simple method of improving the preparation. Such indeed, proved to be the case: deionization of the filtered reaction mixture, prepared as described by Hockett and Hudson[2] followed by simple concentration *in vacuo* and crystallization from methanol or ethanol was found to yield directly D-arabinose of $[\alpha]^{20}\text{D}$ $-102.9°$ to $-104.5°$ (equil. in water) in 41 to 46% yield. Using calcium D-galactonate in the same procedure, D-lyxose of $[\alpha]^{20}\text{D}$ -13.4 to $-14.1°$ (equil. in water) was obtained in 41 to 42% yield. The accepted specific rotation of D-arabinose at equilibrium in water is $-104.5°$ while that of D-lyxose is $-13.8°$. The use of ion-exchange resins thus results in higher yields and a simplified and less time-consuming procedure for the preparation of these sugars.

Attention is drawn to the fact that, contrary to the indications in the earlier literature, the yields of D-arabinose from calcium D-gluconate and D-lyxose from calcium D-galactonate are substantially identical. It is considered probable that the improvements here described may equally well be applied to the preparation of sugars other than D-arabinose and D-lyxose.

Experimental

D-Arabinose from Calcium D-Gluconate.—The procedure employed was, except for the use of ion-exchange resins, practically identical with that reported previously.[2,3] A mixture of 192.3 g. of calcium D-gluconate monohydrate, 20.86 g. of barium acetate monohydrate, 10.2 g. of ferric sulfate and 2 liters of water was boiled with stirring. The mixture was then filtered through a layer of Filter-Cel (500 ml. washings added), cooled to 40° and treated with 120 ml. of 30% hydrogen peroxide. When the temperature again fell to 40°, another 120-ml. portion of hydrogen peroxide was added. After reaction was complete, as shown by the appearance of a dark purple color, the mixture was filtered through decolorizing carbon and then passed successively through a 5.5 × 103 cm.-column of Amberlite IR-120[4] and a 5.5 × 97 cm.-column of Duolite A-4.[5,6] The columns of resin were washed with distilled water until the effluent gave a negative test with Fehling solution; the combined solution and washings (approximately 8 liters) possessed a conductance equivalent to less than 7 p.p.m. (expressed as sodium chloride) as determined by a Barnstead Purity Meter.[7] After concentration *in vacuo* to a stiff sirup (60° bath) and solution in 100 ml. of methanol, the product was left for five days at +5°. In a typical preparation there was thus obtained 57.5 g. (44.4%) of D-arabinose showing an equilibrium rotation in water $[\alpha]^{20}\text{D}$ of $-103.3°$ (c, 0.92). One recrystallization from 0.7 parts of water or from aqueous methanol brought this latter constant to a value of $-104.5°$.

D-Lyxose from Calcium D-Galactonate.—Calcium D-galactonate pentahydrate was degraded exactly as described above. The stiff sirup obtained after concentration of the deionized solution was dissolved in 100 ml. of absolute alcohol and the solution reconcentrated *in vacuo*. After one repetition of this process the clear and practically colorless sirup was dissolved in 100 ml. of hot absolute alcohol and the solution, after seeding, left at room temperature for twelve hours and then at +5° for twenty-four hours. There resulted, in a typical run, 53.6 g. (41.3%) of pure α-D-lyxose showing an equilibrium rotation in water of $-14.0°$ (c, 0.82).

Summary

An improved method for preparing D-arabinose from calcium D-gluconate and D-lyxose from calcium D-galactonate has been described.

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[1] O. Ruff, *Ber.*, **31**, 1573 (1898); **34**, 1362 (1901); O. Ruff and G. Ollendorff, *Ber.*, **33**, 1798 (1900).

[2] R. C. Hockett and C. S. Hudson, THIS JOURNAL, **56**, 1632 (1934).

[3] F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," U. S. Govt. Printing Office, Washington, D. C., 1942, p. 469.

[4] A product of the Resinous Products and Chemical Co., Washington Square, Philadelphia 5, Pa.

[5] A product of Chemical Process Co., 901 Spring St., Redwood City, California.

[6] Yields appear to be adversely affected if the procedure is interrupted at any point prior to deionization; it is therefore advisable to carry the preparation through this process in one day.

[7] Barnstead Still and Sterilizer Co., Inc., Boston, Mass.