

Preparation of 2-deoxy-D- and L-erythro-pentoses by electrooxidative reduction of the respective glucometasaccharinic acids in the presence of cerium(IV) ions

Š. KUČÁR, J. KOZÁK, and J. KUBALA

*Institute of Chemistry, Slovak Academy of Sciences,
CS-842 38 Bratislava*

Received 21 December 1989

By electrooxidation of 3-deoxy-D-ribo-hexonic and 3-deoxy-D-arabino-hexonic acids as well as of their mixture in diluted sulfuric acid under catalytic action of cerium(IV) ions 2-deoxy-D-erythro-pentose has been prepared in about 60 % yield. From the mixture of 3-deoxy-L-ribo-hexonic and 3-deoxy-L-arabino-hexonic acids 2-deoxy-L-erythro-pentose has been obtained in a similar way.

2-Deoxy-D-erythro-pentose as a component of deoxyribonucleic acids plays an important role in biochemistry of saccharides. It is evident also from the great number of methods described in the literature for its preparation. From the point of view of large-scale preparation the methods based on oxidative reduction of glucometasaccharinic acids (mixture of 3-deoxy-D-ribonic and 3-deoxy-D-arabinonic acids) in the presence of iron(III) ions [1—3] are the most significant ones. Though the use of cerium(IV) ions [4] simplifies the reaction, twofold mole excess of cerium(IV) ions with respect to the substrate makes this method disadvantageous from the economic point of view. In electrooxidative reduction of aldonic acids and their lactones, respectively, the consumption of cerium(IV) ions is substantially lower on account of their regeneration during the reaction. By this method D-arabinose was prepared in 60—70 % yield from calcium gluconate using graphite [5] or platinum electrodes [6].

The aim of the present work was to find out optimal conditions for electrooxidative reduction of glucometasaccharinic acids in the presence of cerium(IV) ions and examine the influence of steric arrangement of the used substrates (3-deoxy-D-ribo- and 3-deoxy-D-arabino-hexonic acids and their lactones, respectively) in the preparation of 2-deoxy-D-erythro-pentose.

For electrooxidation of the mixture of glucometasaccharinic acids using graphite electrodes the following conditions were found to be optimal: current density 2.4 A dm^{-2} , temperature 35°C , and time 10 h. At higher current density the rate of electrooxidation was higher however, the formed 2-deoxy-D-erythro-pentose was degraded. Similar phenomenon was observed at elevated reaction temperature and prolonged reaction time. For example, it was advantageous to stop electrooxidation of the mixture of 3-deoxy-D-ribo- and 3-deoxy-D-arabino-

-hexonolactones after 10 h in spite of the fact that about 25 % of 3-deoxy-D-*arabino*-hexonolactone and 10 % of 3-deoxy-D-*ribo*-hexonolactone were still present in the reaction mixture. After isolation of 2-deoxy-D-ribose in the form of anilide, the mother liquor is subjected to further electrooxidation. The total yield of 2-deoxy-N-phenyl-D-ribosylamine is then about 59 %. The yield at longer reaction time or higher current density is by about 10 % lower.

From the aforementioned case it is evident that the rate of electrooxidative reduction of the 3-deoxy-D-*ribo* derivative is higher than that of the 3-deoxy-D-*arabino* derivative. This was confirmed by separate electrooxidative reductions carried out with the derivatives mentioned above at the same reaction conditions. While the yield of 2-deoxy-N-phenyl-D-ribosylamine obtained from the starting 3-deoxy-D-*ribo*-hexonolactone was 63.5 %, that obtained from 3-deoxy-D-*arabino*-hexonolactone was 52.2 %. Electrooxidation of both isomers was followed also in time dependence. By preparative paper chromatography 2-deoxy-D-*erythro*-pentose and the starting lactone were isolated. As seen from Table 1, the conversion of the 3-deoxy-D-*ribo* isomer was higher already after 3 h.

Table 1

Electrooxidation yields (in %) of 3-deoxy-D-*ribo*- and 3-deoxy-D-*arabino*-hexonolactones

<i>t</i> /h	Lactone I	Product	Lactone II	Product
3	48	34	66	25
5	32	46	44	34
10	12	66	25	53
15	6	58	18	43

Lactone I = 3-deoxy-D-*ribo*-hexonolactone

Lactone II = 3-deoxy-D-*arabino*-hexonolactone

Product = 2-deoxy-D-*erythro*-pentose

The experience gained in electrooxidative reduction of glucometasaccharinic acids of the D-series was utilized also in preparation of 2-deoxy-L-ribose. The mixture of 3-deoxy-L-*ribo*- and 3-deoxy-L-*arabino*-hexonolactones was electrooxidized analogously, while 2-deoxy-N-phenyl-L-ribosylamine was obtained in 54.9 % yield.

Experimental

γ -Lactone of 3-deoxy-D-*ribo*-hexonic acid, m.p. = 108–109 °C, $[\alpha](D, 24\text{ }^{\circ}\text{C}, \rho = 10\text{ g dm}^{-3}, \text{H}_2\text{O}) = +26.2^{\circ}$, γ -lactone of 3-deoxy-D-*arabino*-hexonic acid, m.p. = 90–92 °C, $[\alpha](D, 24\text{ }^{\circ}\text{C}, \rho = 10\text{ g dm}^{-3}, \text{H}_2\text{O}) = +5.8^{\circ}$, and their mixture were

prepared according to [7]. Melting points were determined on a Kofler block and optical rotations on a Perkin—Elmer, model 141, polarimeter. For electrooxidation a ZSE 24 V/10 A source of direct current and graphite electrodes were used. The course of electrooxidation was monitored by paper chromatography on a Whatman No. 1 paper, preparative separation of the electrooxidized mixture was carried out on a Whatman No. 3 paper in 2-butanone saturated with water.

Electrooxidation of the mixture of γ -lactones of 3-deoxy-D-ribo- and 3-deoxy-D-arabino-hexonic acids

The mixture of lactones (10 g) dissolved in 0.1 M- H_2SO_4 (520 cm³) and containing $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (2.5 g) was electrooxidized using graphite electrodes and direct current with current density 2.4 A dm⁻² at 35°C for 10 h when the composition of the reaction mixture was optimal. The solution was made neutral with BaCO_3 , filtered, and concentrated to about 80 cm³. By addition of CH_3OH (150 cm³) the residual salts were precipitated, filtered off and the supernatant was evaporated to a sirup. The mixture (7 g) contained 2-deoxy-D-ribose and the unreacted lactones in the ratio of 7 : 3. The sirup was dissolved in water (21 cm³) and ethanol (4 cm³) and aniline (3.5 cm³) were added. 2-Deoxy-N-phenyl-D-ribosylamine (6 g) crystallized after 24 h. M.p. = 170—171°C and $[\alpha]_D^{24}$ (D, 24°C, $\rho = 10 \text{ g dm}^{-3}$, $\text{C}_2\text{H}_5\text{OH}$) = + 21° were in accordance with the literature data [8]. The mother liquor was purified by distillation with water vapours and subjected to further electrooxidative reduction, which provided additional 1.6 g of 2-deoxy-N-phenyl-D-ribosylamine. Total yield was 7.6 g (68.9 %).

When pure γ -lactones were used as starting compounds, the total yield of 2-deoxy-N-phenyl-D-ribosylamine obtained from the 3-deoxy-D-ribo derivative was 8.2 g (63.5 %), while that obtained from the 3-deoxy-D-arabino derivative was 6.7 g (52.2 %).

Similar electrooxidative reduction of the mixture of γ -lactones of 3-deoxy-L-ribo- and 3-deoxy-L-arabino-hexonic acids resulted in 2-deoxy-N-phenyl-L-ribosylamine (7.0 g; 54.9 %).

Time dependence of electrooxidation

The respective 3-deoxy-D-hexonolactone isomer (5 g) was dissolved in 0.1 M- H_2SO_4 (260 cm³) and $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (1.25 g) was added. Electrooxidation was performed at 2.4 A dm⁻² current density and 35°C. At time intervals aliquots (52 cm³) were withdrawn from the reaction mixture, made neutral with BaCO_3 , filtered, and evaporated. The residue was separated quantitatively on a Whatman No. 3 paper. The bands belonging to the starting lactone and to 2-deoxy-D-*erythro*-pentose were eluted with water. The eluates were concentrated to afford the pure products in yields presented in Table 1.

References

1. Richards, G. N., *J. Chem. Soc.* 1954, 3638.
2. Sowden, J. C., *J. Am. Chem. Soc.* 76, 3541 (1954).
3. Diehl, H. W. and Fletcher, H. G., *Chem. Ind.* (London) 1958, 1087.
4. De Lederkremer, R. M. and Sala, L. F., *Carbohydr. Res.* 50, 385 (1975).
5. Kubala, J., Kučár, Š., and Linek, K., *Czechoslov.* 225576 (1983).
6. Nakamura, Y. *Nippon Kagaku Kaishi* 10, 1727 (1982); *Chem. Abstr.* 98, 34860 (1983).
7. Kučár, Š., Zámocký, J., and Bauer, Š., *Collect. Czechoslov. Chem. Commun.* 40, 457 (1975).
8. Deriaz, R. E., Overend, G. W., Stacey, M., Teece, F. G., and Wiggins, L. F., *J. Chem. Soc.* 1949, 1879.

Translated by A. Kardošová