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Studies on Nitro Sugars. IV.[1] The Synthesis of Benzyl 2-Deoxy-3,4-*O*-isopropylidene-2-nitro-β-D-arabino- and ribo-pyranoside

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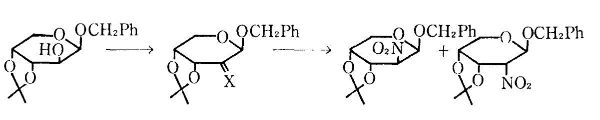
Recently, we reported the syntheses of 3- and 2-nitro furanoses[1-3] through the oxidation of sugar oximes with trifluoroperacetic acid. As an extension of our studies to the pyranose series, we have now examined the oxidation of the 2-oximino-pentopyranoside derivative to the corresponding 2-nitro compound by this method.



1 2: X=O 3: X=NOH 4 5

The dimethyl sulfoxide oxidation[4] of benzyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside (**1**),[5] followed by distillation at 155—157°C/3 mmHg, afforded sirupy 2-ulose (**2**), showing 1756 cm^{-1} (neat); this was immediately converted to benzyl 3,4-*O*-isopropylidene-2-oximino-β-D-*erythro*-pentopyranoside (**3**) in the usual manner in a 27% overall yield from **1**. When **3** was treated with trifluoroperacetic acid in the presence of excess dibasic sodium phosphate as a buffer in acetonitrile, the corresponding 2-nito-pentoses, which consisted of benzyl 2-deoxy-3,4-*O*-isopropylidene-2-nitro-β-D-arabinopyranoside (**4**) and its 2-epimer (**5**) in the ratio of *ca.* 1 : 1, were obtained in a 75% yield. The separation of both the products, according to the small difference in chromatographical mobility, could

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[1] Part III; T. Takamoto, Y. Yokota, R. Sudoh, and T. Nakagawa, This Bulletin, in press.

[2] T. Takamoto, R. Sudoh, and T. Nakagawa, *Tetrahedron Lett.*, **1971**, 2053.

[3] T. Takamoto, R. Sudoh, and T. Nakagawa, *Carbohyd. Res.*, in press.

[4] J. S. Brimacombe, *Angew. Chem.*, **81**, 415 (1969).

[5] H. G. Fletcher Jr., "Methods in Carbohydrate Chemistry," Vol. II, ed. by R. L. Whistler and M. L. Wolfrom, Academic Press, New York (1963), p. 386.

be achieved by using a long silica-gel column.

As is shown in Fig. 1, what was eluted later was identified as the *arabino*-isomer (**4**) on the basis of the coupling constant values, $J_{1,2}=3.7$, $J_{2,3}=8$, and $J_{3,4}=6$ Hz, which would mean a slightly twisted 1C conformation. On the other hand, the first-eluted component, *i.e.*, the *ribo*-isomer (**5**), showed $J_{1,2}=7$, $J_{2,3}=3$, and $J_{3,4}=7$ Hz, which would mean a twisted boat form, as is shown in Fig. 2.

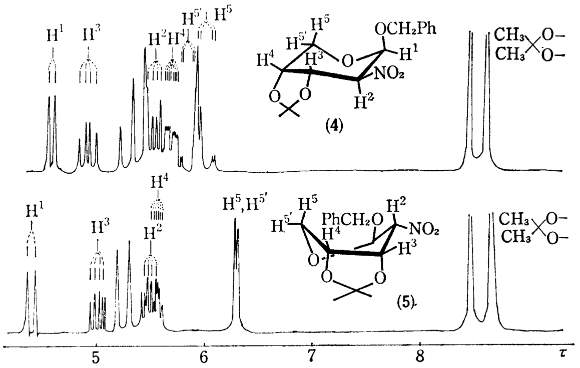

Fig. 1. 100 MHz NMR spectra (in $CDCl_3$).

As an explanation of the stereochemically-interesting results, it appears that an equatorially-oriented nitro group might be effective, but any detailed discussion must await further investigations concerning nitro sugars.

Experimental

The specific rotations were measured with a Carl Zeiss photoelectric polarimeter. The NMR spectra were recorded at 100 MHz with a spectrometer JNM-4H-100 (JEOL), using tetramethylsilane as the internal standard. Column chromatography was carried out on silica gel (100 Mesh, Mallinckrodt, St. Louis). All the evaporations were performed *in vacuo*.

*Benzyl 3,4-*O*-Isopropylidene-2-oximino-β-*D-erythro-*pentopyranoside (3).* To a solution of benzyl 3,4-*O*-isopropylidene β-D-arabinopyranoside (**1**) (58.6 g) in dimethyl sulfoxide (680 ml), acetic anhydride (452 ml) was added with manual stirring. After standing for 48 hr at room temperature, the mixture was evaporated below 60°C. A solution of the residue in chloroform (1 l) was washed with water four times, dried over calcium chloride, and evaporated. The sirup was distilled at 155—157°C/3 mmHg to give 2-ulose (**2**) contaminated with the starting material (**1**). The distilled sirup (43.8 g), showing an absorption band at 1756 cm^{-1} (C=O), was heated under reflux with hydroxylamine hydrochloride (21.9 g) in a mixture of pyridine (438 ml) and ethanol (438 ml) for 2 hr. The solution was evaporated to give a sirupy residue containing pyridine hydrochloride, which was then washed out with water several times. The sirup was crystallized and recrystallized from ethanol–petroleum ether to give crystalline **3** (16.7 g, 27%); mp 161.5—163.5°C (uncorrected); $[\alpha]_D^{20}$ −232° (*c* 1.02, $CHCl_3$); IR (KBr): 3320 cm^{-1} (OH). Found: C, 61.22; H, 6.27; N, 4.87%. Calcd for $C_{15}H_{19}NO_5$: C, 61.42; H, 6.53; N, 4.78%.

*Benzyl 2-Deoxy-3,4-*O*-isopropylidene-2-nitro-β-*D-*arabino-(4) and ribopyranoside (5).* Oxime **3** (100 mg) was stirred into an oxidizing agent, prepared by mixing successively 90% hydrogen peroxide (0.05 ml), trifluoroacetic anhydride (0.3 ml), acetonitrile (5 ml), dibasic sodium phosphate (1.15 g), and urea (5 mg), at room temperature. After 2 hr, the mixture was evaporated, then, the residue was dissolved in methylene chloride (100 ml). After it had been filtered, the solution was evaporated and chromatographed on silica gel with benzene to give a sirupy product (79 mg, 75%), which was subsequently rechromatographed on a silica-gel column (14×2.5 cm) developed slowly with benzene. The eluate was collected in 20 ml portions. Fractions No. 9—12 were combined and evaporated to give **5**, which was too hydroscopic and low-melting to be recrystallized; $[\alpha]_D^{20}$ −121° (*c* 1, $CHCl_3$); IR (neat): 1560 cm^{-1} (NO_2); NMR ($CDCl_3$): τ 4.39 (1H-*d*, $J_{1,2}=7$ Hz, H^1), 5.50 (1H-*q*, $J_{2,3}=3.5$ Hz, H^2), 5.01 (1H-*q*, $J_{3,4}=6.5$ Hz, H^3), 5.56 (1H-*sex*, $J_{4,5}=3.5$ Hz, H^4), 6.32 (2H-*d*, H^5, $H^{5'}$). Found: C, 58.21; H, 6.26; N, 4.45%. Calcd for $C_{15}H_{19}NO_6$: C, 58.24; H, 6.19; N, 4.53%.

The evaporation of Fractions No. 20—25 afforded sirupy **4**; $[\alpha]_D^{20}$ −200° (*c* 1, $CHCl_3$); IR (neat): 1560 cm^{-1} (NO_2); NMR ($CDCl_3$): τ 4.61 (1H-*d*, $J_{1,2}=3.7$ Hz, H^1), 5.55 (1H-*q*, $J_{2,3}=8$ Hz, H^2), 4.95 (1H-*q*, $J_{3,4}=6$ Hz, H^3), 5.71 (1H-*oct*, $J_{4,5}=2.5$ Hz, $J_{4,5'}=1.2$ Hz, H^4), 6.04 (1H-*q*, $J_{5,5'}=13.8$ Hz, H^5), 5.87 (1H-*q*, $H^{5'}$). Found: C, 58.20; H, 6.21; N, 4.40%