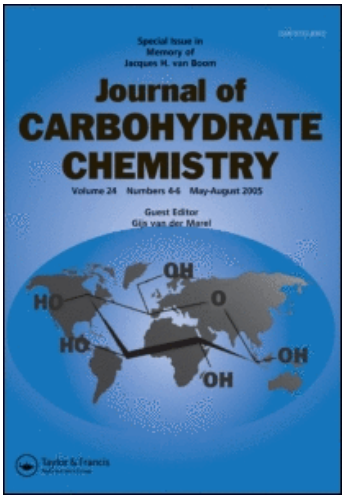

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Shigemasa, Yoshihiro , Tanioka, Shin-ichiro , Furukawa, Hiroyuki , Sashiwa, Hitoshi and Saimoto, Hiroyuki(1991) 'The Favored Formation of Threo-3-Pentulose in the Formose Reaction', Journal of Carbohydrate Chemistry, 10: 1, 97 — 100

To link to this Article: DOI: 10.1080/07328309108543894

URL: http://dx.doi.org/10.1080/07328309108543894

J. CARBOHYDRATE CHEMISTRY, 10(1), 97-100 (1991)

COMMUNICATION

THE FAVORED FORMATION OF threo-3-PENTULOSE IN THE FORMOSE REACTION*

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Received July 13, 1990 - Final form October 9, 1990

The "formose reaction" is the generic name for the base-catalyzed condensation of formaldehyde to give "formose" which is a complex mixture of sugars, alditols, organic acids, etc.[2] Increasing attention has been recently given to this reaction because of its possible importance in the manufacture of edible carbohydrates from a simple material and its possible role in the prebiotic synthesis of carbohydrates.[3] In our recent study[4] on the reaction catalyzed by triethylamine (TEA) and thiamine·HCl in N,N-dimethylformamide (DMF)-water mixed solvent, the formation of 3-pentulose (GP-11-1 corresponding to GLC peak number 11-1) was suggested. P. Decker et al.[5] also reported that at the end of formaldehyde consumption the concentration of 3-pentuloses became smaller because of their higher reactivity (these carbohydrates cannot form stable furanoses or pyranoses) compared to tetroses, pentoses, and hexoses. Although the isolation of 3-pentuloses was not described in that report,[5] erythro-3-pentulose and threo-3-pentulose in a formose were identified by comparison of GLC retention times and mass spectra with those of authentic samples.

*Formose reactions. Part 30. For Part 29, see ref. 1.

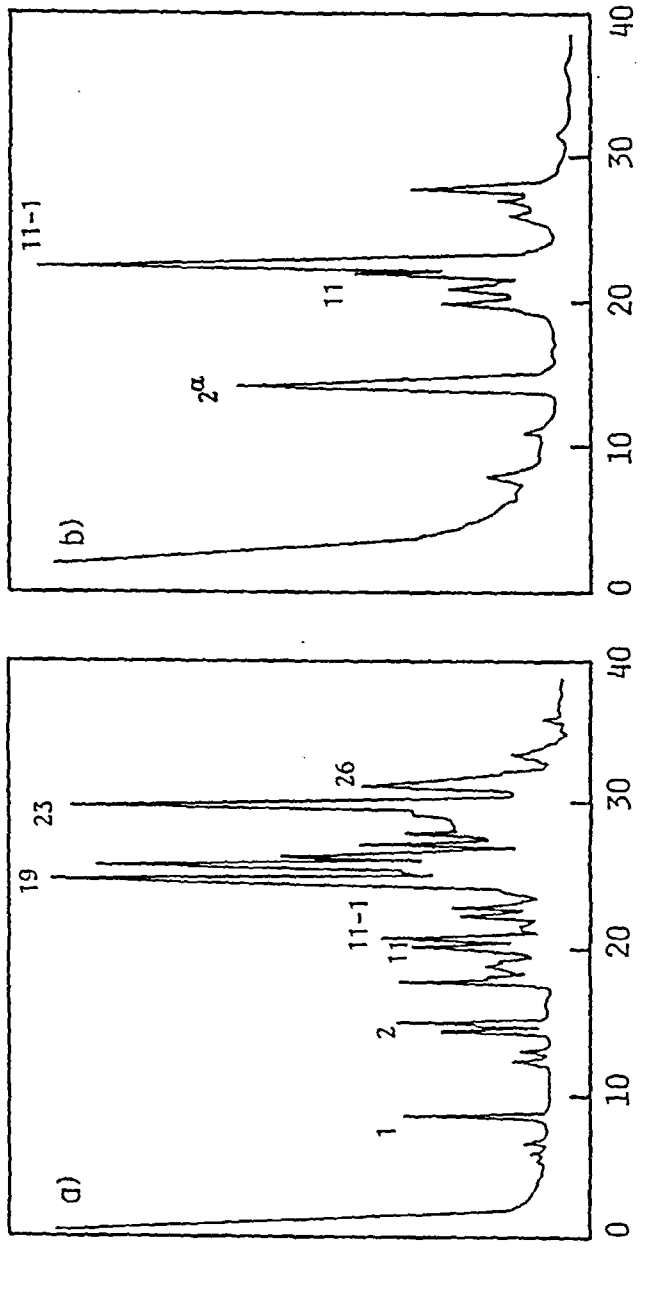

Fig. 1. The GLC patterns of pertrimethylsilylated products obtained from (a) a conventional formose reaction in water starting from [HCHO]=2.0 M and $[Ca(OH)_2]$=0.22 M at 60 °C for 30 min, and (b) the selective formose reaction in DMSO starting from [HCHO]=1.0 M, $[Pb_2O(OH)_2]$=0.08 M, and [Thiamine·HCl]=0.06 M at 50 °C for 150 min.

In the present paper we describe conditions that favor the formation of threo-3-pentulose (GP-11-1) in the formose reaction (see Fig. 1b). The reaction was catalyzed by lead oxyhydroxide ($Pb_2O(OH)_2$) and thiamine·HCl in dimethyl sulfoxide (DMSO) and the improved yield enabled the isolation and structure elucidation of the product.

In a typical experiment, the reaction was performed with a M solution of formaldehyde (4.7 g) in DMSO (150 mL) in the presence of 80 mM lead oxyhydroxide and 60 mM thiamine·HCl at 50 °C for 150 min under nitrogen. At various time intervals, aliquots (5 mL) were transferred into 10-mL flasks and the reaction was quenched immediately by acidification with formic acid (98-100%). These aliquots were analyzed for formaldehyde by the method of Bricker and Johnson,[6] except that the absorbance was measured at 579 nm. The product distribution as pertrimethylsilylated products was determined by GLC, the pattern of which (Fig. 1b) clearly indicated that these conditions favored the formation of a product (GP-11-1) corresponding to peak number 11-1 (19% by GLC).

The reaction mixture (2x150 mL) was concentrated to a syrup under reduced pressure (65-70 °C /4-5 mm Hg), then the concentrated mixture was added to ca. 300 mL of methanol to remove salts, and the methanol solution was passed through an active carbon column.

Concentration of the solution gave a brown syrup (7.6 g, GP-11-1=17% by GLC). GP-11-1 was obtained as a colorless syrup of purity above 85% (by GLC) by repeated chromatography on cellulose powder with wet n-butanol as eluent: ^1H NMR(D_2O; int. standard, DSS) δ 3.90(d, 4H, J=4.3 Hz, $-CH_2OH$), 4.67(t, 2H, J=4.3 Hz, -CHOH-); ^{13}C NMR(D_2O; int. standard, DSS) δ 71.0(t), 83.9(d), and 219.8(s), corresponding to 2 CH_2 and 2 CH groups, and a carbonyl C atom; MS of pertrimethylsilylated derivative (70 eV) m/z 438(96, M^+), 423(5, M^+-CH_3), 335(88, $M^+-CH_2OSiMe_3$), 293(99), 191(97), 149(97), 133(92), 103(79), 89(89); IR (KBr) 3400 (O-H) and 1720 (C=O) cm^{-1}.

Reduction of GP-11-1 with $NaBH_4$ gave the corresponding sugar alcohol whose peracetylated derivative showed the same GLC retention time as the peracetylated derivative of DL-arabinitol but the retention time was different from those of peracetylated ribitol and xylitol. Furthermore, the ^1H NMR spectrum of the acetate of the reduced GP-11-1 was in fair agreement with that of the acetate of DL-arabinitol:

^{1}H NMR($CDCl_3$; int. standard, Me_4Si) δ 2.02, 2.04, 2.05, 2.06, and 2.11(5s, 3H, $-COCH_3$), 3.95(dd, 1H, J=7.3 and 11.7 Hz, -HCHO-), 4.14(dd, 1H, J=7.1 and 12.1 Hz, -HCHO-), 4.24(dd, 1H, J=2.9 and 12.1 Hz, -HCHO-), 4.28(dd, 1H, J=4.9 and 11.7 Hz, -HCHO-), 5.13-5.20(m, 1H, -CHO-), 5.36-5.47(m, 2H, -CHO-).

These results indicate that the product corresponding to peak number 11-1 (GP-11-1) is threo-3-pentulose.

DL-threo-3-Pentulose might be successively formed by the condensation of formaldehyde and DL-tetrulose[4] (the product corresponding to peak number $2^{\alpha i}$ shown in Fig. 1b) formed from dihydroxyacetone. Steric hindrance of the transition state might contribute to suppressing the formation of erythro-3-pentulose. We are now undertaking studies on the mechanistic elucidation for the favored formation of DL-threo-3-pentulose.

REFERENCES

1. Y. Shigemasa, M. Yamamoto, K. Hayashi, H. Sashiwa, and H. Saimoto, Chem. Express, 5, 289 (1990).
2. A. Butlerow, Justus Liebigs Ann. Chem., 120, 295 (1861); O. Loew, J. Prakt. Chem., 34, 51 (1886).
3. N. W. Gabel and C.Ponnamperuma, Nature (London), 216, 453 (1967); R. F. Socha, A. H. Weiss, and M. M. Sakharov, J. Catal., 67, 207 (1981).
4. Y. Shigemasa, T. Ueda, and H. Saimoto, Bull. Chem. Soc. Jpn., 63, 389 (1990).
5. P. Decker and H. Schweer, Origins of Life, 14, 335 (1984).
6. C. E. Bricker and H. R. Johnson, Ind. Eng. Chem., 17, 400 (1945); M. Lambert and A. C. Neish, Can. J. Res., Sect. B, 28, 83 (1950).