Differentiation Effect of Pentacoordinate Phosphorus on Carbohydrate Reaction

Yong JU, Yi CHEN, Yu Fen ZHAO*

Bioorganic Phosphorus Chemistry Laboratory, Department of Chemistry,
Tsinghua University, Beijing 100084

Abstract: The reaction between D-glucose, D-ribose and 2, 2, 2-trimethoxy-4, 5-diphenyl-2, 2-dihydro-1, 3, 2-dioxaphospholene were investigated by ^{31}P NMR and FAB-MS. The results showed that there were a lot of differences in the reactions *via* pentacoordinate phosphorus compound, and it should give significant clue to the metabolism of carbohydrate phosphate in nature.

Keywords: Carbohydrate, pentacoordinate oxyphosphorane, biomimic mechanism.

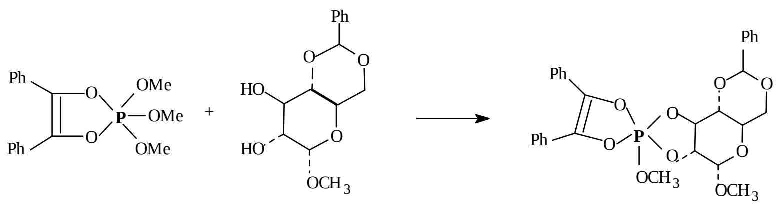
Glycosyl phosphates are of considerable interest as intermediates for the synthesis of nucleotide and oligosaccharides in glycoproteins and glycolipids[1-3]. However, there is no such report to give why only pentose D-ribose is used as the central block in nucleotide and in ATP, but not the hexose D-glucose, despite of D-glucose possessing very rich source. Therefore, it is necessary to investigate the possible reaction mechanism of carbohydrate phosphorylation. The pentacoordinate phosphorus intermediate was proposed to participate in biological process[4-6]. In order to obtain confirmative information about the metabolism of carbohydrate under the phosphorus participation, the reaction of carbohydrates and pentacoordinate oxyphosphorane were investigated and the preliminary result was reported in this paper.

The reactions of different monosaccharides with 2, 2, 2-trimethoxy-4, 5-diphenyl-2, 2-dihydro-1, 3, 2-dioxaphospholene [named P (5)] were studied by using ^{31}P NMR technique. D-Glucose and D-ribose, as models for hexose and pentose respectively, reacted with P (5). The progress of reaction was monitored by the integral area of signal of P (5) in the ^{31}PNMR spectra. The result showed that D-glucose and D-ribose exhibited a different reaction rate with P (5). The reaction of D-ribose was about six times faster than that of D-glucose, D-mannose, and the reaction rate constants were $k_{Glu} = 1.3 \times 10^{-4}$ / mol.sec and $k_{Rib} = 6.2 \times 10^{-4}$ / mol.sec, respectively.

Generally, the reaction of carbohydrate with P (5) might first go through a pentacoordinate phosphorus compound to give a spiro-oxyphosphorane (multipeak signals appeared at δ: ~ 29.0 - 31.5 ppm in the ^{31}PNMR, and the FAB-MS gave molecular ion at m/z= 450 [M^+] for the glucose)[7-8]. The ^{31}PNMR and FAB-MS techniques were used to determine the reaction products of D-ribose and P (5).

The ^{31}PNMR of P-5 showed the signal at δ = -31.5 ppm which belonged to the pentacoordinate spiro-oxyphosphorane, and the EI mass spectrum (M+ m/z: 552 and the other characteristic fragment ions) are confirmed the above results.

Scheme 1.



P-5

However, when the reactions were kept for over two hours, the D-glucose and D-ribose showed that there were very different intermediates by trapping with ^{31}PNMR. In the reaction of D-ribose, except pentacoordinate phosphorus intermediate (δ about -24 .0 ppm in the ^{31}PNMR) like in the reaction of D-glucose, the hexacoordinate spiro-oxaphosphorane intermediate (The signal at δ - 91.0 ppm in the ^{31}PNMR[9]) also appeared and after four hours the signal disappeared.

Finally, the D-glucose usually gave only monophosphate of glucose (in the ^{31}PNMR and M^+ m/z 468 in FAB-MS. The quasi-molecular weight was given at m/z 467.1107 ($C_{21}H_{24}O_{10}P$, calculated: 467.1127) in the high-resolution negative ion FAB-MS. On the contrary, the D-ribose gave pyrophosphate of ribose (δ - 9.10 ppm in the ^{31}PNMR and M^+ m/z 320 for the pyrophosphate in FAB-MS) in addition to the monophosphate (psedomolecular ion $[M+H]^+$ m/z 421 in positive ion FAB-MS). The phenomena might reflect the difference between D-glucose and D-ribose metabolism *via* phosphate in nature. Further studies are in progress.

Conclusion

The investigation results indicated that there were two different types of intermediates exhibited in the reactions of D-ribose and D-glucose with P (5) and resulted in different kinds of products. Therefore, the differentiation of D-glucose and D-ribose in nature might be due to the pentacoordinate phosphorus participation. It should give some significant clue that phosphorus plays an important role in life chemistry.

Acknowledgment

The authors thank the National Natural Science Foundation of China (No. 29672022) and Tsinghua University for financial supports.

References

1. B. Evers, P. Mischnik, J. Thiem, *Carbohydr. Res.* , **1994,** *262*, 335.
2. P. Strees, K. Pupitz, S. G. Wither, *Biochem.* , **1989,** *28*, 1581.
3. E. Tarelli, S. F. Wheeler, *Carbohydr. Res.* **,** **1994**, *261*, 25.
4. L. Lehninger, D. L. Nelson, M. M. Cox, "*Principles of Biochemistry*", 2nd ed. , Worth Publishers Inc. **1993**, p. 400, p. 598.
5. R. R. Holmes, *Main Group Chem. News,* **1994,** *1*, 18.
6. F. Ramirrez, Y. F. Chaw, J. F. Marecek, I. Ugi, *J. Am. Chem. Soc.* , **1974,** *96***,** 2429.
7. X. Chen, Y. F. Zhao, H. Fu, J. Z. Wang, *Org. Mass Spectroscopy*, **1995**, *30*, 755.
8. Q. D. Yan, Y. Ju, Y. Guo, Y. F. Zhao, Q. Z. Wang, *Chinese Chem. Lett.* , **1997,** *8*, 303.
9. J. G. Verkade, L. D. Quin, "*^{31}P NMR Spectroscopy in Stereochemical Analysis*", VCH Publisher Inc. , Florida, **1987**, p. 46.

Received 26 November 1998
Revised 5 March 1999