Evaluation of the aldononitrile acetate ester derivatization method for aldose analysis in products from chemical evolution experiments

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Introduction

Sugars and sugar derivatives play important roles in biological processes on the Earth. Sugars such as ribose, a component of RNA, are essential compounds for the origin of life. Since some sugars have been found in meteorites [1, 2], there is a possibility that some sugars made in space brought to the early Earth by meteorites. As a prebiotic sugar formation reaction, "formose reaction" have been attacked attention [3].

Since there are so many kinds of sugars and sugar derivatives, GC/MS is a promising technique to identify them, but a suitable derivatization technique is required for it. One of the derivatization methods for sugars is aldononitrile acetate ester derivatization. This method is very effective for aldoses [4]. However, previous studies have mainly focused on pentoses [2], and other sugars have not been widely discussed. In this research, we verified the usefulness of the aldononitrile acetate ester derivatization for aldoses other than pentose. In addition, verification of whether sugars were formed or not in products by "formose-like reaction" simulating the interior of meteorite parent bodies.

Experimental

Standard reagents of aldose (C3-C6: glyceraldehyde, erythrose, threose, ribose, lyxose, arabinose, xylose, allose, glucose, galactose) were derivatized by aldononitrile acetate ester derivatization. Then resulting sugar derivatives were analyzed by GC/MS. Limits of detection of all the aldoses were examined.

In order to simulate reactions in the meteorite parent bodies, a mixture of H2O, HCHO and NH3 (molar ratios were 100:5:5, 100:5:1, 100:5:0 and 100:10:0) were prepaird. 200 mL each of the mixture was heated at 150℃ for 3 days. An aliquot of each product was derivatized by the present method, and analyzed by GC/MS.

Result and Discussion

Retention time and major m/z of each aldose were obtained with authentic standards: The retention time (major m/z's) were as follows. Triose: 9.7 min (m/z 86, 103), tetroses: 17.7-18.0 min (m/z 103, 145), pentoses: 24.8-26.0 min (m/z 103, 115, 145), and hexoses : 31.0-33.0 min (m/z 103, 115, 145).There is a correlation between the carbon number and the retention time. The carbon number increases by 1, then the retention time increases by about 7 minutes.

Although varied by the number of carbon, limits of detection of the aldoses were about 2~50 mM.

By comparing the analysis results of aldose standard reagents and the products of the "formose-like reaction" simulating the interior of meteorite parent bodies, peaks similar to those of tetroses and hexoses were detected in all the products. In the 100:5:1 product, pentoses were tentatively detected in addition to tetroses and hexoses. It was suggested that, in the products of 100:5:5, 100:5:0 and 100:10:0, glyceraldehyde (C3) generated in the initial stage of formose-like reaction reacted with unreacted formaldehyde (C1) to form tetroses (C4), or reacted with other glyceraldehyde to form hexoses (C6). The other possibility is that the glycolaldehyde (C2) generated in the initial stage of formose-like reaction reacts with other glycolaldehyde to form tetroses, and this tetroses reacts with glycolaldehyde to form hexoses. In the sample of 100:5:1, slightly added ammonia might act as a catalyst, which promoted the formation of pentoses. Further experiments are required to verify such hypotheses.

References

[1] G. Cooper et al. (2001) *Nature*, 414, 879-883.
[2] Y. Furukawa et al. (2019) *PNAS*, 116, 24440-24445.
[3] H. J. Cleaves II (2008) *Precambrian Res.*, 164,111-118.
[4] K. Kobayashi et al. (1989) Bunseki Kagaku, 38, 608-612.

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