

## Non-canonical nucleoside synthesis through formose-type reaction on the early Earth

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Abiotic nucleoside formation is one of the essential steps for the origin of life. This synthesis has been conducted in previous studies using reactive molecules that were difficult to be accumulated on the early Earth by multistep reactions, including purification of intermediates. Therefore, reactions that are more compatible with the Hadean environments are needed to understand prebiotic RNA synthesis. Ribose, a component of nucleoside, forms in the formose reaction that is the polymerization of formaldehyde by simple heating in alkaline solutions. When ammonia is added to the formose reaction, various amino acids, amines, carboxylic acids, and N-heterocycles form in addition to various sugars. This reaction is simple, and the source materials were definitely available on Hadean Earth. Thus, we investigated the spontaneous synthesis of nucleoside analogs in the formose-type reaction.

Aqueous solutions containing formaldehyde, glycolaldehyde, ammonia, calcium hydroxide (a catalyst of the formose-type reaction), ribose (the sugar of nucleoside component), and borate (a sugar stabilizer) were heated at 60°C or 80°C for 20 hours. The products were diluted by an acidic solution and analyzed by ultra-performance liquid chromatography/tandem mass spectrometry.

The products contained diverse organic compounds, including diverse N-heterocycles, including imidazole and even ribosyl-imidazole, a non-canonical nucleoside. These yields were higher in experiments containing borate. Canonical nucleosides and nucleobases were not detected in the products. Formation of ribosyl-imidazole was also found even in experiments without ribose in the starting material. In this experiment, the formose-type reaction formed both ribose and imidazole and combined them to form the non-canonical nucleoside in a one-pot reaction from simple aldehyde and ammonia. This finding opens up a possibility of the spontaneous formation of diverse nucleoside analogs, potentially including canonical nucleosides in the formose-type reaction on the prebiotic Earth.

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