

Glyceraldehyde and glycolaldehyde in interstellar ice analogues and the role of aldehydes in cosmochemical evolution

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Abstract

Our understanding of the molecular origin of life is based on amino acids, ribose, and nucleobases that – after their selection by prebiotic processes – initiated the evolutionary assembly of catalytic and informational polymers, being proteins and ribonucleic acids. Following previous amino acid identifications in the room-temperature residues of simulated circumstellar/interstellar ices [1,2] we have searched for a different family of molecules of potential prebiotic interest. Using multidimensional gas chromatography coupled to time-of-flight mass spectrometry, we have detected ten aldehydes, including the sugar-related glycolaldehyde and glyceraldehyde – two species considered as key prebiotic intermediates in the first steps toward the synthesis of ribonucleotides in a planetary environment.

1. Introduction

Amino acids, sugar-like molecules, and nucleobases have been detected in exogenous samples of carbonaceous chondrite meteorites and also in interstellar ice analogues. Glycine was identified by the help of the Stardust mission in a sample of comet 81P/Wild 2. Recently, experimental evidence was given, revealing that the origin of ribonucleotides bypassed the classical chemical synthesis and proceeded from the starting materials glycolaldehyde and glyceraldehyde via pentose amino-oxazolines [3]. Analogously, meteoritic amino acids were suggested to originate from aldehyde precursors in a manner that chiral aldehydes stereo-dictated the chirality of meteoritic amino acids [4]. Despite of the importance of aldehydes in ribonucleotide evolution and amino

acid handedness, pre-biotic aldehyde intermediates escaped so far direct systematic detection due to their chemical reactivity and instability. Here we report the detection of aldehydes including glycolaldehyde and chiral glyceraldehyde (Figure 1) in the room-temperature residue of an interstellar ice analogue that was ultraviolet-irradiated in a high vacuum at cryogenic temperature.

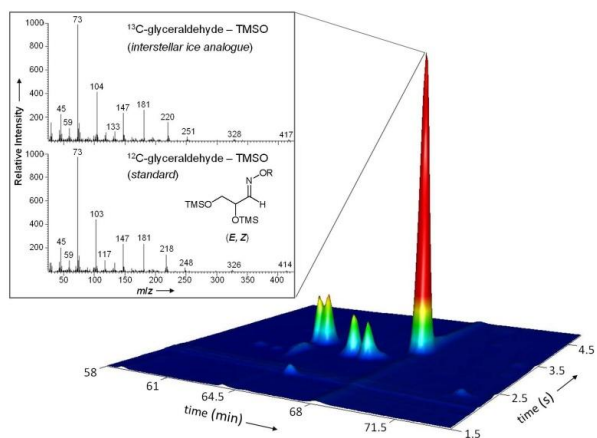


Figure 1: Glyceraldehyde detected in simulated cometary matter. Identification of glyceraldehyde as O pentafluorobenzyl oxime (R) trimethylsilyl ether (TMSO) in simulated cometary ice residues using multidimensional gas chromatography. The corresponding external glyceraldehyde standard shows identical retention times and logically ^{12}C isotopic signatures in its mass spectra. The mass fragmentation reveals that glyceraldehyde formed in the residue is entirely composed of ^{13}C -isotopes provided by the $^{13}\text{CH}_3\text{OH}$ reactant present in the original interstellar ice mixture.

2. Results

We used new multidimensional gas chromatography coupled to time-of-flight mass spectrometry for the detection of ten different aldehydes [5]. Some of the identified aldehydes are also found in cometary ices. Chiral implications in the photochemical generation of glyceraldehyde in the ice samples are of special interest since this process could proceed through a formose-type reaction process with autocatalytic feedback and possible asymmetric amplification. In this context the chiral glyceraldehyde was subjected to anisotropy spectroscopy [6] revealing high anisotropies which make this aldehyde a suitable recipient for the chirality of circularly polarized light. Our results show that the spontaneous generation of aldehydes in the interstellar medium is possible, allowing to understand intermediate steps in chemical evolution towards enantioselective amino acid and ribonucleotide formation.

3. Perspectives

The reported identification of aldehydes is of importance for two reasons: This identification allows for a better understanding of the origin of biomolecular asymmetry in the context of asymmetric ribonucleotide synthesis and in the context of asymmetric amino acid synthesis. Furthermore these results help in the ongoing data interpretation of the Rosetta mission that landed on a cometary nucleus on 12 November 2014 [7,8] to perform in-situ measurements of cometary ices, particularly with the COSAC instrumentation which contains a GC-MS device specifically designed for the characterization of organic molecules [9].

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