

Formation of complex organic molecules in astrophysical environments: Sugars and derivatives

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Abstract. Carbonaceous meteorites contain a large variety of complex organic molecules, including amino acids, nucleobases, sugar derivatives, amphiphiles, and other compounds of astrobiological interest. Photoprocessing of ices condensed on cold grains with ultraviolet (UV) photons was proposed as an efficient way to form such complex organics in astrophysical environments. This hypothesis was confirmed by laboratory experiments simulating photo-irradiation of ices containing H₂O, CH₃OH, CO, CO₂, CH₄, H₂CO, NH₃, HCN, etc., condensed on cold (~10–80 K) substrates. These experiments resulted in the formation of amino acids, nucleobases, sugar derivatives, amphiphilic compounds, and other organics comparable to those identified in carbonaceous meteorites. This work presents results for the formation of sugars, sugar alcohols, sugar acids, and their deoxy variants from the UV irradiation of ices containing H₂O and CH₃OH in relative proportions 2:1, and their comparison with meteoritic data. The formation mechanisms of these compounds and the astrobiological implications are also discussed.

Keywords. astrochemistry, astrobiology, molecular processes, methods: laboratory, ISM: molecules

1. Introduction

Laboratory experiments simulating radiation processes of ices in cold astrophysical environments have shown that the UV irradiation of ices composed of H₂O, CH₃OH, CO, CO₂, CH₄, NH₃, etc. (Allamandola *et al.* 1999; Dartois 2005; Ehrenfreund & Charnley 2000; Gibb *et al.* 2004) leads to the formation of complex organic compounds stable at room temperature, commonly called residues. These residues contain a large number of molecules (Dworkin *et al.* 2004), some of which are of astrobiological interest, e.g., amino acids (Bernstein *et al.* (2002); Muñoz Caro *et al.* 2002; Nuevo *et al.* 2008), amphiphiles (Dworkin *et al.* 2001), nucleobases (Nuevo *et al.* 2014; Materese *et al.* 2018), and other compounds such as urea and hydantoin (Nuevo *et al.* 2010; de Marcellus *et al.* 2011).

Carbonaceous meteorites such as Murchison and Murray contain similar organic compounds of astrobiological interest (Cronin & Pizzarello 1997; Deamer 1985; Martins *et al.* 2008; Callahan *et al.* 2011), including sugar derivatives (Cooper *et al.* 2001). Sugar derivatives were long searched for in laboratory residues, but because of their wide variety and structural complexity (linear, furanose, pyranose), there was no systematic search for these until our group developed a GC-MS method to identify sugars, sugar alcohols,

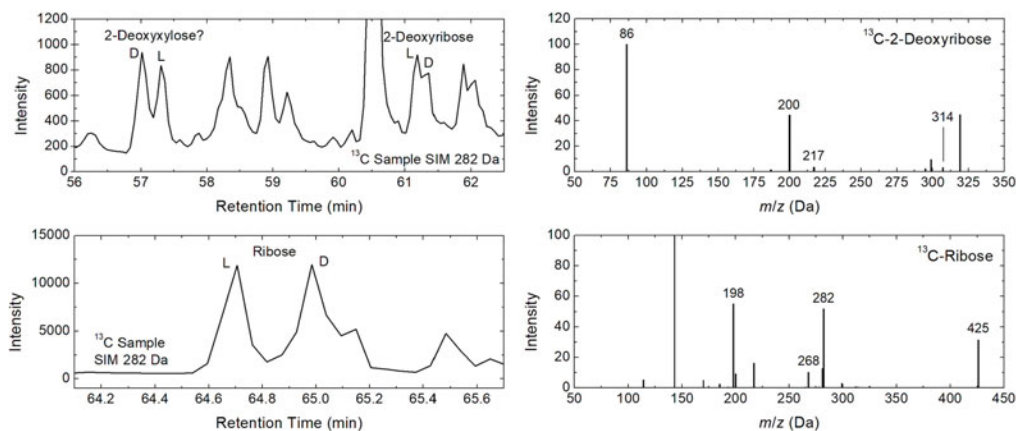


Figure 1. (Left) Single-ion chromatograms (SIM) showing the identification of 2-deoxyribose (200 Da, top) and ribose (282 Da, bottom) in ^{13}C -labeled residues. (Right) Mass spectra of the peaks identified as ^{13}C -2-deoxyribose (top) and ^{13}C -ribose (bottom).

and sugar derivatives in residues (Nuevo *et al.* 2015). This method was applied to residues produced from the UV irradiation of $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ice mixtures at 10 K and led to the identification of several sugar alcohols, sugars, and sugar acids (in decreasing abundances) with up to 5 carbon atoms (Nuevo *et al.* 2015). An independent study confirmed this result and reported the identification of more sugar derivatives including ribose, the sugar of RNA (Meinert *et al.* 2016). In addition, in that study the authors proposed that all these sugar derivatives were formed via a formose reaction mechanism (Buttlerow 1861; Breslow 1959), i.e., a polymerization of formaldehyde, although no experimental proof was provided.

In this work we present recent results regarding the identification of sugar derivatives in residues produced from the UV irradiation of $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ices. We show that in addition to sugar derivatives, residues also contain several deoxysugar derivatives (i.e., sugar derivatives that have lost one or more OH groups), including 2-deoxyribose, the sugar of DNA (Nuevo *et al.* 2018).

2. Results and Discussion

The experimental protocol of preparation of $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ (2:1) gas mixtures, deposition of these gases onto a cold substrate at 10 K, irradiation of the resulting ices with UV photons, warm-up of the ices to room temperature, and gas chromatography–mass spectrometry (GC-MS) analysis of the resulting residues is explained in detail elsewhere (Nuevo *et al.* 2018; and references therein).

All the residues analyzed were found to contain a wide variety of sugar alcohols, sugars (including ribose), and sugar acids, confirming previous studies (Nuevo *et al.* 2015; Meinert *et al.* 2016), as well as several deoxysugar alcohols and 2-deoxyribose (Nuevo *et al.* 2018; Fig. 1). The distribution of these compounds suggest a formation pathway involving H_2O -catalyzed CH_3OH polymerization into sugar alcohols of increasing carbon chain length, followed by an oxidation of sugar alcohols into sugars, themselves oxidized into sugars acids (Nuevo *et al.* 2015). Experiments in which the starting CH_3OH ice was labeled with ^{13}C confirmed that these compounds are formed via ice photoprocesses rather than resulting from any contamination (Nuevo *et al.* 2018).

However, the distribution of sugar derivatives is different in residues and meteorites, as no sugars have been found in meteorites except dihydroxyacetone (Cooper *et al.* 2001). In meteorites, sugar alcohols (most abundant) and sugar acids are present in

Table 1. Absolute and relative abundances between 2-deoxyribose and ribose in our residues.

2-Deoxyribose (L+D, μmol)	Ribose (L+D, μmol)	Ratio (L+D)	2-Deoxyribose (L, μmol)	Ribose (L, μmol)	Ratio (L)
217–3855	237–2467	0.2–3.3	170–1970	153–1461	0.2–4.4

large quantities. In contrast, residues produced from $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ices do not contain a lot of sugar acids. This discrepancy may be due to the fact that (1) astrophysical ices also contain other carbon sources (CO , CO_2 , CH_4), while only CH_3OH was used in our experiments, or (2) meteorites have experienced aqueous alteration and thermal metamorphism between the time they formed and the time they fall on Earth. These processes affect the composition of meteoritic organics (Browning *et al.* 1996; Palmer & Lauretta 2011).

The detection of 2-deoxyribose in laboratory residues is the first reported under such simulated astrophysical conditions (Nuevo *et al.* 2018). Only two other abiotic synthesis of 2-deoxyribose have been previously reported in the literature. In the first study, acetaldehyde, glyceraldehyde or formaldehyde, and calcium oxide were reacted together at 50°C in an aqueous solution, resulting in the production of 2-deoxyribose with a 3% yield (Oró & Cox 1962). In the second study, 2-deoxyribose was produced from the photo-induced deoxygenation of ribose and/or arabinose, when mixed with a solution of $\text{H}_2\text{O}/\text{D}_2\text{O}$ and catalytic salts at 37°C and pH 7, and when subjected to 254-nm UV light (Ritson & Sutherland 2014). After 6 hours of irradiation, more than half of the starting ribose/arabinose was converted into several photoproducts, including 2-deoxyribose.

The relative abundances between 2-deoxyribose and ribose vary quite significantly in the residues, as in some residues 2-deoxyribose is more abundant than ribose, while in other residues it is the opposite (Table 1). In Table 1, L and D refer to the enantiomers of 2-deoxyribose and ribose. Biological systems only use the D enantiomers in DNA and RNA, so our results show that the abundance ratios between 2-deoxyribose and ribose remain constant when we add up the abundances of both enantiomers or only consider L enantiomers. Therefore, the abundances of 2-deoxyribose and ribose in the residues do not favor any formation mechanism for sugar and deoxysugar derivatives, i.e., neither from small molecules to larger ones (e.g., Oró & Cox 1962), nor from the photo-induced degradation of larger molecules (e.g., Ritson & Sutherland 2014). Rather, the formation pathway for these compounds is likely a combination of several mechanisms, due to the stochastic nature of the processes taking place during the irradiation of ices at low temperature, as it was demonstrated for the formation of amino acids (Elsila *et al.* 2007). We are currently working on a paper in which we demonstrate that sugar derivatives are probably formed from via combination of different mechanisms rather than a pure formose reaction pathway as suggested previously (Meinert *et al.* 2016).

In addition to 2-deoxyribose, another pair of peaks eluting at ~ 57 min in the GC-MS chromatograms of the residues were tentatively assigned to 2-deoxyxylose, the only possible 2-deoxy isomer of 2-deoxyribose (Nuevo *et al.* 2018; Fig. 1). This tentative identification is based on the retention time of these peaks (close to 2-deoxyribose) and on the mass spectra of both peaks which are very similar to those for 2-deoxyribose. However, the identification of 2-deoxyxylose could not be confirmed because there is no commercial standard for this compound.

Finally, several deoxysugar alcohols were identified in these residues: 1,2-propanediol, 1,3-propanediol, 2-methyl-1,3-propanediol, 1,2,3-butanetriol, and 1,2,4-butanetriol (Nuevo *et al.* 2018). Of these deoxysugar alcohols, 1,2-propanediol and 1,2,4-butanetriol were also identified in the Murchison meteorite, but not the others (Nuevo *et al.* 2018). Besides these two compounds, another deoxysugar alcohol, namely, 2-(hydroxymethyl)-1,3-propanediol was identified in Murchison but not in the residues (Nuevo *et al.* 2018).

3. Conclusion

The UV irradiation of H₂O:CH₃OH ice mixtures under simulated astrophysical conditions leads to the formation of several sugar and deoxysugar derivatives, including ribose and 2-deoxyribose. The distribution of these compounds suggests that they form via several mechanistic pathways. Their distribution in residues is also different from that in meteorites, which could be due to differences in the starting ice mixture composition and/or the fact that meteorites experience chemical and thermal processing affecting the organics. Understanding the link between ice photochemistry and meteoritic organics may shed light on the inventory of compounds that seeded the primitive Earth and their role in the origin of life.

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