Sugars and Sugar Derivatives in Residues Produced from the UV Irradiation of Astrophysical Ice Analogs

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Outline

• Brief introduction to (Experimental) Astrochemistry
• Formation of complex organics in the laboratory
• Formation of sugars and sugar derivatives
• Summary
• Work in Progress
• Future Work
IR Observations of Molecular Clouds

Protostar
IR continuum source
- dust heated by star
  (500-1000 K)

Clouds of cold ice and dust

Infrared light (IR)

IR absorption spectrum
IR "Black Body" continuum

Infrared observatories

ABE

SOFIA

IRTF
IR Observations of Molecular Clouds

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Infrared observatories

ABE
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## Astrophysical Ices

### Observation of ices in the ISM & comets

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<td>CO(_2)</td>
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<td>CH(_3)OH</td>
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Photoprocesses on Grains (Greenberg Model)
Delivery of Organics to the Earth

Exogenous Delivery
- Diffuse Medium
- Dense Cloud
- Stellar Death and Mass Ejection
- Star and Planet Formation
- Comets
- Asteroids
- Interplanetary Dust Particles
- Meteorites

Endogenous Synthesis
- Volcanic Outgassing
- Hydrothermal Vents
- Miller Urey Syntheses
Asteroids

Seen by ROSETTA (ESA)
Asteroids

Itokawa, seen and visited by Hayabusa (JAXA)
Interplanetary Dust Particles (IDPs)
Ingredients to Make Life

Primordial

Cambells

Condensed

Quick & Easy Directions
WARM WATER UNDER REDUCING (HYDROGEN-RICH) ATMOSPHERE ON THE SURFACE OF A TERRESTRIAL PLANET. SPARK WITH LIGHTNING. COLLECT ORGANIC MOLECULES OVER MANY YEARS, SERVE WHEN ORGANISMS ARISE.

Professor Stanley's 2-Step Earthy Planet Sandwich
Cook Time: 15 Million Years
1. Spark wet, warm reducing atmosphere.
2. Flavor with exogenous organics, to taste.

Ingredients:
TOMATO PUREE (WATER, TOMATO PASTE), HIGH FRUCTOSE CORN SYRUP, WHEAT FLOUR, SALT, SPICE EXTRACT, VITAMIN C (ASCORBIC ACID), CITRIC ACID, CAMBELL SOUP COMPANY, CAMDEN, NM U.S.A. 78103-1701

Nutritional Facts
Amount/serving %DV
Total Amino acids 20g 7%
Nucleobases 2g 1%
Ribose and other sugars

Vitamin A 10% • Vitamin C 10% • Calcium 6% • Iron 4%

Inhabitable planet guaranteed on your hydrogen fuel. Please have your solar system and planet numbers available. Call (800) 234-3263.

0011-005-10

For information & more, visit: http://www.cambellssoup.com
Ingredients to Make Life

Primordial
Experimental Set-up & Protocol

- Vacuum chamber
- H₂ UV lamp
- Cryocooler
- Bulb containing the gas mixtures
- Pressure in the chamber (torr)
Experimental Set-up & Protocol

UV photon energy: Lyman α (121.6 nm) + H₂ transitions (~150–170 nm)
Experimental Set-up & Protocol

Horse Head Nebula (Orion)
Experimental Set-up & Protocol
UV Irradiation of Ices – IR Spectroscopy

CH$_3$OH:NH$_3$ = 1:1 mixture, 46-hr UV irradiation @ 80 K

$\sim$10$^7$ years of irradiation in dense astrophysical environments
<table>
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<th>Position (cm(^{-1}))</th>
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<tr>
<td>3600–3000</td>
<td>3.33–3.78</td>
<td>Alcohols, amines, carboxylic acids (OH, NH)</td>
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<td>Carbon chains (alkanes) (CH(_3), CH(_2))</td>
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<tr>
<td>~2880</td>
<td>~3.47</td>
<td>H(_2)CO (CH(_2) str.)</td>
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<tr>
<td>2342</td>
<td>4.27</td>
<td>CO(_2) (C=O str.)</td>
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<tr>
<td>~2260</td>
<td>~4.42</td>
<td>HNCO*</td>
</tr>
<tr>
<td>~2165</td>
<td>~4.62</td>
<td>OCN(^-) (C≡N str.)</td>
</tr>
<tr>
<td>2135</td>
<td>4.68</td>
<td>CO (C≡O str.)</td>
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<tr>
<td>~1850</td>
<td>~5.41</td>
<td>HCO**</td>
</tr>
<tr>
<td>~1720</td>
<td>~5.81</td>
<td>H(_2)CO (C=O str.)</td>
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<td>~1695</td>
<td>~5.90</td>
<td>NH(_2)CHO (C=O str.)**</td>
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<tr>
<td>~1387</td>
<td>~7.21</td>
<td>NH(_2)CHO**</td>
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<td>~7.66</td>
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</tr>
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<td>~8.03</td>
<td>H(_2)CO (CH(_2) rock.)</td>
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*HNCO and HCO*: no detection in ISM in the solid phase

**NH\(_2\)CHO**: tentatively detected
Warm up to Room Temperature

Chen et al. (2007)
Residues – IR Microscope Images

$\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3 = 1:1:1$ mixture
Residues – IR Microscope Images

$\text{H}_2\text{O}:\text{CO}_2:\text{NH}_3 = 1:1:1$ mixture

Chen et al. (2008)
Residues – Mass Spectrometry

Organic residues produced from the UV irradiation of ice mixtures consisting of $\text{H}_2\text{O}$, $\text{CH}_3\text{OH}$, $\text{CO}$, $\text{CO}_2$, $\text{NH}_3$, etc., analyzed with laser-desorption mass spectrometry.

Every peak in this mass spectrum is potentially one new molecule!
Residues – IR Spectroscopy

\( (a) \ \text{CH}_3\text{OH}:\text{NH}_3 = 1:1 \ (46\text{-hr UV irradiation}) \\
(b) \ \text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{NH}_3 = 1:1:1 \ (47\text{-hr UV irradiation}) \)
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Residues – XANES Spectroscopy

X-ray Absorption Near-Edge Structure (XANES) 390-eV images of 4 residues produced from the UV irradiation of 4 different starting ice mixtures.

M1 \( \text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3 = 100:50:1:1 \)
M2 \( \text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO} = 100:50:1 \)
M3 \( \text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3:\text{C}_3\text{H}_8 = 100:50:1:1:10 \)
M4 \( \text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3:\text{C}_{10}\text{H}_8 = 100:50:1:1:1 \)

Nuevo et al. (2011)
Residues – XANES Spectroscopy

Full-range C-, N-, and O-XANES 1s spectra of the M1, M2, M3, and M4 residues

- All residues show significant contributions from C, N, and O organics
- N from NH$_3$ is very efficiently incorporated into organic molecules
Residues – XANES Spectroscopy

M1 $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3 = 100:50:1:1$

M2 $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO} = 100:50:1$

M3 $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3$:C$_2$H$_8 = 100:50:1:1:10$

M4 $\text{H}_2\text{O}:\text{CH}_3\text{OH}:\text{CO}:\text{NH}_3$:C$_{10}$H$_8 = 100:50:1:1:1$

Elemental composition:

- N/C: 0.11–0.28
- O/C: 0.43–0.61

$\Rightarrow \sim$2 times larger than Stardust particles

Nuevo et al. (2011)

- 285.1 eV: CH$_x$ (aromatic)
- 285.8 eV: C=\(\equiv\)
- 286.6 eV: C\(\equiv\)N or C=\(\equiv\)C=O
- 287.4 eV: CH$_x$ (aliphatic)
- 288.7 eV: O–C=O (carboxyl)

- 399.3 eV: C\(\equiv\)N
- 398.8 eV: C\(\equiv\)N (?)
- 401.7 eV: CONH (amide)

- 531.3 eV: C=O (ketone)
- 532.2 eV: O–C=O (carboxyl)
Formation of Complex Organics

High-performance liquid chromatography (HPLC)

Gas chromatography – mass spectrometry (GC–MS)

(H₂O:CH₃OH:NH₃:HCN = 20:2:1:1)

Bernstein et al. (2002a)

(H₂O:CH₃OH:NH₃:CO₂ = 2:1:1:1:1)

Muñoz Caro et al. (2002)

Several amino acids detected in organic residues produced from the UV irradiation of different starting ice mixtures with different techniques.
Formation of Complex Organics

Starting with ice mixtures containing $\text{H}_2\text{O}$
+ carbon source(s) [$\text{CH}_3\text{OH}$, $\text{CO}$, $\text{CO}_2$, $\text{CH}_4$, and/or $\text{HCN}$]
+ nitrogen source(s) [$\text{NH}_3$, $\text{N}_2$, and/or $\text{HCN}$]
+ UV photo-irradiation at low temperature

Amino acids

Amphiphilic compounds

Bernstein et al. (2002a)
Muñoz Caro et al. (2002)
Nuevo et al. (2008)

Dworkin et al. (2001)
Formation of Complex Organics

Starting with ice mixtures containing $\text{H}_2\text{O}$
+ aromatic compounds [PAHs or $N$-heterocycles]
+ $\text{H}_2$, $\text{CH}_3\text{OH}$, $\text{CO}_2$, $\text{CH}_4$, $\text{NH}_3$, $\text{HCN}$, etc.
+ UV photo-irradiation at low temperature

**Functionalized PAHs**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAHs</td>
<td>$\text{H}_2$</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_3\text{OH}$</td>
</tr>
</tbody>
</table>

Bernstein et al. (2002b,c)

**Nucleobases**

Materese et al. (2013)
Sandford et al. (2014)
Sugars: Background & Motivation

- Laboratory experiments have shown that the photochemistry of simple ices (H$_2$O, CH$_3$OH, CO, CO$_2$, CH$_4$, NH$_3$, etc.) leads to the formation of amino acids, amphiphilic molecules, and nucleobases [e.g., Bernstein et al. 2002; Muñoz Caro et al. 2002; Dworkin et al. 2004; Nuevo et al. 2008, 2009, 2012, 2014; Materese et al. 2013].
- Carbonaceous meteorites contain a large variety of organic compounds, which include amino acids, amphiphilic molecules, nucleobases, sugars, and sugar derivatives [e.g., Cronin & Pizzarello 1997, 1999; Cooper et al. 2001; Dworkin et al. 2001; Callahan et al. 2011].
- But no systematic search for sugars and related compounds has been reported before this one. Now other people are also searching for the same compounds in residues [de Marcellus et al. 2015; Meinert et al. 2016].
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### Sugars: Background & Motivation

**Sugar-related compounds in Murchison and Murray**

<table>
<thead>
<tr>
<th>Sugars</th>
<th>Sugar Alcohols</th>
<th>Sugar Acids</th>
<th>Dicarboxylic Sugar Acids</th>
<th>Deoxy Sugar Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C</td>
<td>CH₂OH&lt;br&gt;C=O&lt;br&gt;CH₂OH</td>
<td>CH₂OH&lt;br&gt;H-C-O-H&lt;br&gt;CH₂OH</td>
<td>CO₂H&lt;br&gt;H-C-O-H&lt;br&gt;CH₂OH</td>
<td>——</td>
</tr>
<tr>
<td></td>
<td>Dihydroxyacetone</td>
<td>Glycerol 160 nmol/g (100%)</td>
<td>Glyceric acid 80 nmol/g</td>
<td>2-Methyl glyceric acid</td>
</tr>
<tr>
<td>4C</td>
<td>CH₂OH&lt;br&gt;H-C-O-H&lt;br&gt;CH₂OH</td>
<td>CH₂OH&lt;br&gt;H-C-O-H&lt;br&gt;CH₂OH</td>
<td>CO₂H&lt;br&gt;H-C-O-H&lt;br&gt;CH₂OH</td>
<td>2, 4 Dihydroxybutyric acid</td>
</tr>
<tr>
<td></td>
<td>Erythritol &amp; Threitol (1%)</td>
<td>Erythronic &amp; Threonic acid (4nmol/g)</td>
<td>Tartaric &amp; Mesotartaric acid</td>
<td>2, 3 Dihydroxybutyric acid (diastereomer)</td>
</tr>
<tr>
<td>5C</td>
<td>CH₂OH&lt;br&gt;H-C-O-H&lt;br&gt;CH₂OH</td>
<td>CH₂OH&lt;br&gt;H-C-O-H&lt;br&gt;CH₂OH</td>
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</tr>
<tr>
<td></td>
<td>Ribitol &amp; Isomers</td>
<td>Ribonic acid &amp; Isomers</td>
<td>2, 3, 4-Trihydroxy Pentaneoic acid</td>
<td>2-Deoxypentonic acids</td>
</tr>
<tr>
<td>6C</td>
<td>CH₂OH&lt;br&gt;H-O-C-H&lt;br&gt;CH₂OH</td>
<td>CH₂OH&lt;br&gt;H-O-C-H&lt;br&gt;CH₂OH</td>
<td>CO₂H&lt;br&gt;H-C-O-H&lt;br&gt;CH₂OH</td>
<td>2-Deoxyhexonic acids</td>
</tr>
<tr>
<td></td>
<td>Glucitol &amp; Isomers</td>
<td>Gluonic acid &amp; Isomers</td>
<td>Gluconic acid &amp; Isomers</td>
<td>3-Deoxyhexonic acid</td>
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Cooper et al. (2001)
Sugars: Background & Motivation

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- But no systematic search for sugars and related compounds has been reported before this one. Now other people are also searching for the same compounds in residues [de Marcellus et al. 2015; Meinert et al. 2016].
Why is it complicated to search for sugar derivatives?

- There are a LOT of possible compounds among all sugars, sugar acids, and sugar alcohols, not to mention dicarboxylic sugar acids, deoxy sugar derivatives, etc.
- Sugars and (most of) sugar derivatives are chiral molecules, so each of them exists in two enantiomeric forms (D and L).
- Each $>\text{C}_4$ sugar (and some sugar acids) can either be in a linear or a cyclic configuration.
- For $\text{C}_5$ and $\text{C}_6$ sugars (aldoses), cyclic forms include furanose and pyranose forms, and each of these forms has two anomeric conformations (α and β).
Sugars (Aldoses)

3 C atoms

4 C atoms

5 C atoms

6 C atoms
Sugars (Aldoses)

3 C atoms
- D-Glyceraldehyde
- Dihydroxyacetone

4 C atoms
- D-Threose
- D-Erythrose

5 C atoms
- D-Lyxose
- D-Xylose
- D-Arabinose
- D-Ribose

6 C atoms
- D-Talose
- D-Galactose
- D-Idose
- D-Gulose
- D-Mannose
- D-Glucose
- D-Altrose
- D-Allose
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- D-Gulose
- D-Mannose
- D-Glucose
- D-Altrose
- D-Alloze
Sugars Acids & Sugar Alcohols

Sugar acids

Sugar alcohols
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Why is it complicated to search for sugar derivatives?
Experimental Set-up & Protocol

• Mix $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ vapors in a bulb to prepare $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ gas mixtures with different relative proportions (5:1 and 2:1).

• Deposit mixtures onto cold substrate (Al foil, ~10 K) and low pressure ($\sim 2 \times 10^{-8}$ torr), and simultaneously irradiate with $\text{H}_2$ lamp for 18–20 h.

• After irradiation, warm up to RT and recover the foil with the residue, dissolve it in a solvent (liquid $\text{H}_2\text{O}$/other).

• Analyze with GC-MS (BSTFA derivatization).
GC-MS Analysis

- Use of non-chiral GC column, so D and L enantiomers cannot be separated (good!), but still 8–10 peaks for each standard!
- Add pyridine to standards (and samples) to decrease the number of peaks to 1–2 main peaks for each compound.
- Identifications rely on comparison of both retention times and mass spectra of commercial standards, however...
GC-MS Analysis

L-Glucose + BSTFA

Lots of peaks!!!

Cyclic forms

Linear chains
GC-MS Analysis

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GC-MS Analysis

L-Glucose + BSTFA + pyridine

Better!
GC-MS Analysis

• Use of non-chiral GC column, so D and L enantiomers cannot be separated (good!), but still 8–10 peaks for each standard!
• Add pyridine to standards (and samples) to decrease the number of peaks to 1–2 main peaks for each compound.
• Identifications rely on comparison of both retention times and mass spectra of commercial standards, however...
GC-MS Analysis

D-Threose

D-Arabinose

D-Glucose
**GC-MS Analysis**

- **D-Threose**
- **D-Arabinose**
- **D-Glucose**

No peaks at high masses
GC-MS Analysis

D-Lyxose

D-Xylose

D-Arabinose

D-Ribose

![Chemical structures of D-Lyxose, D-Xylose, D-Arabinose, and D-Ribose.](image)

![GC-MS spectra of D-Lyxose, D-Xylose, D-Arabinose, and D-Ribose.](image)
GC-MS Analysis

D-Threose

D-Threonic acid

D-Threitol
GC-MS Analysis

D-Threose

D-Threonic acid

D-Threitol

Characteristic of sugar acids
Results

$\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV}$

Nuevo et al. (submitted)
Results

$\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV}$

Sugar alcohols

Nuevo et al. (submitted)
Results

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Sugar alcohols

Nuevo et al. (submitted)
Results

$H_2O:CH_3OH = 2:1 + UV$

Sugar alcohols

Nuevo et al. (submitted)
Results

Peak 1

Sample peak @ 11.81 min (/1.5)

Glycerol

Nuevo et al. (submitted)
Results

\[ \text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV} \]

Sugar alcohols

*Nuevo et al. (submitted)*
Results

Peak 2

Sample peak @ 16.94 min

Erythritol (m/z 18)

Peak 3

Sample peak @ 17.10 min

Threitol (m/z 14)

Nuevo et al. (submitted)
Results

H$_2$O:CH$_3$OH = 2:1 + UV

Sugar alcohols

Nuevo et al. (submitted)
Results

Peaks 5+6

Nuevo et al. (submitted)
Results

$\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV}$

*Nuevo et al. (submitted)*
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$\text{H}_2\text{O} : \text{CH}_3\text{OH} = 2:1 \ + \ \text{UV}$

*Nuevo et al. (submitted)*
Results

$H_2O:CH_3OH = 2:1 + UV$

**Sugars + Sugar acids**

_Nuevo et al. (submitted)_
Results

\[ \text{H}_2\text{O} : \text{CH}_3\text{OH} = 2:1 + \text{UV} \]

Nuevo et al. (submitted)
Results

H₂O:CH₃OH = 2:1 + UV

Sugars + Sugar acids

Nuevo et al. (submitted)
Results

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\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV}
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Sugars + Sugar acids

Nuevo et al. (submitted)
Results

\[ \text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV} \]

Sugars

Nuevo et al. (submitted)
Results

Peak 3

Sample peak @ 15.77 min

Threose (/60)

Peak 4

Sample peak @ 16.07 min

Erythrose (/1300)

Nuevo et al. (submitted)
Results

$\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV}$

Nuevo et al. (submitted)
Results

H$_2$O:CH$_3$OH = 2:1 + UV

Sugar acids (SIC 292 Da)

Nuevo et al. (submitted)
Results

$\text{H}_2\text{O} : \text{CH}_3\text{OH} = 2:1 + \text{UV}$

Sugar acids (SIC 292 Da)

Nuevo et al. (submitted)
Results

$\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV}$

Peak 2

Sample peak @ 14.16 min

Glyceric acid (/190)

Nuevo et al. (submitted)
Results

$\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV}$

Sugar acids
(SIC 292 Da)

Nuevo et al. (submitted)
Results

$\text{H}_2\text{O}:\text{CH}_3\text{OH} = 2:1 + \text{UV}$

Sugar acids (SIC 292 Da)

Nuevo et al. (submitted)
Results

\[ H_2O:CH_3OH = 2:1 + UV \]

Sugar acids (SIC 292 Da)

Nuevo et al. (submitted)
Results

Peak 5

Sample peak @ 18.74 min

Erythronic acid (m/z 650)

Peak 6

Sample peak @ 19.54 min

Threonic acid (m/z 2060)

Nuevo et al. (submitted)
Results

Peak 5

Sample peak @ 18.74 min

Erythronic acid (m/z 650)

147
220
205

Peak 6

Sample peak @ 19.54 min

Threonic acid (m/z 2060)

147
292

Nuevo et al. (submitted)
Results

Peak 5

Sample peak @ 18.74 min

Erythronic acid (m/z 650)

Peak 6

Sample peak @ 19.54 min

Threonic acid (m/z 2060)

Nuevo et al. (submitted)
## Results

<table>
<thead>
<tr>
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<th>Relative abundance (Meteorites)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol (C$_3$)</td>
<td>100</td>
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</tr>
<tr>
<td>Erythritol + threitol (C$_4$)</td>
<td>1.4–6.6</td>
<td>1</td>
</tr>
<tr>
<td>Ribitol + arabitol + xylitol (C$_5$)</td>
<td>0.1–1.3</td>
<td>(Not reported)</td>
</tr>
<tr>
<td>Dihydroxyacetone (C$_3$)</td>
<td>0–14.8</td>
<td>(Not reported)</td>
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<tr>
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<td>50</td>
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Nuevo et al. (submitted)
## Results

~190 nmol

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Nuevo et al. (submitted)
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Nuevo et al. (submitted)
Formation pathway?

\[ \text{CH}_3\text{OH/} \]
\[ \cdot\text{CH}_2\text{OH} \]
Formation pathway?

CH₃OH/ •CH₂OH → CH₂OH

CH₃OH/ •CH₂OH → CH₂OH

CH₃OH/ •CH₂OH → CH₂OH
Formation pathway?

\[ \text{CH}_3\text{OH/} \text{•CH}_2\text{OH} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{OH} \rightarrow \ldots \]
Formation pathway?

\[ \text{CH}_3\text{OH}/\cdot\text{CH}_2\text{OH} \rightarrow \]

Oxidation (H\(_2\)O)

\[ \text{CHO} \]

Oxidation (H\(_2\)O)

\[ \text{COOH} \]
Formation pathway?

\[ \text{CH}_3\text{OH}/\text{•CH}_2\text{OH} \rightarrow \text{CH}_2\text{OH} \]

Oxidation (H\(_2\)O)

\[ \text{CHO} \]

Oxidation (H\(_2\)O)

\[ \text{COOH} \]
Formation pathway?

\[
\text{CH}_3\text{OH}/\text{CH}_2\text{OH} \rightarrow \text{CHO} \rightarrow \text{COOH}
\]

Oxidation (H\textsubscript{2}O)

\[
\text{CH}_3\text{OH}/\text{CH}_2\text{OH} \rightarrow \text{CHO} \rightarrow \text{COOH}
\]

Oxidation (H\textsubscript{2}O)
Ribose and related sugars from ultraviolet irradiation of interstellar ice analogs

Comelia Meinert, Inelia Mygorodskaya, Pierre de Marcellus, Thomas Buhse, Laurent Nahon, Suren V. Hoffmann, Louis Le Sergeant d'Hendecourt, Uwe J. Meierhenrich

Ribose is the central molecular subunit in RNA, but the prebiotic origin of ribose remains unknown. We observed the formation of substantial quantities of ribose and a diversity of structurally related sugar molecules such as arabino, xylose, and lyxose in the room-temperature organic residues of photo-processed interstellar ice analogs initially composed of H₂O, CH₃OH, and NH₃. Our results suggest that the generation of numerous sugar molecules, including aldopentose ribose, may be possible from photochemical and thermal treatments of cosmic ices in the late stages of the solar nebula. Our detection of ribose provides plausible insights into the chemical processes that could lead to formation of biologically relevant molecules in suitable planetary environments.

D NA is the genetic source code for all known living organisms. It is currently thought that DNA evolved from a primordial ribonucleic acid RNA world state (1, 2), in which ribose chemically binds and orients the complementary purine and pyrimidine nucleobases for efficient base pairing. Ribose thereby forms the essential part of the RNA backbone. However, ribose is difficult to form, and the source of the ribose subunits in the sugars that constitute the key stereoindicating elements in nucleic acid structure remained unknown (3, 4). We describe here the identification of precursor molecules, including ribose, in simulated precometary ice using the sensitive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS) technique.

Our astrophysical scenario involves the simulation of the photo- and thermo-chemistry of precometary ices. It is based on the assumption that planetesimals (including asteroids, comets, and the parent bodies of meteorites) were formed in the solar nebula from the aggregation of icy grains.
Fig. 2. Multidimensional gas chromatogram showing ribose and other monosaccharides in the organic residue from an evolved precometary ice analog. See also fig. S1 and movie S1 (7). The atomic mass units 206 and 294 were selected for the multidimensional chromatographic representation. \( \alpha \)- and \( \beta \)-enantiomers of the monosaccharides were not resolved.
Summary

- UV irradiation of $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ ice mixtures leads to the formation of sugar alcohols, sugars, and sugar acids.
- Suggests a pathway in which sugar alcohols are formed first (from methanol/formaldehyde?), then sugars, then sugar acids (increasing oxidation products).
- This distribution is different from Murchison and Murray (no sugars except dihydroxyacetone).
- Many other GC-MS peaks are consistent with the presence of other sugar-like compounds [NIST library], including unidentified deoxy versions of sugars and sugar derivatives, carboxylic acids/diacids, and ketones with several OH groups.
## Sugar-related compounds in meteorites

Cooper et al. (2001)

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<td>C=O</td>
<td>H-C-OH</td>
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<td></td>
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<tr>
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<td>CH₂OH</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Dihydroxyacetone</td>
<td>Glycerol</td>
<td>Glyceric acid</td>
<td>80 nmol/g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>160 nmol/g (100%)</td>
<td></td>
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<td>H-C-OH</td>
<td>CO₂H</td>
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<td>Erythronic &amp; Threonic acid (40 nmol/g)</td>
<td>Tartaric &amp; Meso-tartaric acid</td>
<td>2-Methyl glyceric acid</td>
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<td></td>
<td></td>
<td>2, 4 Dihydroxy butyric acid</td>
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<td></td>
<td></td>
<td></td>
<td>2, 3 Dihydroxy butyric acid (diastereomer)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>3, 4 Dihydroxy butyric acid</td>
</tr>
<tr>
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<td>CO₂H</td>
<td>H₂C-OH</td>
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<tr>
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<td>CH₂OH</td>
<td>2, 3, 4-Trihydroxy Pentanedioic acid</td>
<td>2-Deoxypentonic acids</td>
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<td>Ribitol &amp; Isomers</td>
<td>Ribonic acid &amp; Isomers</td>
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<tr>
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<td>Glucitol &amp; Isomers</td>
<td>Gluconic acid &amp; Isomers</td>
<td>Glucaric acid &amp; Isomers</td>
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<td>3-Deoxyhexonic acid</td>
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• Use of $^{13}$C-labeled methanol ($^{13}$CH$_3$OH) shows that all photoproducts seen are made in the experiment and are not due to any biological contamination.

• Add CO$_2$ as a carbon source in the starting ice mixtures: UV irradiation of H$_2$O:CO$_2$ and H$_2$O:CH$_3$OH:CO$_2$ ices leads to the formation of more sugar acids.

• Add NH$_3$ to the starting mixtures: UV irradiation of H$_2$O:CH$_3$OH:NH$_3$ (10:5:1) ice mixtures leads to the formation of shorter and smaller amounts of sugar alcohols, sugars, and sugar acids, suggesting an inhibiting effect of NH$_3$. 
Future Work

- Perform similar experiments with starting ice mixtures which include other carbon sources (CO) and/or nitrogen sources (HCN).
- Perform similar experiments with starting mixtures mimicking more realistic astrophysical ices (containing H₂O, CH₃OH, CO, CO₂, CH₄, and NH₃).
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Any questions?

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http://www.astrochem.org/