

26. M. D. Groner, F. H. Fabreguette, J. W. Elam, S. M. George, *Chem. Mater.* **16**, 639–645 (2004).  
 27. J. Lee, J. H. Kim, S. Im, *Appl. Phys. Lett.* **83**, 2689 (2003).  
 28. L. A. Majewski, R. Schroeder, M. Grell, *J. Phys. D Appl. Phys.* **37**, 21–24 (2004).  
 29. C. Tedeschi, H. M $\ddot{o}$ hwald, S. Kirstein, *J. Am. Chem. Soc.* **123**, 954–960 (2001).

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## SUPPLEMENTARY MATERIALS

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## ASTROCHEMISTRY

# Ribose and related sugars from ultraviolet irradiation of interstellar ice analogs

Cornelia Meinert,<sup>1\*</sup> Iuliia Myrgorodska,<sup>1,2</sup> Pierre de Marcellus,<sup>3</sup> Thomas Buhse,<sup>4</sup> Laurent Nahon,<sup>2</sup> Søren V. Hoffmann,<sup>5</sup> Louis Le Sergeant d'Hendecourt,<sup>3</sup> Uwe J. Meierhenrich<sup>1\*</sup>

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 arabinose, xylose, and lyxose in the room-temperature organic residues of photo-processed interstellar ice analogs initially composed of H<sub>2</sub>O, CH<sub>3</sub>OH, and NH<sub>3</sub>. Our results suggest that the generation of numerous sugar molecules, including the aldopentose ribose, may be possible from photochemical and thermal treatment 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 orien-

tates 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 consti-

tute the key stereodictating elements in nucleic acid structure remained unknown (3, 4). We describe here the identification of precursor molecules, including ribose, in simulated precometary ices 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

<sup>1</sup>Université Nice Sophia Antipolis, Institut de Chimie de Nice, UMR 7272 CNRS, 28 Avenue Valrose, 06108 Nice, France.

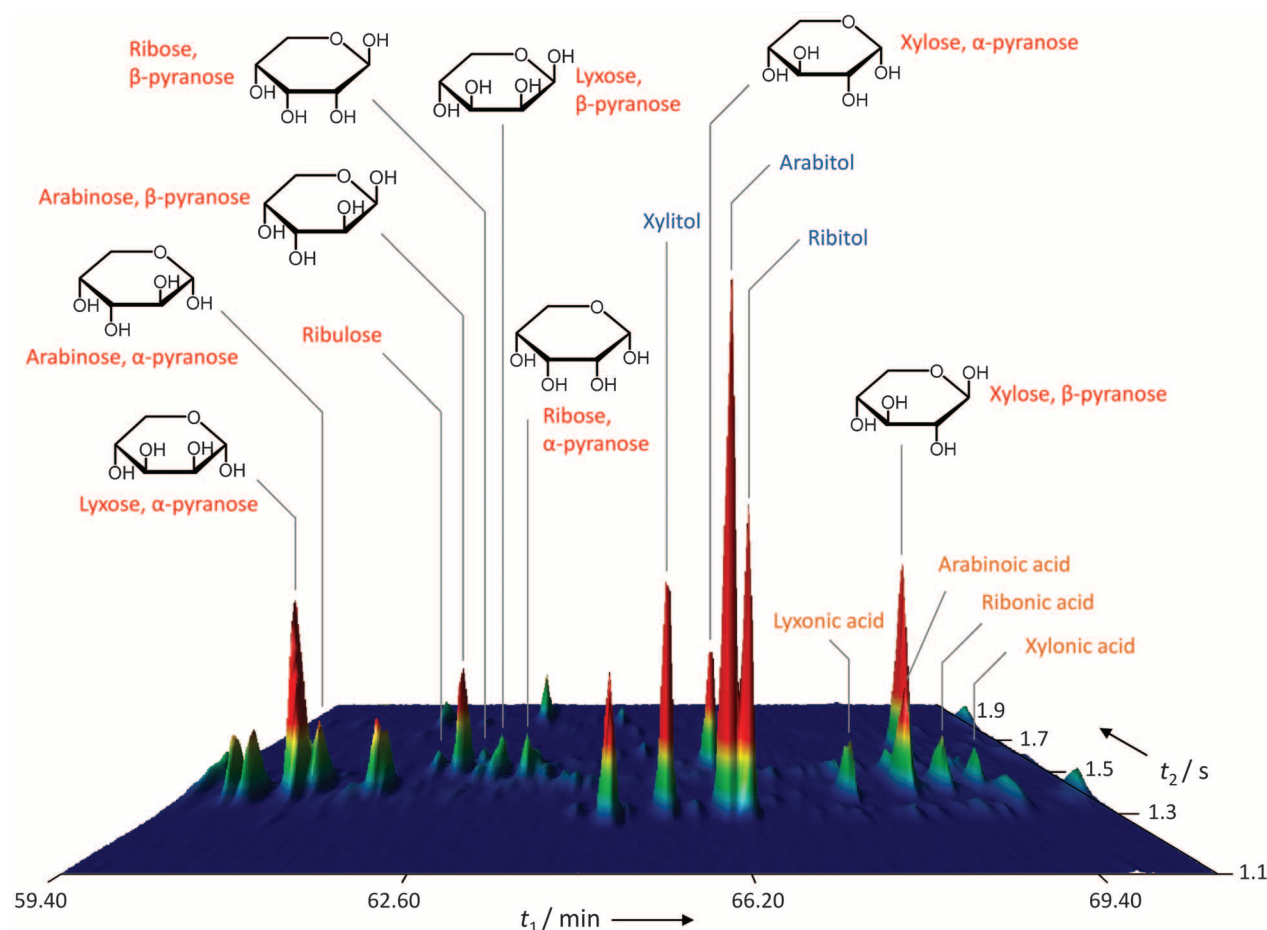
<sup>2</sup>Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin BP48, 91192 Gif-sur-Yvette, France. <sup>3</sup>Institut d'Astrophysique Spatiale, CNRS, Université Paris-Sud, Université Paris-Saclay, bât 121, 91405 Orsay, France. <sup>4</sup>Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, 62209 Cuernavaca, Mexico.

<sup>5</sup>Aarhus University, Department of Physics and Astronomy, Ny Munkegade 120, 8000 Aarhus, Denmark.

\*Corresponding author. E-mail: cornelia.meinert@unice.fr (C.M.); uwe.meierhenrich@unice.fr (U.J.M.)

**Fig. 1. Aldoses and ketoses as identified in a sample generated under simulated precometary conditions.** The structures of sugar alcohols, mono-saccharides, and saccharinic acids are indicated along with the amount of the identified analyte in the simulated ice sample. Identified C-6 analytes are not included. The Fischer projections indicate the D-enantiomer form only. ppm, parts per million by mass; q.l., quantification limit; d.l., detection limit.

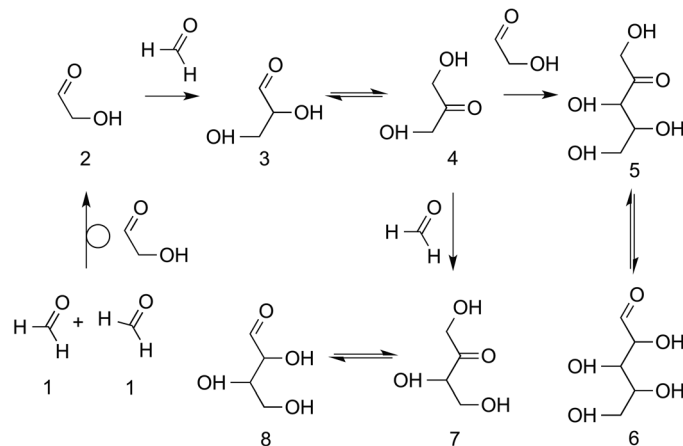
	Aldoses				Ketoses	
C-2	$\begin{array}{c} \text{R} \\   \\ \text{CH}_2\text{OH} \end{array}$ R = CH <sub>2</sub> OH, Ethylene glycol (550 ppm) = CHO, Glycolaldehyde (2390 ppm) = COOH, Glycolic acid (6330 ppm)					
C-3	$\begin{array}{c} \text{R} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ R = CH <sub>2</sub> OH, Glycerol (2860 ppm) = CHO, Glyceraldehyde (302 ppm) = COOH, Glyceric acid (2440 ppm)				$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{CH}_2\text{OH} \end{array}$ Dihydroxyacetone (540 ppm)	
C-4	$\begin{array}{c} \text{R} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ R = CH <sub>2</sub> OH, Erythritol (5070 ppm) = CHO, Erythrose (< q.l.) = COOH, Erythronic acid (960 ppm)		$\begin{array}{c} \text{R} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ R = CH <sub>2</sub> OH, Threitol (7200 ppm) = CHO, Threose (< d.l.) = COOH, Threonic acid (840 ppm)		$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ Erythrulose (37 ppm)	
C-5	$\begin{array}{c} \text{R} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ R = CH <sub>2</sub> OH, Ribitol (560 ppm) = CHO, Ribose (260 ppm) = COOH, Ribonic acid (82 ppm)	$\begin{array}{c} \text{R} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ Arabitol (1150 ppm) Arabinose (200 ppm) Arabinic acid (165 ppm)	$\begin{array}{c} \text{R} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ Xylitol (630 ppm) Xylose (240 ppm) Xylonic acid (67 ppm)	$\begin{array}{c} \text{R} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ Arabitol (1150 ppm) Lyxose (145 ppm) Lyxonic acid (140 ppm)	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ Ribulose (2010 ppm)	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C}=\text{O} \\   \\ \text{HO}-\text{C}-\text{H} \\   \\ \text{H}-\text{C}-\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$ Xylulose (470 ppm)



**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. D- and L-enantiomers of the monosaccharides were not resolved.

### Fig. 3. The formose reaction.

Formaldehyde **1** condenses under autocatalytic reaction kinetics to form glycolaldehyde **2**, which undergoes an aldol reaction by forming glyceraldehyde **3**. Dihydroxyacetone **4** is formed by aldose-ketose isomerization of **3** and reacts with **2**, forming pentulose **5**, which isomerizes to an aldopentose **6** such as ribose. In an alternative pathway, dihydroxyacetone **4** reacts with **1**, producing ketotetrose **7** and aldotetrose **8** (18).



already present and processed at the late molecular cloud stages. This also took place within the protoplanetary disk phase, owing to vertical/radial mixing of the protostellar materials (5). As a model, these dust particles are composed of silicate (or

carbon) grains surrounded by icy mantles containing  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{NH}_3$ , and other volatile species (6). In this environment, dust particles and icy mantles are expected to be subjected to ultraviolet photons and cosmic-ray irradiation, leading to a

complex chemistry in the condensed phase. We empirically simulated this process in the laboratory at low temperature ( $T = 78\text{ K}$ ) and low pressure ( $p = 10^{-7}\text{ mbar}$ ). Volatile molecules  $\text{H}_2\text{O}$ ,  $^{13}\text{C}_3\text{OH}$ , and  $\text{NH}_3$  in a 10:3.5:1 ratio were condensed on the cooled surface, while being irradiated with ultraviolet photons, and then warmed up to room temperature, leading to the formation of an organic residue (7).  $^{13}\text{C}$  isotopic labeling of the methanol allowed us to distinguish between the reaction products and potential contamination during manipulation of the sample and through the analytical procedure. A precise description of the experimental setup is provided in the supplementary materials.

The samples were extracted with water, derivatized, and submitted to GC×GC-TOFMS analysis (8). The analytical multidimensional separation apparatus consisted of a 0.25-mm capillary column with a  $\beta$ -cyclodextrin stationary phase in the first dimension and a polyethylene glycol capillary column of 100  $\mu\text{m}$  inner diameter in the second dimension. A cryogenic modulator connected both capillary columns (7). A reflectron time-of-flight (TOF) mass spectrometer has been used for recording retention times and mass

**Table 1. Identified sugars and related organic compounds in interstellar ice analogs initially composed of H<sub>2</sub>O:<sup>13</sup>CH<sub>3</sub>OH:NH<sub>3</sub>, #C, quantity of carbon atoms; R<sub>t1</sub>, GC×GC retention time 1st dimension; R<sub>t2</sub>, GC×GC retention time 2nd dimension.**

#C	Compound	R <sub>t1</sub> (min)	R <sub>t2</sub> (sec)	MS-fragmentation/ <sup>13</sup> C sample		MS-fragmentation/ <sup>12</sup> C standard	
				(M <sup>+</sup> )	Other important ions (m/z)	(M <sup>+</sup> )	Other important ions (m/z)
Monosaccharides							
3	L-Glyceraldehyde	33.48	1.78	237	207, 206, 191, 147, 119, 104, 73, 29	234	205, 204, 189, 147, 117, 103, 73, 28
	D-Glyceraldehyde	34.03	1.74		see L-Glyceraldehyde		
	Dihydroxyacetone	43.37	1.88	237	222, 191, 147, 104, 73	234	219, 189, 147, 103, 73
4	D,L-Erythrose, α-furanose	49.46	1.52	340	235, 221, 220, 206, 192, 147, 104, 73	336	231, 218, 217, 203, 191, 147, 103, 73
	D,L-Erythrulose	54.51	1.82	340	309, 235, 207, 191, 147, 119, 104, 73	336	306, 231, 205, 189, 147, 117, 103, 73
5	D,L-Lyxose, α-pyranose	60.90	1.41	443	see Ribose		
	D,L-Arabinose, α-pyranose	61.15	1.42		see Ribose		
	D,L-Ribulose, ketol	62.50	1.46	443	339, 310, 249, 220, 192, 147, 132, 104, 73	438	335, 307, 245, 218, 191, 147, 129, 103, 73
	D,L-Arabinose, β-pyranose	62.85	1.51		see Ribose		
	D,L-Ribose, β-pyranose	63.15	1.45	443	308, 294, 220, 206, 192, 147, 119, 104, 103, 73	438	305, 291, 217, 204, 191, 147, 117, 103, 101, 73
	D,L-Lyxose, β-pyranose	63.40	1.48	443	see Ribose		
	D,L-Ribose, α-pyranose	63.70	1.46	443	308, 294, 220, 206, 192, 147, 119, 103, 73	438	305, 291, 217, 204, 191, 147, 117, 103, 101, 73
	D,L-Xylulose, ketol*†	64.30	1.54	443	339, 310, 249, 220, 192, 147, 132, 104, 73	438	335, 307, 245, 218, 191, 147, 129, 103, 73
	D,L-Xylose, α-pyranose	66.20	1.52	443	see Ribose		
	D,L-Xylose, β-pyranose	69.04	1.61	443	see Ribose		
Sugar acids (saccharinic acids)							
3	D,L-Glyceric acid	44.42	1.64	325	310, 294, † 220, 207, 191, 177, 147, 119, 103, 73	322	307, 292, † 217, 205, 189, 175, 147, 117, 102, 73
4	D,L-Erythronic acid	56.96	1.47	428	413, 382, 294, † 222, 207, 147, 104, 73	424	409, 379, 292, † 220, 205, 147, 103, 73
	D,L-Threonic acid	58.10	1.49	428	413, 382, 294, † 222, 207, 147, 104, 73	424	409, 379, 292, † 220, 205, 147, 103, 73
5	D,L-Lyxonic acid†	67.79	1.39	531	see Ribonic acid		
	D,L-Arabinic acid†	68.59	1.41	531	see Ribonic acid		
	D,L-Ribonic acid†	69.09	1.41	531	337, 310, 294, † 279, 220, 207, 191, 147, 119, 104, 73	526	333, 307, 292, † 277, 217, 205, 189, 147, 117, 103, 73
	D,L-Xylonic acid†	69.54	1.42	531	see Ribonic acid		
Sugar alcohols							
3	Glycerol	40.58	1.43	311	296, 221, 207, 147, 119, 104, 73	308	293, 218, 205, 147, 117, 103, 73
4	D,L-Threitol	54.56	1.38	414	324, 310, 295, 220, 207, 191, 147, 119, 104, 73	410	320, 307, 293, 217, 205, 189, 147, 117, 103, 73
	Erythritol	54.86	1.38	414	324, 310, 295, 220, 207, 191, 147, 119, 104, 73	410	320, 307, 293, 217, 205, 189, 147, 117, 103, 73

continued on next page

#C	Compound	$R_{t1}$ (min)	$R_{t2}$ (sec)	MS-fragmentation/ $^{13}\text{C}$ sample		MS-fragmentation/ $^{12}\text{C}$ standard	
				( $M^{++}$ )	Other important ions ( $m/z$ )	( $M^{++}$ )	Other important ions ( $m/z$ )
5	D,L-Xylitol	65.54	1.33	517	337, 323, 310, 220, 207, 191, 147, 119, 104, 73	512	332, 319, 307, 217, 205, 189, 147, 117, 103, 73
	D,L-Arabitol	66.29	1.32	517	337, 323, 310, 220, 207, 191, 147, 119, 104, 73	512	332, 319, 307, 217, 205, 189, 147, 117, 103, 73
	D,L-Ribitol (Adonitol)*†	66.49	1.31	517	337, 323, 310, 220, 207, 191, 147, 119, 104, 73	512	332, 319, 307, 217, 205, 189, 147, 117, 103, 73
6	D,L-Mannitol	82.54§	1.63	620	426, 323, 310, 220, 207, 147, 104, 73	614	421, 319, 307, 217, 205, 147, 103, 73
	D,L-Sorbitol	83.24§	1.65	620	426, 323, 310, 220, 207, 147, 104, 73	614	421, 319, 307, 217, 205, 147, 103, 73
	D,L-Allitol*	83.49§	1.67	620	see Mannitol		
	D,L-Dulcitol (Galactitol)	83.69§	1.67	620	426, 323, 310, 220, 207, 147, 104, 73	614	421, 319, 307, 217, 205, 147, 103, 73
	D,L-Talitol (Altritol)*	84.04§	1.67	620	see Mannitol		
Branched-chain sugar acids and polyols							
4	2-Methylglycerol†	40.03	1.31	326	311, 235, 222, 147, 104, 73	322	307, 232, 219, 147, 103, 73
	2-Methylglyceric acid*	43.02	1.48	340	325, 309, ‡ 296, 236, 222, 206, 191, 147, 104, 73	336	321, 306, ‡ 293, 233, 219, 203, 189, 147, 103, 73
	2-Hydroxymethylglycerol*	52.81	1.33	414	310, 220, 191, 147, 132, 104, 73		
5	2-Hydroxymethyltetritol*	64.90	1.29	517	323, 310, 220, 147, 104, 73		
Hydroxycarboxylic acids							
2	Glycolic acid	31.39	1.69	222	207, 178, † 162, 147, 104, 73	220	205, 177, † 161, 147, 103, 73
3	D-Lactic acid	24.94	1.66	237	222, 193, 147, 119, 103, 73	234	219, 191, 147, 117, 101, 73
	L-Lactic acid	25.24	1.66	237	222, 193, 147, 119, 103, 73	234	222, 191, 147, 117, 101, 73
	3-Hydroxypropanoic acid	36.63	1.60	237	222, 178, 147, 118, 103, 73	234	219, 177, 147, 116, 101, 73
4	2-Hydroxyisobutyric acid	24.00	1.52	252	237, 208, † 147, 134, 73	248	233, 205, † 147, 131, 73
	(R)-2-Hydroxybutyric acid	29.54	1.65	252	237, 208, † 147, 134, 73	248	233, 205, † 147, 131, 73
	(S)-2-Hydroxybutyric acid	29.79	1.63	252	237, 208, † 147, 134, 73	248	233, 205, † 147, 131, 73
	3-Hydroxyisobutyric acid†	34.73	1.58	252	237, 221, 208, 178, 162, 147, 104, 73	248	233, 218, 205, 177, 158, 147, 103, 73
	(R)-3-Hydroxybutyric acid	35.63	1.57	252	237, 206, † 193, 147, 119, 73	248	233, 204, † 191, 147, 117, 73
	(S)-3-Hydroxybutyric acid	36.13	1.55				
	4-Hydroxybutyric acid	42.52	1.62	252	237, 206, 147, 119, 73	248	233, 204, 147, 117, 73
	D,L-Malic acid	55.81	1.77	354	339, 310, 249, 236, 191, 147, 119, 73	350	335, 307, 245, 233, 189, 147, 117, 73
Dicarboxylic acids							
4	Succinic acid	48.37	2.05	266	251, 176, 147, 132, 73	262	247, 172, 147, 129, 73
	Fumaric acid	51.76	1.96	264	249, 220, 147, 118, 73	260	245, 217, 147, 115, 73
Miscellaneous							
2	Ethylene glycol	16.00	1.38	208	193, 147, 104, 73	206	191, 147, 103, 73
	Oxamic acid*†	37.68	1.61	235	220, 191, 147, 117, 73	233	218, 190, 147, 116, 73
	Glycolaldehyde¶	36.18	2.16		304, 288, 215, 191, 147, 73		302, 286, 214, 189, 147, 73
		36.48	2.12		304, 288, 215, 191, 147, 73		302, 286, 214, 189, 147, 73
3	D,L-1,3-Propanediol	27.69	1.36	223	208, 178, 147, 133, 73	220	205, 177, 147, 130, 73

\*Identification is based on literature data on the formose reaction (19, 20), former ice simulation experiments, as well as chromatographic retention properties of sugar and sugar-related molecules (7). †Identification is based on National Institute of Standards and Technology mass spectral database and retention time prediction. ‡McLafferty and McLafferty-type (ester migration) rearrangement. §Retention time shift by +3 min because of changes in column flow. ||Temperature program of first dimension: 40°C (1 min), 10°C min<sup>-1</sup>, 80°C (10 min), 2°C min<sup>-1</sup>, 180°C (5 min). ¶Stereoisomers of dimeric or anhydrol form.

spectra. The GC×GC-TOFMS analysis in combination with our derivatization protocol (7) provided the simultaneous resolution and identification of the sugar and sugar-related compounds, which has not been possible with classical chromatographic devices because of coelution of analytes.

We detected aldoses and ketoses in these simulated interstellar ice analogs as schematically represented by the Fischer projections in Fig. 1. The monosaccharides ribose, arabinose, xylose, and lyxose belong to the aldopentoses; ribulose and xylulose are ketopentoses. The aldopentoses were resolved and identified in

both  $\alpha$ - and  $\beta$ -pyranose form (Fig. 2), and the ketopentoses show ketol form. Besides aldopentoses and ketopentoses, we identified the ketotetrose erythrose. Mass spectra of the analytes and the interpretation of characteristic fragmentation pathways leading to unambiguous identification are provided (supplementary text),

along with details on the quantification of the analytes.

The corresponding saccharinic acids (sugar acids) were identified. We also detected the corresponding sugar alcohols, along with threitol, erythritol, mannitol, and sorbitol. We further found the related series of hydroxycarboxylic acids.

A systematic representation of the identified molecular species is given in Table 1, which indicates the analytes' retention times in the first and second chromatographic dimension and mass spectra of analyzed sample and standard. The analytes detected in the organic residue were found to contain  $^{13}\text{C}$  isotopes, whereas the standard samples used for identification were made of the natural isotopic composition dominated by  $^{12}\text{C}$  (figs. S3 to S5). We therefore exclude experimental contamination and conclude that all described analytes were formed by the  $\text{H}_2\text{O}$ ,  $^{13}\text{CH}_3\text{OH}$ , and  $\text{NH}_3$  volatile reactants that were deposited under simulated interstellar precometary conditions (fig. S2).

The molecular complexity in the evolved ices reported here suggests a far larger similarity to meteoritic organic materials than previously assumed. Thus, molecular evolution of meteoritic organic species available for planetary environments could have benefited from accretion of protostellar material. The sugars, dicarboxylic acids, C-4 hydroxycarboxylic acids, and branched-chain molecules described here have not previously been identified, although aldehydes, including glycolaldehyde and glyceraldehyde, have been found in similar laboratory residues (9), along with lower hydroxycarboxylic acids (10). Sugar-related alcohols and acids have previously been detected in the Murchison meteorite (11). Glycolaldehyde has been found sublimating from the nucleus of comet Lovejoy (C/2014 Q2) (12) and by means of millimeter-wave rotational transitions in emission toward the Galactic center source Sagittarius B2(N) (13). Glycolaldehyde was recently also detected in solar-type protostars (14). Moreover, glycolaldehyde and ethylene glycol were characterized by means of infrared spectroscopy in radiation chemistry of laboratory ices (15).

The diversity of sugar molecules formed from  $\text{H}_2\text{O}$ ,  $^{13}\text{CH}_3\text{OH}$ , and  $\text{NH}_3$  under interstellar conditions can be understood in the framework of a photochemically initiated formose-type reaction. Reactant and intermediate species of the formose reaction (16–18) are formaldehyde and glycolaldehyde that undergo aldol condensations to produce hydroxyl aldehydes and hydroxyl ketones with linear and branched structures (Fig. 3 and fig. S6). As in our case, sugar alcohols and sugar acids typically accompany the sugars formed by the formose reaction. We further detected the branched chain molecules hydroxymethylglycerol and hydroxymethyltetritol, which indicate a formose-type reaction mechanism (19, 20). The classical formose reaction is known to require a divalent metal catalyst such as  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ , or  $\text{Tl}^{2+}$  for the stabilizing effect of chelating ions on enediols (18), a condition not needed in the present work. Final steps of the formose-type reaction might

have occurred above 78 K during temperature increase of the sample to room temperature, in which reactants diffuse and react within the labile and sublimating ice matrix.

The parts-per-million values of the photo-products described in Fig. 1 sum up to greater than 35,000 (table S1), which corresponds to a value  $>3.5\%$  (by mass) (7). Thus, sugars, sugar alcohols, and sugar acids are present notably above trace or ultratrace quantities and are therefore considered major molecular constituents of the condensed interstellar organics. The relative yield of ribose, which is known to be very small in the classical formose reaction, resulted in higher values during our cold scenario. We regard this result as central for an implication for prebiotic chemistry because it shows that even at this initial level of molecular “simplicity,” we observe an autocatalytic reaction. This, in turn, may be interpreted as a link between astrochemistry and astrobiology. The acquisition of kinetic data and enantioseparation will be necessary to rationalize the reaction mechanism of the sugar formation and to search for asymmetric autocatalytic effects.

The identification of ribose in the organic residues obtained from evolved precometary ices does not necessarily indicate the prebiotic evolutionary pathway. Besides ribose, we identified threose in its oxidized and reduced form, threonic acid and threitol, respectively. Threose is the molecular component of threose nucleic acid (TNA), a nucleic acid analog discussed to have preceded RNA (21). We further detected glycol and glycerol, which provide the molecular backbones of glycol and glycerol nucleic acids (GNAs) (22, 23). The molecular building blocks of peptide nucleic acids (PNAs), *N*-(2-aminoethyl) glycine and 2,4-diaminobutanoic acid, were previously detected in organic residues from similar ice experiments (24). In this experimental frame, precursors of both proteins (amino acids) (25) and genetic material (sugars and their derivatives) are produced in large amounts so that if delivered from meteorites in the Earth's environment, their coevolution may be considered one of the standing issues in prebiotic chemistry (26).

Our samples are fully soluble in water (as well as in other polar solvents), a condition that is essential for any further prebiotic activity. In aqueous solution, sugar molecules, including ribose, develop chemical equilibria between the open form (Fig. 1), the cyclic furanose and pyranose forms (Fig. 2), and in between the various constitutional isomers such as ribose and arabinose. Our experiments demonstrate plausible physical and chemical environmental conditions that allow for abiotic ribose synthesis.

Our findings support the identification of organic molecules in cometary samples taken in situ by the Philae Lander (27, 28) part of the cometary Rosetta mission (29). Our analytical results demonstrate the usefulness of multidimensional chromatographic techniques for the chemical analyses of extraterrestrial samples, which are often available only in small quan-

ties, in which sugar molecules including ribose may be present.

## REFERENCES AND NOTES

- R. F. Gesteland, T. R. Cech, J. F. Atkins, *The RNA World* (Cold Spring Harbor Laboratory Press, 2005).
- C. Woese, *The Genetic Code* (Harper & Row, 1967), pp. 179–195.
- F. H. C. Crick, *J. Mol. Biol.* **38**, 367–379 (1968).
- L. E. Orgel, *J. Mol. Biol.* **38**, 381–393 (1968).
- F. J. Ciesla, S. A. Sandford, *Science* **336**, 452–454 (2012).
- J. M. Greenberg, in *The Chemistry of Life's Origins*, J. M. Greenberg, Ed. (Kluwer, Dordrecht, 1993) pp. 195–207.
- Materials and methods are available as supplementary materials on Science Online.
- C. Meinert, U. J. Meierhenrich, *Angew. Chem. Int. Ed. Engl.* **51**, 10460–10470 (2012).
- P. de Marcellus et al., *Proc. Natl. Acad. Sci. U.S.A.* **112**, 965–970 (2015).
- V. K. Agarwal et al., *Orig. Life Evol. Biosph.* **16**, 21–40 (1985).
- G. Cooper et al., *Nature* **414**, 879–883 (2001).
- N. Biver et al., *Sci. Adv.* **1**, e1500863 (2015).
- J. M. Hollis, F. J. Lovas, P. R. Jewell, *Astrophys. J.* **540**, L107–L110 (2000).
- J. K. Jørgensen et al., *Astrophys. J.* **757** (L4), 1–6 (2012).
- R. L. Hudson, M. H. Moore, A. M. Cook, *Adv. Space Res.* **36**, 184–189 (2005).
- M. A. Butlerow, C. R. Séances Acad. Sci. **53**, 145–147 (1861).
- M. A. Butlerow, *Ann. Chem.* **120**, 295–298 (1861).
- R. Breslow, *Tetrahedron Lett.* **21**, 22–26 (1959).
- Y. Shigemasa, Y. Matsuda, C. Sakazawa, T. Matsuura, *Bull. Chem. Soc. Jpn.* **50**, 222–226 (1977).
- T. Zweckmair et al., *J. Chromatogr. Sci.* **52**, 169–175 (2014).
- H. Yu, S. Zhang, J. C. Chaput, *Nat. Chem.* **4**, 183–187 (2012).
- L. Zhang, A. Peritz, E. Meggers, *J. Am. Chem. Soc.* **127**, 4174–4175 (2005).
- C.-H. Tsai, J. Chen, J. W. Szostak, *Proc. Natl. Acad. Sci. U.S.A.* **104**, 14598–14603 (2007).
- C. Meinert, J.-J. Filippi, P. de Marcellus, L. le Sergeant d'Hendecourt, U. J. Meierhenrich, *ChemPlusChem* **77**, 186–191 (2012).
- G. M. Muñoz Caro et al., *Nature* **416**, 403–406 (2002).
- D. J. Ritson, J. D. Sutherland, *Angew. Chem. Int. Ed. Engl.* **52**, 5845–5847 (2013).
- F. Goesmann et al., *Science* **349**, aab0689 (2015).
- I. P. Wright et al., *Science* **349**, aab0673 (2015).
- U. J. Meierhenrich, *Comets and their Origin* (Wiley-VCH, 2015).

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## SUPPLEMENTARY MATERIALS

[www.sciencemag.org/content/352/6282/208/suppl/DC1](http://www.sciencemag.org/content/352/6282/208/suppl/DC1)  
Materials and Methods  
Supplementary Text  
Figs. S1 to S6  
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**Ribose and related sugars from ultraviolet irradiation of interstellar ice analogs**

Cornelia Meinert, Iuliia Myrgorodska, Pierre de Marcellus, Thomas Buhse, Laurent Nahon, Søren V. Hoffmann, Louis Le Sergeant d'Hendecourt and Uwe J. Meierhenrich (April 7, 2016)  
*Science* **352** (6282), 208-212. [doi: 10.1126/science.aad8137]

Editor's Summary

**Making ribose in interstellar ices**

Astrobiologists have long speculated on the origin of prebiotic molecules such as amino acids and sugars. Meinert *et al.* demonstrated that numerous prebiotic molecules can be formed in an interstellar-analog sample containing a mixture of simple ices of water, methanol, and ammonia. They irradiated the sample with ultraviolet light under conditions similar to those expected during the formation of the solar system. This yielded a wide variety of sugars, including ribose—a major constituent of ribonucleic acid (RNA).

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