

## TECHNICAL RESPONSE

## ASTROCHEMISTRY

# Response to Comment on “Ribose and related sugars from ultraviolet irradiation of interstellar ice analogs”

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We detected ribose and related sugars in the organic residues of simulated interstellar ices using multidimensional gas chromatography. Kawai questions the formation of sugar compounds in the ices and suggests that they arise from a classical formose reaction during sample workup for analysis. We disagree with this hypothesis and present additional data to argue that Kawai's criticism does not apply.

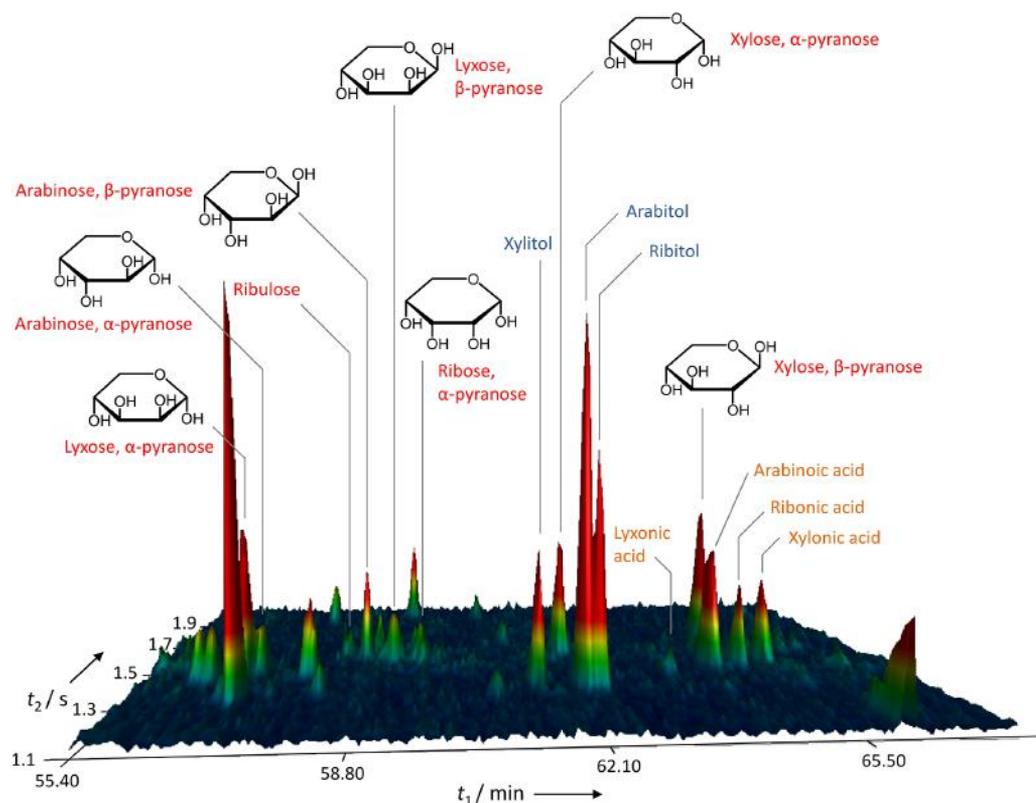
**W**e simulated astrophysical ices by condensing water, methanol, and ammonia in a vacuum chamber at low temperature ( $T = 78$  K) while irradiating with ultraviolet light. We found ribose and other related sugars in the residues that formed when the material was later warmed up to room temperature ( $T$ ). The simultaneous generation of these compounds together with high quantities of branched-chain sugar alcohols allows us to

assume a photochemically induced formose-type reaction because the reaction products resemble those of classical formose reactions (2). However, no base and no divalent metal catalysts are required in the discovered cold formose-type reaction. Moreover, the amount of ribose and its sister aldopentoses detected in the organic residues of simulated interstellar ices largely exceeds the yields known to be produced in the classical formose reaction.

Kawai (3) proposes that most of our identified molecules have been formed during sample workup and derivatization—a necessary step in our analytical protocol for the identification based on two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOFMS). Here, we add complementary data and discuss the criticism to show that our original finding and conclusion on the formation of ribose in astrophysical ices is correct.

One spare sample of the astrophysical ice analog was analyzed with *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) only—i.e., without the additional use of pyridine. After extraction of the organic residue of this sample with 150  $\mu$ L CHROMASOLV water, the sample was dried under a gentle stream of nitrogen and derivatized with 50  $\mu$ L BSTFA and 10  $\mu$ L trimethylchlorosilane for 3 hours at 80°C. The derivatized extract was transferred into a glass vial equipped with a 100- $\mu$ L glass insert together with 10  $\mu$ L of the internal standard methyl laurate in *n*-hexane ( $5 \times 10^{-5}$  M) and subsequently analyzed with GC×GC-TOFMS. An almost identical set of sugar

**Fig. 1. Multidimensional gas chromatogram showing ribose and other monosaccharides in the organic residue from an evolved precometary ice analog.** The atomic mass units 206 and 294 were selected for the multidimensional chromatographic representation. This sample was identical to that shown in figure 2 of (1), except that pyridine was not used during the analysis.



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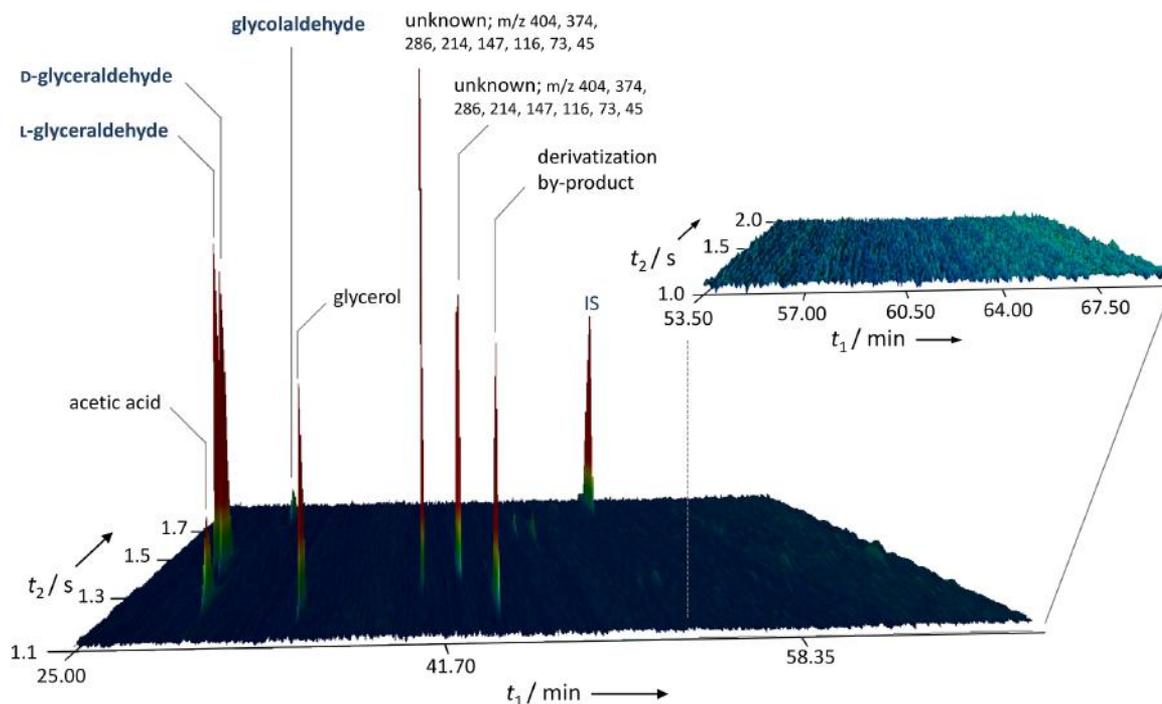
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**Fig. 2. Multidimensional gas chromatogram demonstrating the absence of ribose and other monosaccharides when derivatizing formaldehyde, glycolaldehyde, and glyceraldehyde in the presence of pyridine.**

The atomic mass units 204 and 291 were selected for the multidimensional chromatographic representation that correspond to the  $^{13}\text{C}$ -labeled masses 206 and 294, respectively. The z axis (abundance) of the close-up view of the two-dimensional elution space of C5 monosaccharides, sugar alcohols, and sugar acids was increased by a factor of 3.



compounds was identified in this sample (Fig. 1), as compared with the sample previously published (*I*). The lower abundances observed in the “BSTFA-only” derivatized sample are explained by a higher dilution factor for the overall solvent used, and the missing catalytic effect of pyridine for the transformation of sugar molecules into volatile, and thus detectable, derivatization products. We therefore reveal that in our experiment, pyridine is not required for the formation of aldopentoses. In a simple experiment, Kawai repeated the classical formose reaction and concluded that, in his case, pyridine is required as a base catalyst. We conclude that the aldopentoses and related sugar molecules in our experiment do not form in a classical formose reaction in aqueous, alkaline solution during sample workup.

Kawai argued in his Comment that distinguishing products formed by ultraviolet irradiation from those produced during workup is best done by lyophilizing samples to remove volatile substances before product manipulation. In fact, all our samples were systematically lyophilized before chemical analyses, as we described. Frozen samples of interstellar ice analogs were kept under reduced pressure ( $P = 1 \times 10^{-7}$  mbar) while the temperature was being constantly increased to room temperature. The volatiles were controlled via in situ infrared spectroscopy under the described conditions, and before venting the system, all initial volatiles sublimated out of the ice. This is well known in experimental astrophysics and consistent with literature data. Schutte *et al.* (*4*, *5*) stated that during the warm-up of their astrophysical ice analog, all the original components evaporated by 150 K; by 190 K, only an organic residue remained on the sample window.

We contend that all initial volatiles were removed in our experiments before sample workup. Neither the reactants nor the required high pH for a formose reaction were present during our sample workup.

Without analytical evidence, Kawai asserted the formation of sugar molecules, including ribose, in his experiment, based on the fact that the solution turned light brown. Our astrophysical residue is yellow, light brownish at the window before extraction. This indicates the formation of aldopentoses in the ices and/or during sample warm-up to room temperature and not during sample workup. Our subsequent analysis has ultimately proven the presence of aldopentoses in the organic residues. However, we have undertaken a further experiment to demonstrate this. We prepared a solution of formaldehyde, glycolaldehyde, and glyceraldehyde (1.14:5:1;  $5 \times 10^{-5}$  M)—aldehydes that were previously detected in identical ice simulation experiments (*6*) (as correctly stated by Kawai) and therefore expected to be part of the organic residue before sample analysis. This solution was derivatized and analyzed in the exact same manner as the interstellar ice analog published in (*I*). After drying this aldehyde solution under nitrogen, 10  $\mu\text{L}$  BSTFA and 25  $\mu\text{L}$  pyridine were added and the reaction mixture heated for 2 hours at 80°C. The silylated sample was dried; 30  $\mu\text{L}$  of the internal standard methyl laurate in *n*-hexane was added and then analyzed with GC $\times$ GC-TOFMS. Potential ribose formation starting from the intermediates of the formose reaction formaldehyde, glycolaldehyde, and glyceraldehyde under our derivatization conditions was clearly ruled out as aldopentoses were quantitatively absent in the

chromatogram as well as all other sugar molecules, sugar alcohols, and sugar acids that are typically formed in formose reactions (Fig. 2).

During the preparation of the astrophysical ices, infrared monitoring was used. The 3.4- $\mu\text{m}$  feature, which consists of two subfeatures at 2925  $\text{cm}^{-1}$  (3.42  $\mu\text{m}$ ) and 2875  $\text{cm}^{-1}$  (3.48  $\mu\text{m}$ ) indicative to the presence of  $\text{CH}_2\text{OH}$  groups (*7*), was recorded in our ice during a temperature increase to 230 K when the sublimation of water, methanol, and ammonia is almost finished. Below 230 K, the sample is optically too thick for the detection of the 3.4- $\mu\text{m}$  feature. The 3.4- $\mu\text{m}$  feature indicates the formation of  $\text{CH}_2\text{OH}$  groups—i.e., sugar alcohols, sugar acids, and sugars, in the astrophysical ice before sample post-treatment.

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#### ACKNOWLEDGMENTS

This work was funded by the Agence Nationale de Recherche grant ANR-12-IS07-0006 and Consejo Nacional de Ciencia y Tecnología (CONACYT) grant C001-CONACYTANR-188689. L.L.S.d'H. thanks the Centre National d'Études Spatiales for the continuous support of the MICMOC (Matière Interstellaire et Cométaire: Molécules Organiques Complexes) experiment.

17 June 2016; accepted 28 November 2016  
10.1126/science.aah3756



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*Science* **355** (6321), 141. [doi: 10.1126/science.aah3756]

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