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

Michel Nuevo[1,2], Scott A. Sandford[1], John. M. Saunders[3], and George Cooper[1]

[1]*NASA Ames Research Center, Moffett Field, CA, USA*
[2]*BAER Institute, Petaluma, CA, USA*
[3]*University of California, Santa Cruz, CA, USA*

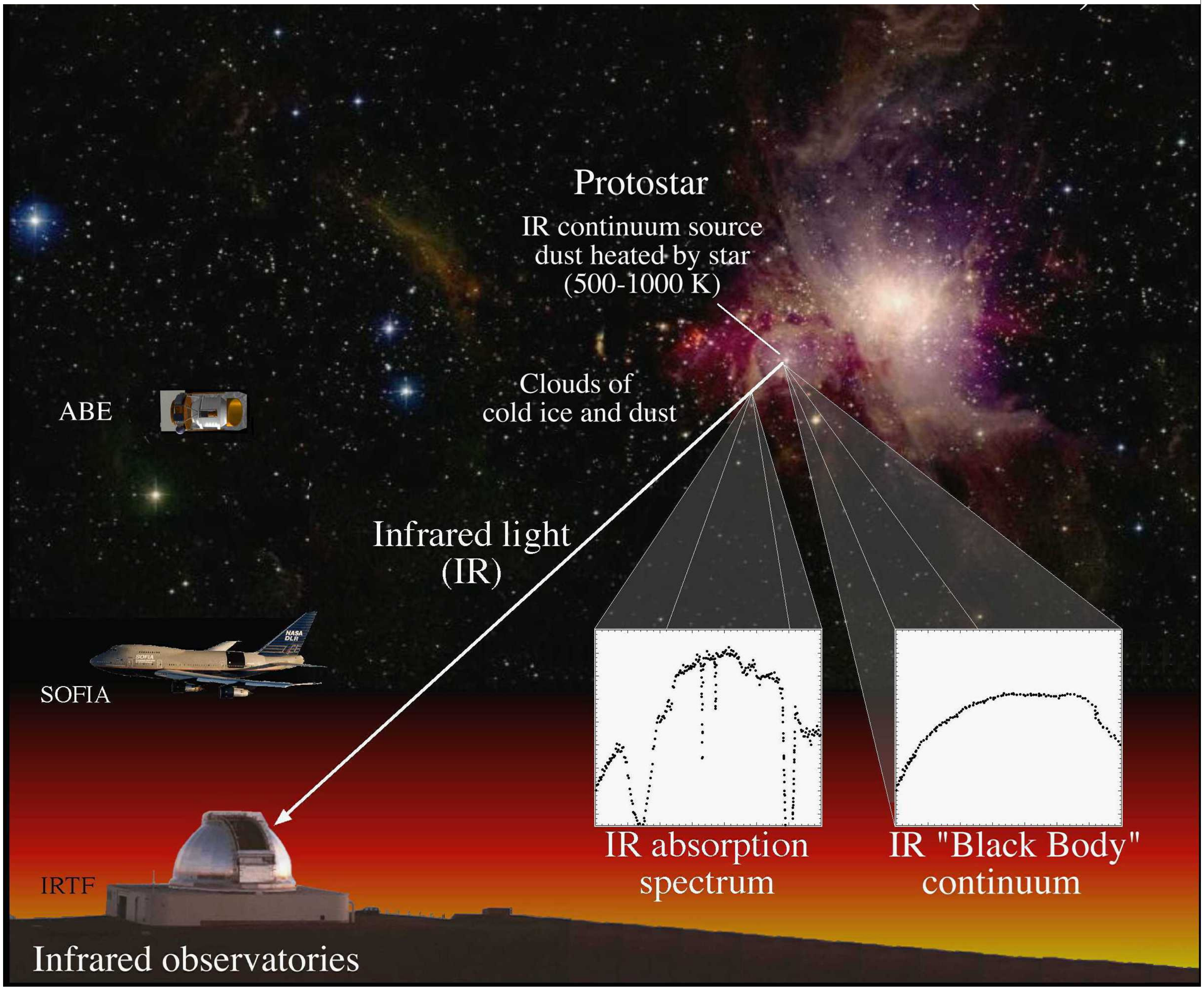
ISWA – Campinas, SP, Brazil – 4 July 2016

photo credit: Jenny Mottar

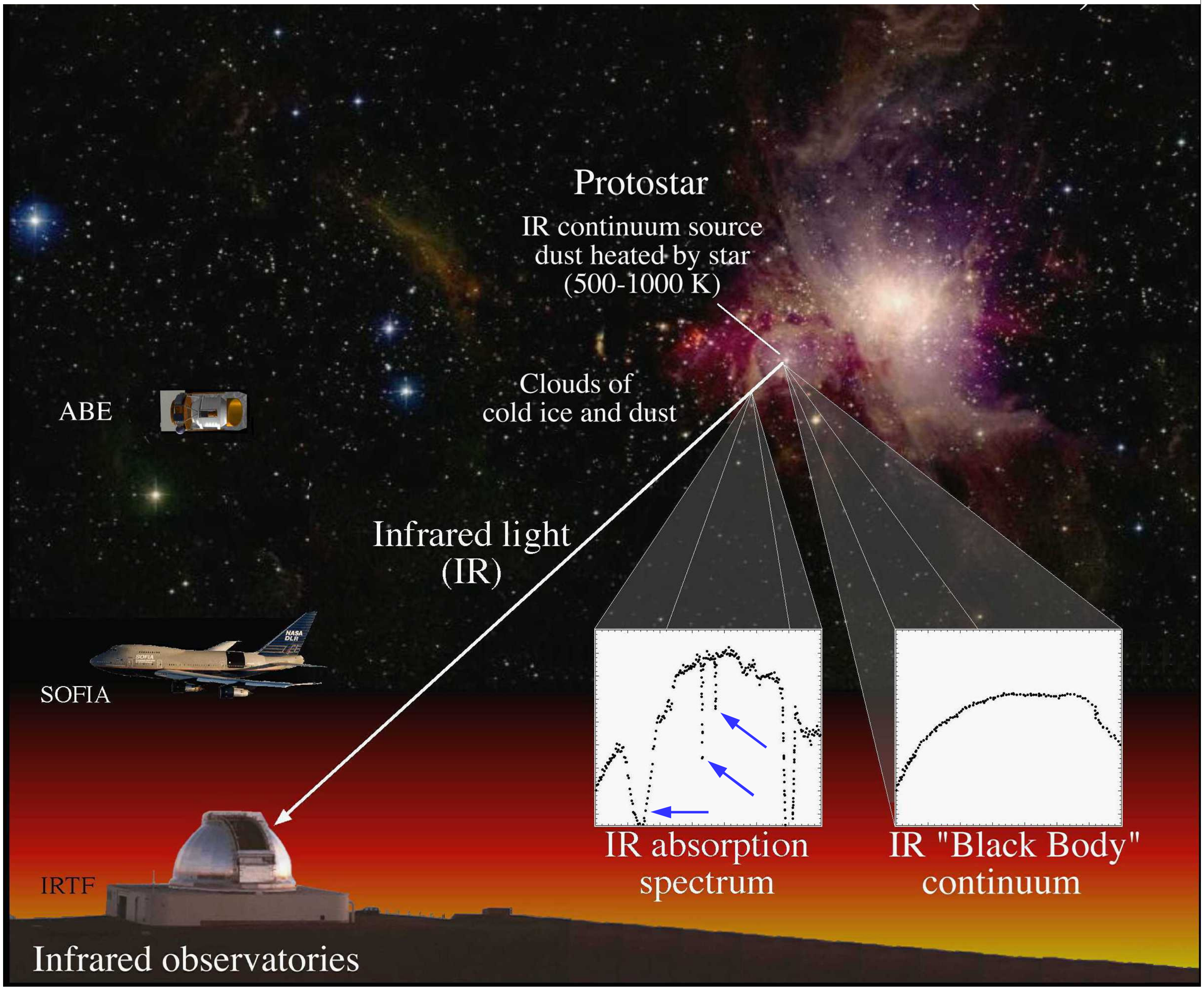
Outline

- 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



IR Observations of Molecular Clouds



Astrophysical Ices

Observation of ices in the ISM & comets

Species	RAFGL 7009S[a]	NGC 7538 IRS9[b]	W33A[c]	Elias 16[c]	Comets[c]
H_2O	100	100	100	100	100
CO	15	12	8	25	5–30
CO_2	21	15	13	18	3–20
CH_3OH	30	4–12	18	<3	0.3–5
CH_4	3.6	2	0.4	–	1
NH_3	–	13[d]	15	≤ 9	0.1–1.8
OCN^-	3.7	2	3.5	< 0.5	–

(*a*) *d'Hendecourt et al. (1996)*
(*b*) *Whittet et al. (1996)*
(*c*) *Gibb et al. (2000)*
(*d*) *Lacy et al. (1998)*

Astrophysical Ices

Observation of ices in the ISM & comets

Species	RAFGL 7009S[a]	NGC 7538 IRS9[b]	W33A[c]	Elias 16[c]	Comets[c]
H_2O	100	100	100	100	100
CO	15	12	8	25	5–30
CO_2	21	15	13	18	3–20
CH_3OH	30	4–12	18	<3	0.3–5
CH_4	3.6	2	0.4	–	1
NH_3	–	13[d]	15	≤ 9	0.1–1.8
OCN^-	3.7	2	3.5	< 0.5	–

(*a*) *d'Hendecourt et al. (1996)*
(*b*) *Whittet et al. (1996)*
(*c*) *Gibb et al. (2000)*
(*d*) *Lacy et al. (1998)*

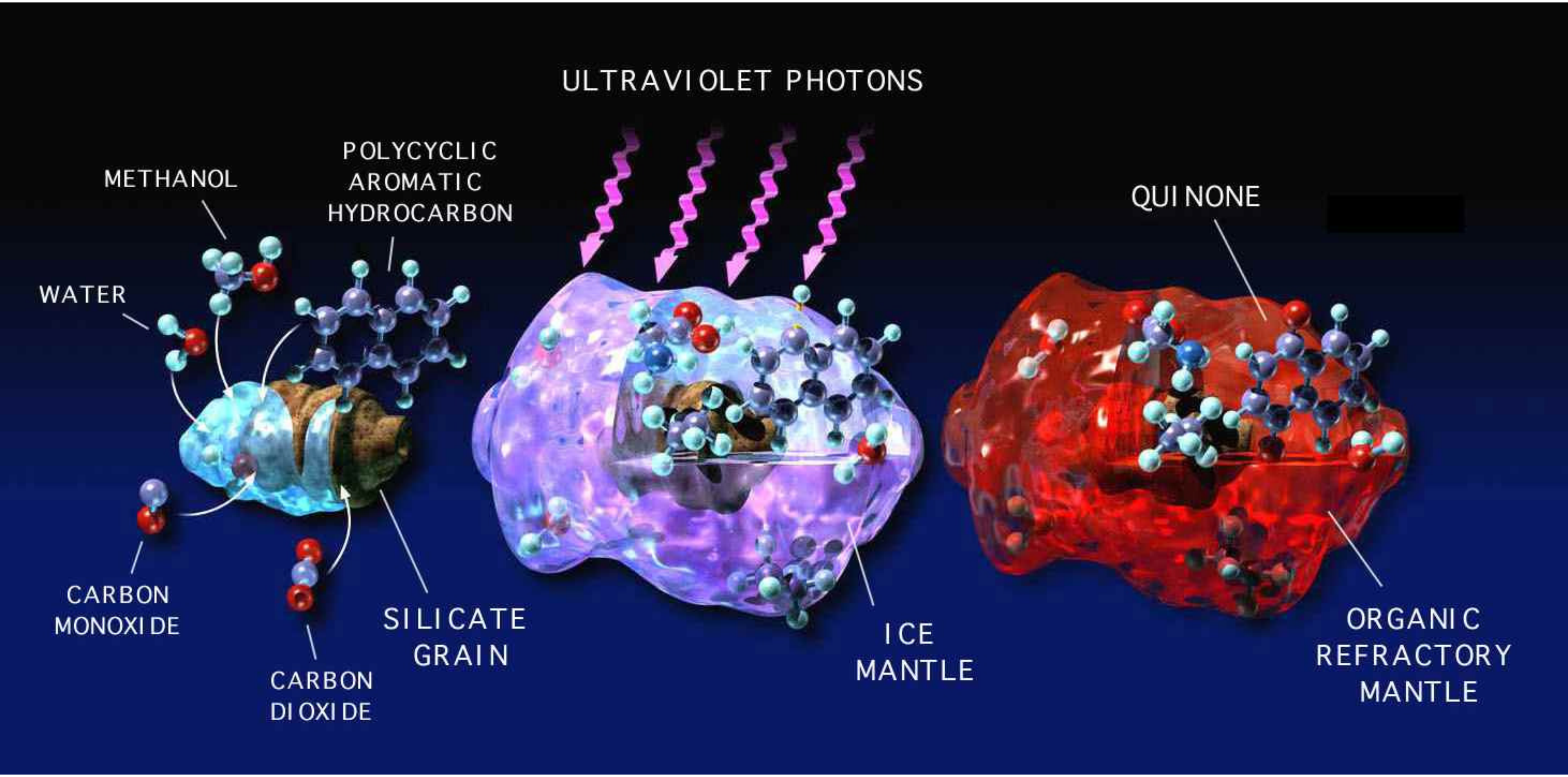
Astrophysical Ices

Observation of ices in the ISM & comets

Species	RAFGL 7009S[a]	NGC 7538 IRS9[b]	W33A[c]	Elias 16[c]	Comets[c]
H_2O	100	100	100	100	100
CO	15	12	8	25	5–30
CO_2	21	15	13	18	3–20
CH_3OH	30	4–12	18	<3	0.3–5
CH_4	3.6	2	0.4	–	1
NH_3	–	13[d]	15	≤ 9	0.1–1.8
OCN^-	3.7	2	3.5	< 0.5	–

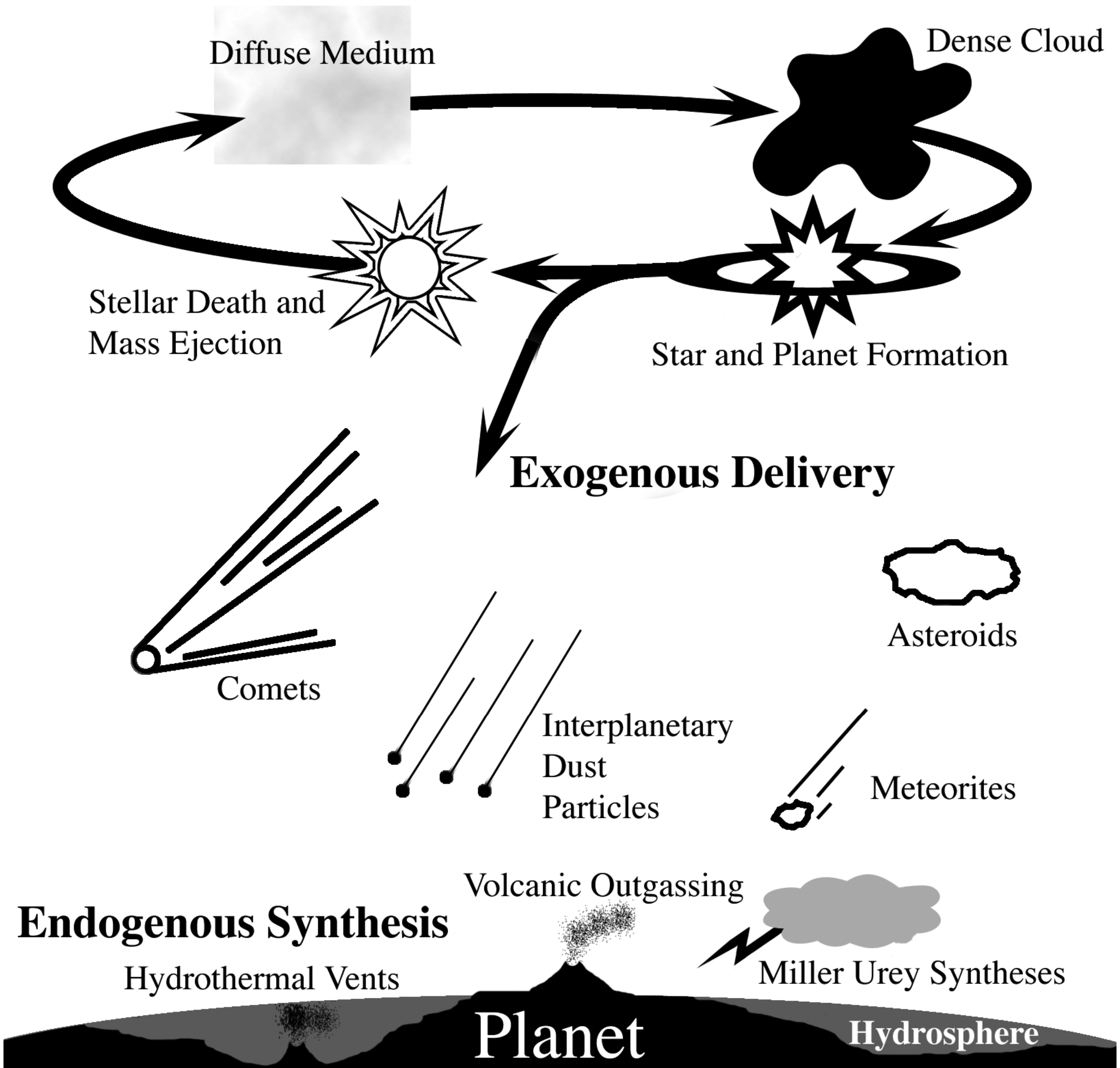
(*a*) *d'Hendecourt et al. (1996)*
(*b*) *Whittet et al. (1996)*
(*c*) *Gibb et al. (2000)*
(*d*) *Lacy et al. (1998)*

Photoprocesses on Grains (Greenberg Model)



Bernstein et al. (1999)

Delivery of Organics to the Earth



Comets

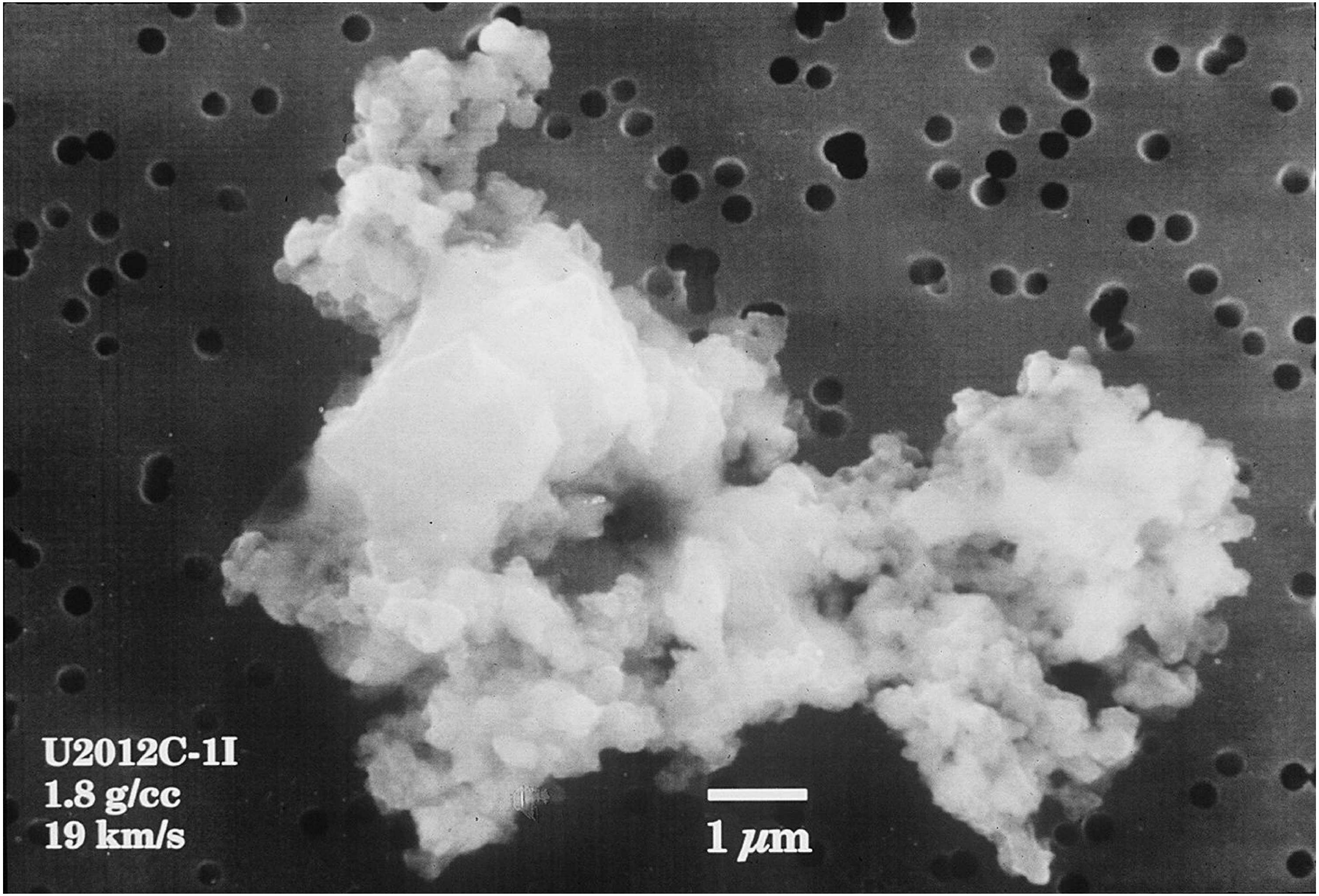
Asteroids

Seen by ROSETTA (ESA)

Asteroids

Itokawa, seen and visited by Hayabusa (JAXA)

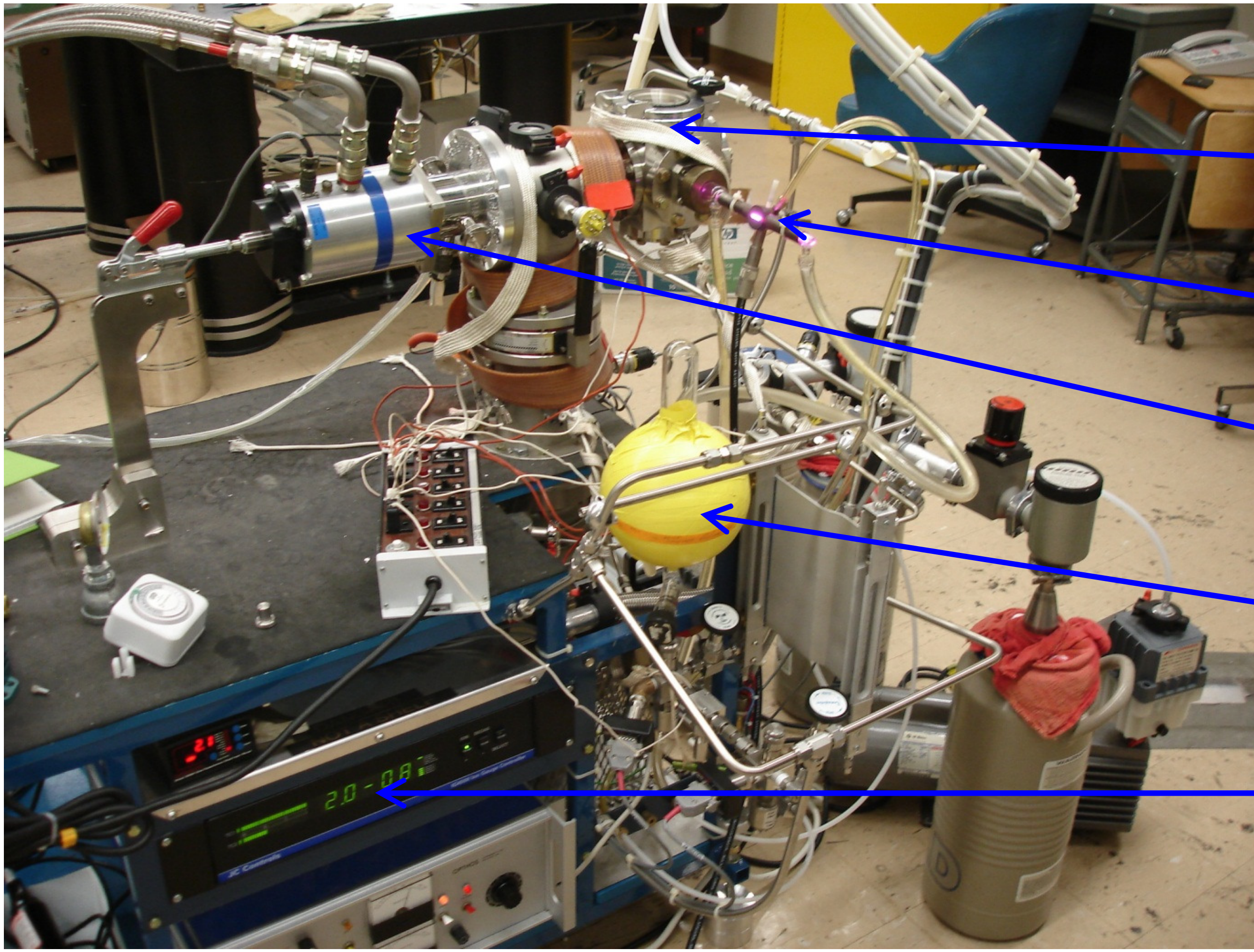
Interplanetary Dust Particles (IDPs)



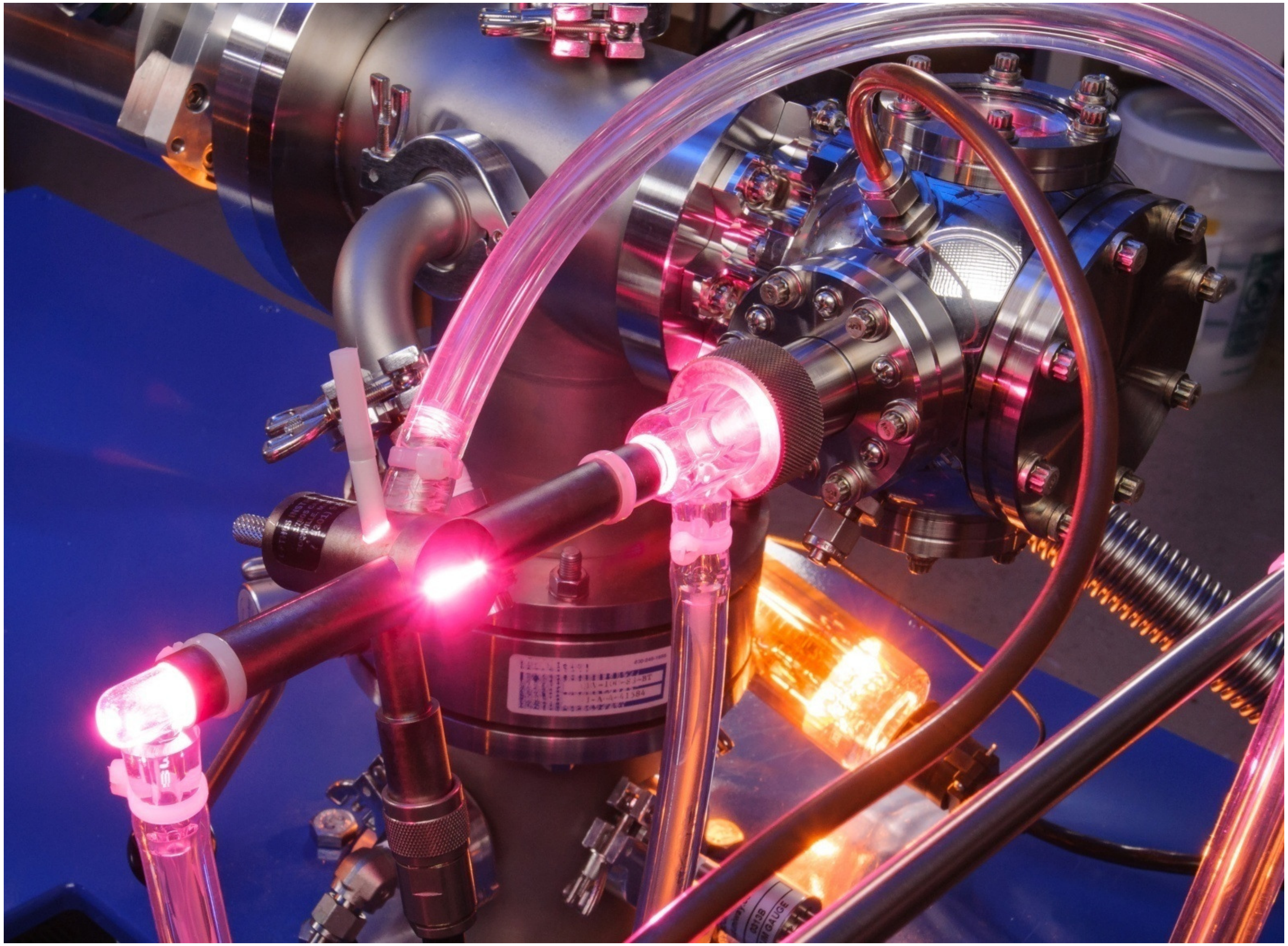
Ingredients to Make Life

Ingredients to Make Life

Experimental Set-up & Protocol



Experimental Set-up & Protocol

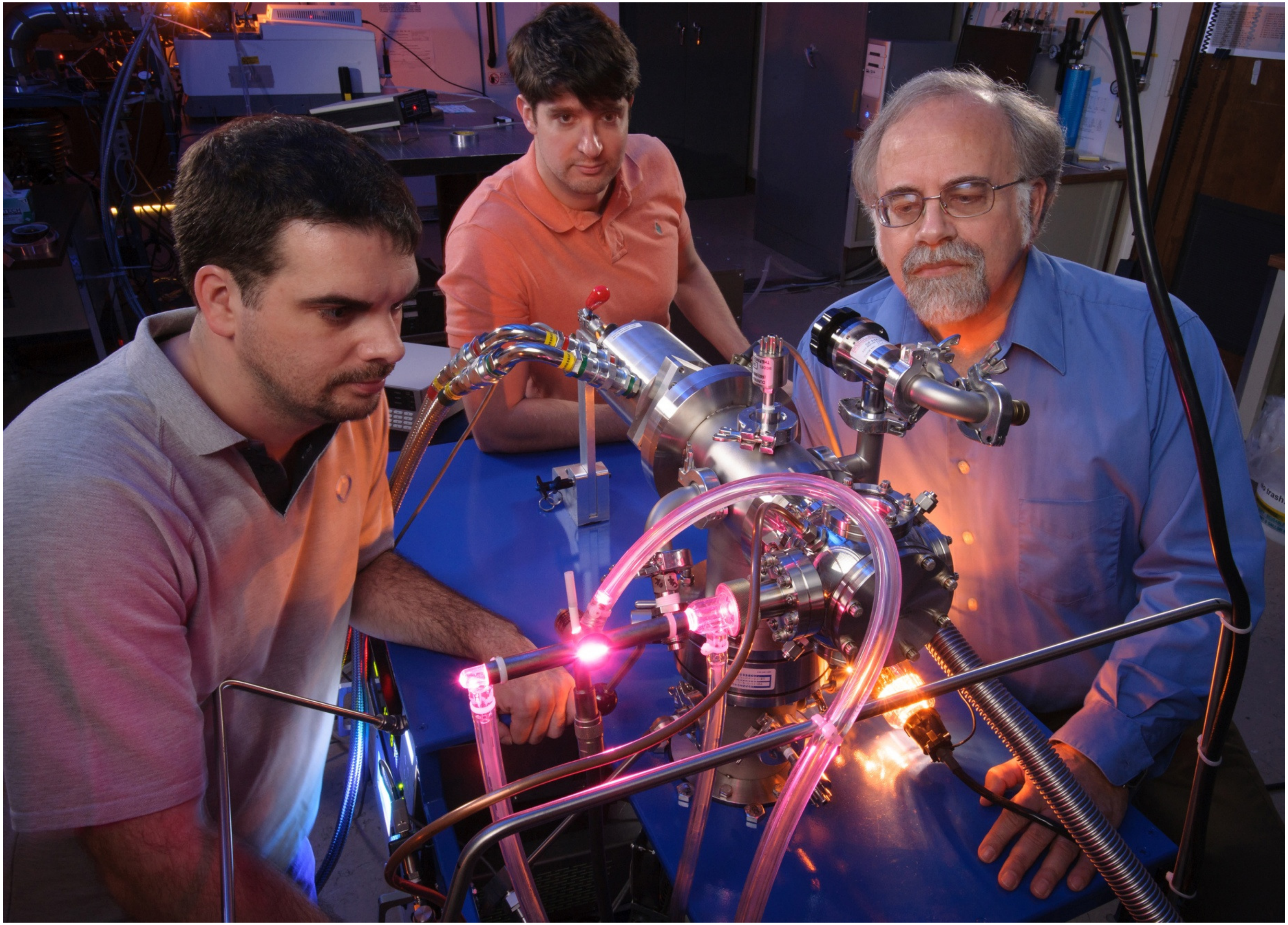


UV photon energy: Lyman α (121.6 nm) + H_2 transitions (~150–170 nm)

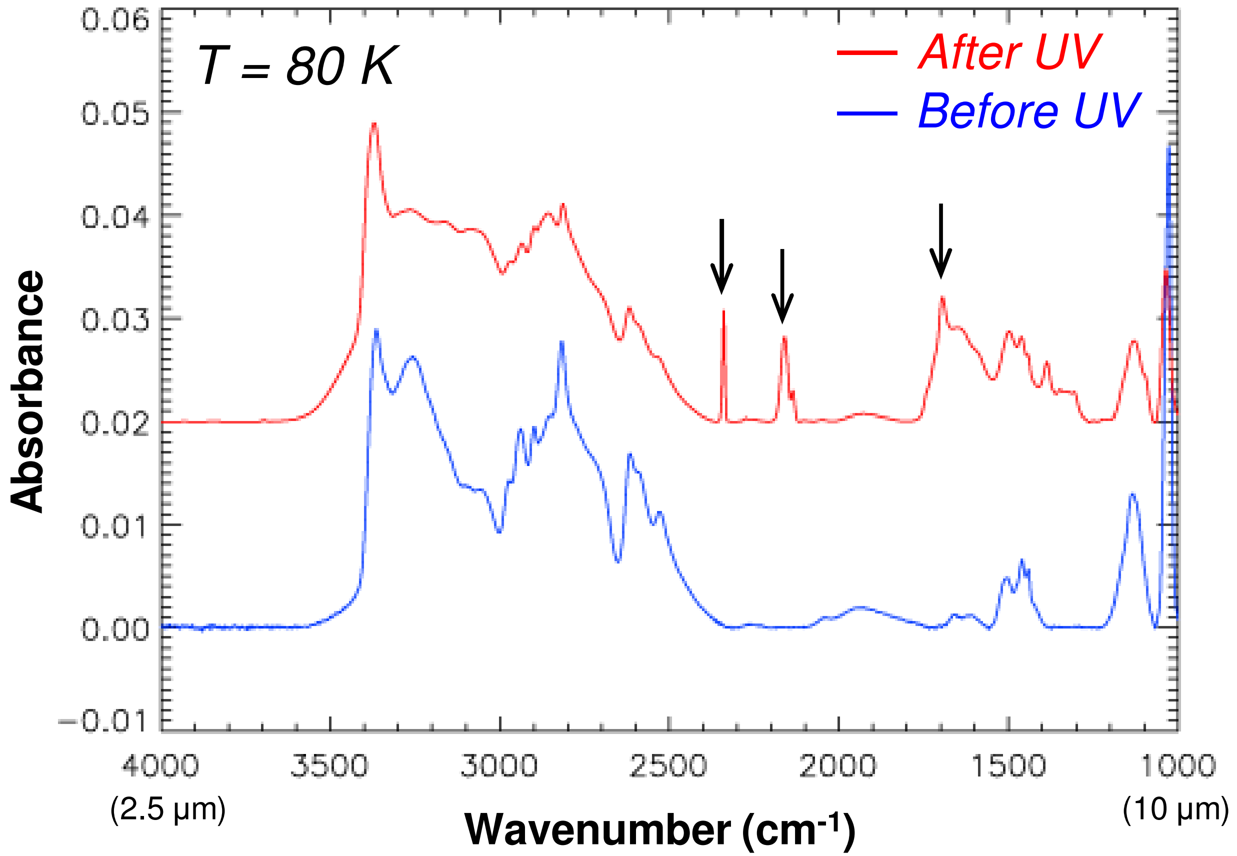
Experimental Set-up & Protocol

Horse Head Nebula (Orion)

Experimental Set-up & Protocol



UV Irradiation of Ices – IR Spectroscopy



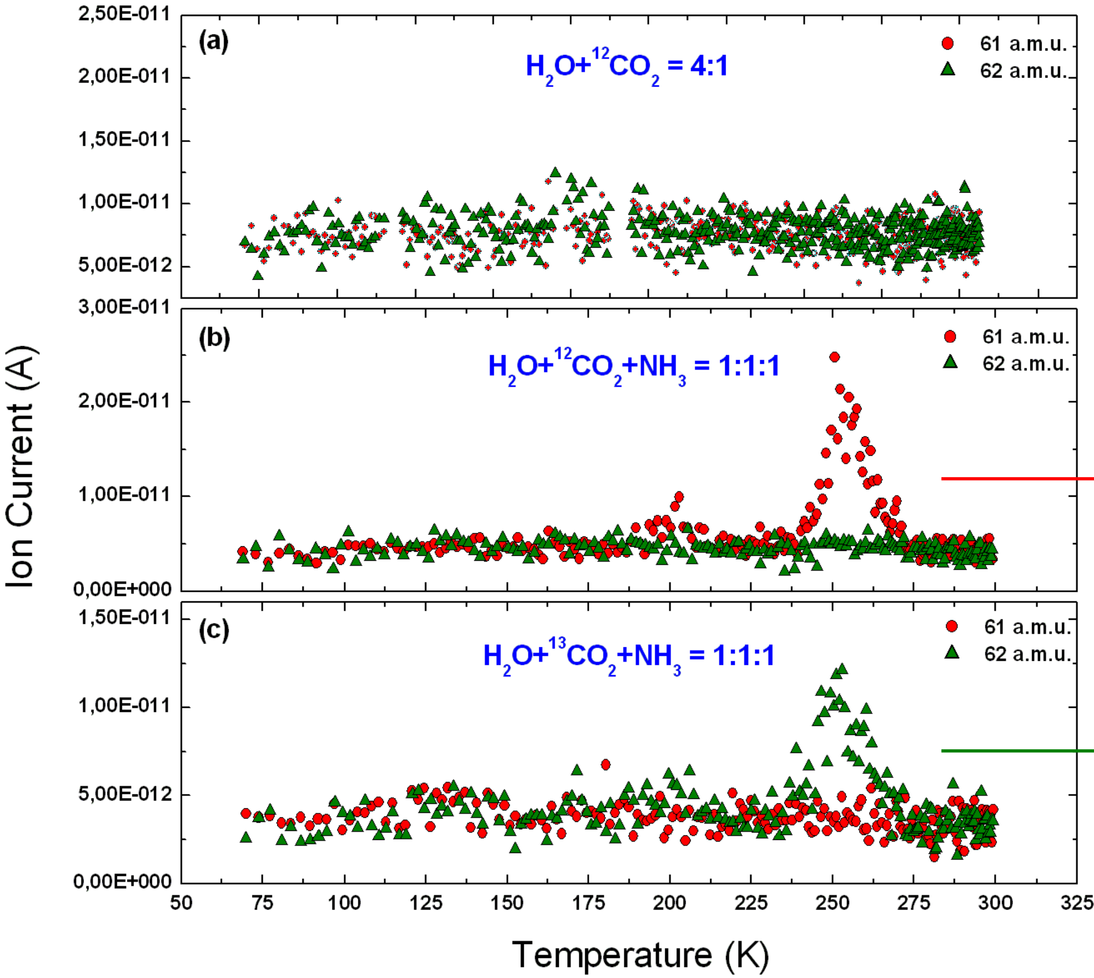
$CH_3OH:NH_3$ = 1:1 mixture, 46-hr UV irradiation @ 80 K

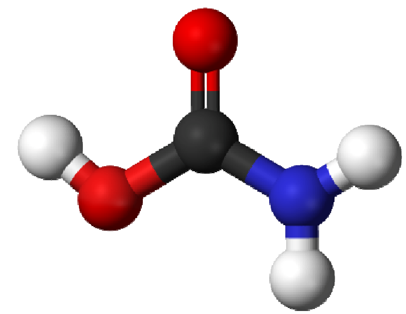
~10^7 years of irradiation in dense astrophysical environments

Position (cm^{-1})	Position (µm)	Identification of produced bands
3600–3000	3.33–3.78	Alcohols, amines, carboxylic acids (OH, NH)
3010–2815	3.32–3.55	Carbon chains (alkanes) (CH_3, CH_2)
~2880	~3.47	H_2CO (CH_2 str.)
2342	4.27	CO_2 (C=O str.)
~2260	~4.42	HNCO*
~2165	~4.62	OCN^- (C≡N str.)
2135	4.68	CO (C≡O str.)
~1850	~5.41	HCO• *
~1720	~5.81	H_2CO (C=O str.)
~1695	~5.90	NH_2CHO (C=O str.)**
~1387 ~1305	~7.21 ~7.66	NH_2CHO**
~1245	~8.03	H_2CO (CH_2 rock.)

*HNCO and HCO• : no detection in ISM in the solid phase **NH_2CHO : tentatively detected

Warm up to Room Temperature



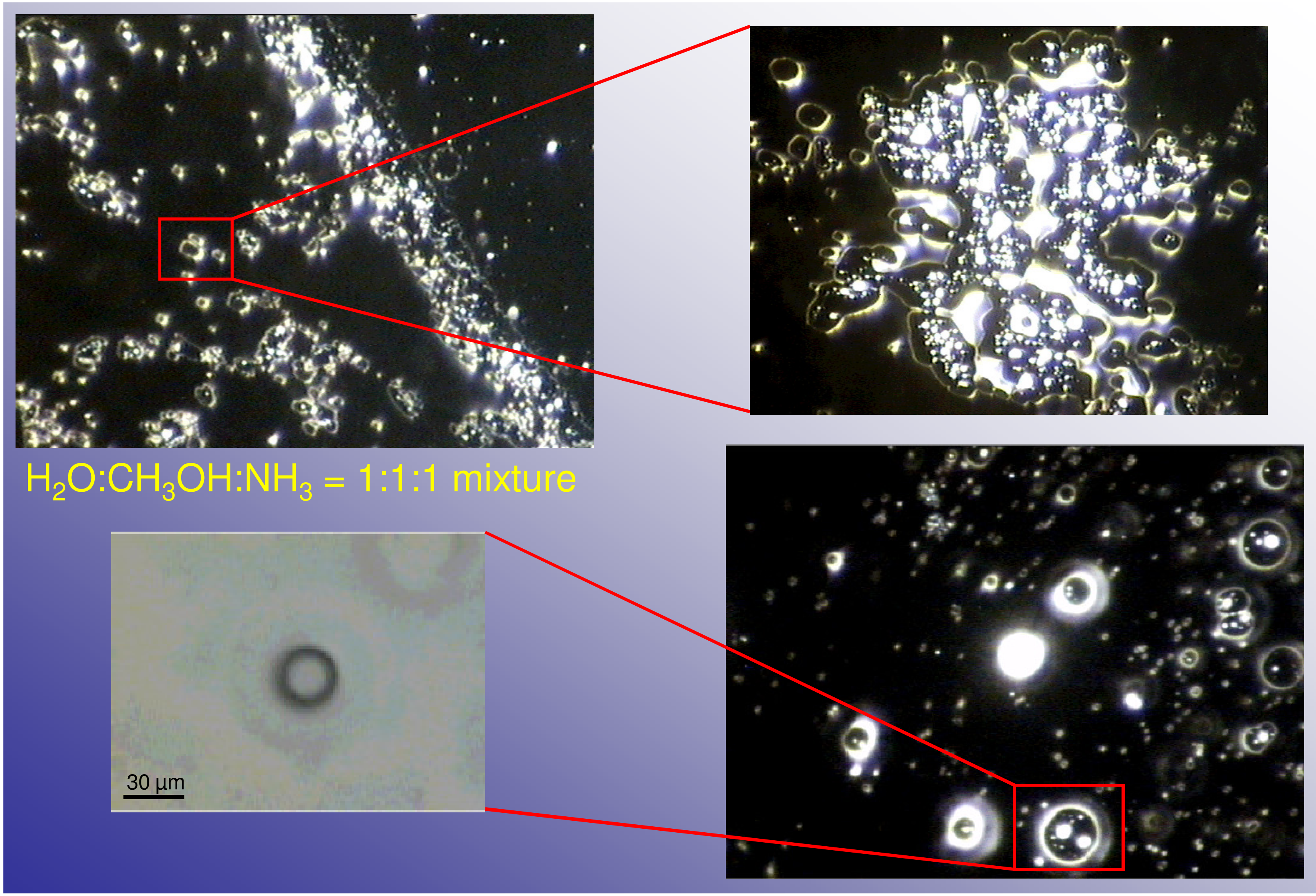


Carbamic acid
NH_2COOH
$m/z = 61$ amu

^{13}C-Carbamic acid
$NH_2{}^{13}COOH$
$m/z = 62$ amu

Chen et al. (2007)

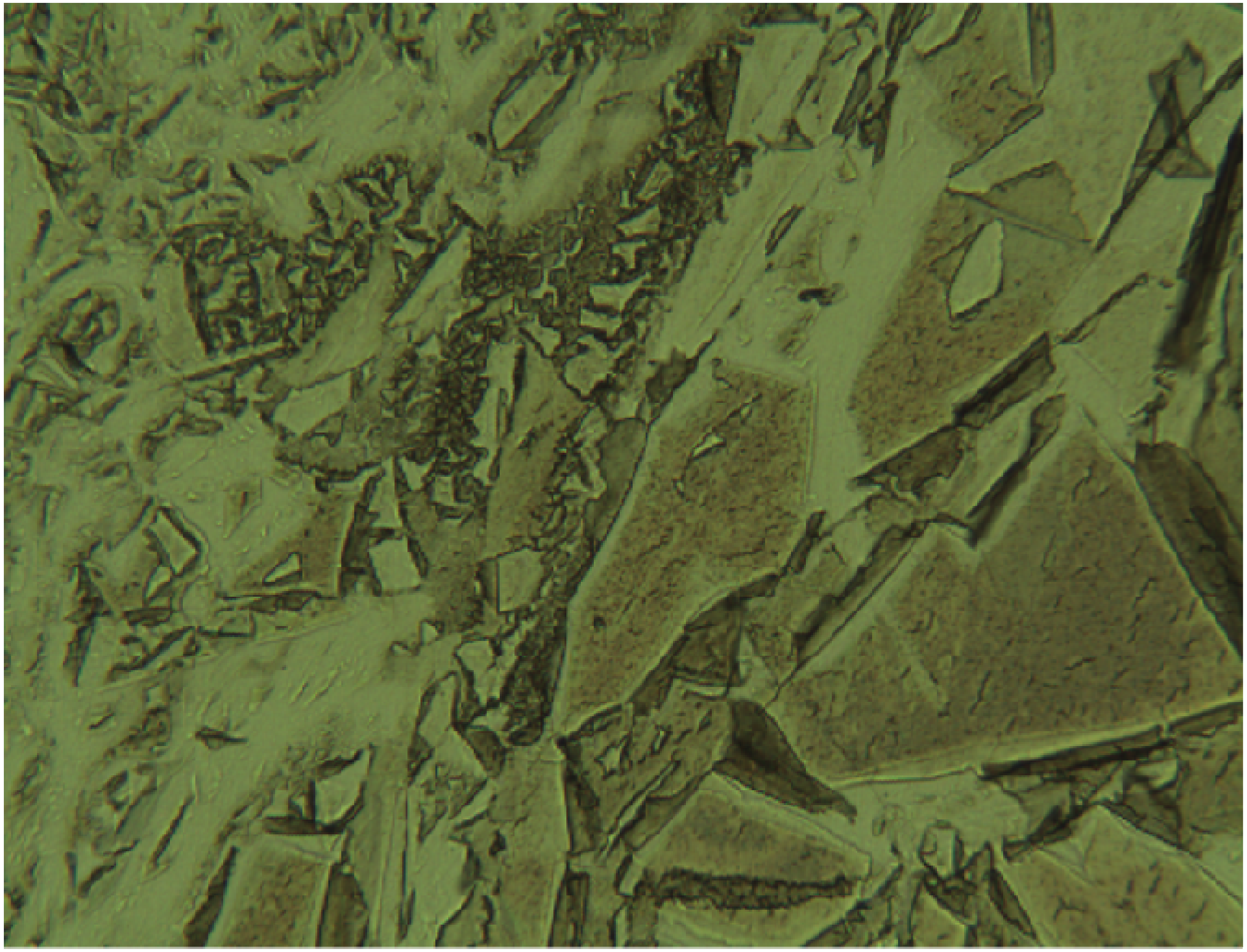
Residues – IR Microscope Images



Nuevo (2012)

Residues – IR Microscope Images

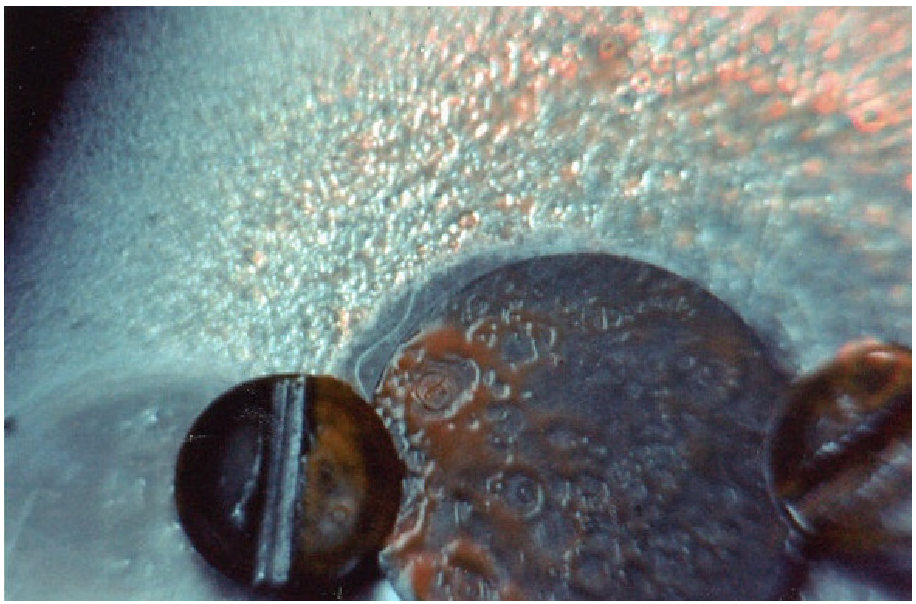
$H_2O:CO_2:NH_3$ = 1:1:1 mixture

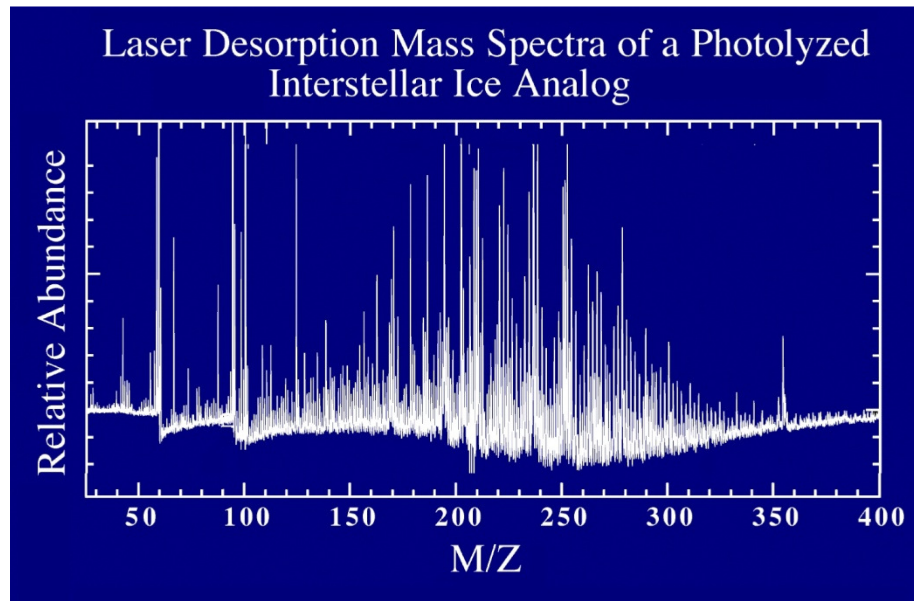


Chen et al. (2008)

Residues – Mass Spectrometry

Organic residues produced from the UV irradiation of ice mixtures consisting of H_2O, CH_3OH, CO, CO_2, NH_3, etc., analyzed with laser-desorption mass spectrometry

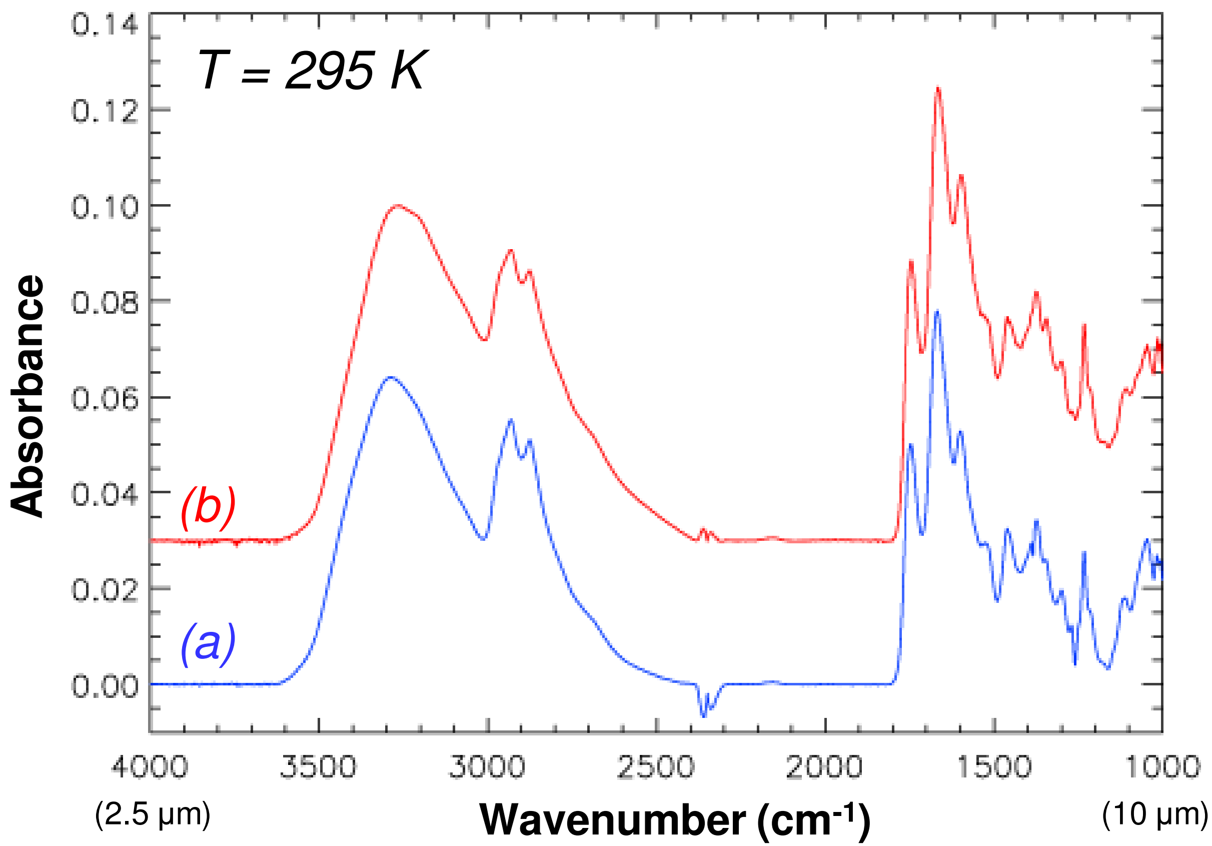




Dworkin et al. (2004)

Every peak in this mass spectrum is potentially one new molecule!

Residues – IR Spectroscopy



(*a*) $CH_3OH:NH_3$ = 1:1 (46-hr UV irradiation)
(*b*) $H_2O:CH_3OH:NH_3$ = 1:1:1 (47-hr UV irradiation)

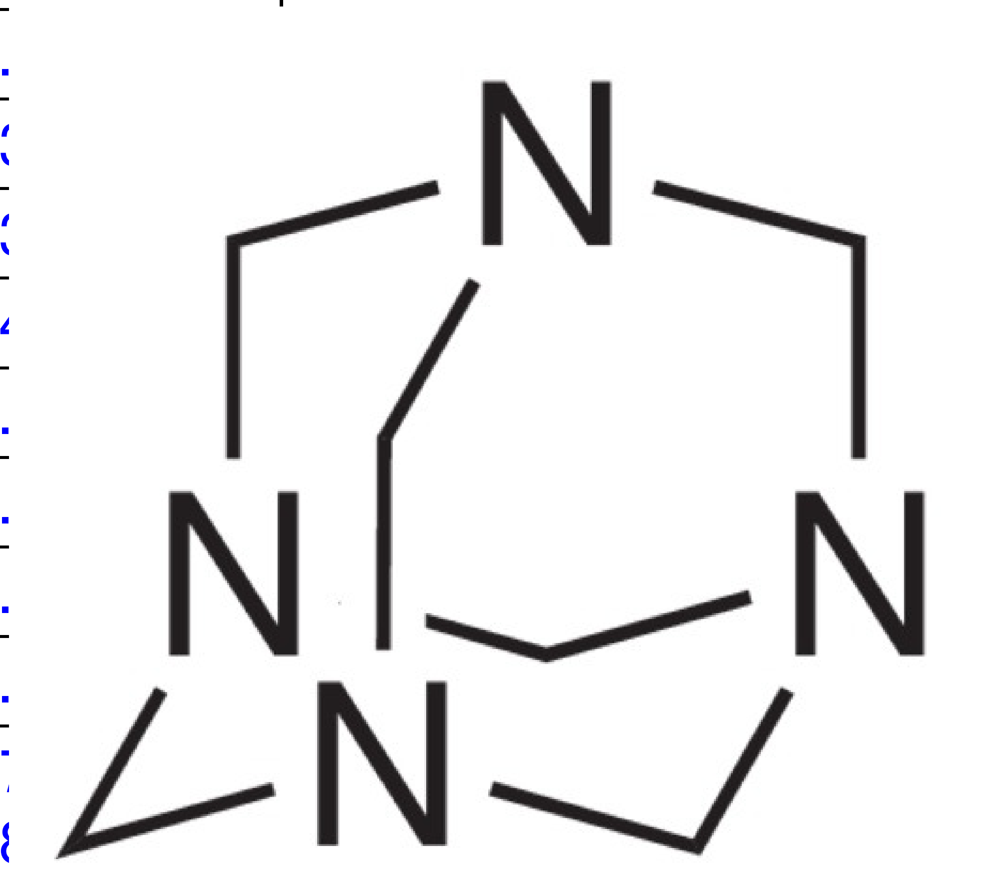
Position (cm^{-1})	Position (µm)	Identification of bands
3600–3000	3.33–3.78	Alcohols, amines, carb. acids (OH, NH)
2950–2850	3.39–3.51	Carbon chains (alkanes) (CH_3, CH_2)
~2935	~3.41	HMT[a] ($2\nu_{19}$, $\nu_2+\nu_{19}$)
~2875	~3.48	HMT[a] (CH_2 ν_{18}), NH_4^+[b] (N–H, $2\nu_4$)
~2160	~4.63	Nitriles, isonitriles (C≡N str.) (?)
1745–1730	5.73–5.78	Esters (C=O str.)
1685–1665	5.93–6.01	Ketones, amides (C=O str.)
1600–1580	6.25–6.33	Carboxylates (salts) COO^-
1470–1455	6.80–6.87	NH_4^+[b] (ν_4)
~1380 ~1235	~7.25 ~8.10	HMT[a] (CH, C–N ν_{21})
~1090	~9.17	Carboxylates (salts) COO^-
~1005	~9.95	HMT[a] (C–N ν_{22})

(a) Bernstein et al. (1995) ; (b) Wagner & Hornig (1950)

Position (cm^{-1})	Position (µm)	Identification of bands
3600–3000	3.33–3.78	Alcohols, amines, carb. acids (OH, NH)
2950–2850	3.39–3.51	Carbon chains (alkanes) (CH_3, CH_2)
~2935	~3.41	HMT[a] ($2\nu_{19}$, $\nu_2+\nu_{19}$)
~2875	~3.48	HMT[a] (CH_2 ν_{18}), NH_4^+ [b] (N–H, $2\nu_4$)
~2160	~4.63	Nitriles, isonitriles (C≡N str.) (?)
1745–1730	5.73–5.78	Esters (C=O str.)
1685–1665	5.93–6.01	Ketones, amides (C=O str.)
1600–1580	6.25–6.33	Carboxylates (salts) COO^-
1470–1455	6.80–6.87	NH_4^+ [b] (ν_4)
~1380 ~1235	~7.25 ~8.10	HMT[a] (CH, C–N ν_{21})
~1090	~9.17	Carboxylates (salts) COO^-
~1005	~9.95	HMT[a] (C–N ν_{22})

(a) Bernstein et al. (1995) ; (b) Wagner & Hornig (1950)

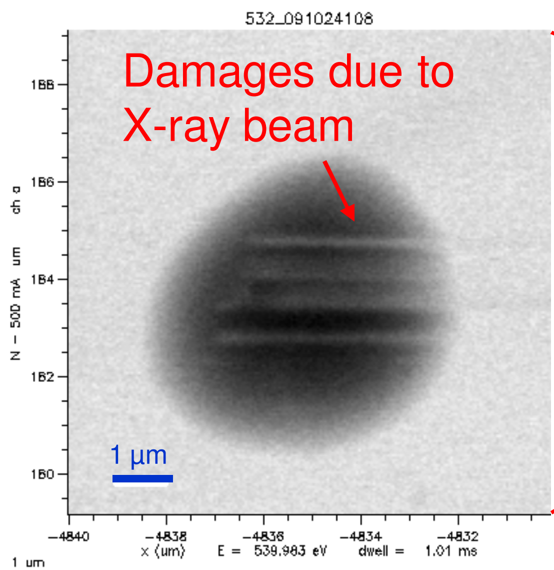
Position (cm^{-1})	Position (µm)	Identification of bands
3600–3000	3.33–3.78	Alcohols, amines, carb. acids (OH, NH)
2950–2850	3.	CH_3, CH_2)
~2935	~	
~2875	~	-H, 2ν_4)
~2160	~	) (?)
1745–1730	5.	
1685–1665	5.	)
1600–1580	6.	
1470–1455	6.	
~1380 ~1235	~ ~	
~1090	~9.17	Carboxylates (salts) COO^-
~1005	~9.95	HMT[a] (C–N ν_{22})

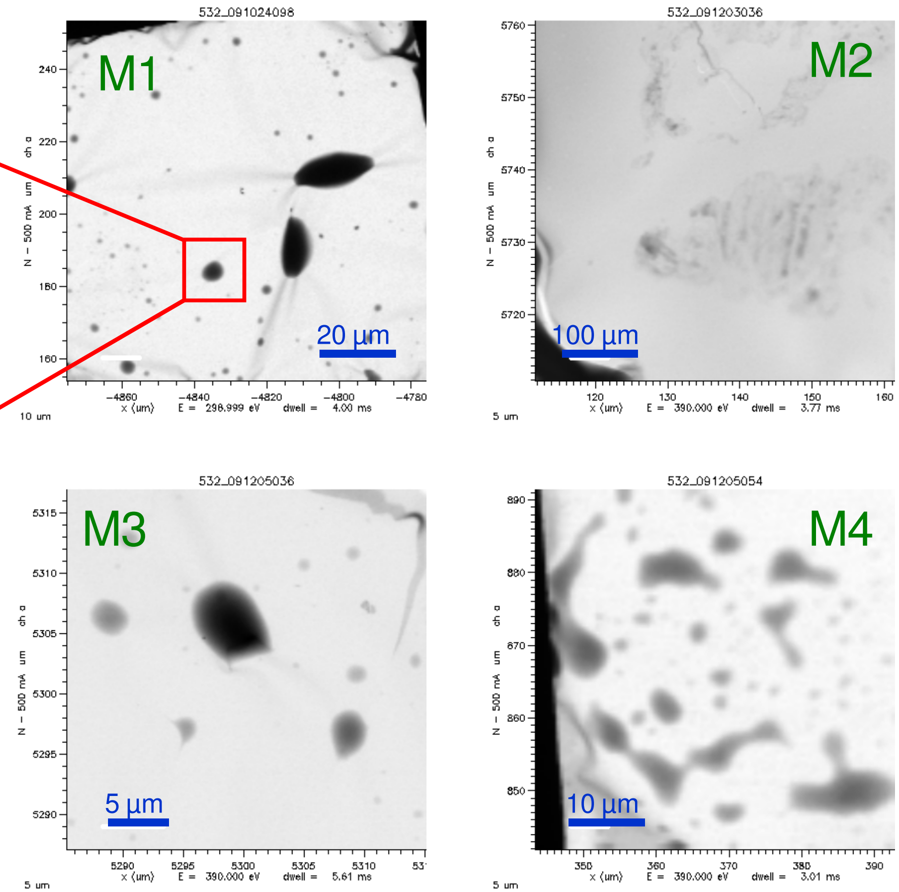


(a) Bernstein et al. (1995) ; (b) Wagner & Hornig (1950)

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 $H_2O:CH_3OH:CO:NH_3$ = 100:50:1:1

M2 $H_2O:CH_3OH:CO$ = 100:50:1

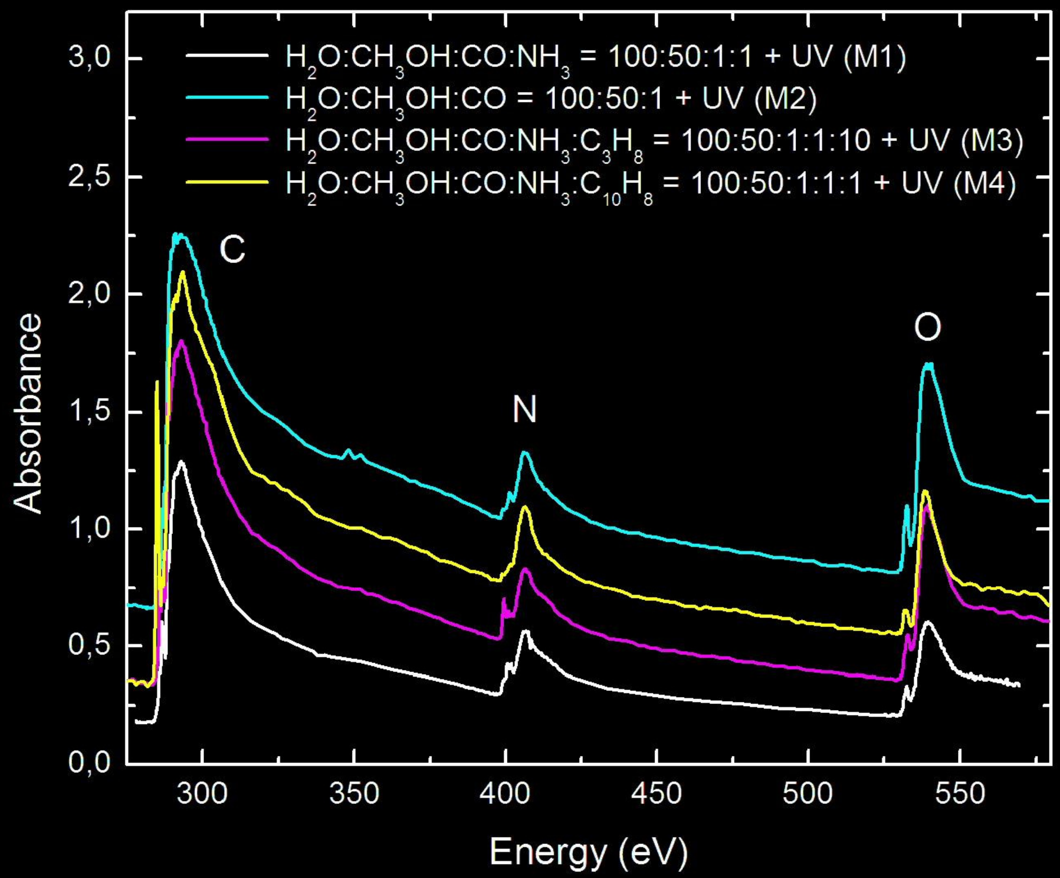
M3 $H_2O:CH_3OH:CO:NH_3:C_3H_8$ = 100:50:1:1:10

M4 $H_2O:CH_3OH:CO:NH_3:C_{10}H_8$ = 100:50:1:1:1

Nuevo et al. (2011)

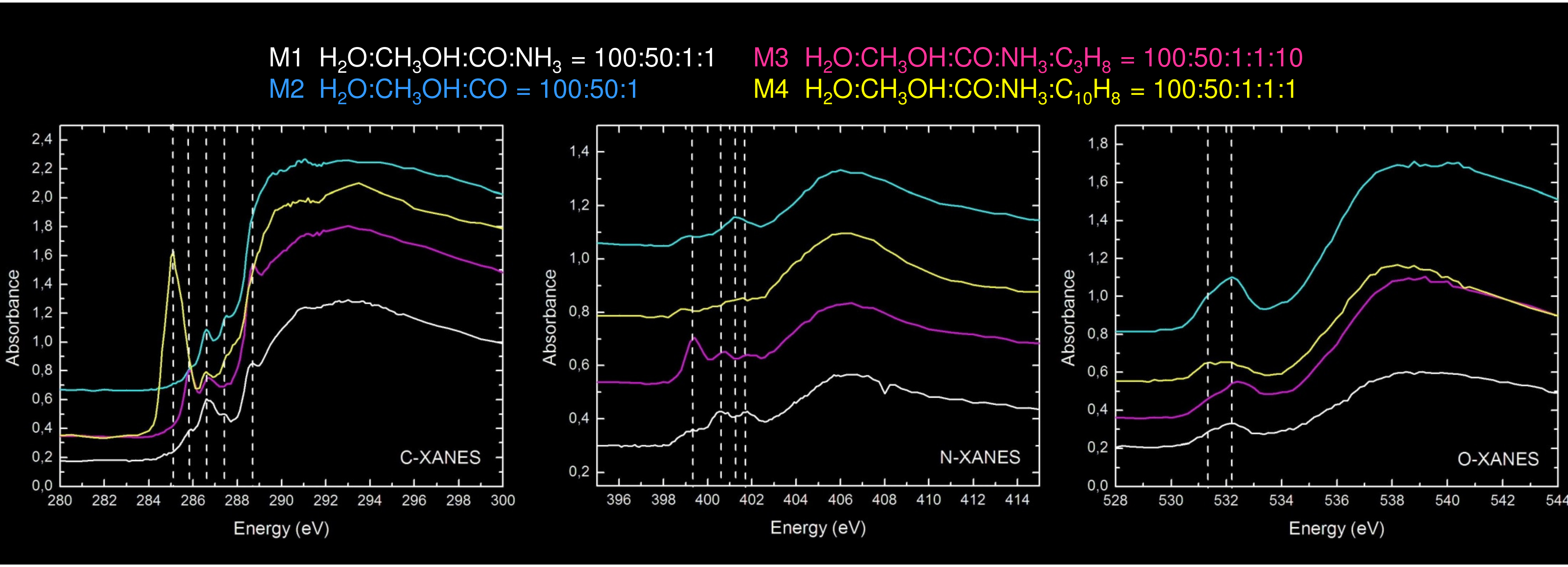
Residues – XANES Spectroscopy

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



285.1 eV CH_x (aromatic)
285.8 eV C=C
286.6 eV C≡N or C=C–C=O
287.4 eV CH_x (aliphatic)
288.7 eV O–C=O (carboxyl)

399.3 eV C≡N
398.8 eV C=N (?)
401.7 eV CONH (amide)

531.3 eV C=O (ketone)
532.2 eV O–C=O (carboxyl)

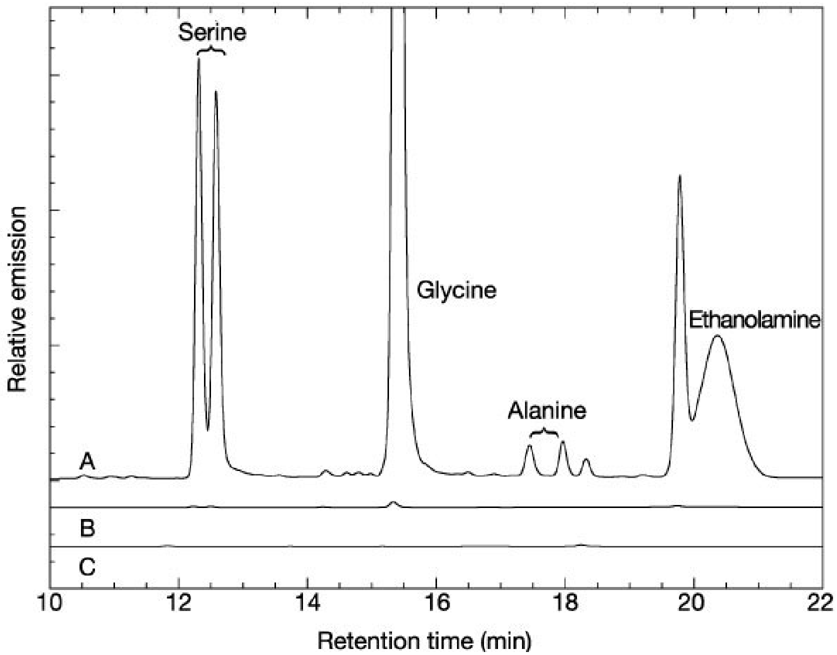
Elemental composition: N/C 0.11–0.28
O/C 0.43–0.61

⇒ ~2 times larger than Stardust particles

Nuevo et al. (2011)

Formation of Complex Organics

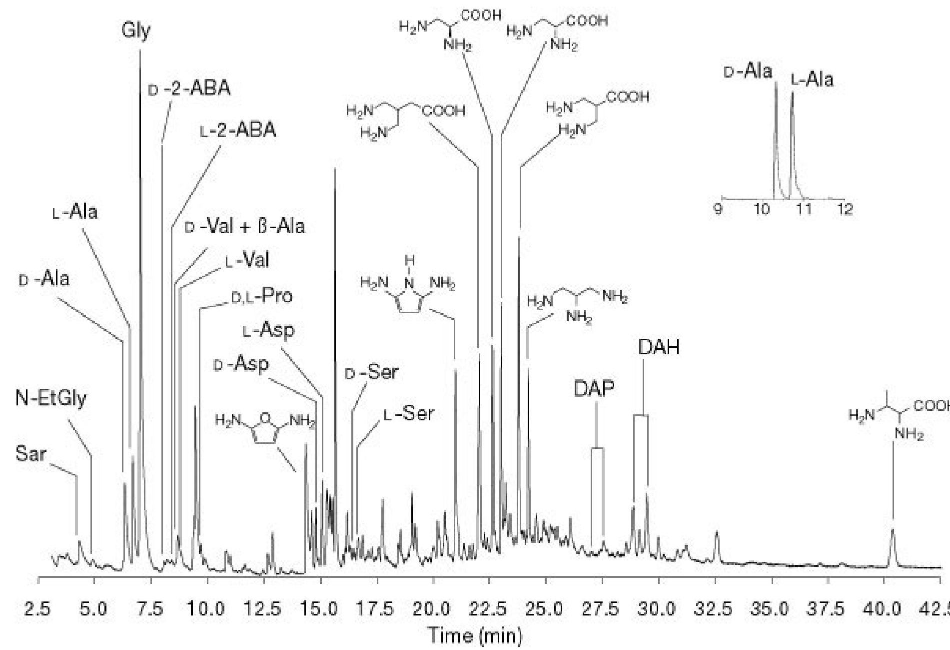
High-performance liquid chromatography (HPLC)



$(H_2O:CH_3OH:NH_3:HCN = 20:2:1:1)$

Bernstein et al. (2002a)

Gas chromatography – mass spectrometry (GC–MS)



$(H_2O:CH_3OH:NH_3:CO:CO_2 = 2:1:1:1:1)$

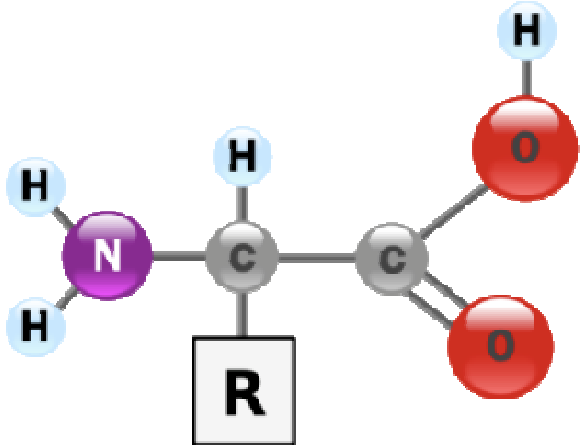
Muñoz Caro et al. (2002)

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

Formation of Complex Organics

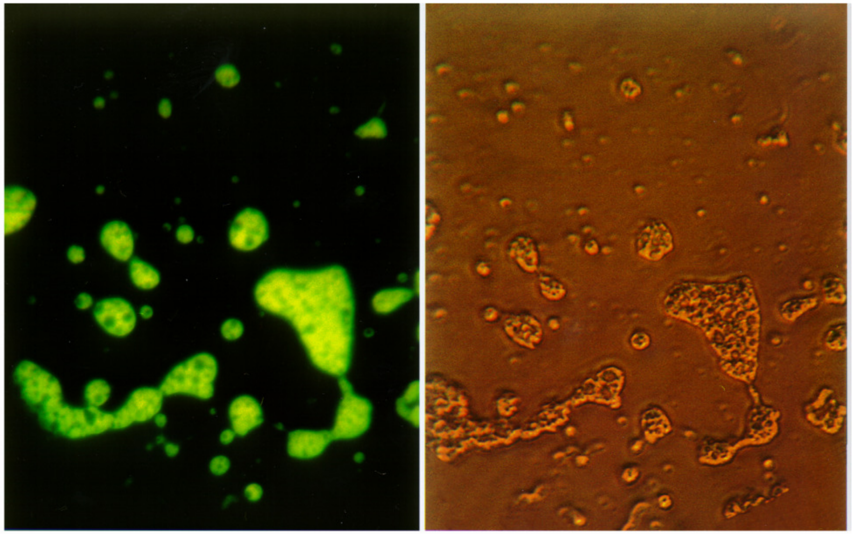
Starting with ice mixtures containing H_2O
+ carbon source(s) [CH_3OH, CO, CO_2, CH_4, and/or HCN]
+ nitrogen source(s) [NH_3, N_2, and/or HCN]
+ UV photo-irradiation at low temperature

Amino acids



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

Amphiphilic compounds

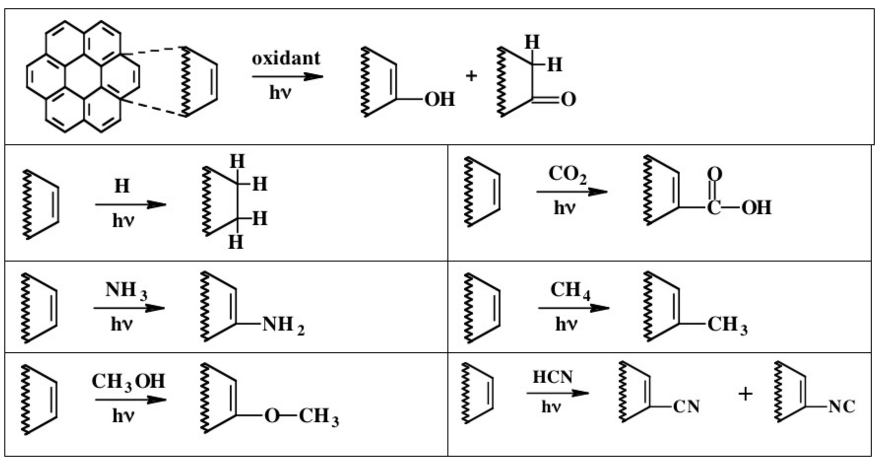


Dworkin et al. (2001)

Formation of Complex Organics

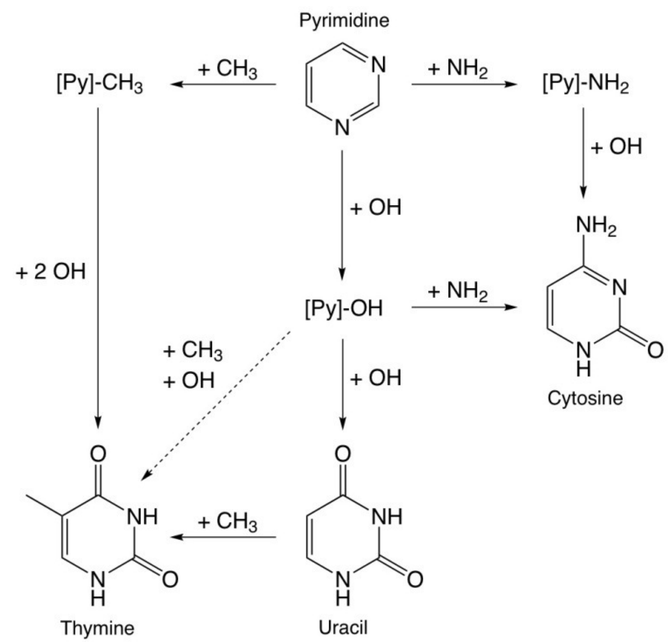
Starting with ice mixtures containing H_2O
+ aromatic compounds [PAHs or *N*-heterocycles]
+ H_2, CH_3OH, CO_2, CH_4, NH_3, HCN, etc.
+ UV photo-irradiation at low temperature

Functionalized PAHs



Bernstein et al. (2002b,c)

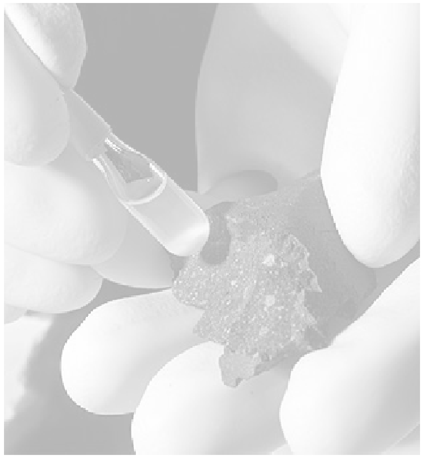
Nucleobases



Nuevo et al. (2009, 2012, 2014)
Materese et al. (2013)
Sandford et al. (2014)

Sugars: Background & Motivation

- Laboratory experiments have shown that the photochemistry of simple ices (H_2O, CH_3OH, 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]*.

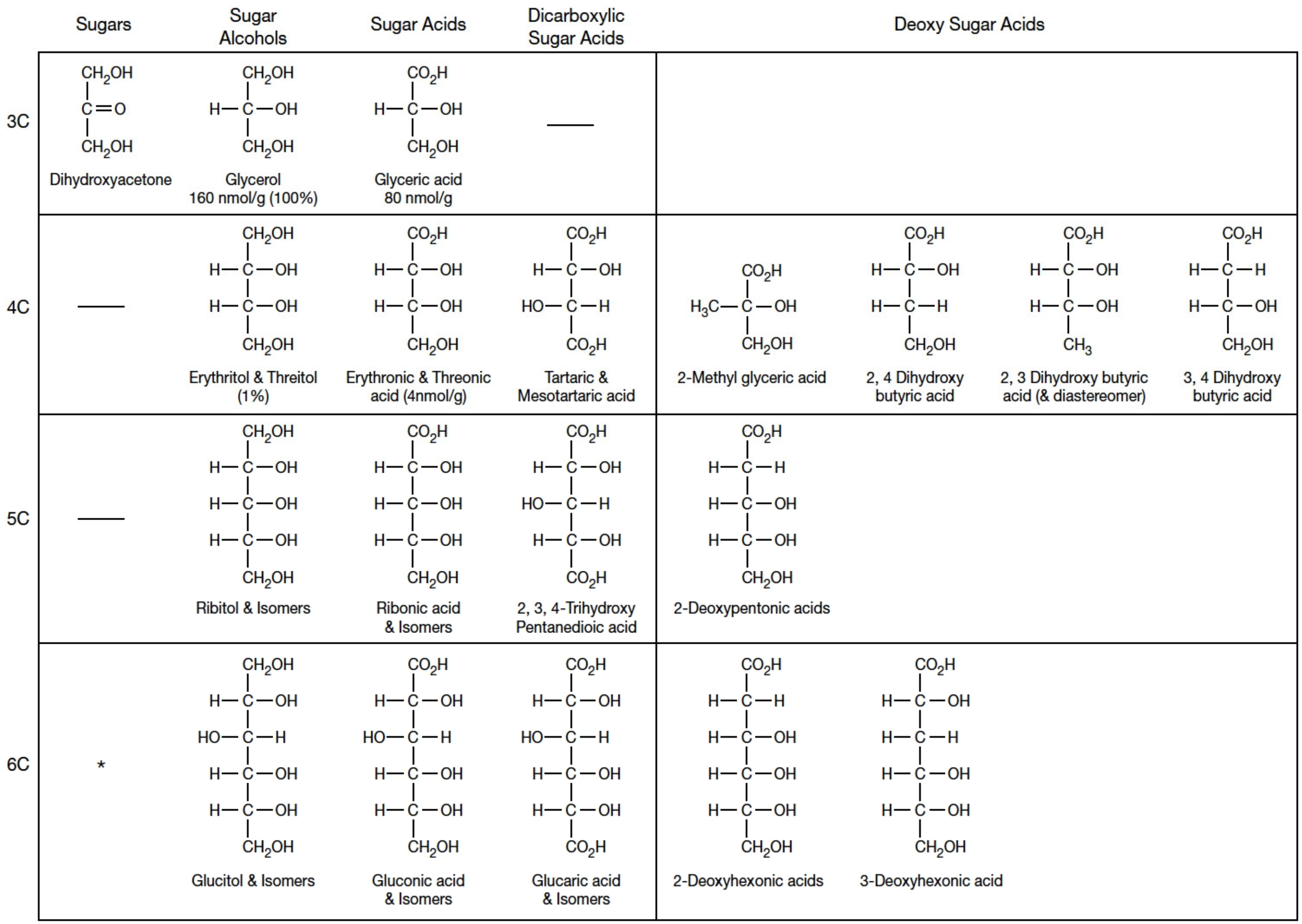
Sugars: Background & Motivation

- Laboratory experiments have shown that the photochemistry of simple ices (H_2O, CH_3OH, 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]*.

Sugars: Background & Motivation

Sugar-related compounds in Murchison and Murray



Cooper et al. (2001)

Sugars: Background & Motivation

- Laboratory experiments have shown that the photochemistry of simple ices (H_2O, CH_3OH, 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]*.

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 >C_4 sugar (and some sugar acids) can either be in a linear or a cyclic configuration.
- For C_5 and C_6 sugars (aldoses), cyclic forms include furanose and pyranose forms, and each of these forms has two anomeric conformations (α and β).

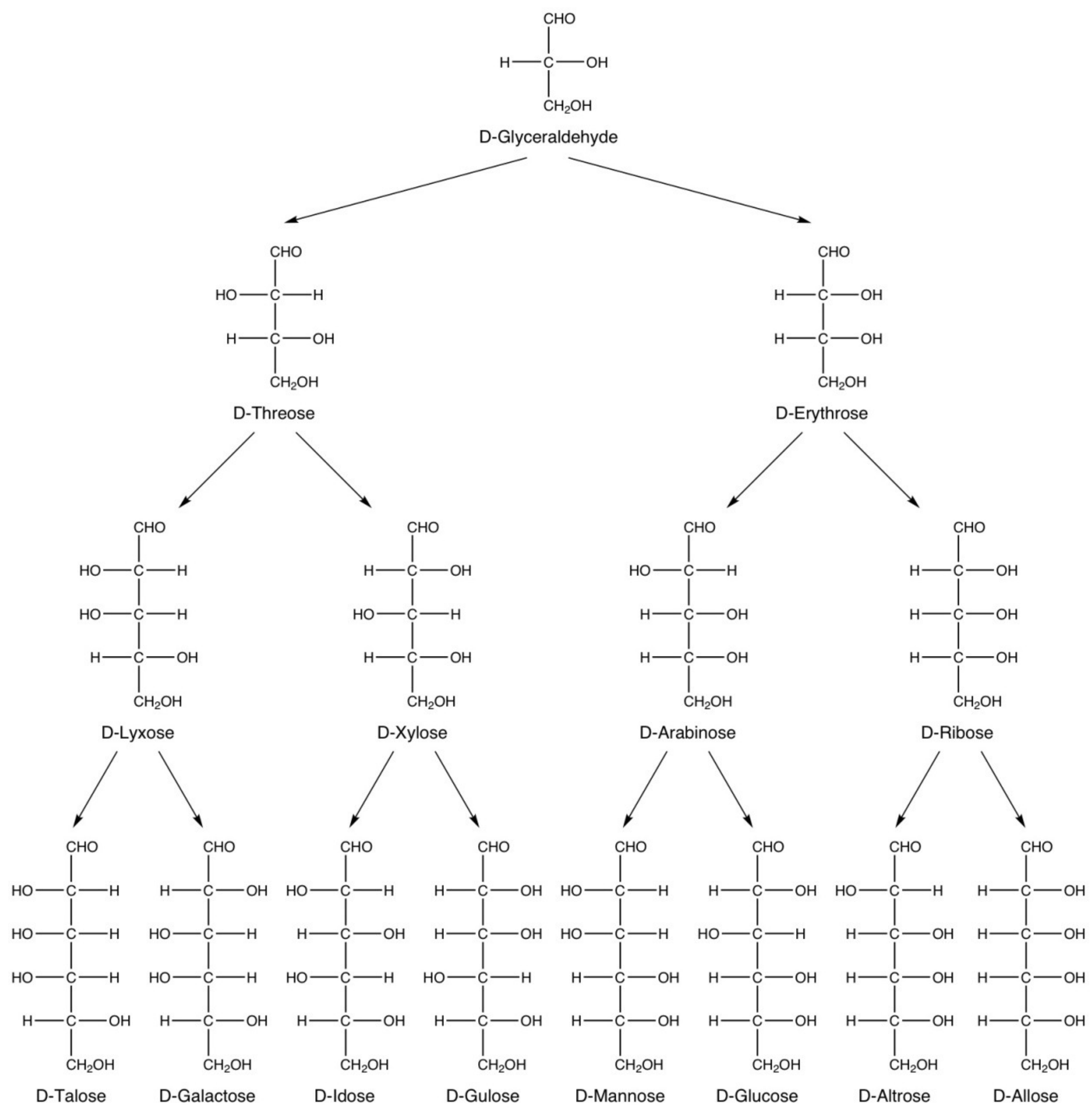
Sugars (Aldoses)

3 C atoms

4 C atoms

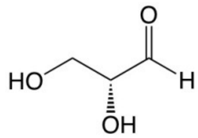
5 C atoms

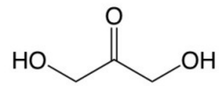
6 C atoms



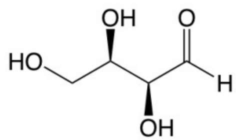
Sugars (Aldoses)

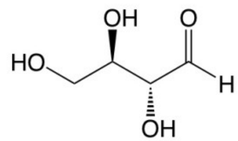
3 C atoms


D-Glyceraldehyde

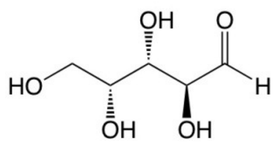

Dihydroxyacetone

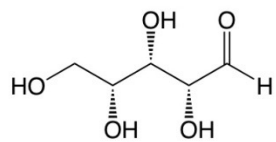
4 C atoms

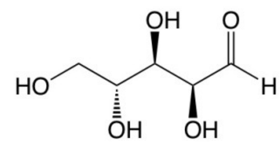

D-Threose

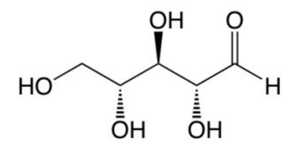

D-Erythrose

5 C atoms

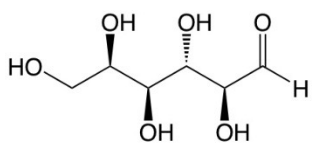

D-Lyxose

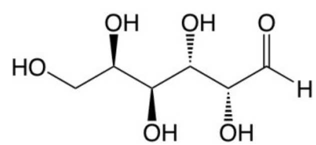

D-Xylose

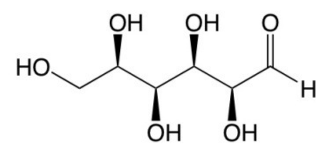

D-Arabinose

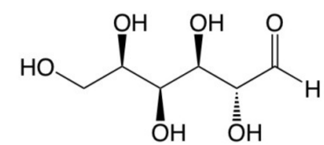

D-Ribose

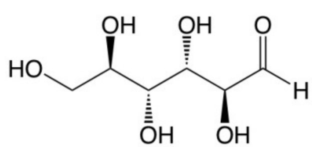
6 C atoms

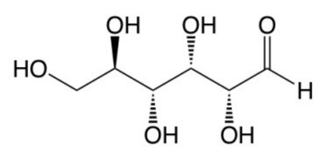

D-Talose

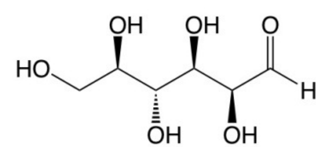

D-Galactose

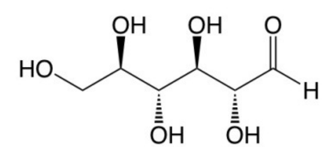

D-Idose


D-Gulose


D-Mannose

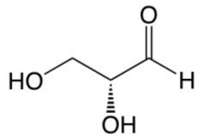

D-Glucose


D-Altrose

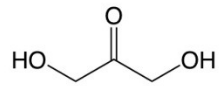

D-Allose

Sugars (Aldoses)

3 C atoms

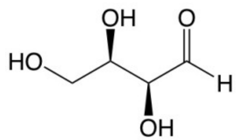


D-Glyceraldehyde

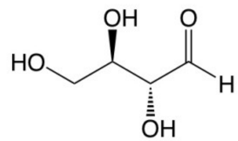


Dihydroxyacetone

4 C atoms

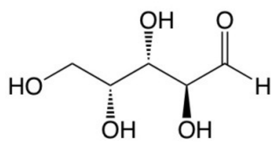


D-Threose

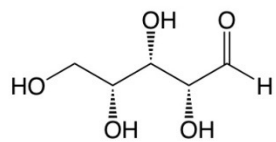


D-Erythrose

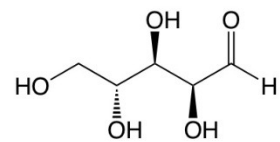
5 C atoms



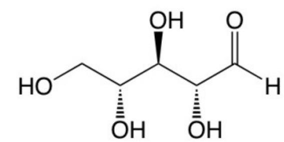
D-Lyxose



D-Xylose

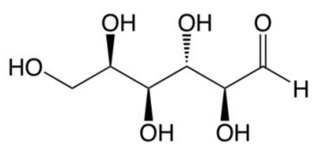


D-Arabinose

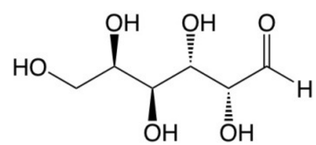


D-Ribose

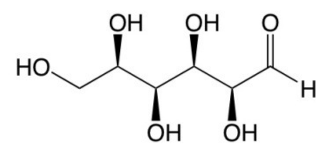
6 C atoms



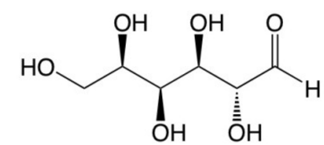
D-Talose



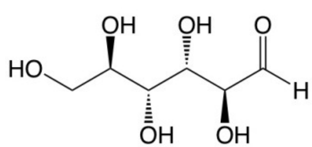
D-Galactose



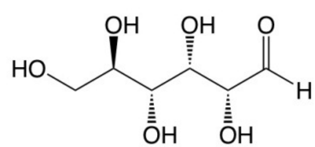
D-Idose



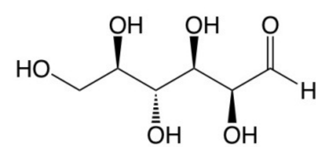
D-Gulose



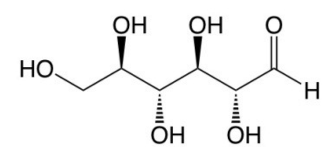
D-Mannose



D-Glucose

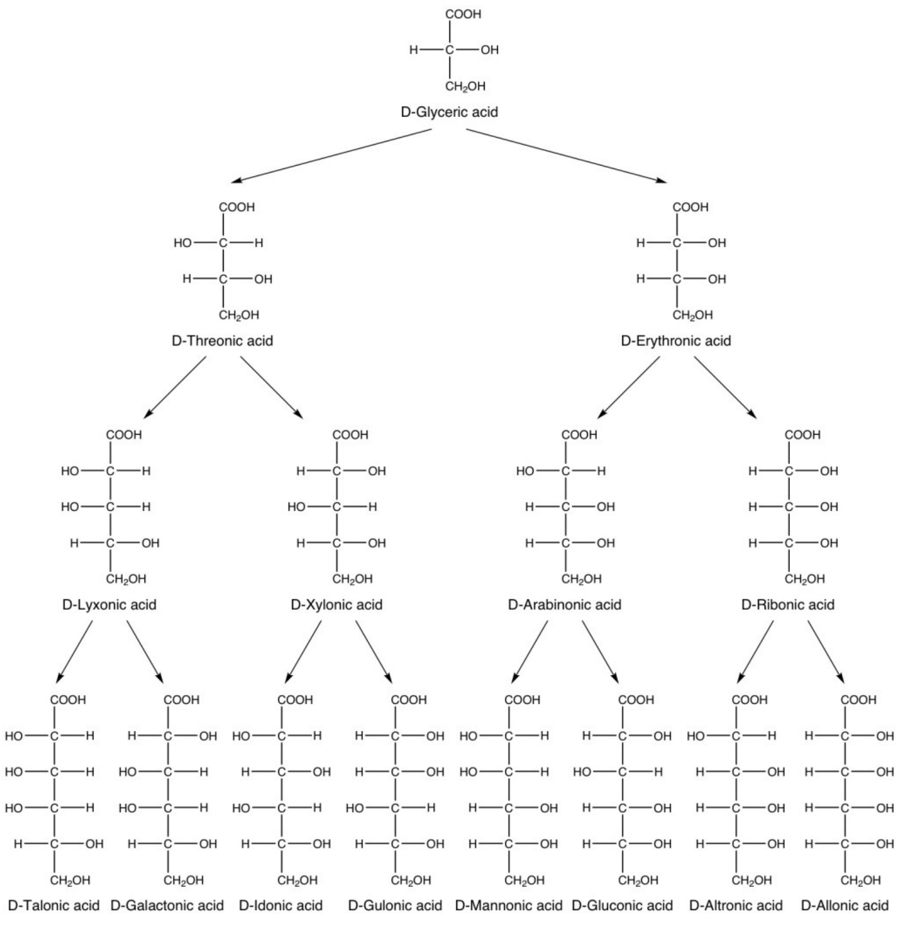


D-Altrose

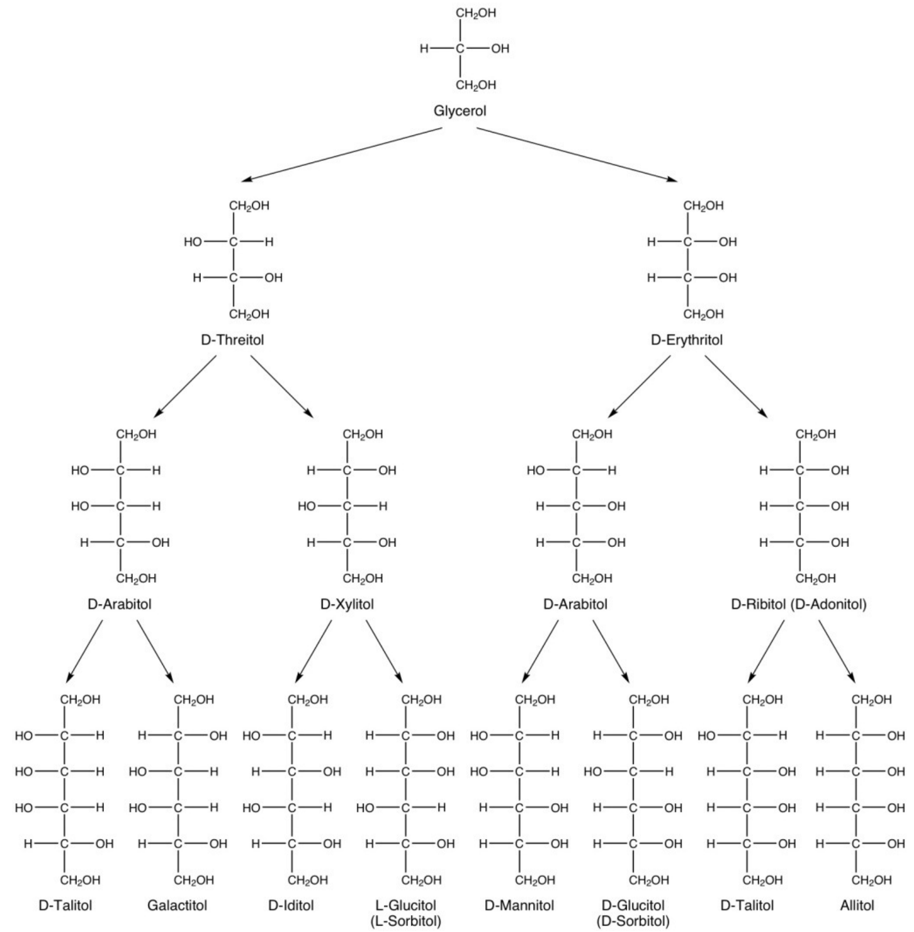


D-Allose

Sugars Acids & Sugar Alcohols



Sugar acids



Sugar alcohols

Why is it complicated to search for sugar derivatives?

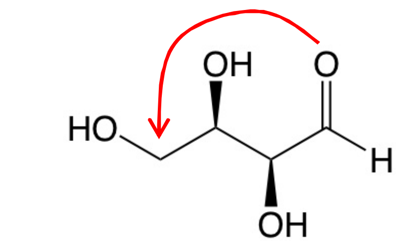
- There are a LOT of possible compounds among all sugars, sugar acids, and sugar alcohols, not to mention dicarboxylic sugar acids, deoxy sugar derivatives, etc.
- Sugars and (most of) sugar derivatives are chiral molecules, so each of them exists in two enantiomeric forms (D and L).
- Each $>C_4$ sugar (and some sugar acids) can either be in a linear or a cyclic configuration.
- For C_5 and C_6 sugars (aldoses), cyclic forms include furanose and pyranose forms, and each of these forms has two anomeric conformations (α and β).

Why is it complicated to search for sugar derivatives?

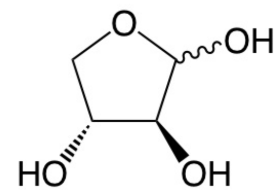
- There are a LOT of possible compounds among all sugars, sugar acids, and sugar alcohols, not to mention dicarboxylic sugar acids, deoxy sugar derivatives, etc.
- Sugars and (most of) sugar derivatives are chiral molecules, so each of them exists in two enantiomeric forms (D and L).
- Each >C_4 sugar (and some sugar acids) can either be in a linear or a cyclic configuration.
- For C_5 and C_6 sugars (aldoses), cyclic forms include furanose and pyranose forms, and each of these forms has two anomeric conformations (α and β).

Why is it complicated to search for sugar derivatives?

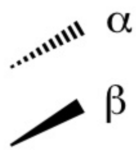
Linear	Furanose	Pyranose

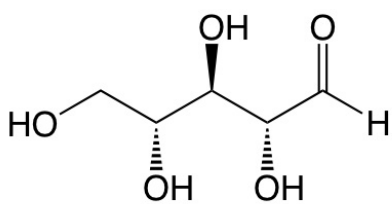


D-Threose

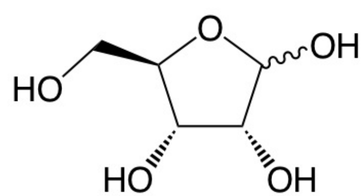


D-Threofuranose

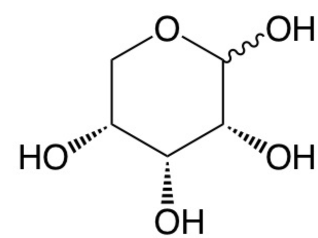




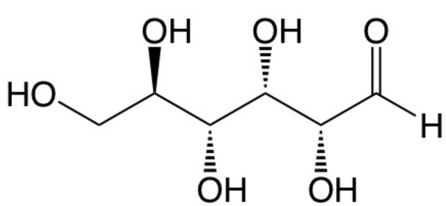
D-Ribose



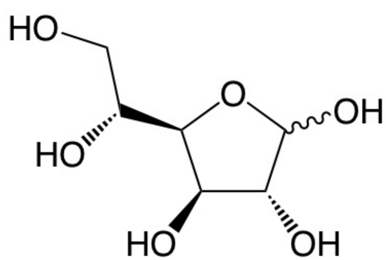
D-Ribofuranose



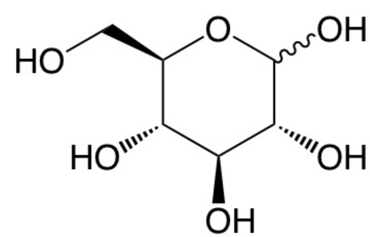
D-Ribopyranose



D-Glucose



D-Glucofuranose



D-Glucopyranose

Experimental Set-up & Protocol

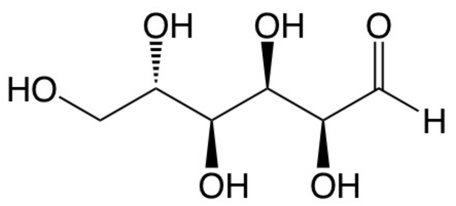
- Mix H_2O/CH_3OH vapors in a bulb to prepare $H_2O:CH_3OH$ gas mixtures with different relative proportions (5:1 and 2:1).
- Deposit mixtures onto cold substrate (Al foil, ~10 K) and low pressure ($\sim 2\times10^{-8}$ torr), and simultaneously irradiate with H_2 lamp for 18–20 h.
- After irradiation, warm up to RT and recover the foil with the residue, dissolve it in a solvent (liquid H_2O/other).
- Analyze with GC-MS (BSTFA derivatization).

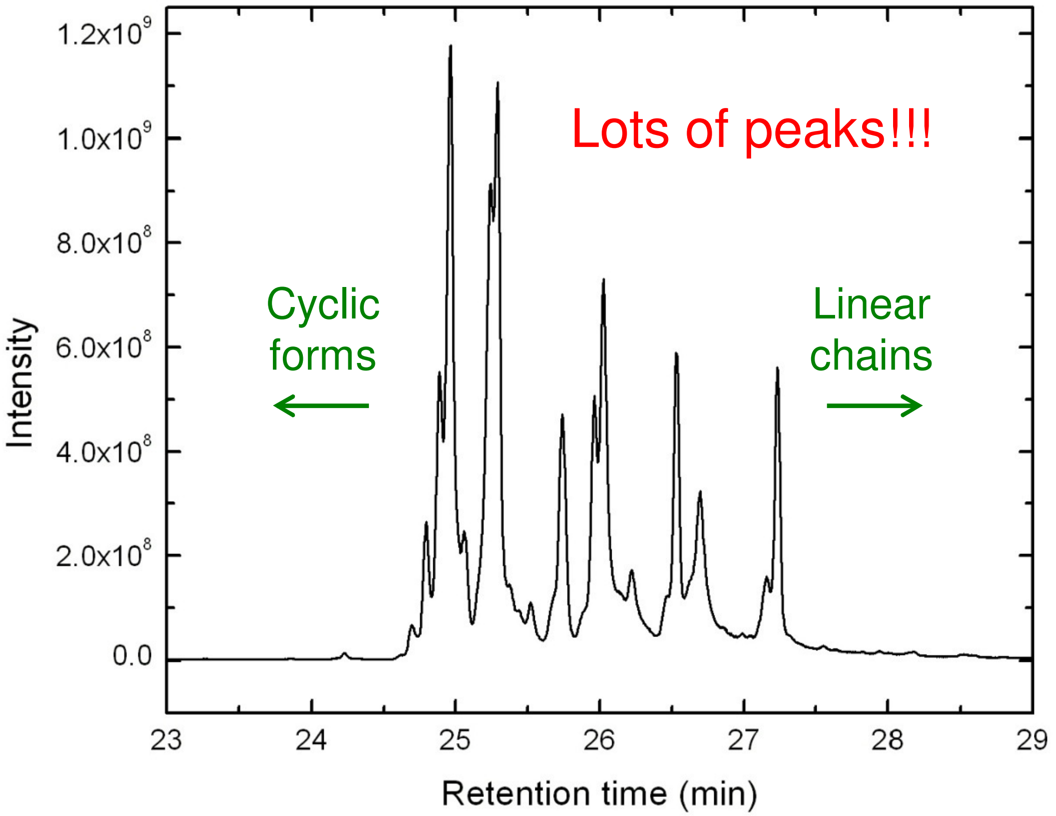
GC-MS Analysis

- 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



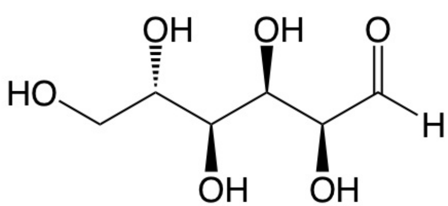


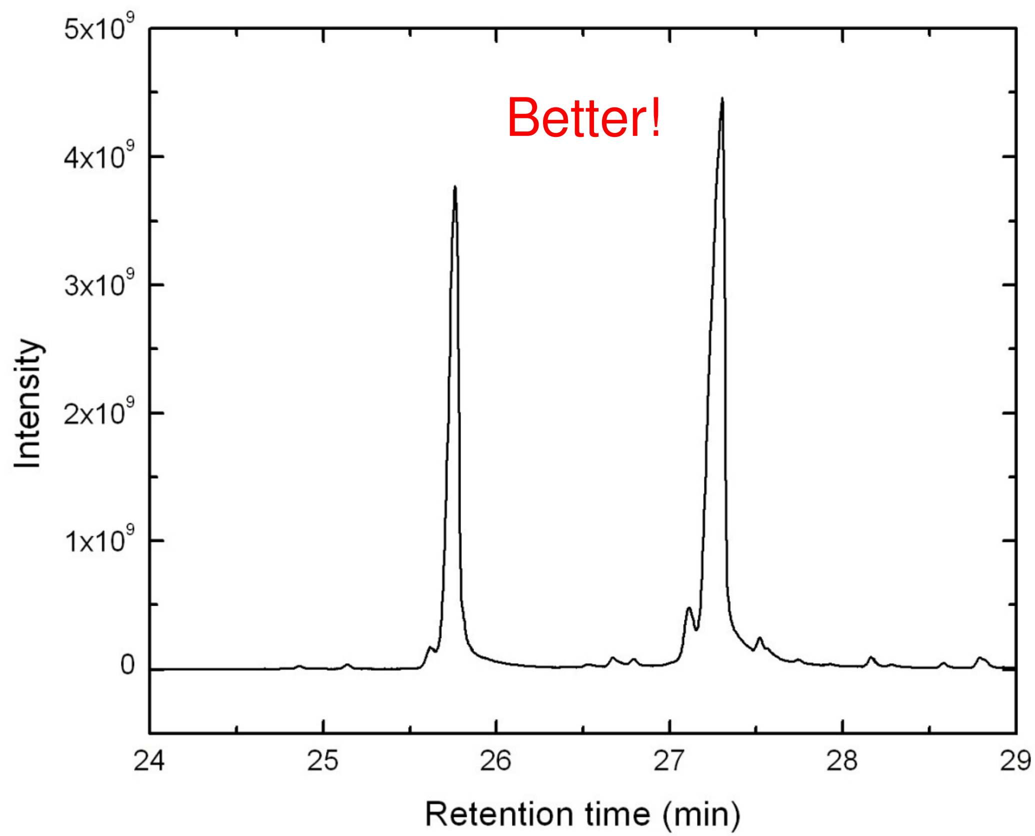
GC-MS Analysis

- 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
+ pyridine



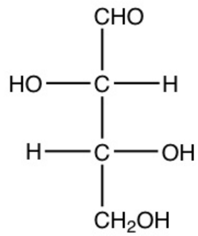


GC-MS Analysis

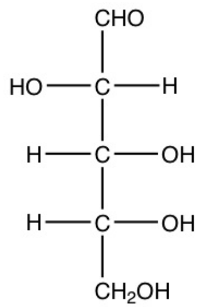
- Use of non-chiral GC column, so D and L enantiomers cannot be separated (good!), but still 8–10 peaks for each standard!
- Add pyridine to standards (and samples) to decrease the number of peaks to 1–2 main peaks for each compound.
- Identifications rely on comparison of both retention times and mass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

GC-MS Analysis

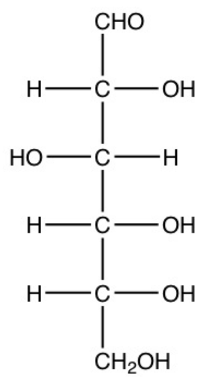
D-Threose

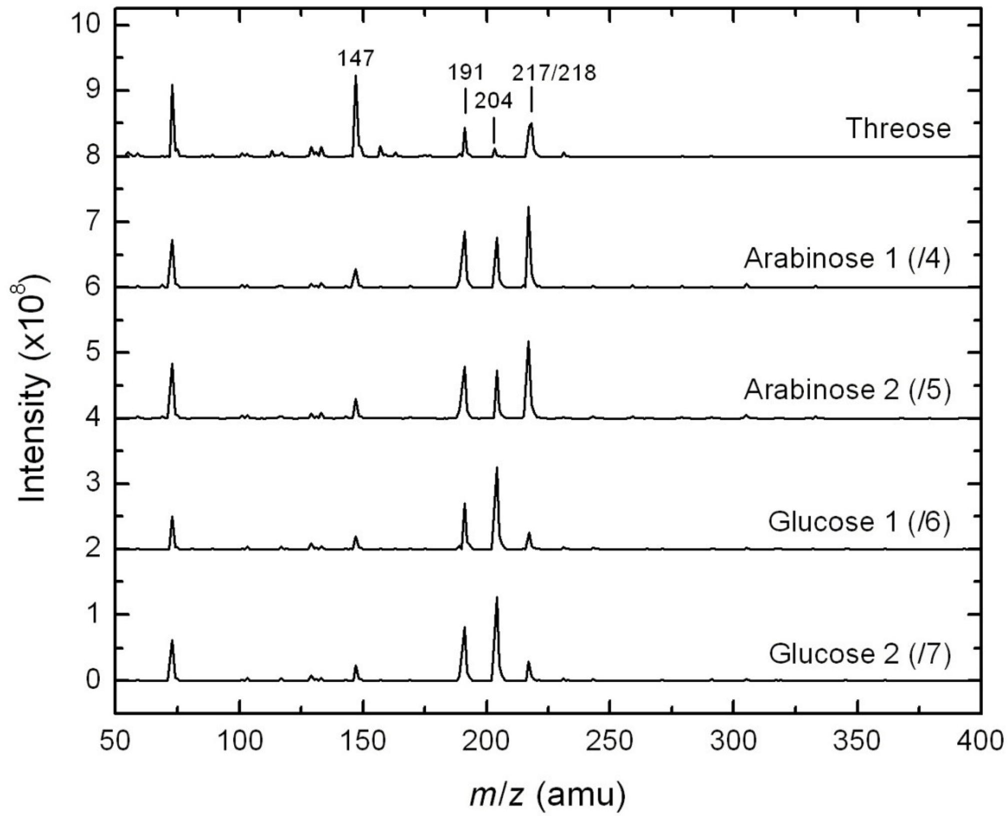


D-Arabinose



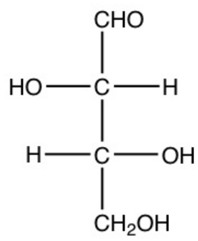
D-Glucose



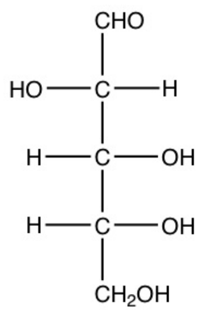


GC-MS Analysis

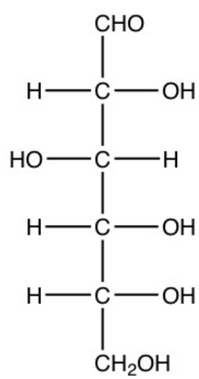
D-Threose

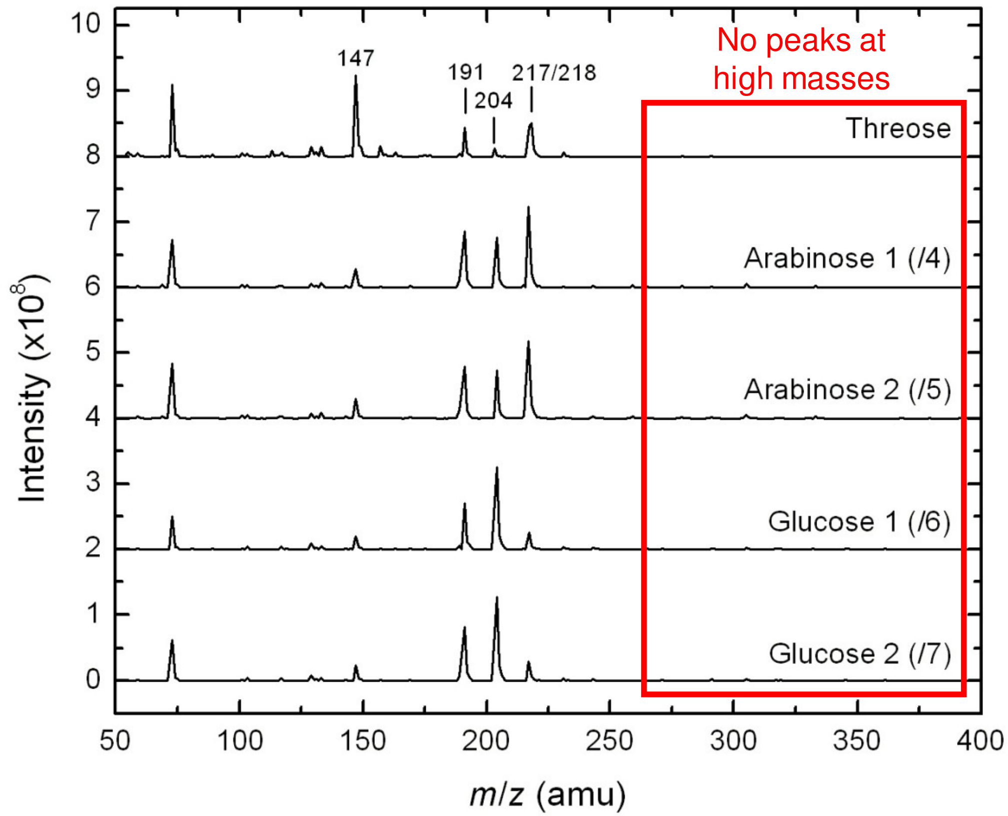


D-Arabinose



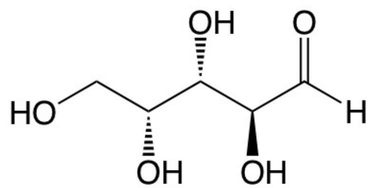
D-Glucose



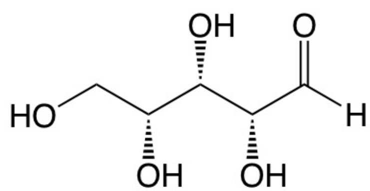


GC-MS Analysis

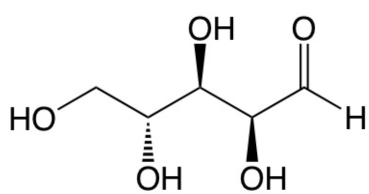
D-Lyxose



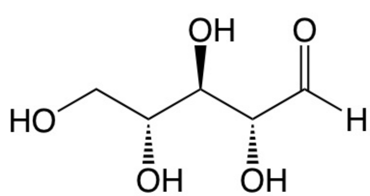
D-Xylose

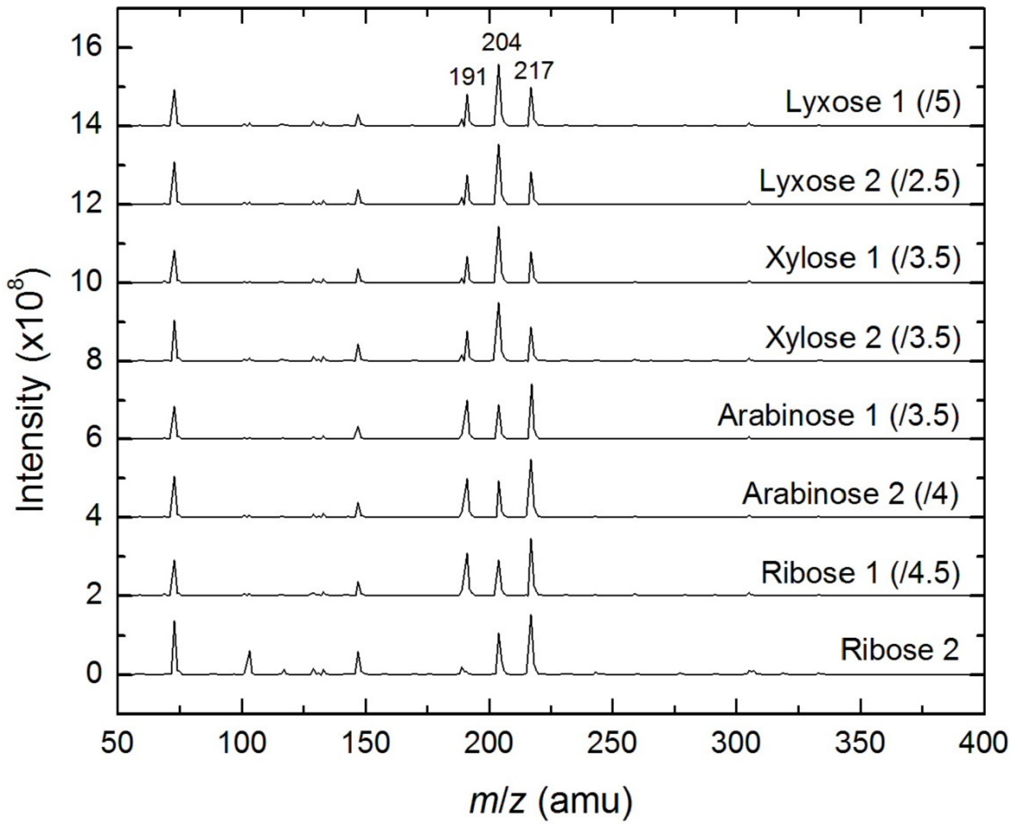


D-Arabinose



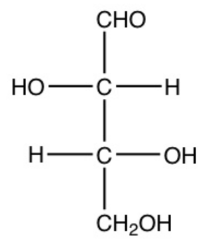
D-Ribose



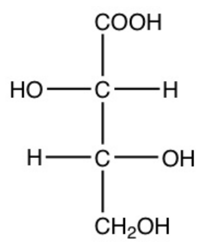


GC-MS Analysis

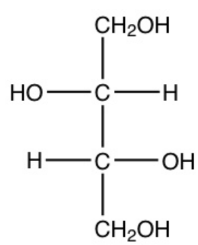
D-Threose

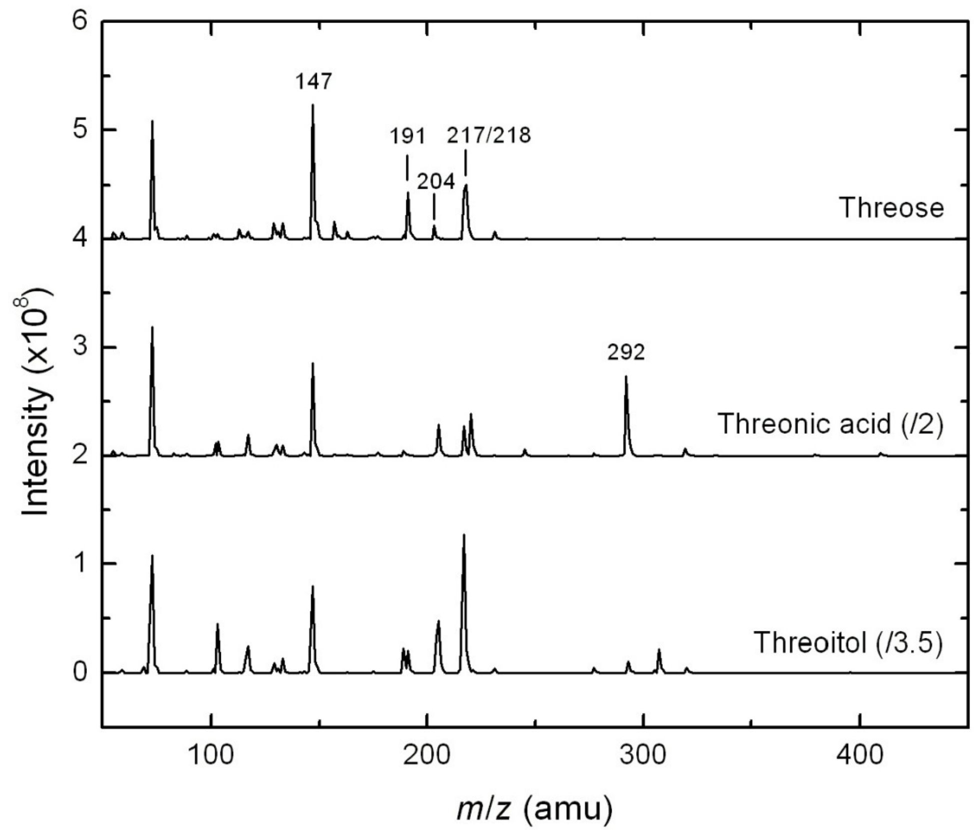


D-Threonic acid



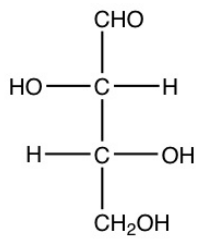
D-Threitol



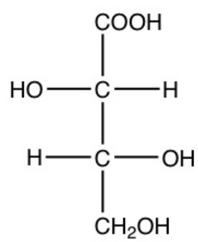


GC-MS Analysis

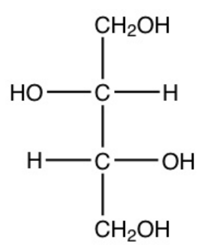
D-Threose

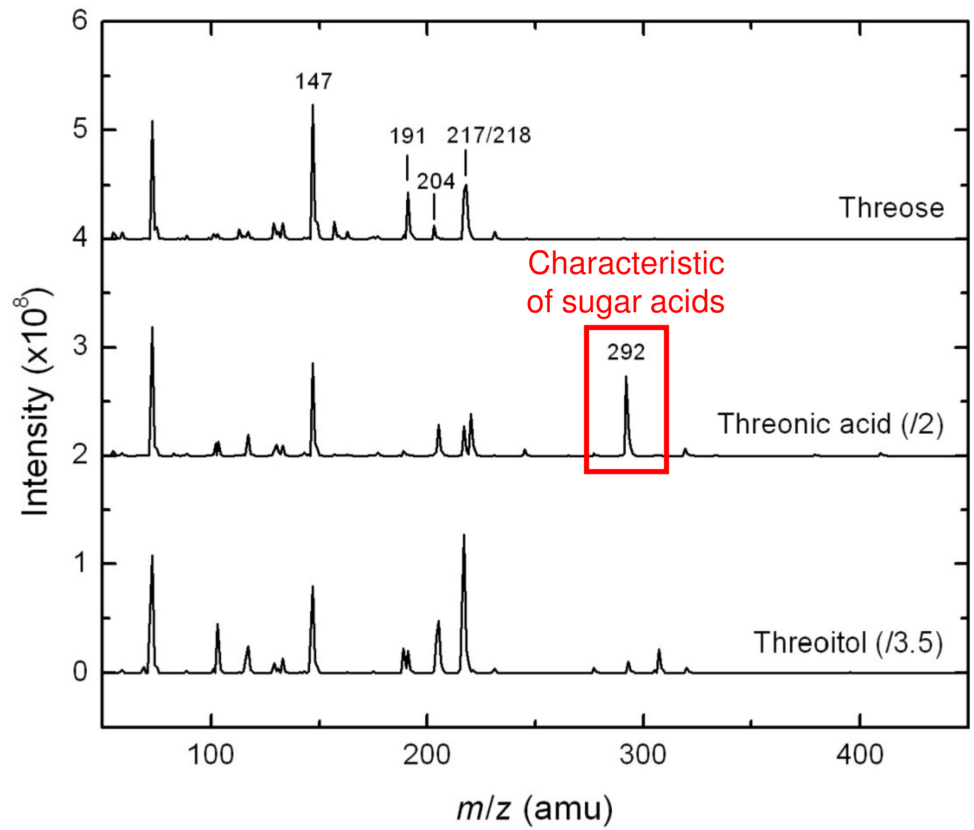


D-Threonic acid



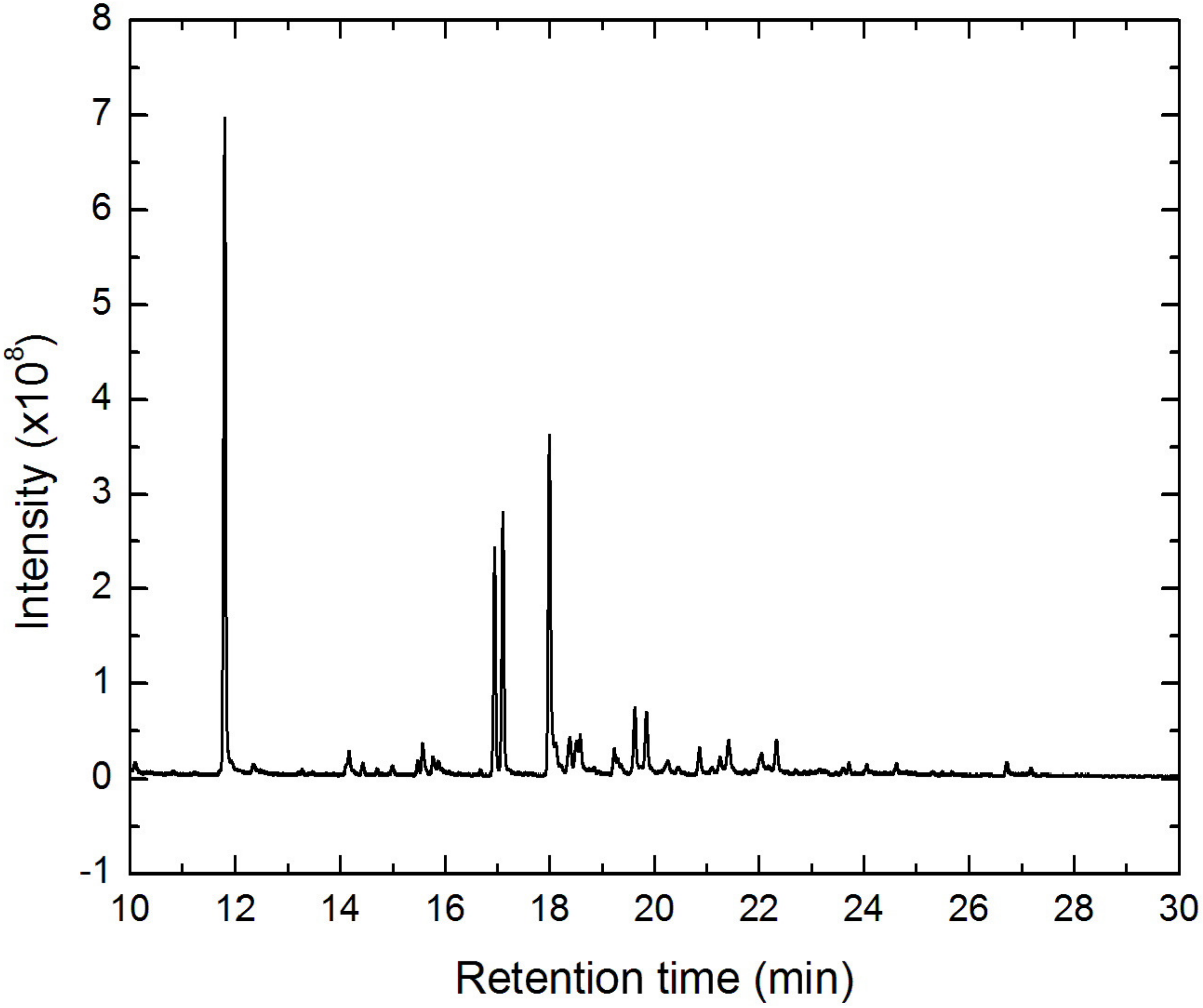
D-Threitol





Results

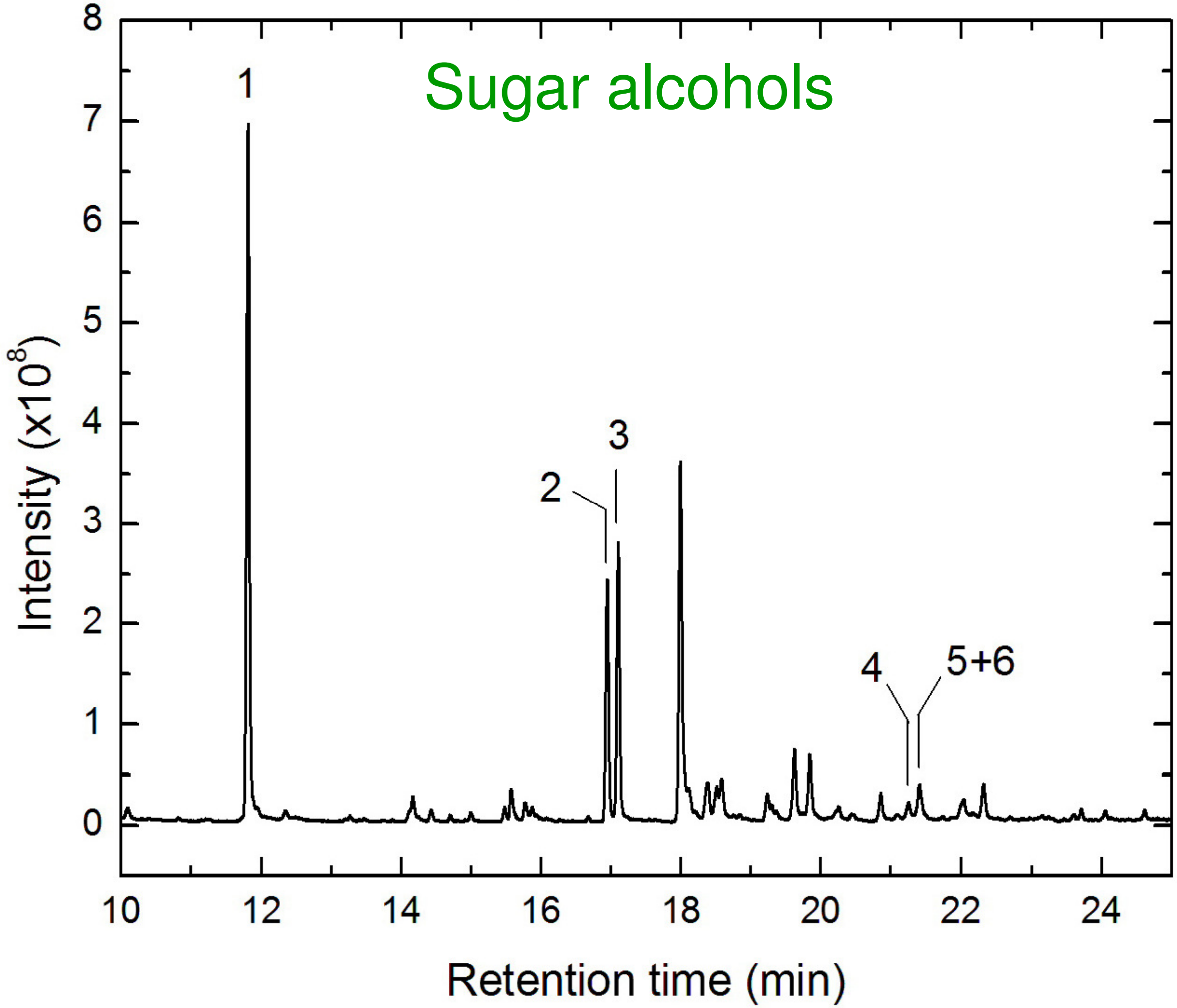
$H_2O:CH_3OH$ = 2:1 + UV



Nuevo et al. (submitted)

Results

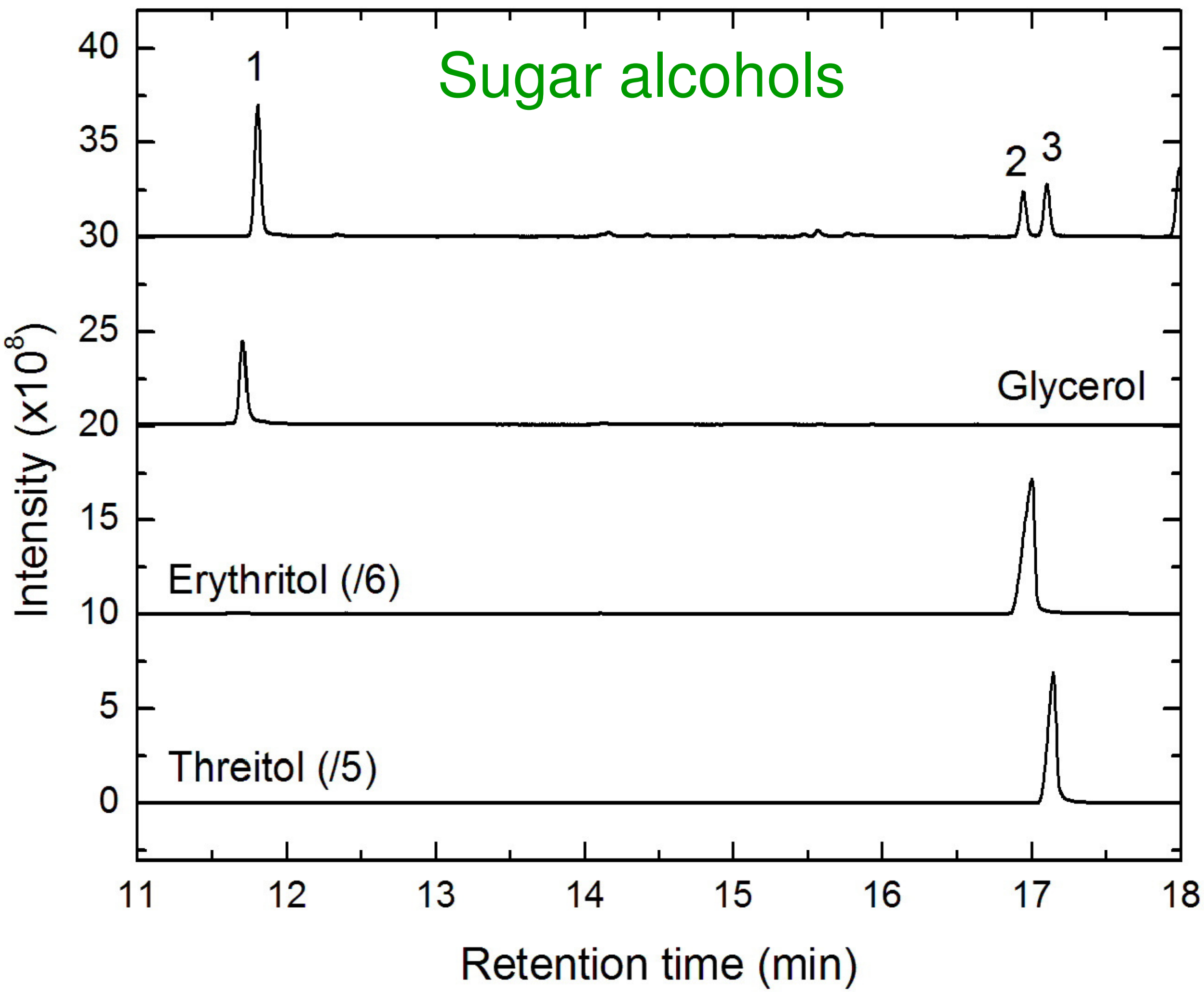
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

Results

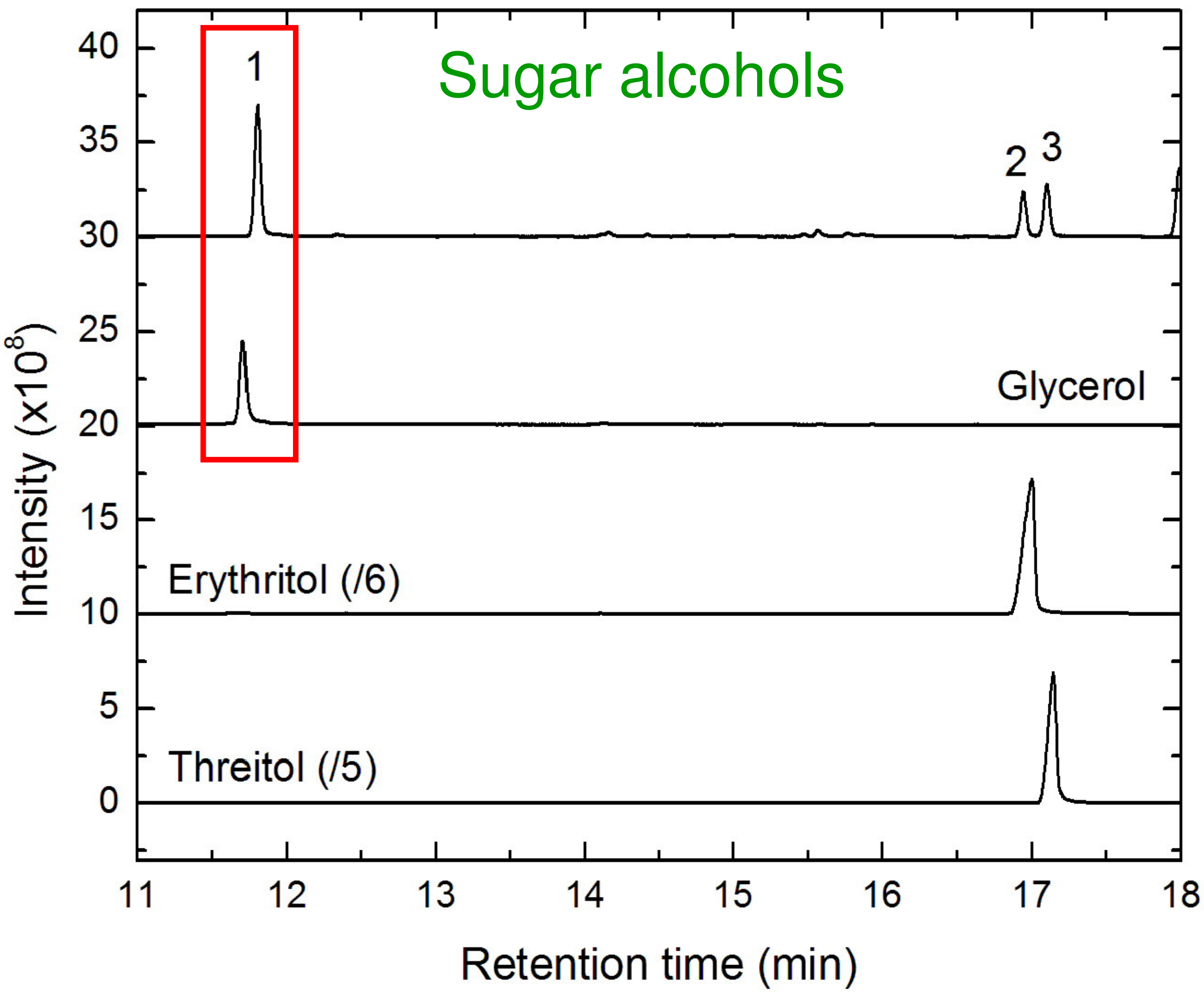
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

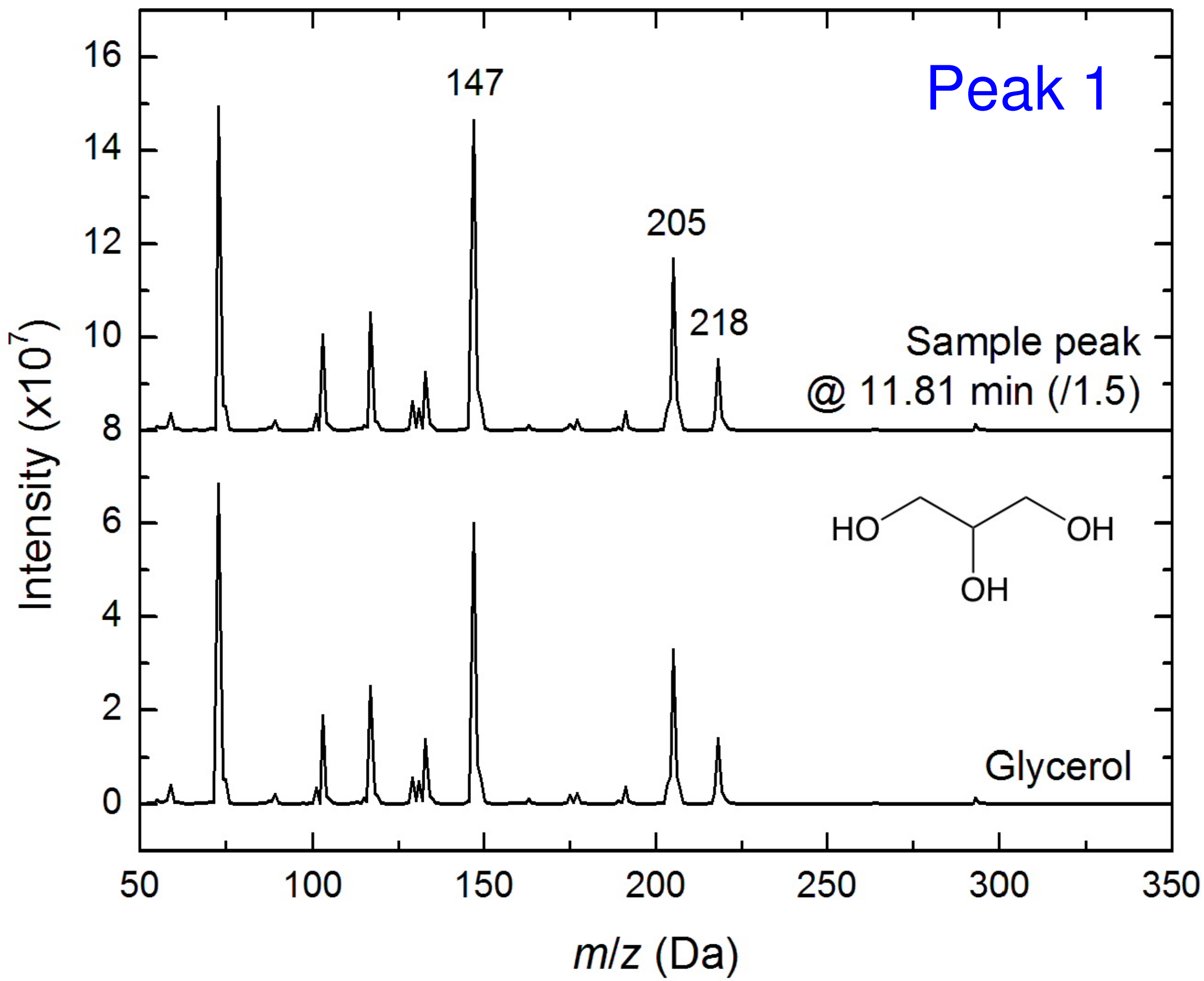
Results

$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

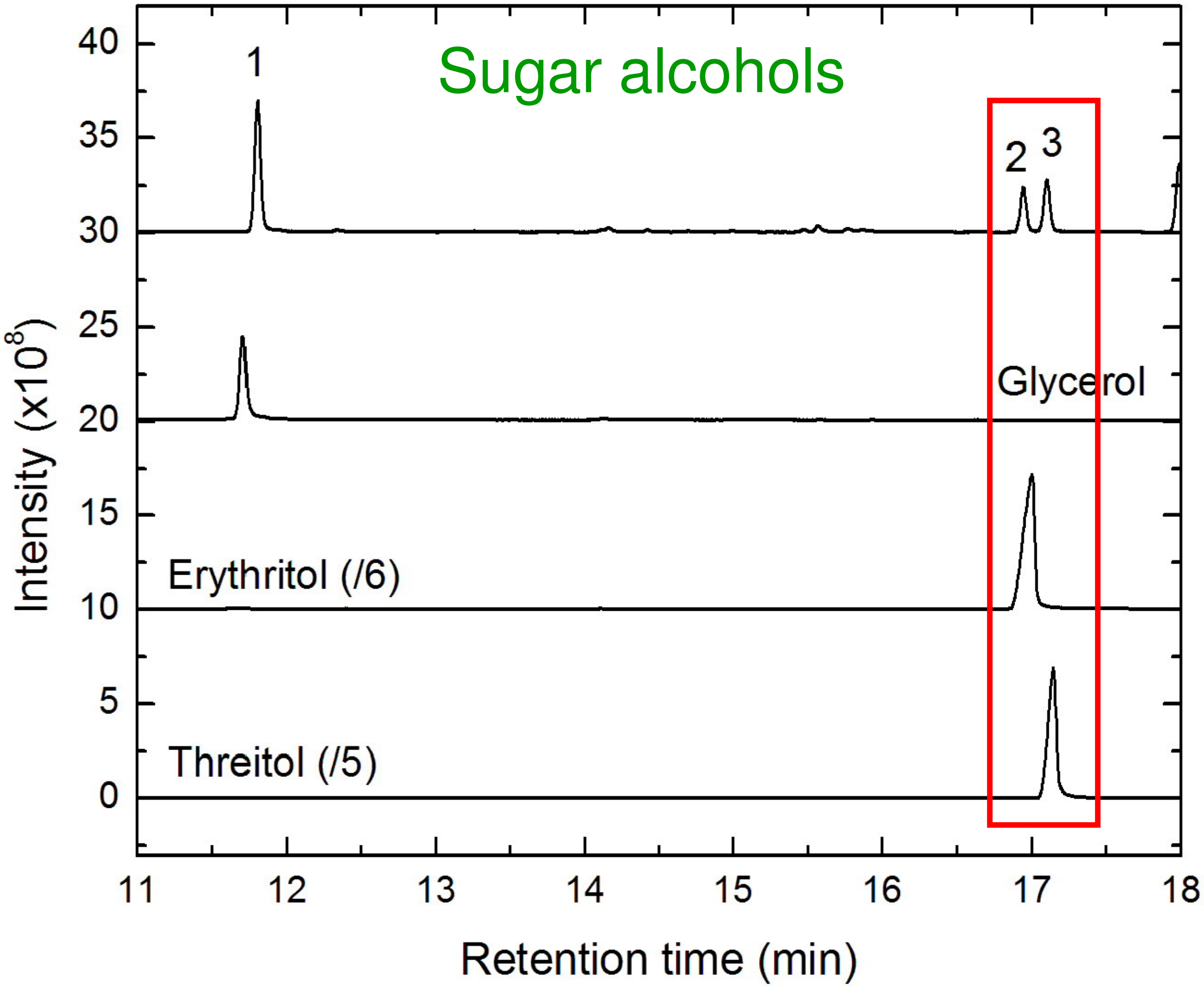
Results



Nuevo et al. (submitted)

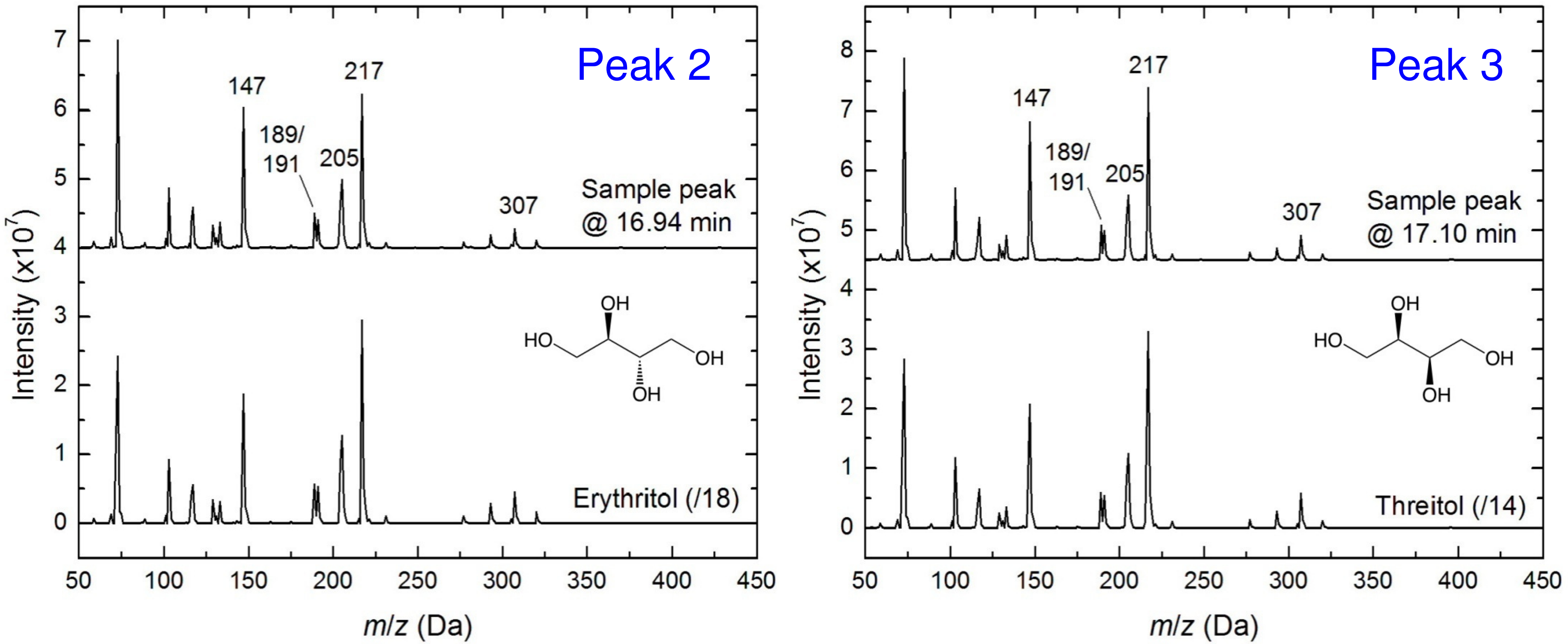
Results

$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

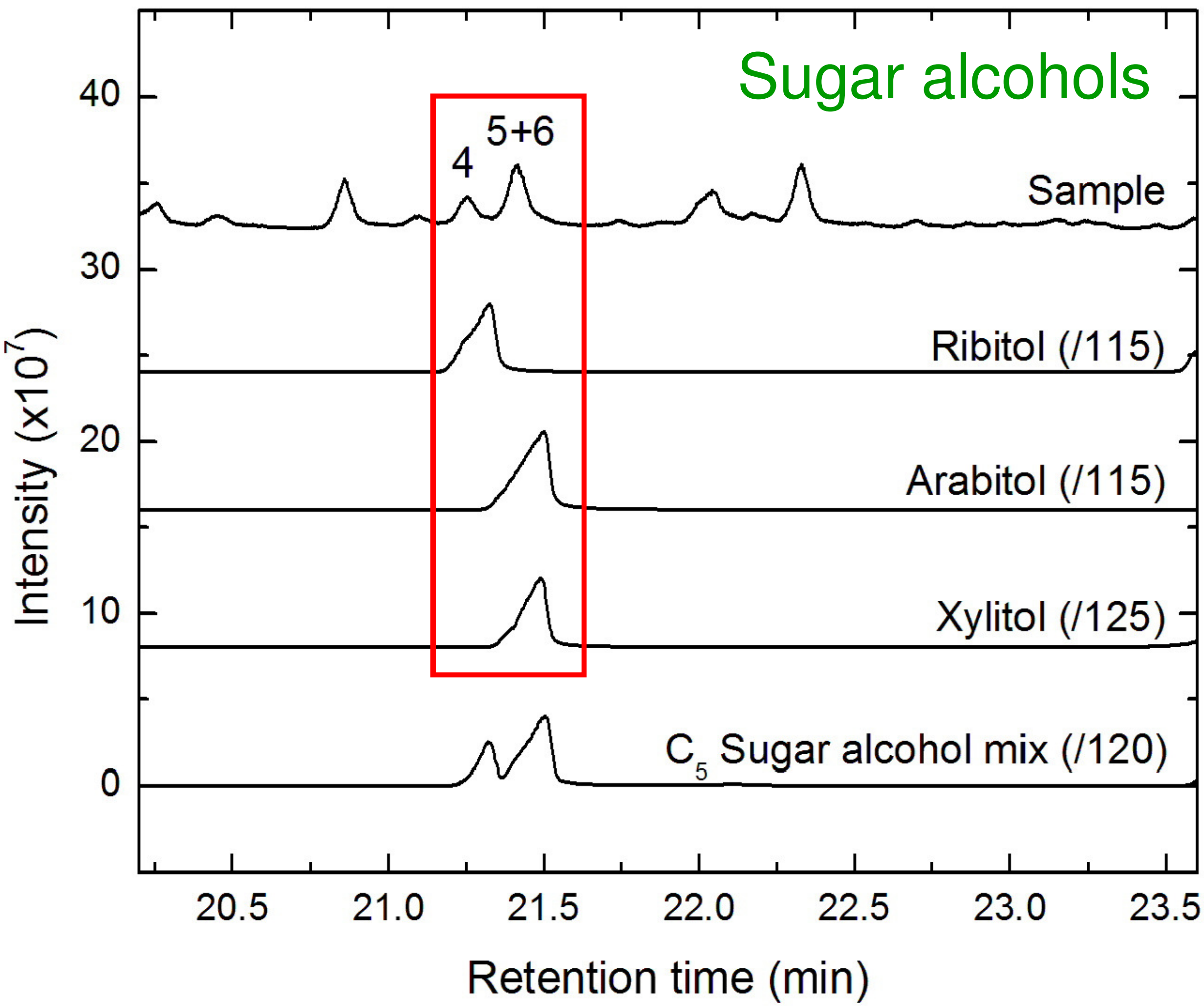
Results



Nuevo et al. (submitted)

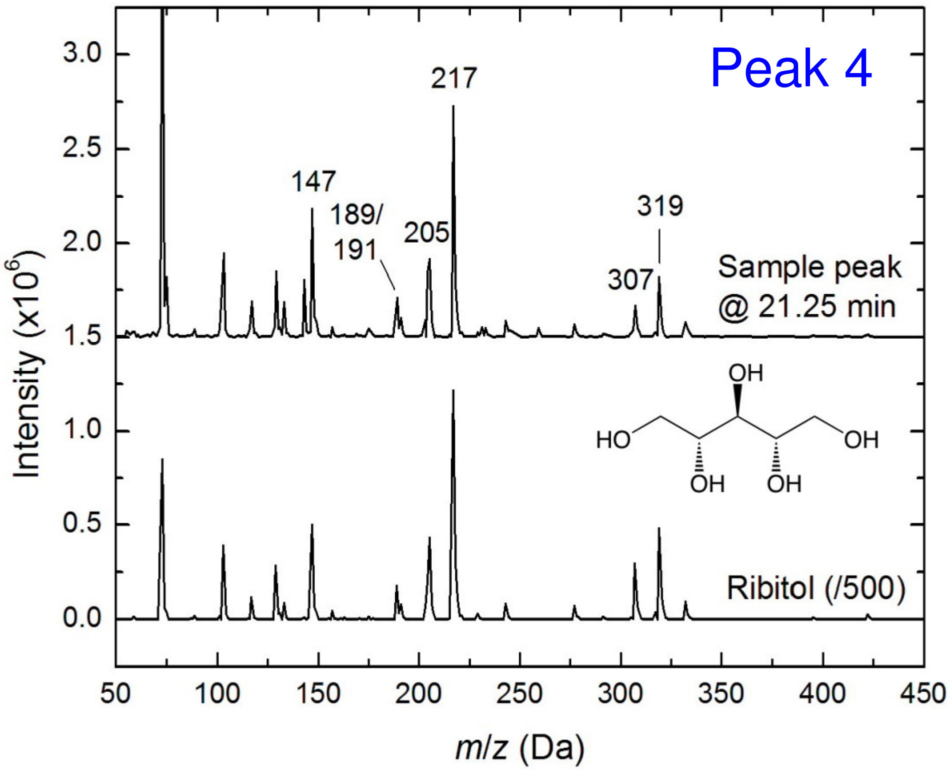
Results

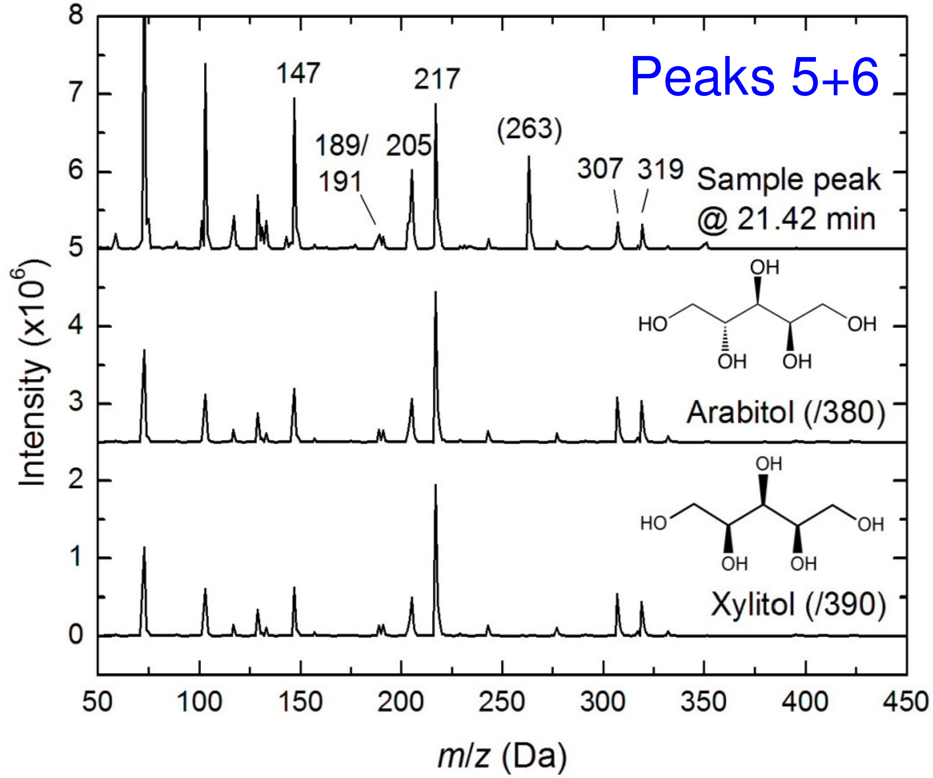
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

Results

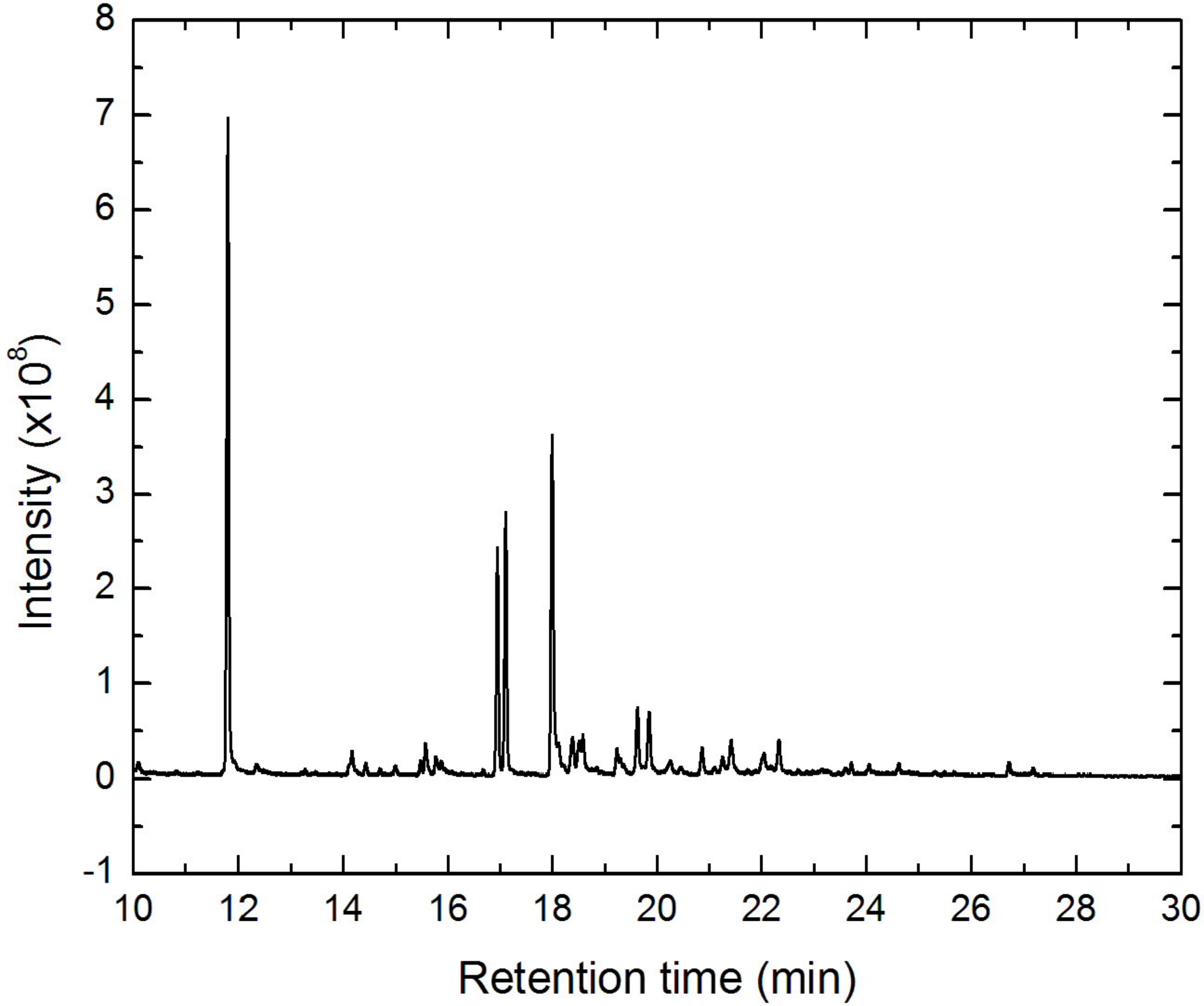




Nuevo et al. (submitted)

Results

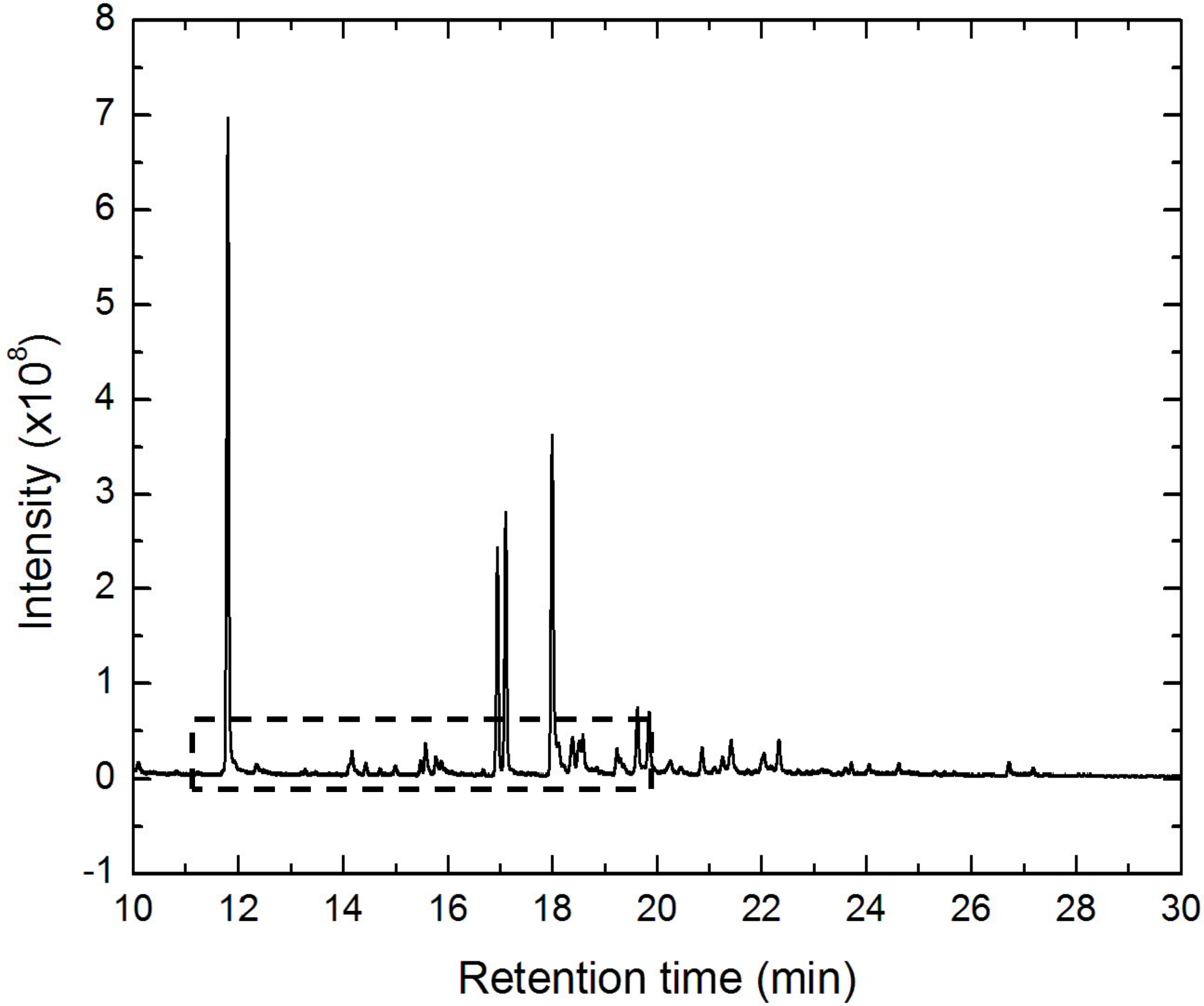
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

Results

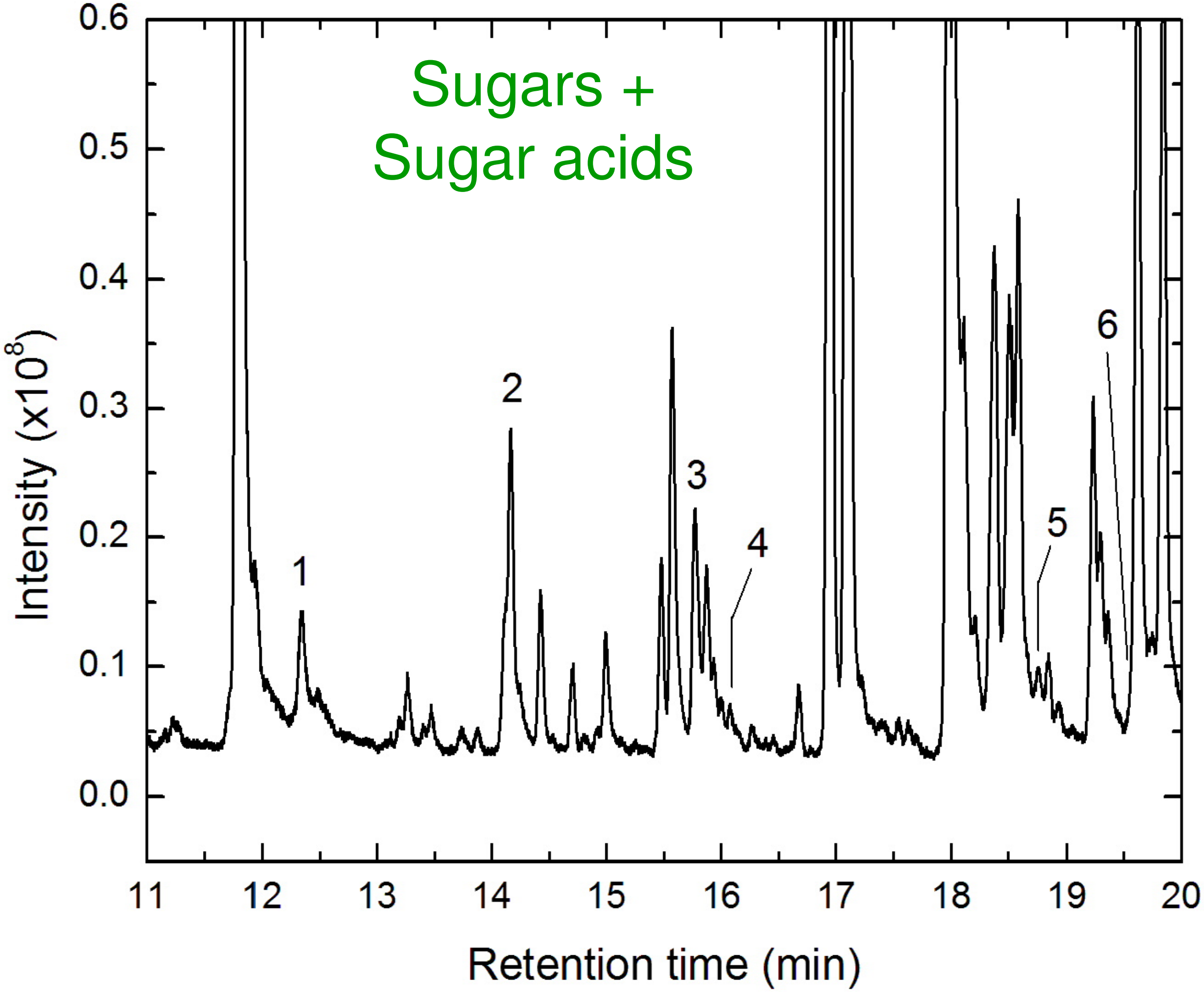
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

Results

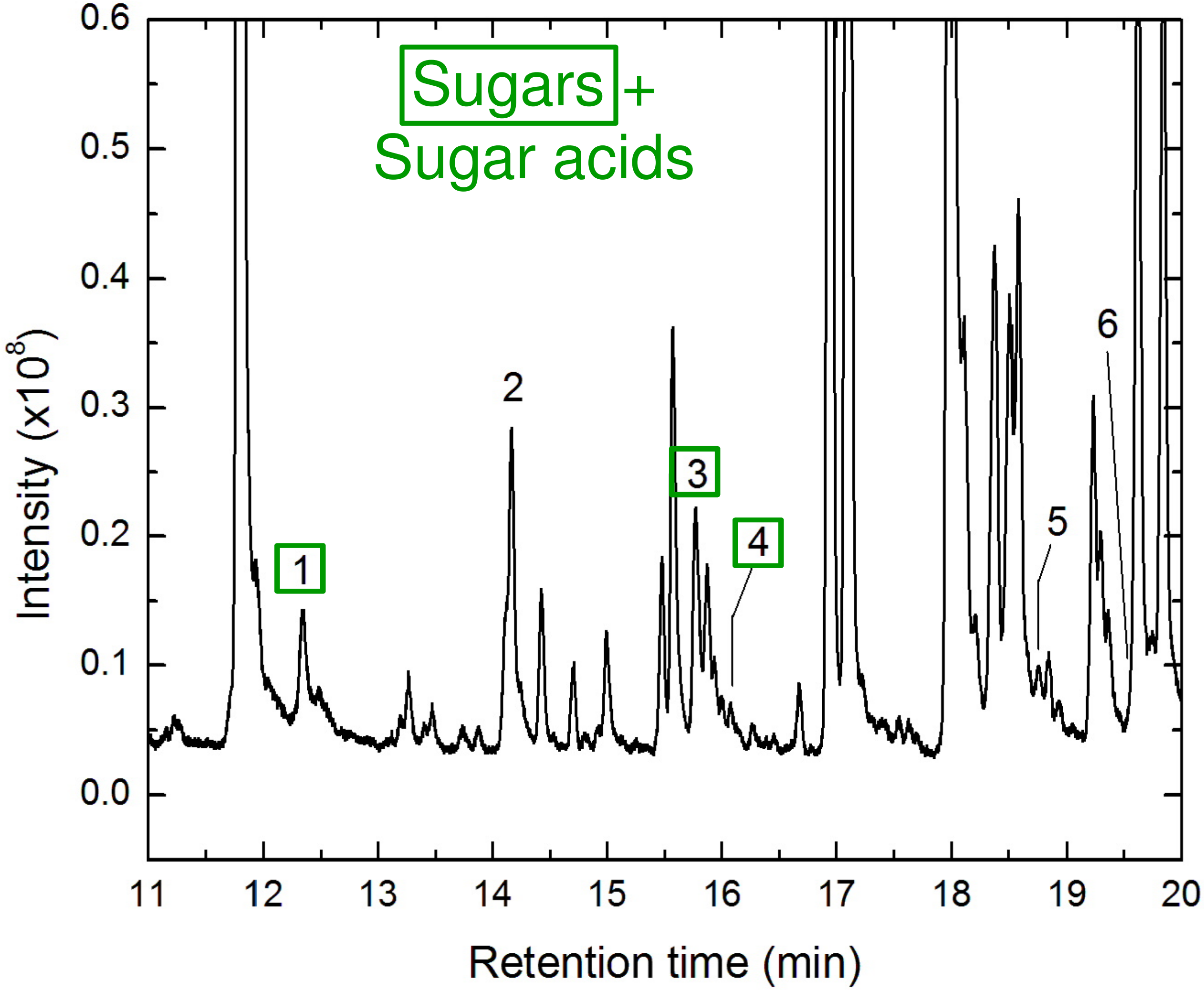
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

Results

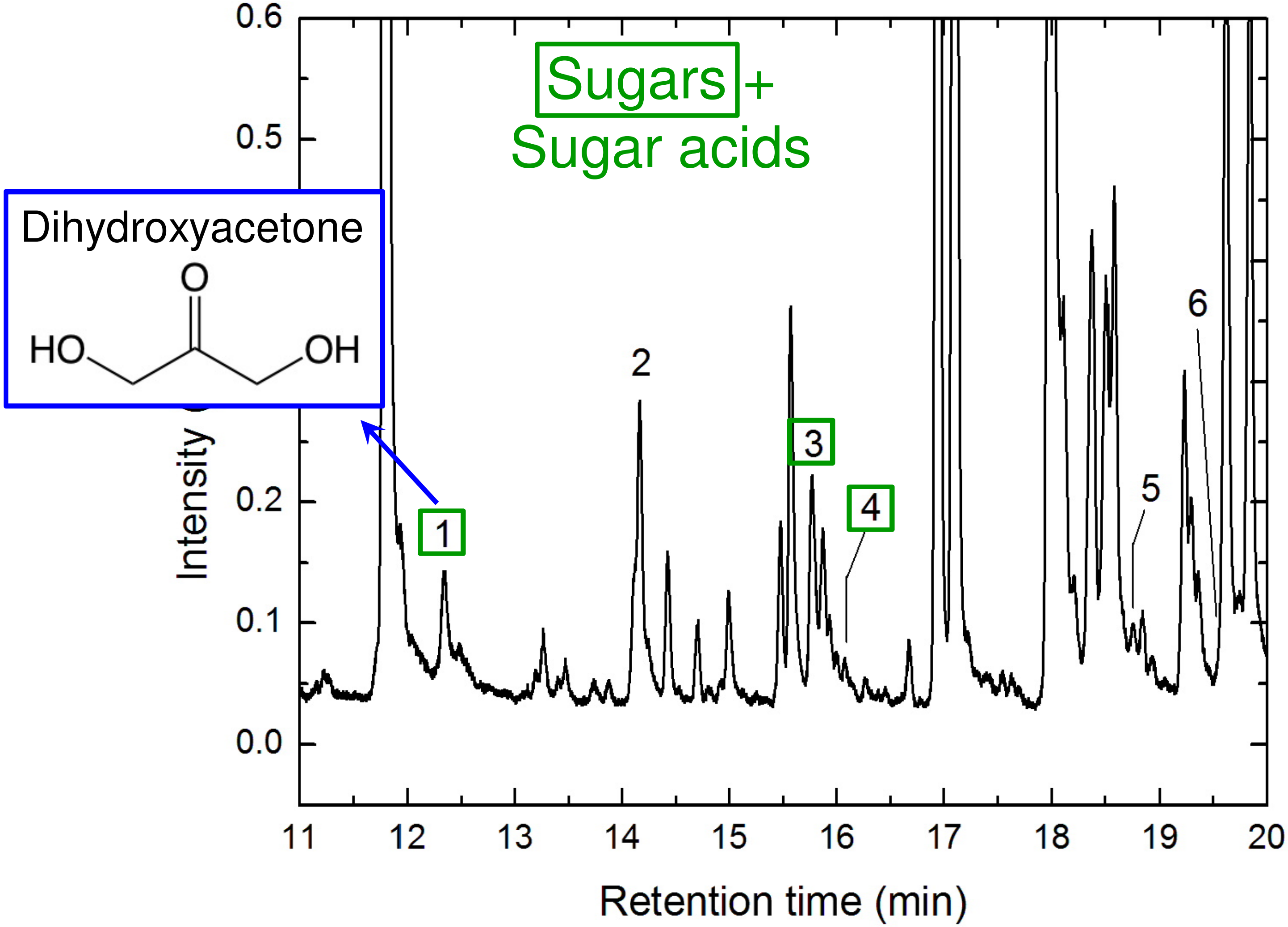
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

Results

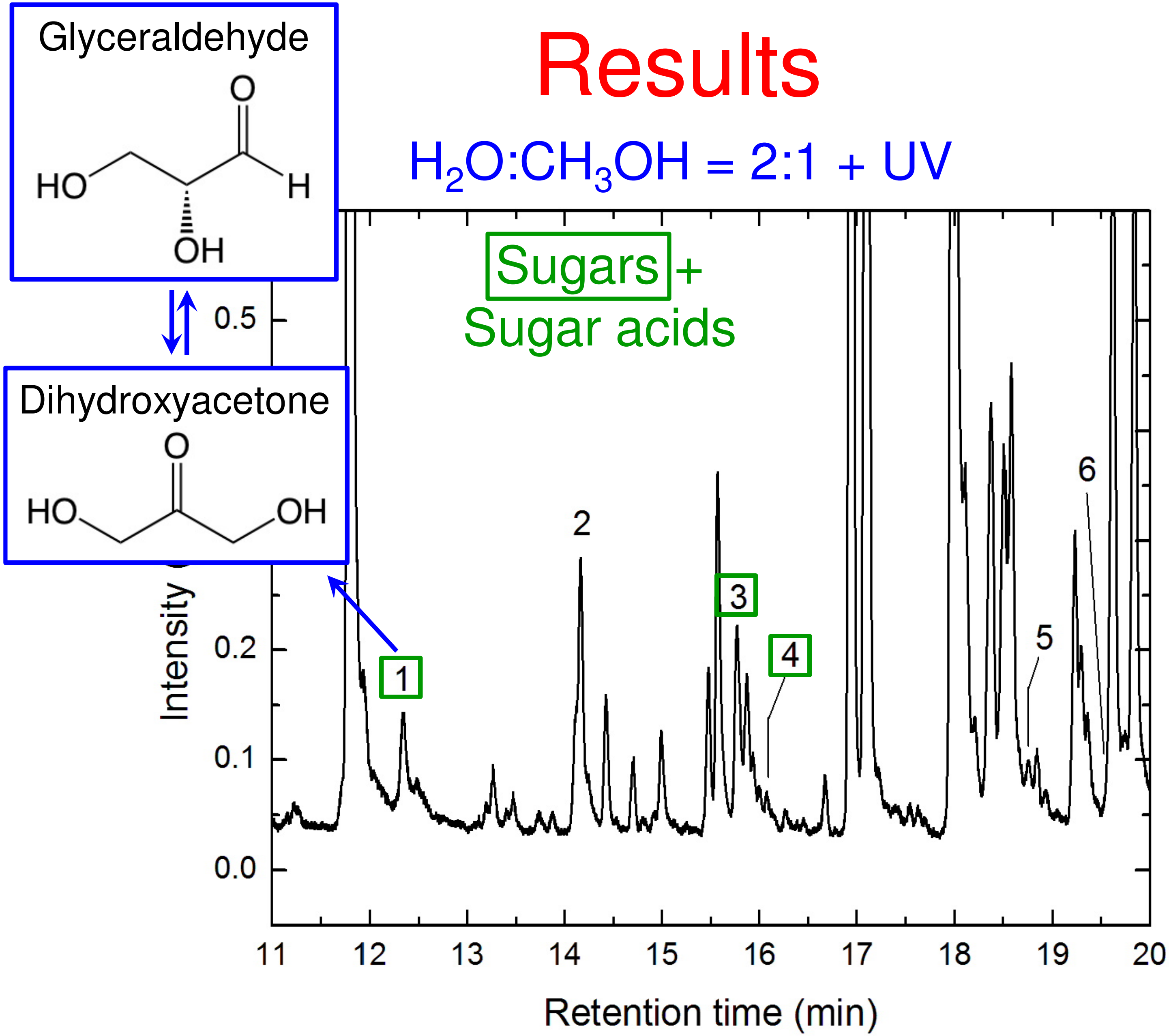
$H_2O:CH_3OH$ = 2:1 + UV



Nuevo et al. (submitted)

Results

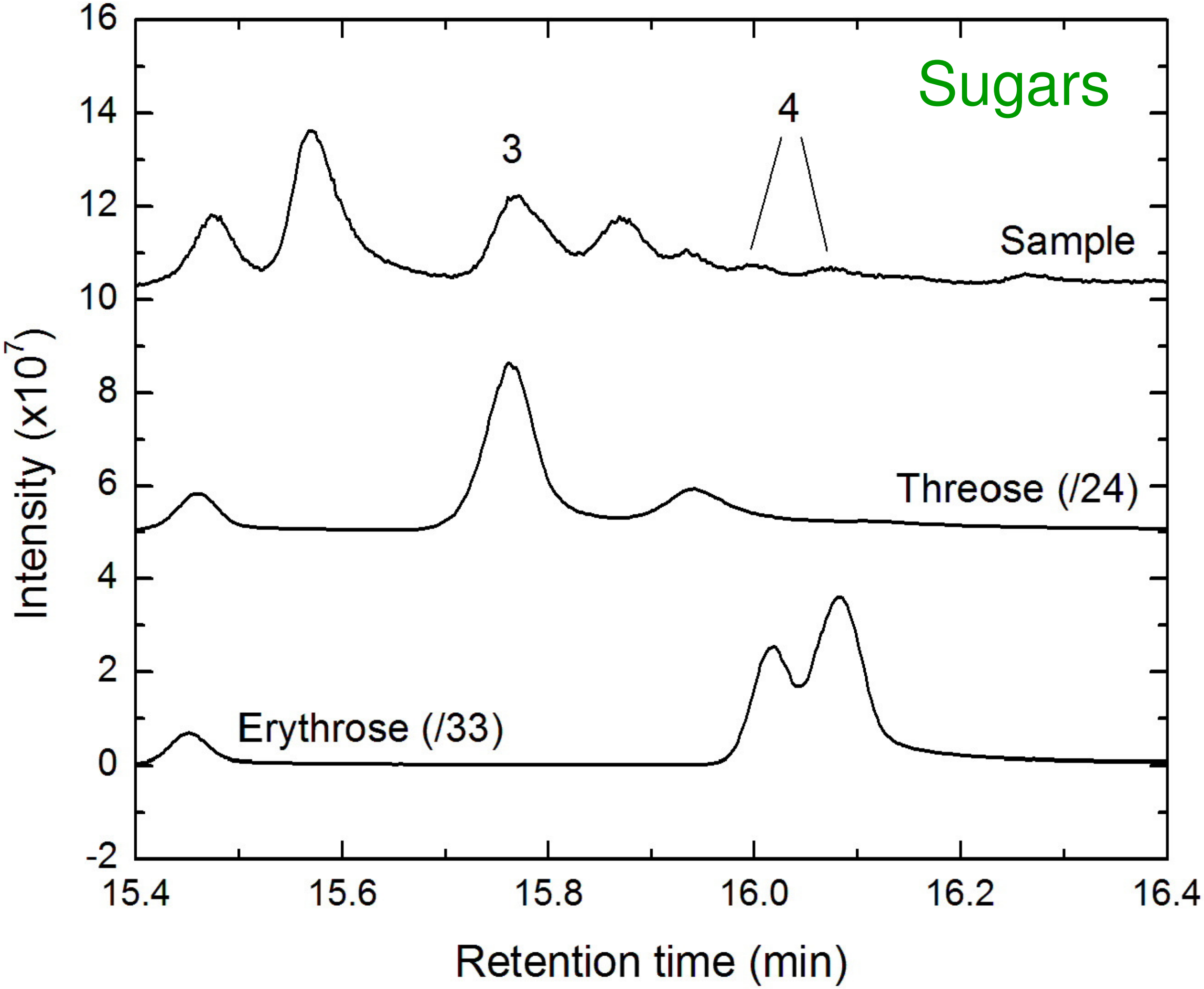
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

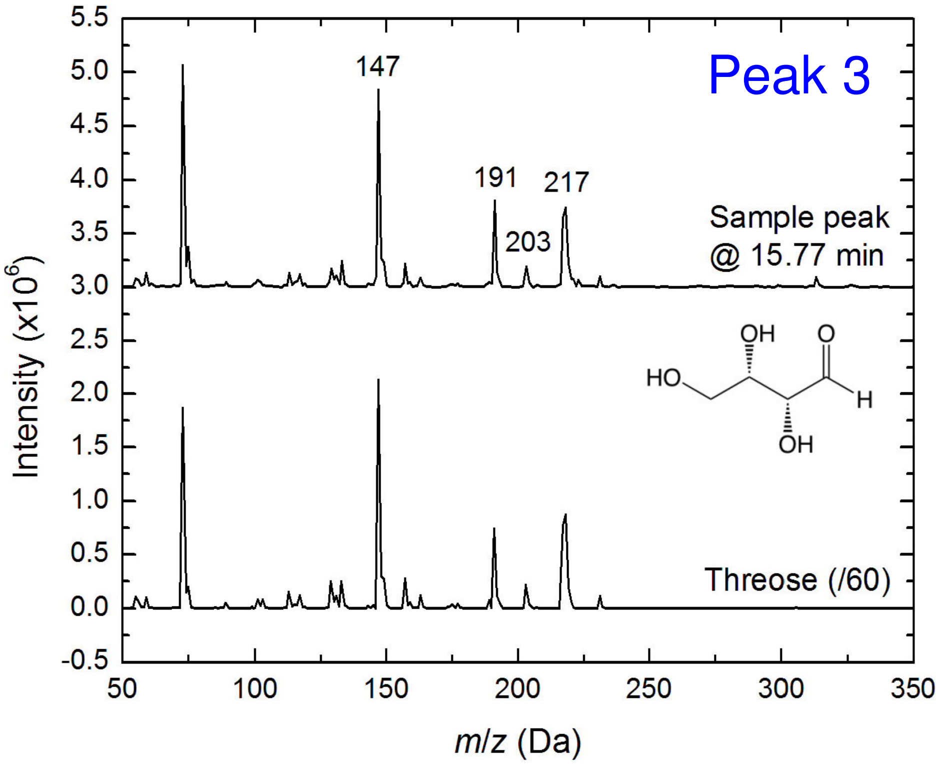
Results

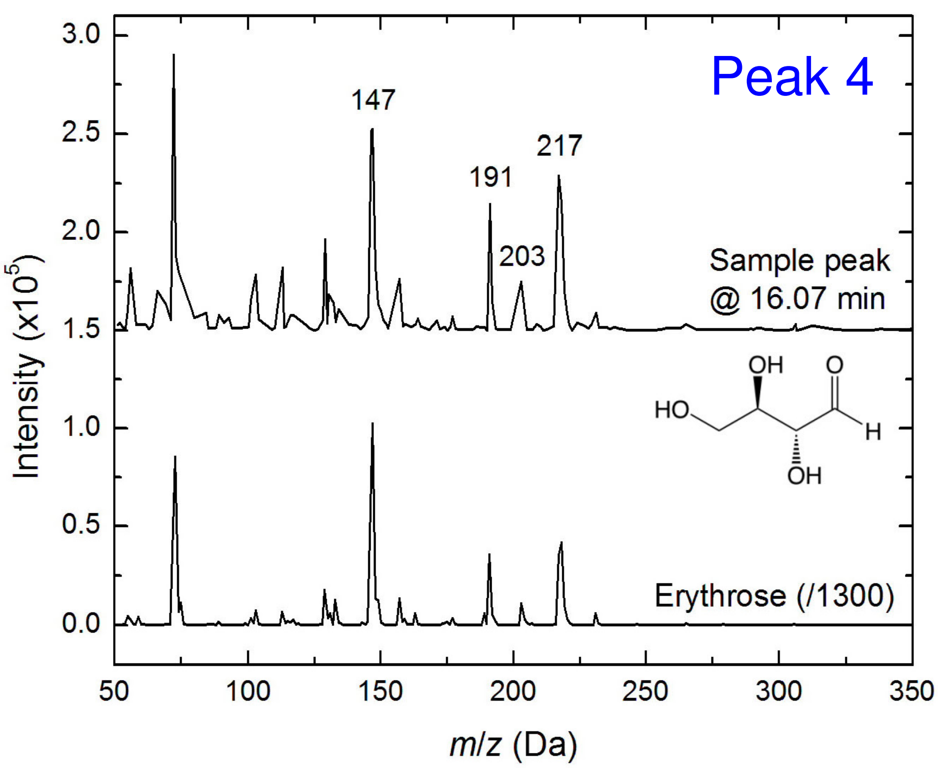
$H_2O:CH_3OH$ = 2:1 + UV



Nuevo et al. (submitted)

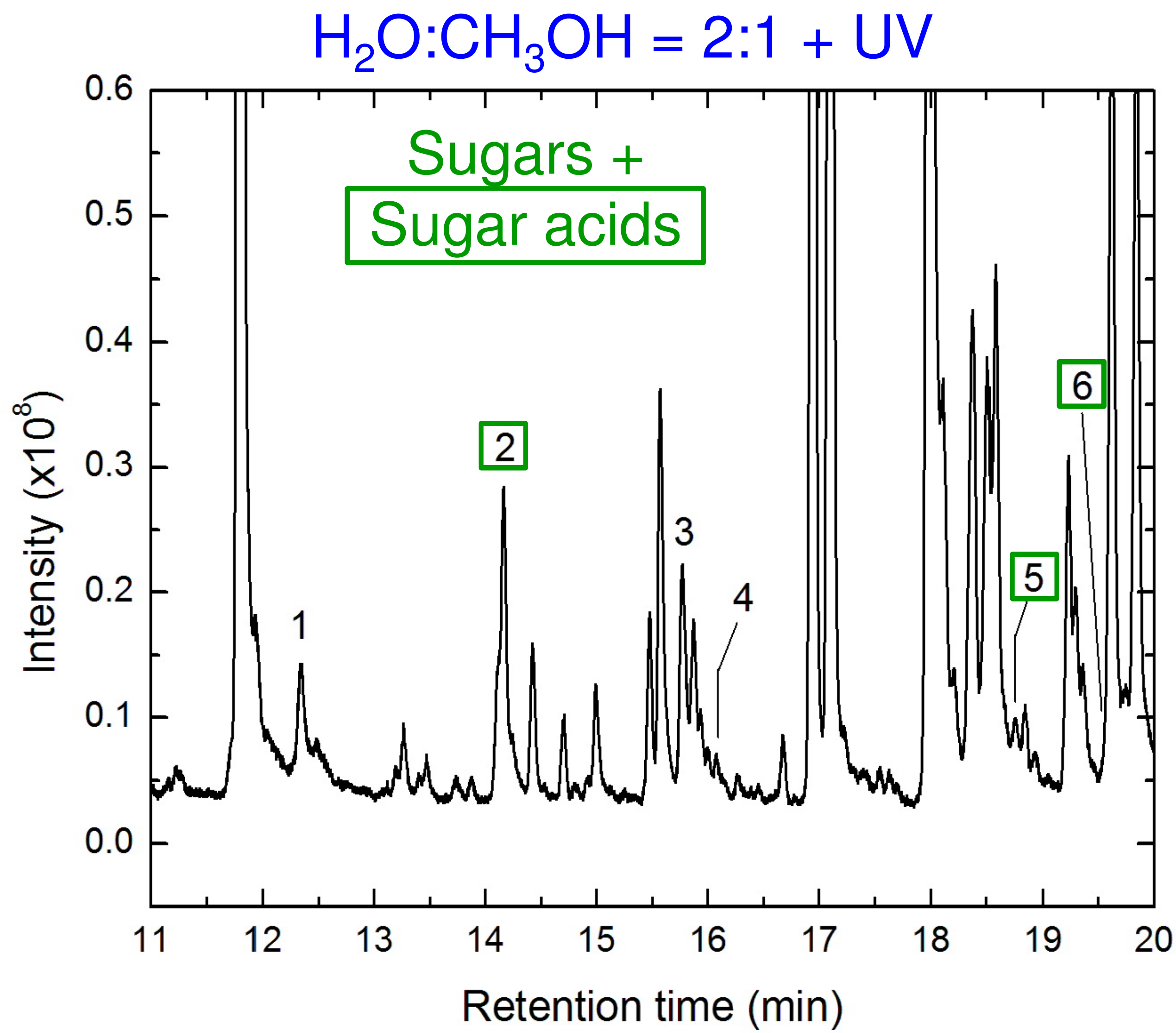
Results





Nuevo et al. (submitted)

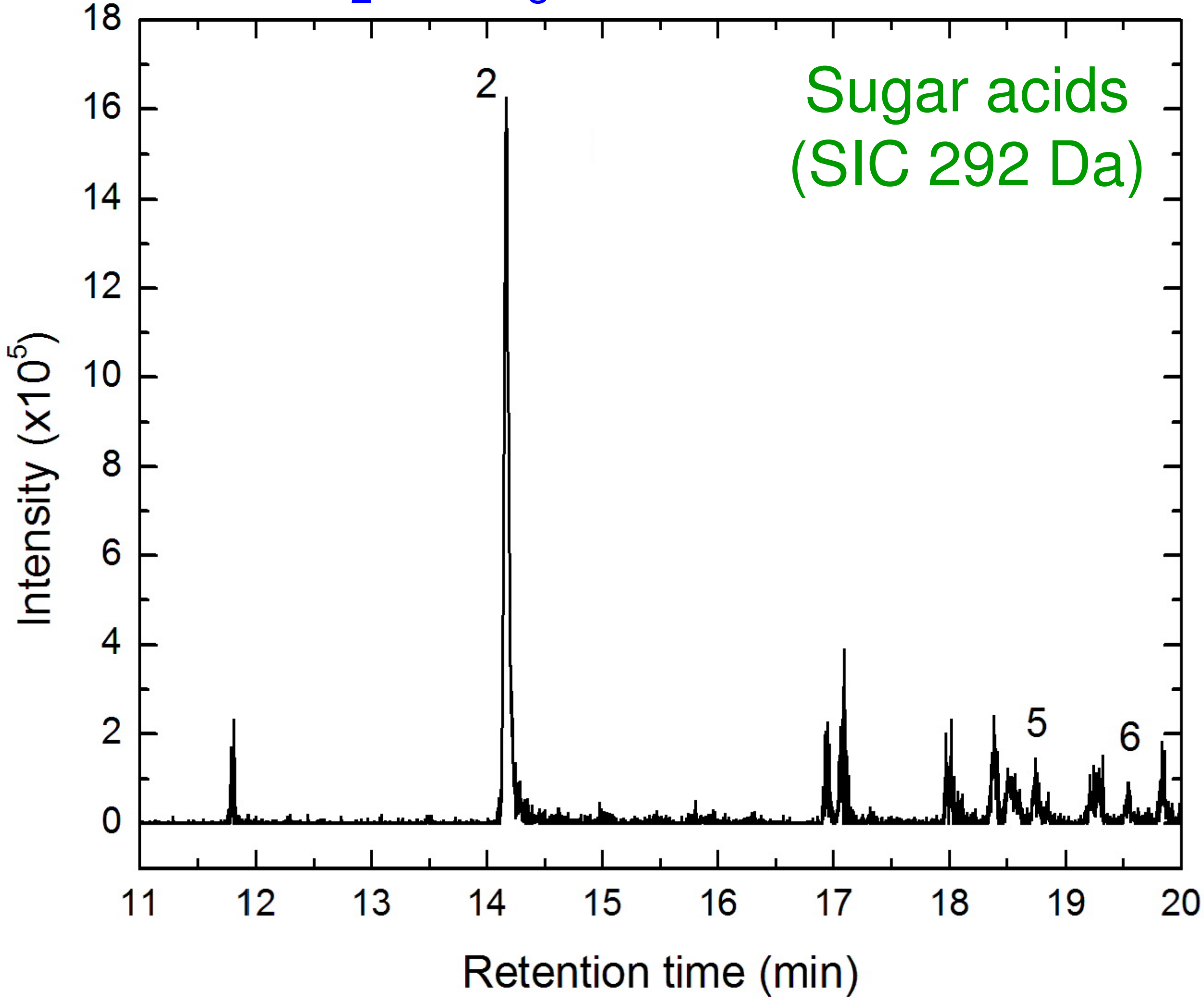
Results



Nuevo et al. (submitted)

Results

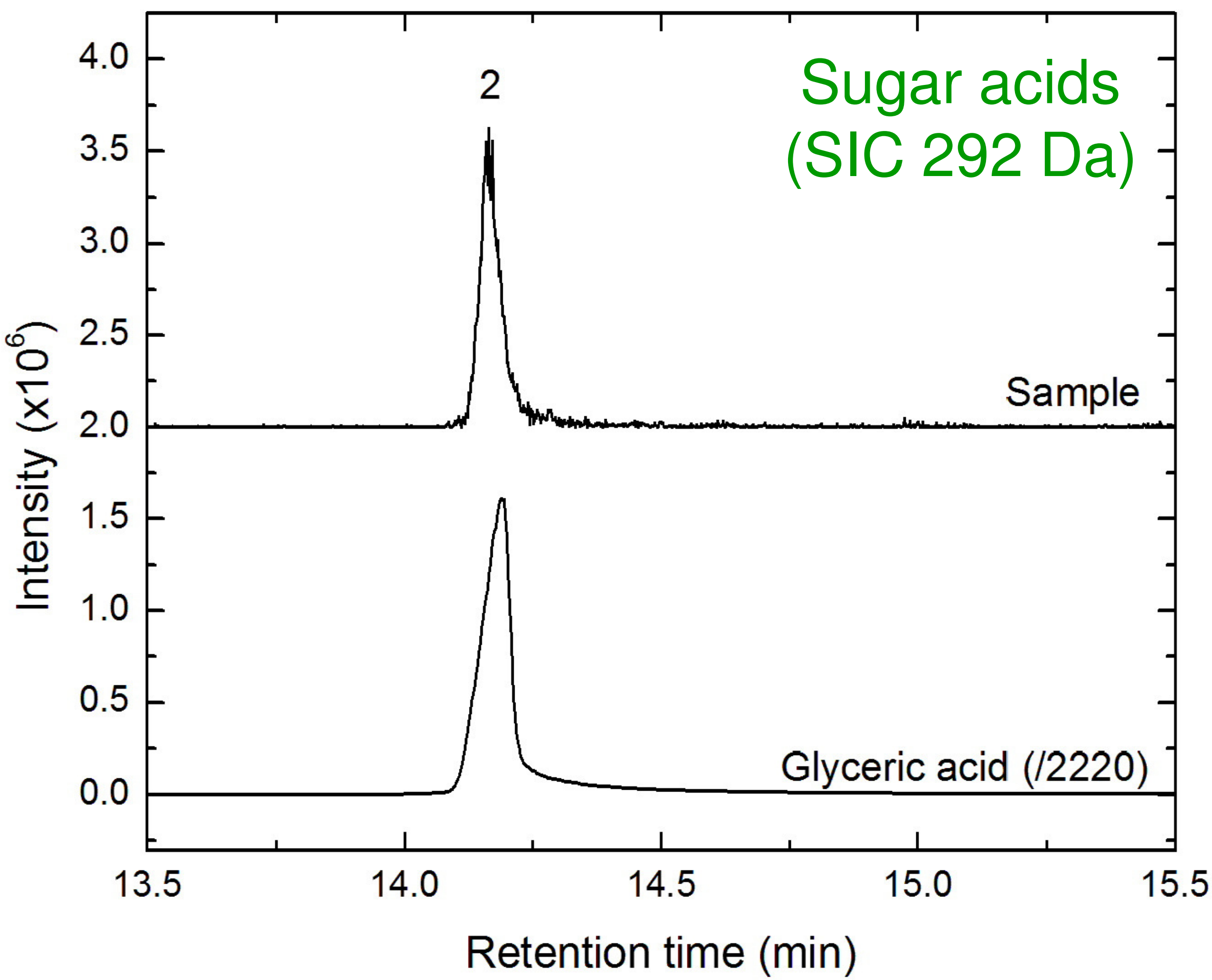
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

Results

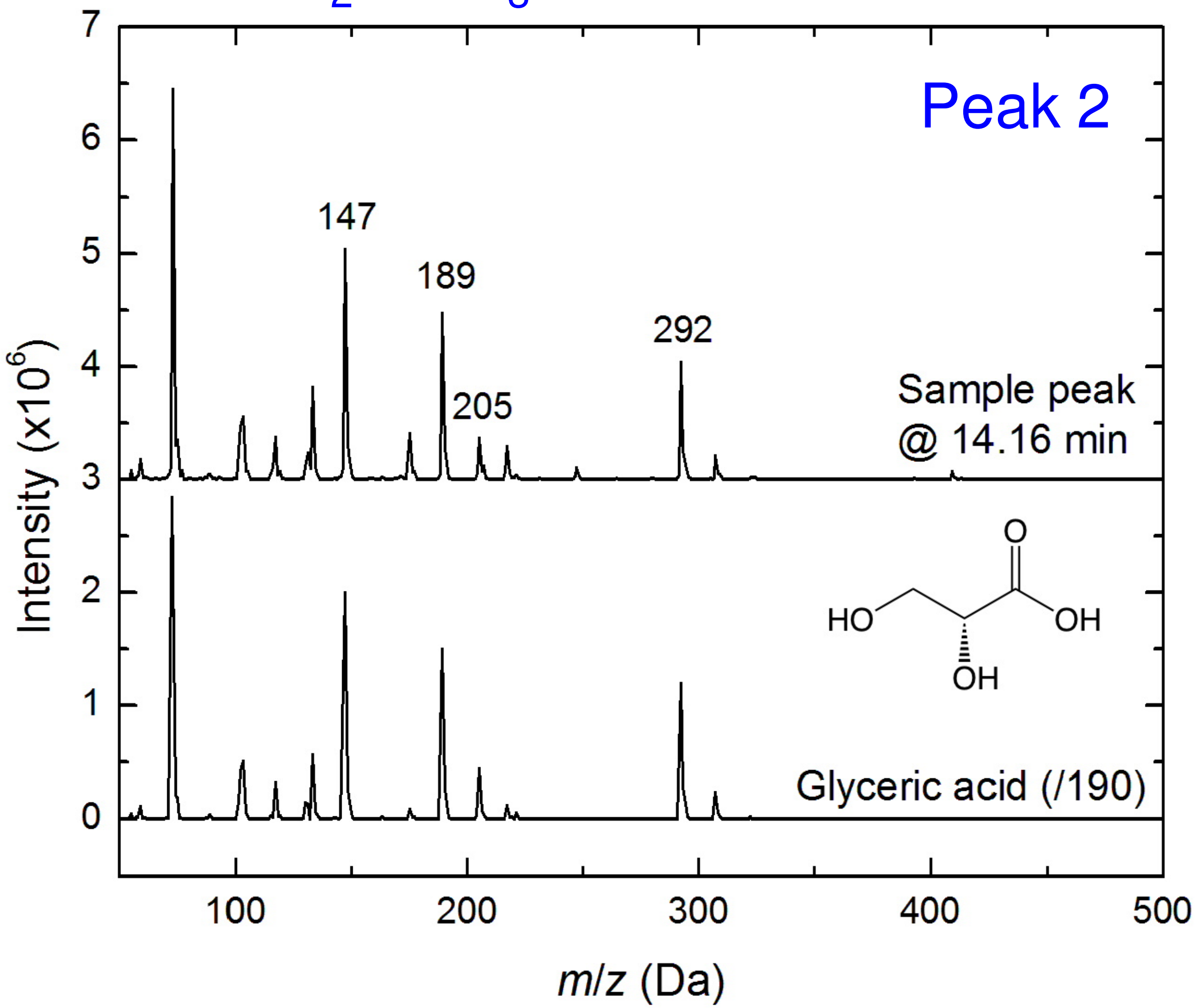
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

Results

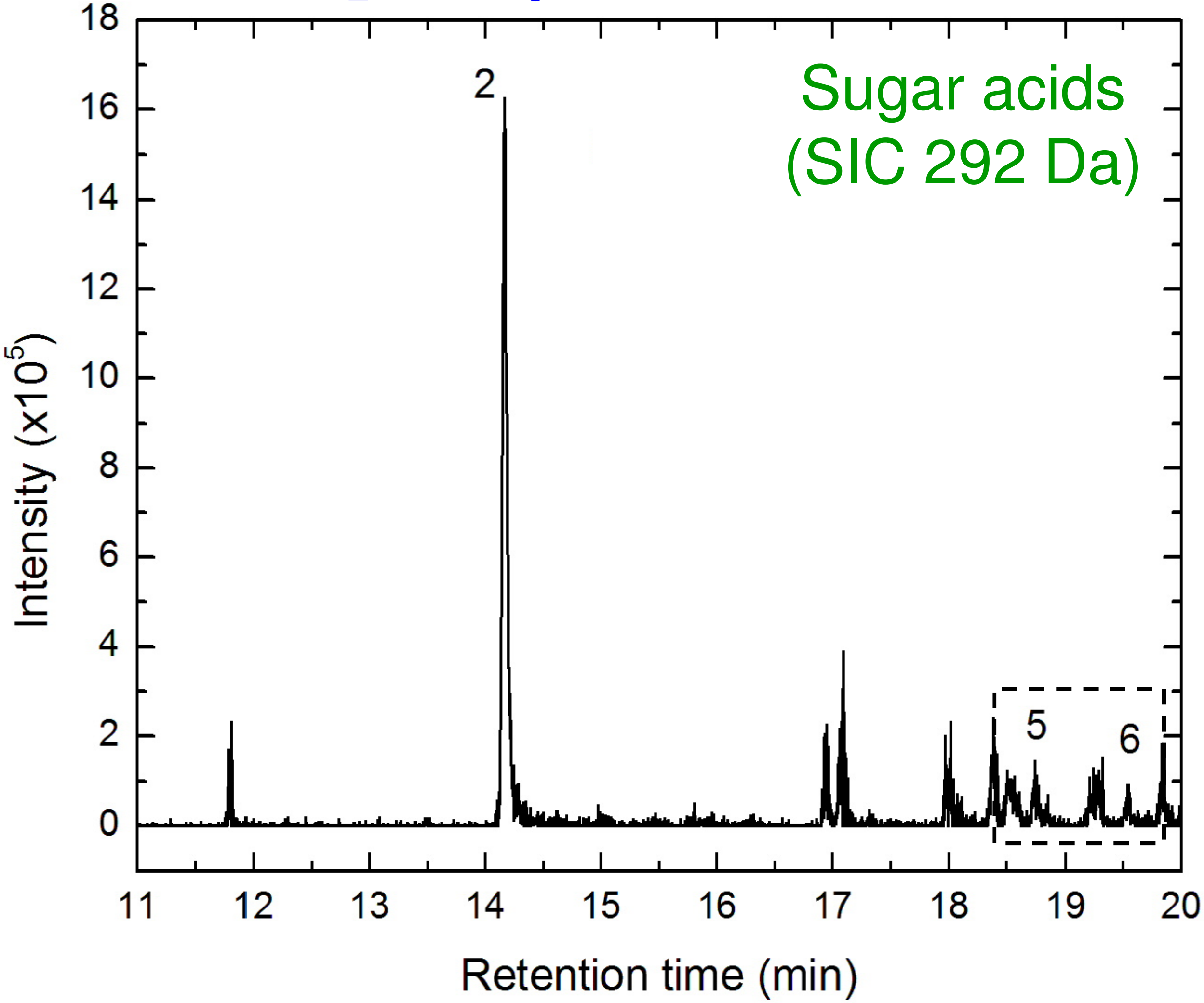
$H_2O:CH_3OH = 2:1 + UV$



Nuevo et al. (submitted)

Results

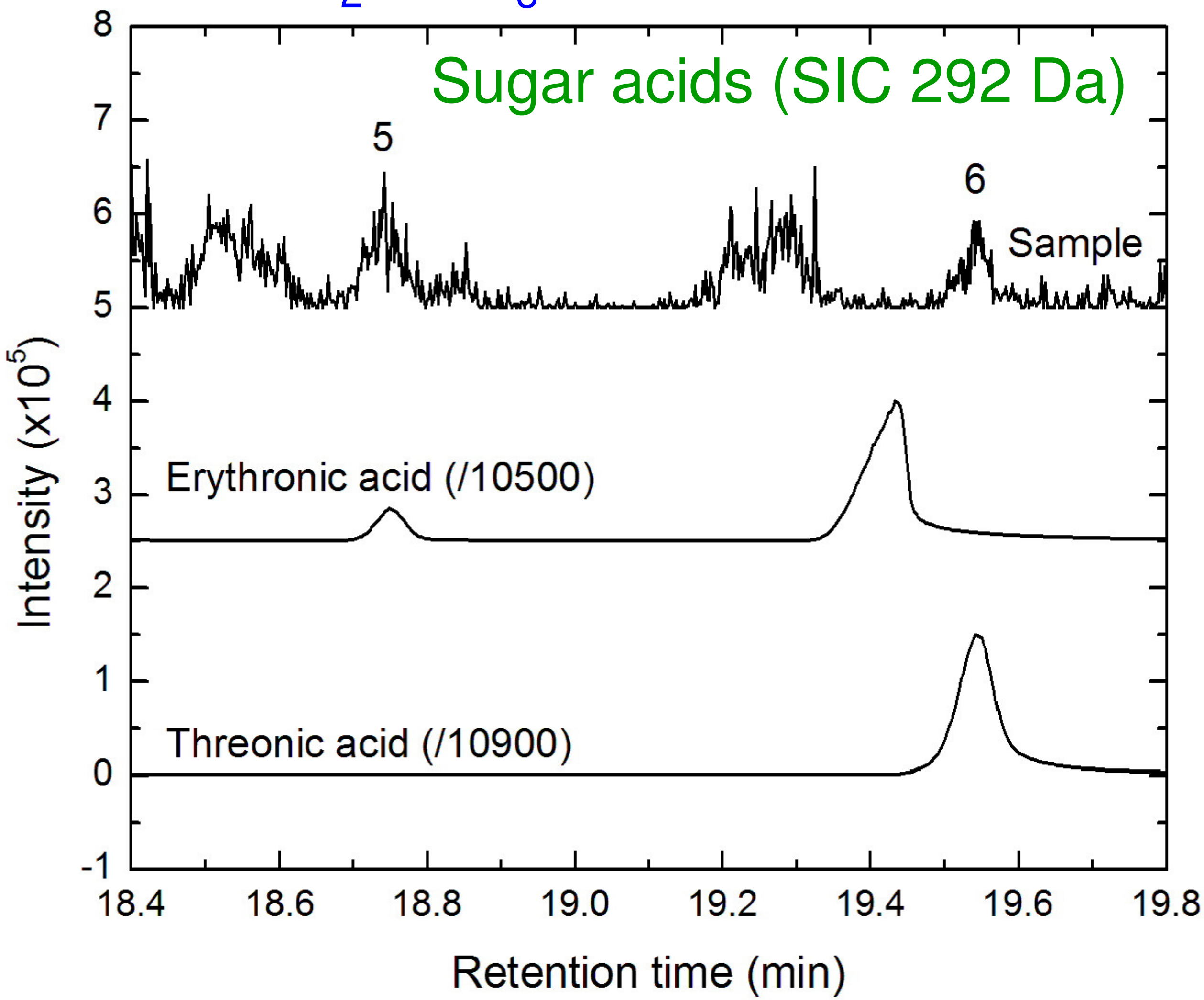
$H_2O:CH_3OH$ = 2:1 + UV



Nuevo et al. (submitted)

Results

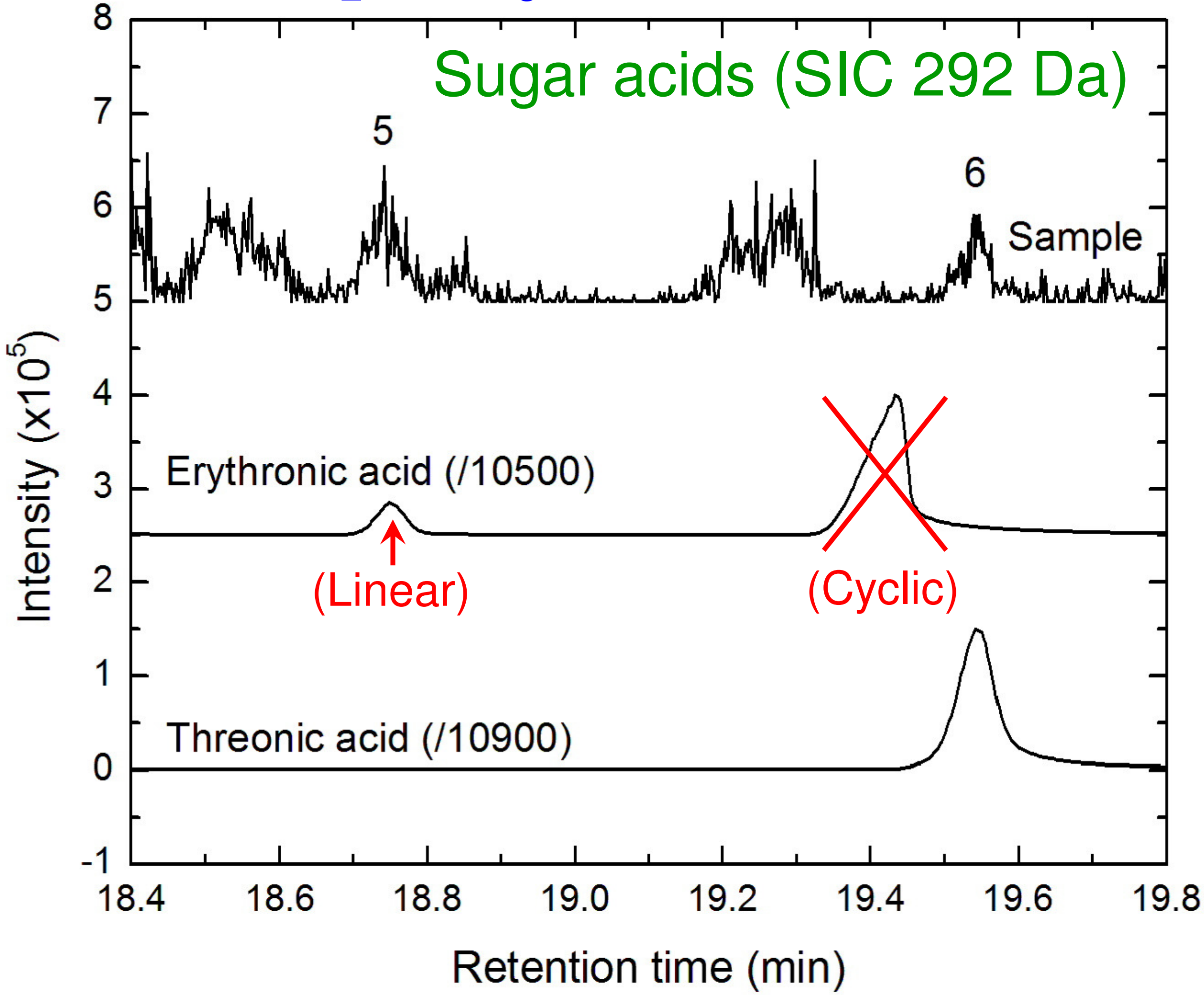
$H_2O:CH_3OH$ = 2:1 + UV



Nuevo et al. (submitted)

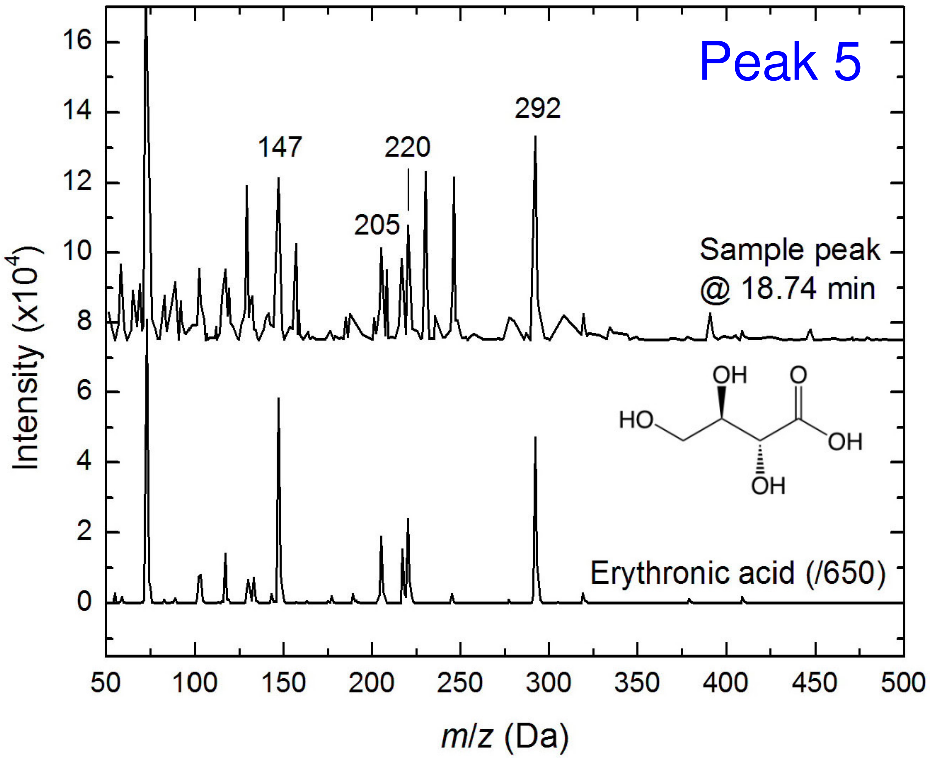
Results

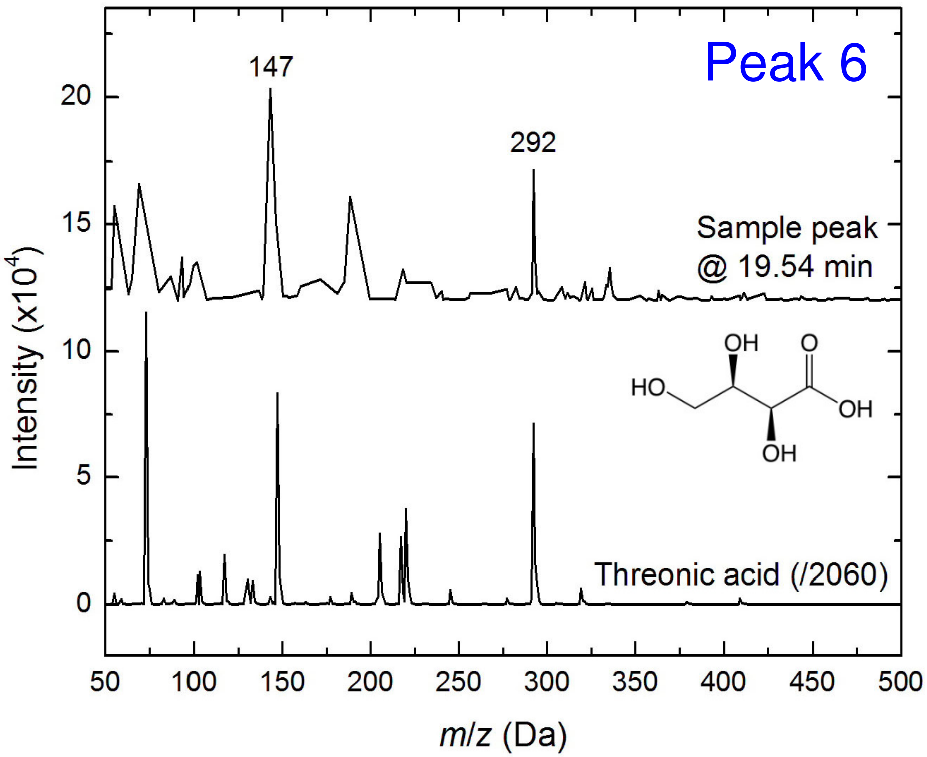
$H_2O:CH_3OH$ = 2:1 + UV



Nuevo et al. (submitted)

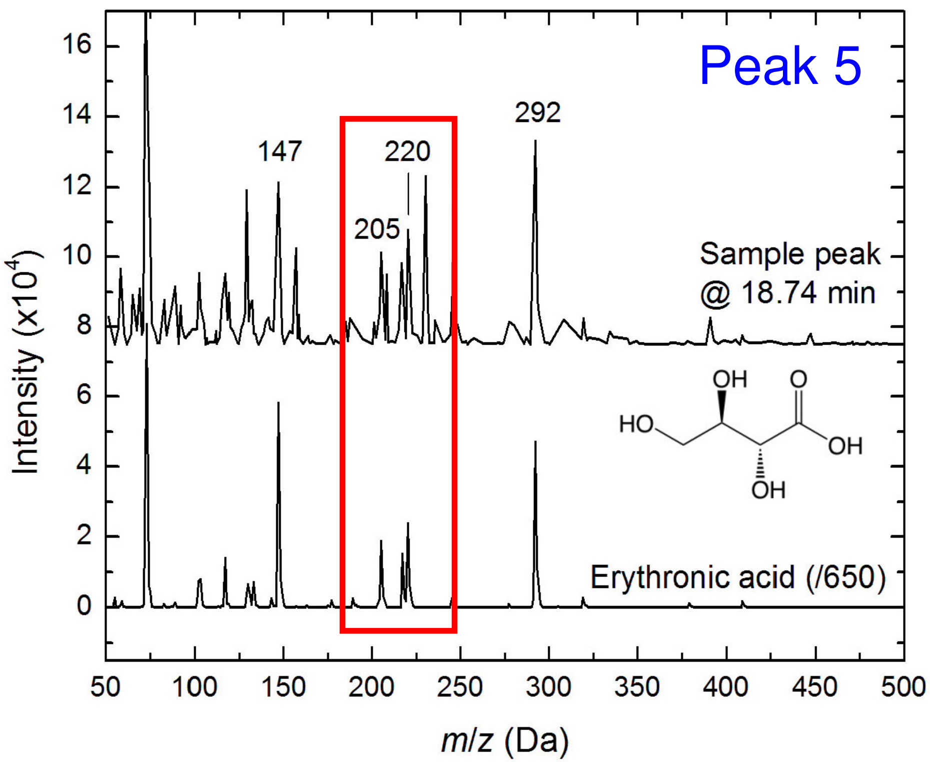
Results

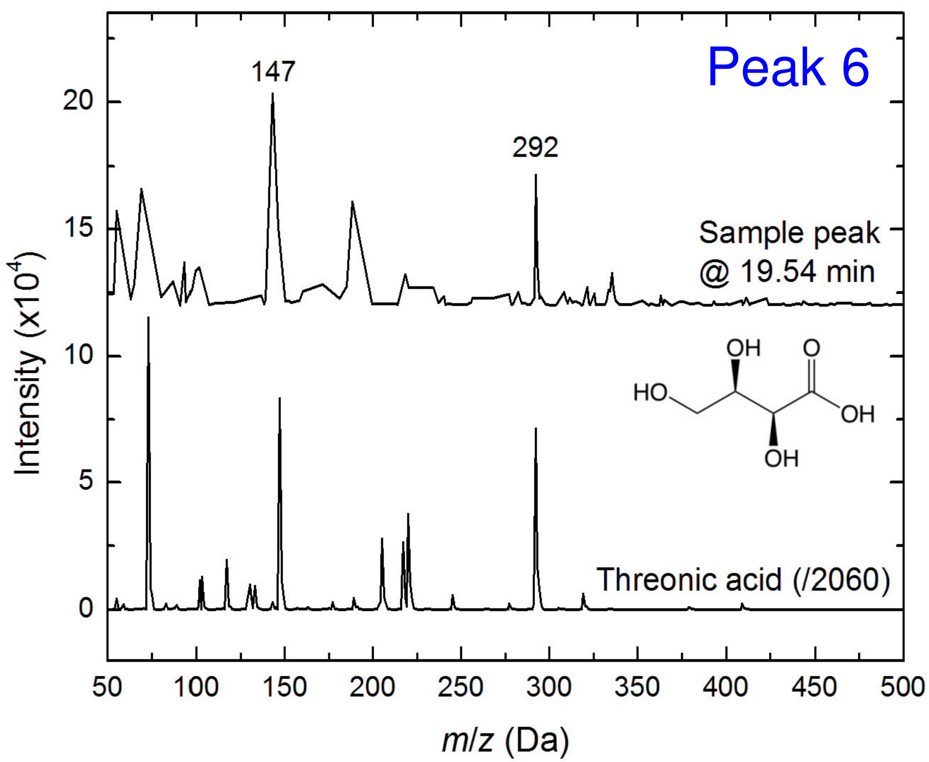




Nuevo et al. (submitted)

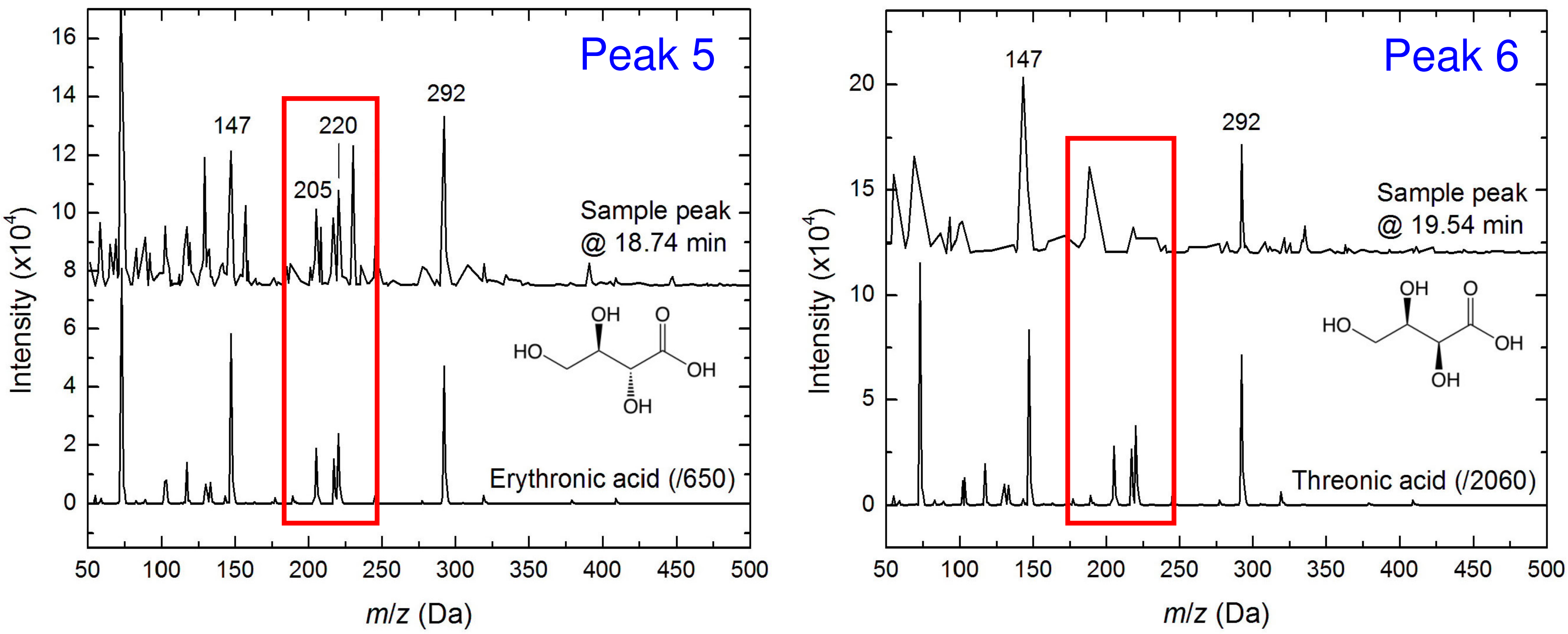
Results





Nuevo et al. (submitted)

Results



Nuevo et al. (submitted)

Results

	Compounds	Relative abundance (Residues)	Relative abundance (Meteorites)
Sugar alcohols	Glycerol (C_3)	100	100
	Erythritol + threitol (C_4)	1.4–6.6	1
	Ribitol + arabitol + xylitol (C_5)	0.1–1.3	(Not reported)
Sugars	Dihydroxyacetone (C_3)	0–14.8	(Not reported)
	Threose + erythrose (C_4)	0.4–6.5	(Not detected)
Sugar acids	Glyceric acid (C_3)	0.1–0.7	50
	Erythronic + threonic acids (C_4)	0.1–0.9	2.5

Nuevo et al. (submitted)

Results

~190 nmol

	Compounds	Relative abundance (Residues)	Relative abundance (Meteorites)
Sugar alcohols	Glycerol (C_3)	100	100
	Erythritol + threitol (C_4)	1.4–6.6	1
	Ribitol + arabitol + xylitol (C_5)	0.1–1.3	(Not reported)
Sugars	Dihydroxyacetone (C_3)	0–14.8	(Not reported)
	Threose + erythrose (C_4)	0.4–6.5	(Not detected)
Sugar acids	Glyceric acid (C_3)	0.1–0.7	50
	Erythronic + threonic acids (C_4)	0.1–0.9	2.5

Nuevo et al. (submitted)

Results

~190 nmol

~160 nmol/g

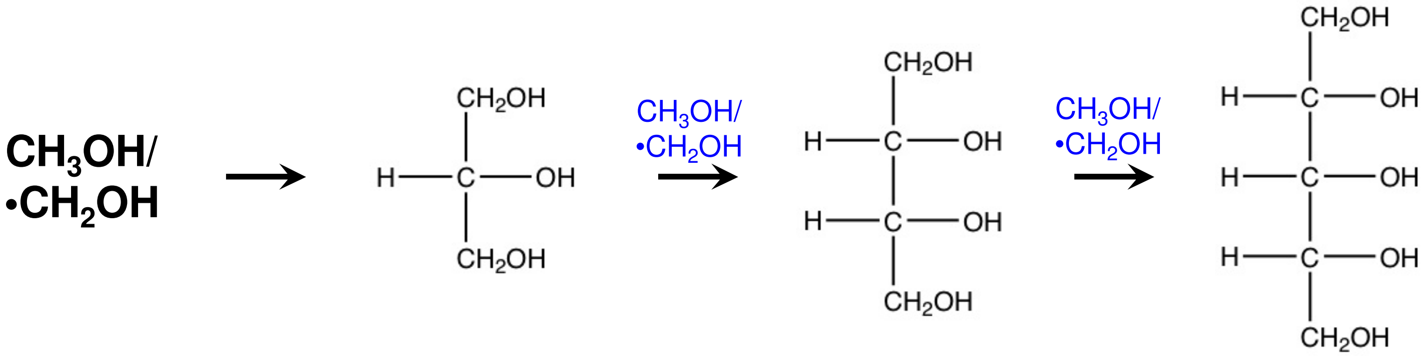
	Compounds	Relative abundance (Residues)	Relative abundance (Meteorites)
Sugar alcohols	Glycerol (C_3)	100	100
	Erythritol + threitol (C_4)	1.4–6.6	1
	Ribitol + arabitol + xylitol (C_5)	0.1–1.3	(Not reported)
Sugars	Dihydroxyacetone (C_3)	0–14.8	(Not reported)
	Threose + erythrose (C_4)	0.4–6.5	(Not detected)
Sugar acids	Glyceric acid (C_3)	0.1–0.7	50
	Erythronic + threonic acids (C_4)	0.1–0.9	2.5

Nuevo et al. (submitted)

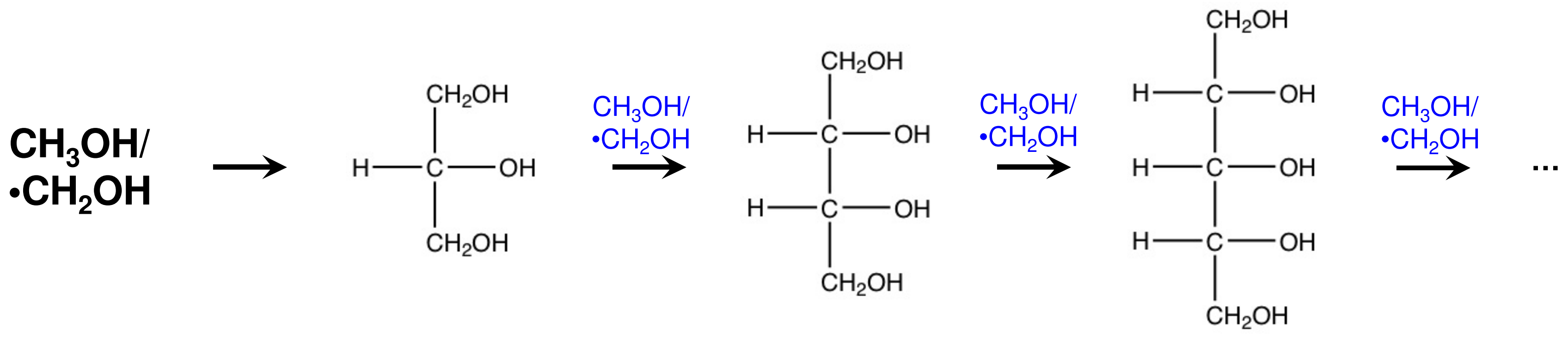
Formation pathway?

CH_3OH/
•CH_2OH

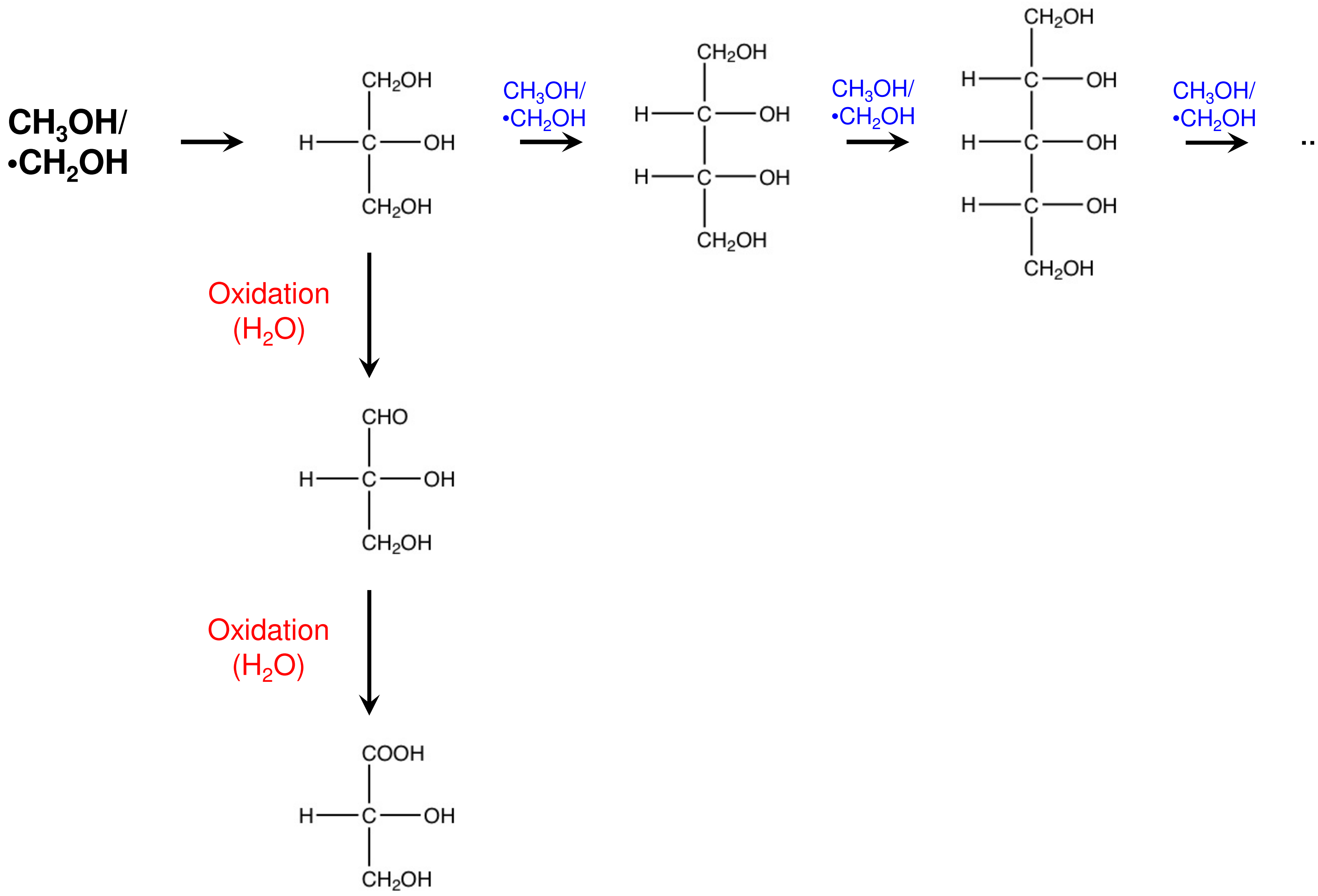
Formation pathway?



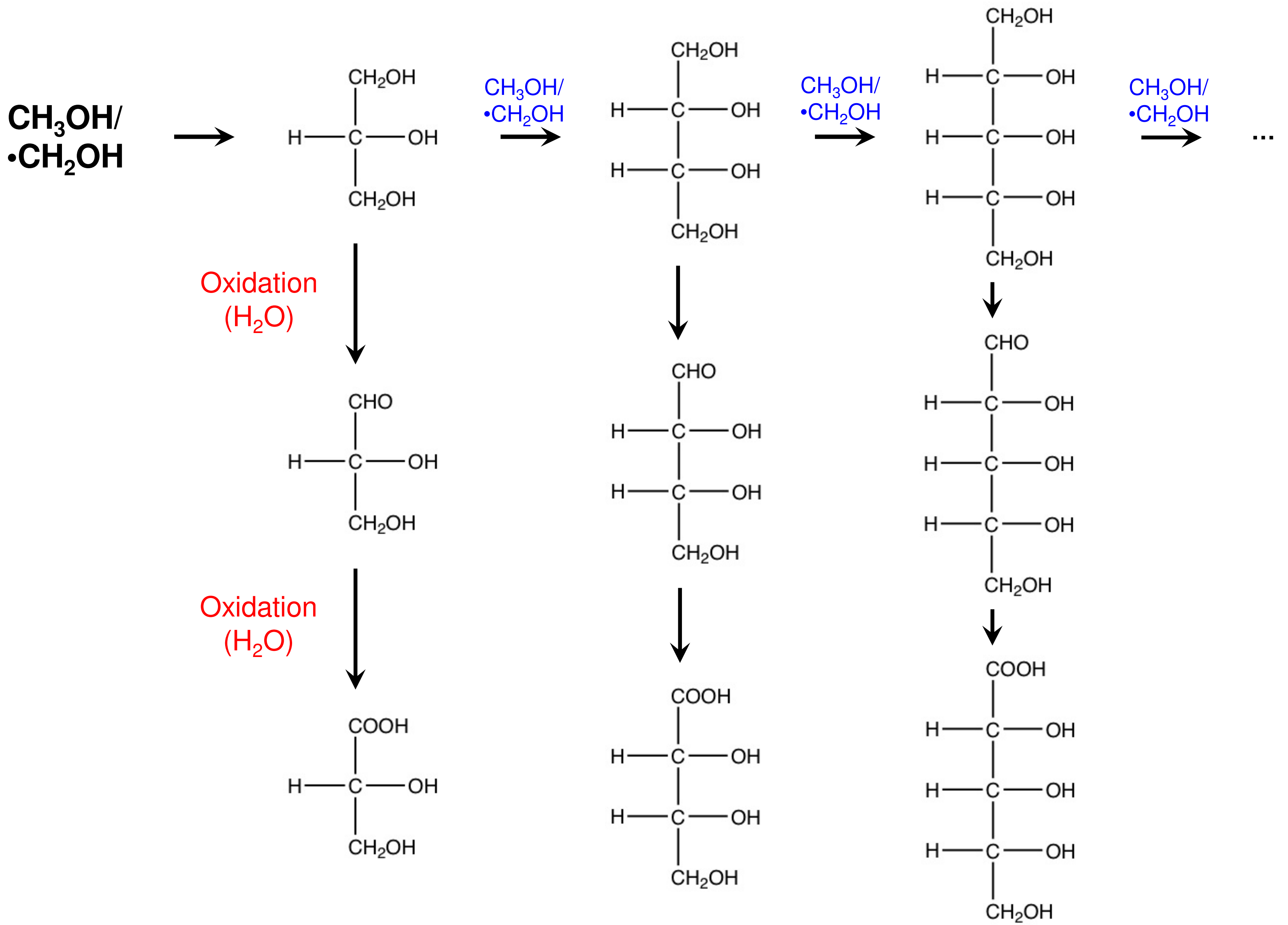
Formation pathway?



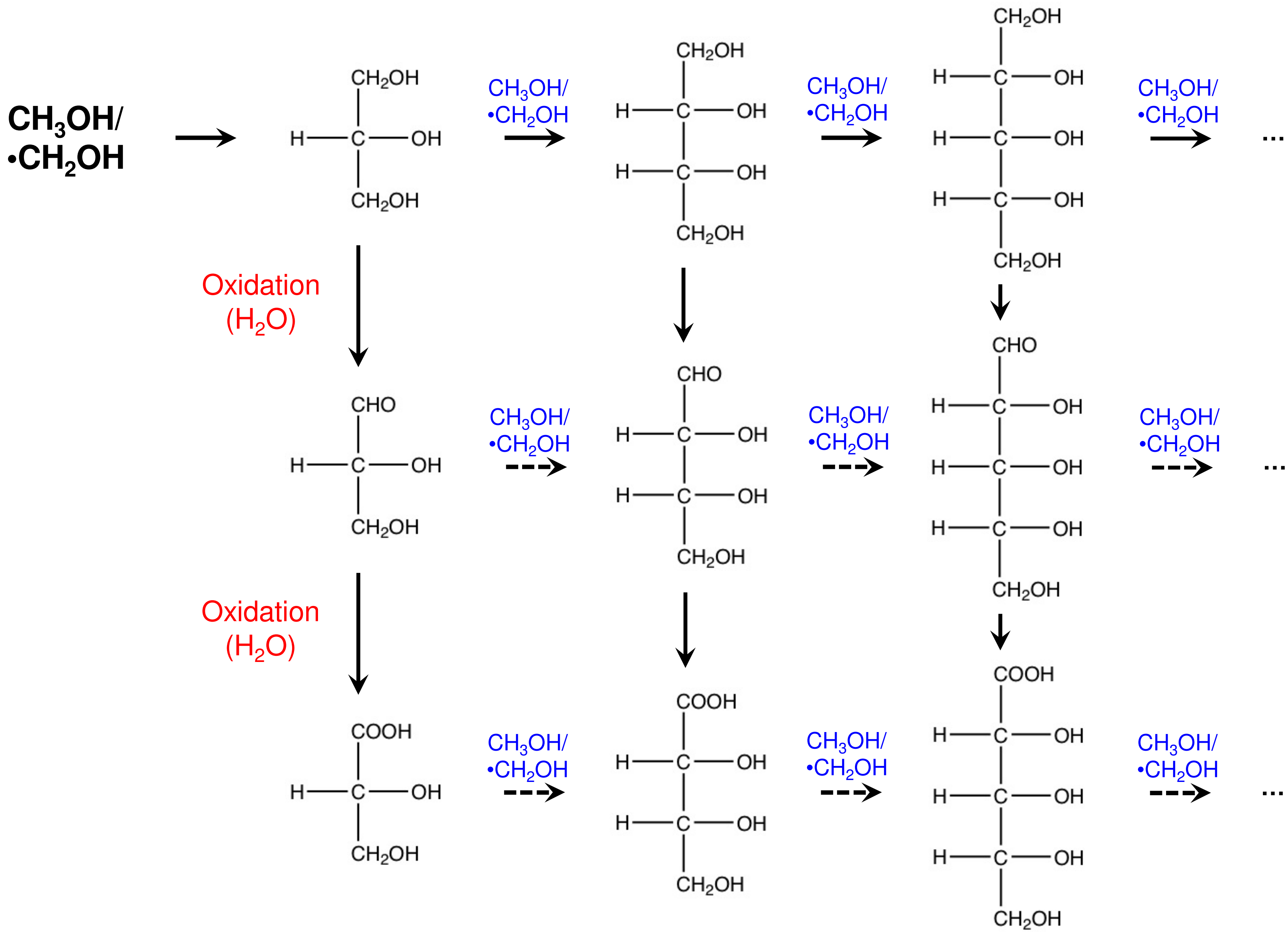
Formation pathway?



Formation pathway?



Formation pathway?



Sugars!!

ASTROCHEMISTRY

Ribose and related sugars from ultraviolet irradiation of interstellar ice analogs

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

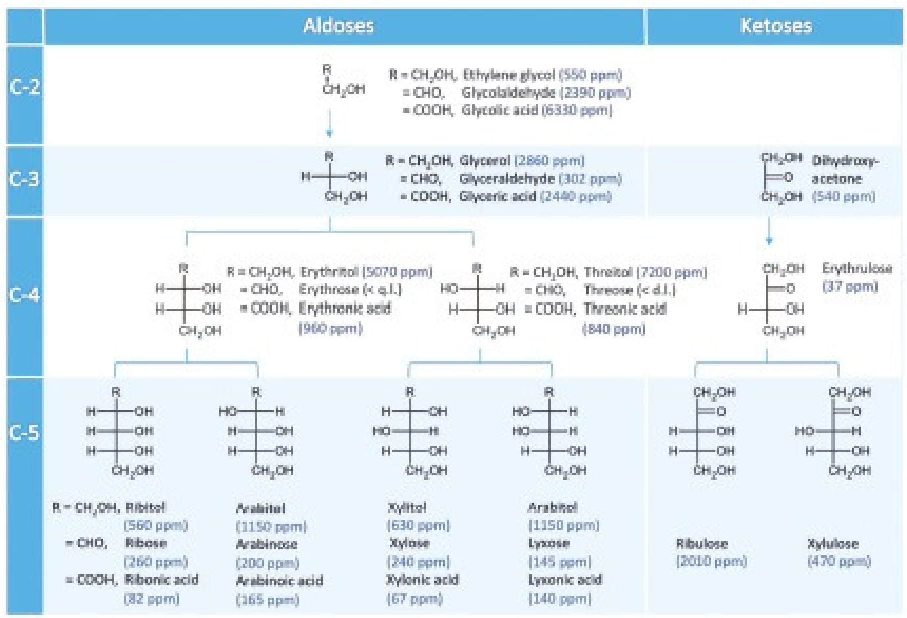
Ribose is the central molecular subunit in RNA, but the prebiotic origin of ribose remains unknown. We observed the formation of substantial quantities of ribose and a diversity of structurally related sugar molecules such as arabinose, xylose, and lyxose in the room-temperature organic residues of photo-processed interstellar ice analogs initially composed of H_2O, CH_3OH, and NH_3. 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.

DNA 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 orientates 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 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

[1]Université Nice Sophia Antipolis, Institut de Chimie de Nice, UMR 7272 CNRS, 28 Avenue Valrose, 06108 Nice, France. [2]Synchrotron SOLEIL, L'Orme des Merisiers, St Aubin BP48, 91192 Gif-sur-Yvette, France. [3]Institut d'Astrophysique Spatiale, CNRS, Université Paris-Sud, Université Paris-Saclay, bât 121, 91405 Orsay, France. [4]Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Avenida Universidad 1001, 62209 Cuernavaca, Mexico. [5]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, monosaccharides, 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.



Sugars!!

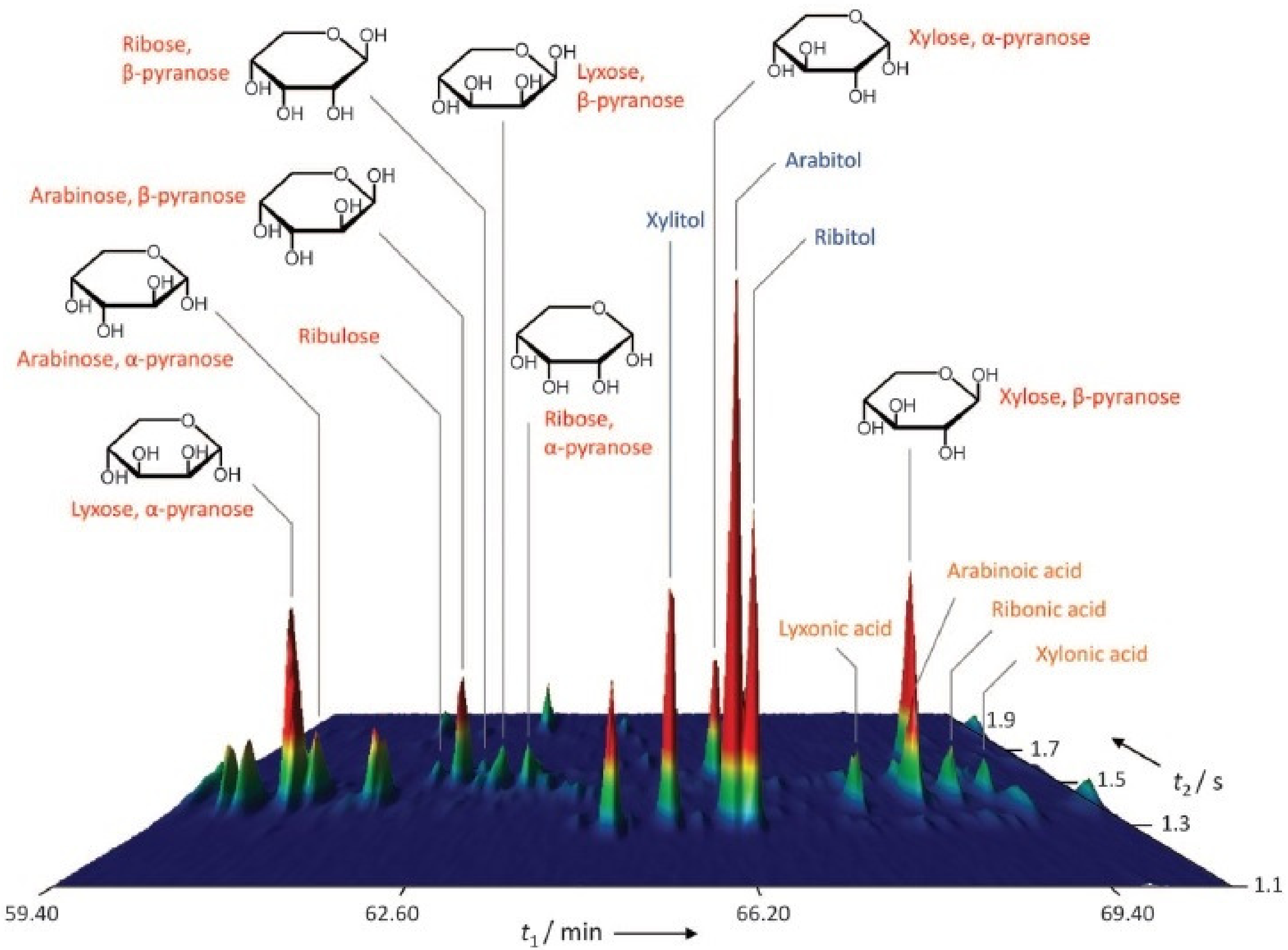
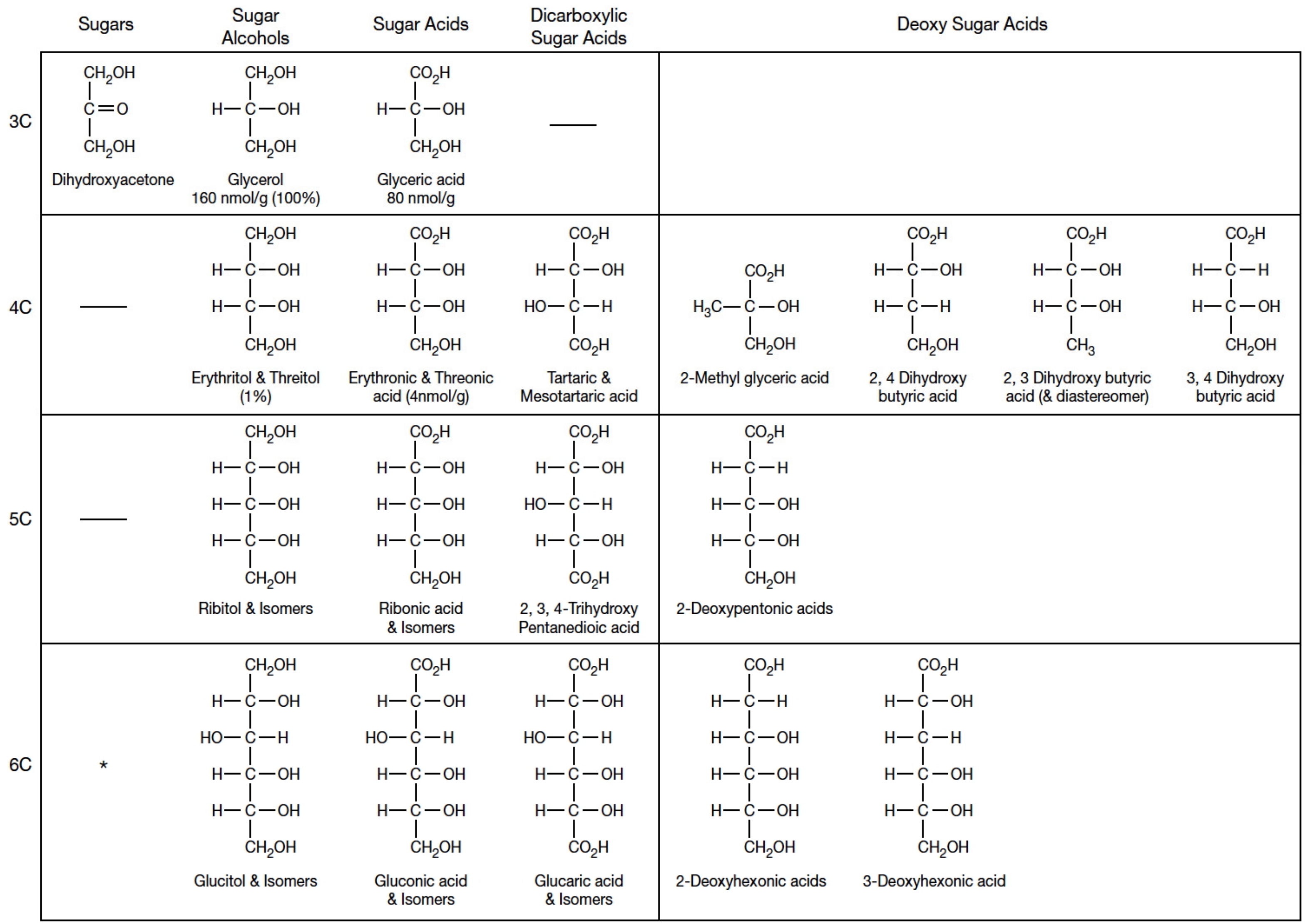


Fig. 2. Multidimensional gas chromatogram showing ribose and other monosaccharides in the organic residue from an evolved precometary ice analog. See also fig. S1 and movie S1 (7). The atomic mass units 206 and 294 were selected for the multidimensional chromatographic representation. D- and L-enantiomers of the monosaccharides were not resolved.

Summary

- UV irradiation of $H_2O:CH_3OH$ 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)

Work in Progress

- Use of ^{13}C-labeled methanol ($^{13}CH_3OH$) 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 $H_2O:CO_2$ and $H_2O:CH_3OH:CO_2$ ices leads to the formation of more sugar acids.
- Add NH_3 to the starting mixtures: UV irradiation of $H_2O:CH_3OH:NH_3$ (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).
- Perforom similar experiments with starting mixtures mimicking more realistic astrophysical ices (containing H_2O, CH_3OH, CO, CO_2, CH_4, and NH_3)

Acknowledgments

- People:
  - Scott Sandford (NASA Ames)
  - George Cooper (NASA Ames)
  - John Michael Saunders (UC Santa Cruz)
  - Christopher Materese (NASA Ames)
- Funding:
  - NASA Exobiology Program
  - NASA Astrobiology Institute

Astrochemistry Laboratory at NASA Ames Research Center

http://www.astrochem.org/