Supplementary Information (SI) for ChemComm.

Supplementary Information

A Selective Non-Enzymatic Synthesis of Ribose Simply from Formaldehyde, Metal Salts and Clays

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General Information of Reagents:

D-Ribose (CAS 50-69-1) was purchased from Sigma-Aldrich (99%), TCI (>98%), Aladdin (>98%). L-Arabinose (CAS 87-72-9) was purchased from Macklin (>98%). D-Erythrose (CAS 583-50-6) were purchased from Adamas (75%). D-Xylose (CAS 6763-34-4) was purchased from Bidepharm (>97%). D-Mannose (CAS 3458-28-4) and D-galactose (CAS 59-23-4) were purchased from Adamas (>99%). D-Glucose (CAS 492-62-6) was purchased from Aldrich (>96%, anhydrous). D-Lyxose (CAS 1114-34-7), L-threose (CAS 95-44-3) and L-gulose (CAS 6027-89-0) were purchased from Shanghai Yuanye Bio-Technology Co., Ltd (99%). D-Allose (CAS 2595-97-3) were purchased from Shanghai Yuanye Bio-Technology Co., Ltd (>97%). D-Talose (CAS 2595-98-4) was purchased from Bidepharm (98%). D-Altrose (CAS 1990-29-0) was purchased from 9dingchem (99%). D-Idose (CAS 5978-95-0) was purchased from J&K Scientific (0.141 M in water). Xylitol was (CAS 87-99-0) purchased from Adamas-beta (99%). D-Sorbitol was (CAS 50-70-4) purchased from Adamas-beta (98%). L-Sorbitol was (CAS 533-50-6) purchased from Macklin (90%). 1,3-Dihydroxyacetone was (CAS 96-26-4) purchased from Adamas-beta (98%). Montmorillonite K-10 (CAS 1318-93-0) was purchased from Adamas-beta. Iron (II) chloride (CAS 7758-94-3) was purchased from Macklin (99.5%). Anhydrous magnesium chloride (CAS 7786-26-2) was purchased from Adamas-beta (99%). Manganese (II) chloride (CAS 13446-34-9) was purchased from TCI (98%). Acetic anhydride (CAS 108-24-7) was purchased from Sinopharm Chemical Reagent Co., Ltd (AR, >98.5%). Pyridine (CAS 110-86-1) was purchased from J&K Scientific (water ≤ 30 ppm). Hydroxylamine hydrochloride (CAS 5470-11-1) was purchased from Adamas-beta (99%). Formaldehyde (CAS 50-00-0) was purchased from Alfa Aesar (37–40% in water). Glycolaldehyde dimer (CAS 23147-58-2) was purchased from Bidepharm (95%). Hydrochloric acid (CAS 7647-01-0) was purchased from Sinopharm Chemical Reagent Co., Ltd (36.0～38.0%). Sodium hydroxide (CAS 1310-73-2) was purchased from General-Reagent (>98%).

General Information of Instruments:

The magnetic stirrer (C-MAG HS 7) was manufactured by IKA®. The centrifugation separation was performed on a centrifuge manufactured by Flying Pigeon. Gas chromatography (GC) was performed on a GC-9860 manufactured by Shanghai Qiyang Information Technology Co. Ltd with an auto-injector (AOC-20i, Shimadzu) using an ACR5 column (30 m, 0.32 mm i.d., film thickness 0.25 μm, TRAJAN GC column). The injector inlet was set to a temperature of 250 °C, and the split mode was applied (ratio: 1/15). The GC was used with the following temperature program: oventemp/°C: 50, 150, 280; rate/°C•min^{-1}: 0, 20, 10; time/min: 3, 1, 2. Gas chromatography mass spectrometric (GCMS) analysis was performed on GCMS-QP2010 Ultra with an auto-injector (AOC-20s, Shimadzu) using a Rtx-5MS column (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 μm). The injector inlet was set to a temperature of 250 °C, the split mode was applied (ratio: 1/20). The GC was used with the following temperature program: oventemp/°C: 50, 150, 280; rate/°C•min^{-1}: 0, 20, 10; time/min: 3, 1, 2. Mass spectrometer was used with an Electron Impact Ionization Mode. Transmission electron microscope (TEM) and element mapping were acquired on JEM-1011 (JEOL Ltd., Japan) with an accelerating voltage of 200 kV.

Procedure for the aldoses, ketoses, and sugar alcohols derivatization:

To a mixture of aldoses in pyridine (1 mL) was added hydroxylamine hydrochloride (10 mg, 0.14 mmol) and stirred at 90 °C for 0.5 h. The aldoses include D-erythrose (5 mg, 0.042 mmol), L-threose (5 mg, 0.042 mmol), D-ribose (5 mg, 0.033 mmol), L-arabinose (5 mg, 0.033 mmol), D-lyxose (5 mg, 0.033 mmol), D-xylose (5 mg, 0.033 mmol), D-mannose (5 mg, 0.028 mmol), D-galactose (5 mg, 0.028 mmol), D-glucose (5 mg, 0.028 mmol), L-gulose (5 mg, 0.028 mmol), D-altrose (5 mg, 0.028 mmol), D-allose (5 mg, 0.028 mmol), D-talose (5 mg, 0.028 mmol), and D-idose (0.5 mg, 0.003 mmol). 1,3-Dihydroxyacetone (5 mg, 0.056 mmol), L-erythrulose (5 mg, 0.042 mmol), erythritol (5 mg, 0.041 mmol), adonitol (5 mg, 0.033 mmol), arabitol (5 mg, 0.033 mmol), xylitol (5 mg, 0.033 mmol), mannitol (5 mg, 0.027 mmol), sorbitol (5 mg, 0.027mmol), dulcitol (5 mg, 0.027 mmol). After cooling to room temperature, acetic anhydride (10.6 mmol, 1 mL) was added to the mixture for acetylation in an ice bath. The mixture was again stirred at 90 °C for 0.5 h. The mixture was then cooled to room temperature, followed by dilution with chloroform. The mixture was decanted into sample vials for analysis by GC and GC-MS.

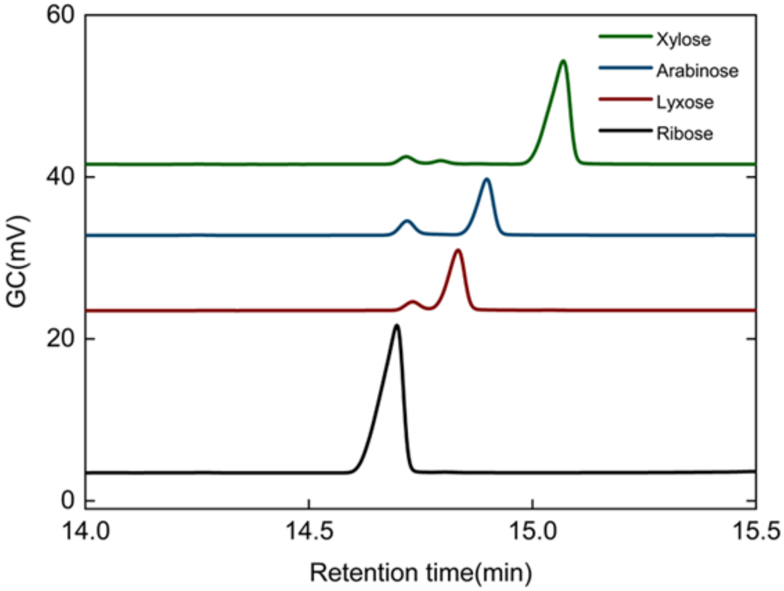
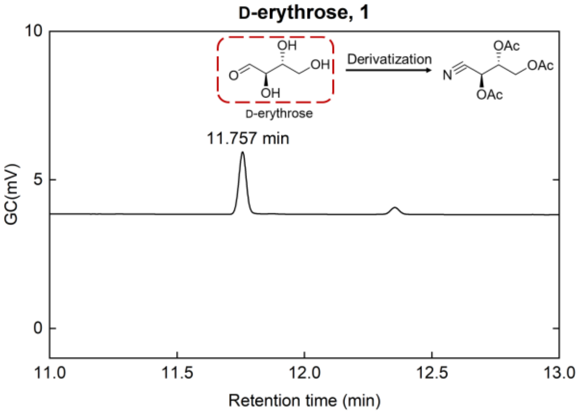


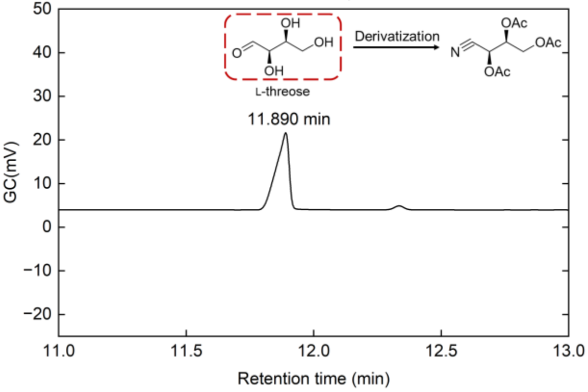
Fig. S1. GC traces of the pentoses derivatized with hydroxylamine hydrochloride and acetic anhydride

(1) Derivatized aldoses:

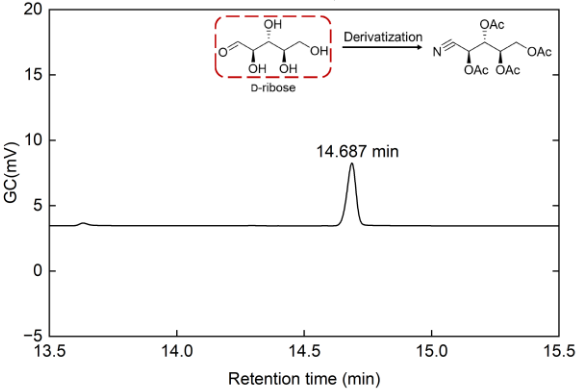
D-erythrose, 1



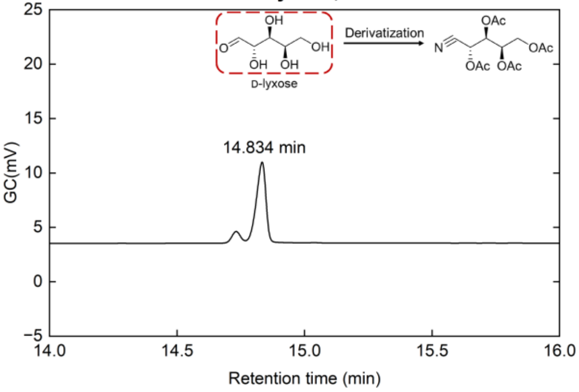
L-threose, 2



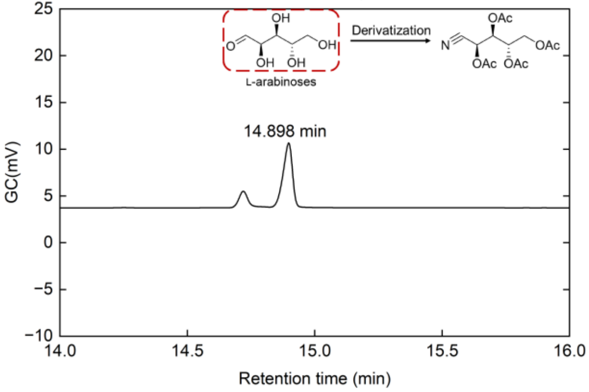
D-ribose, 3



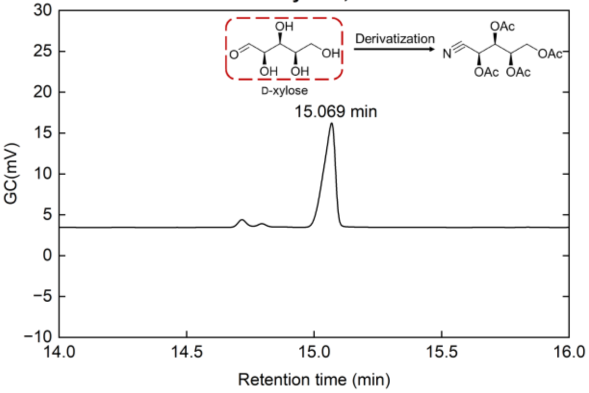
D-lyxose, 4



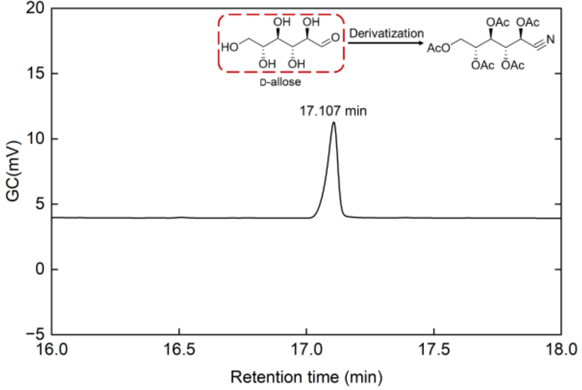
L-arabinose, 5



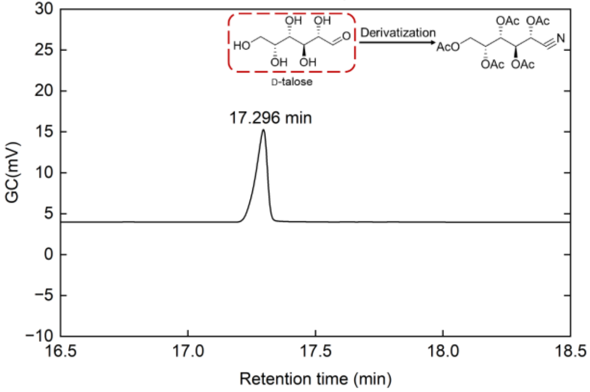
D-xylose, 6



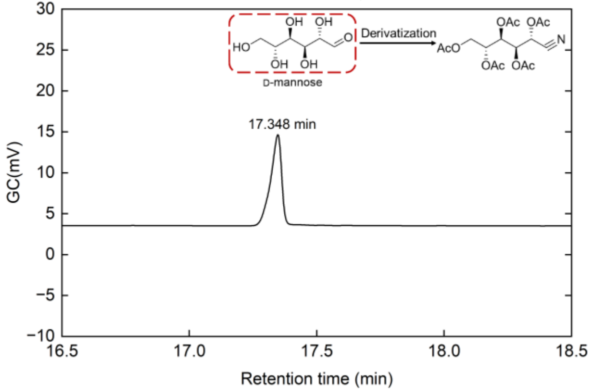
D-allose, 7



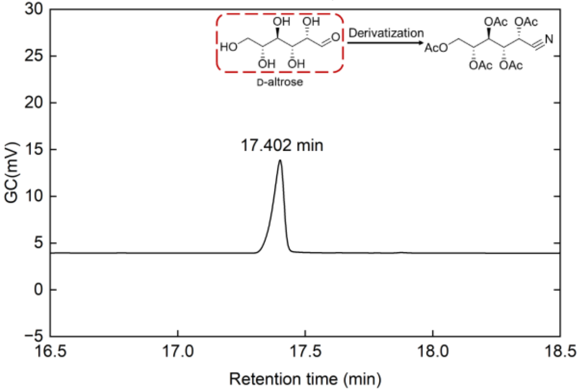
D-talose, 8



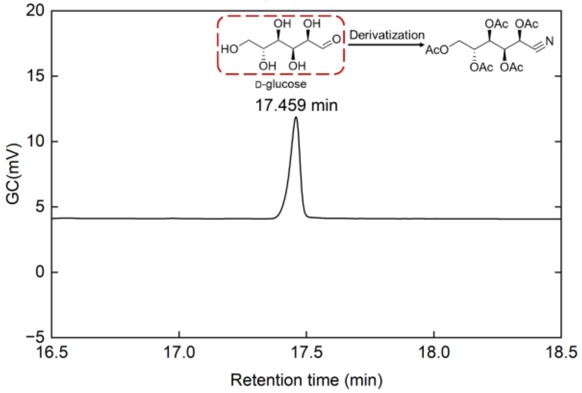
D-mannose, 9



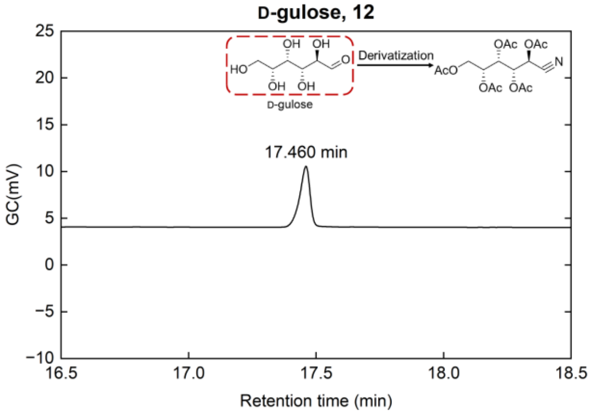
D-altrose, 10

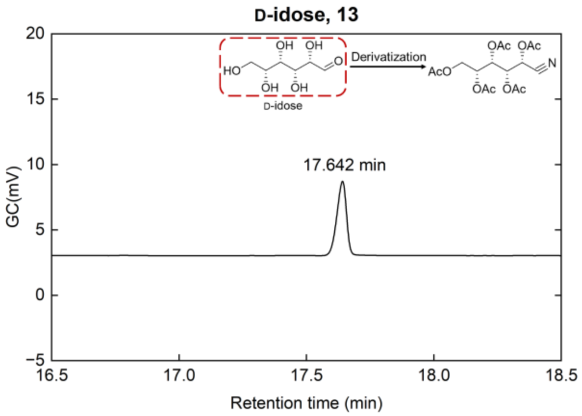


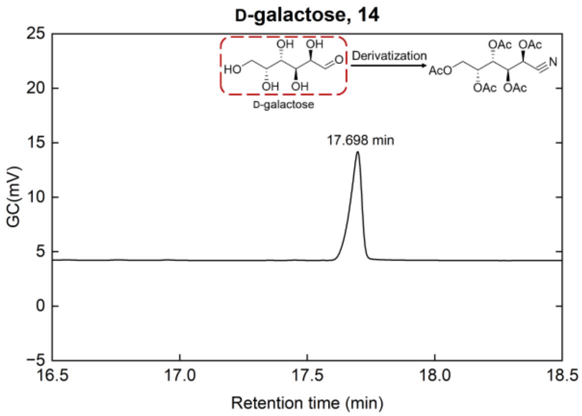
D-glucose, 11



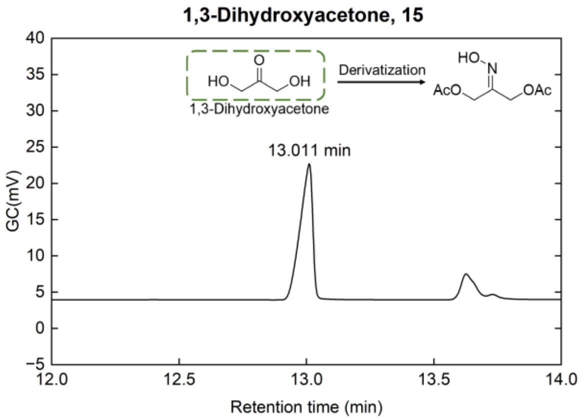
D-gulose, 12

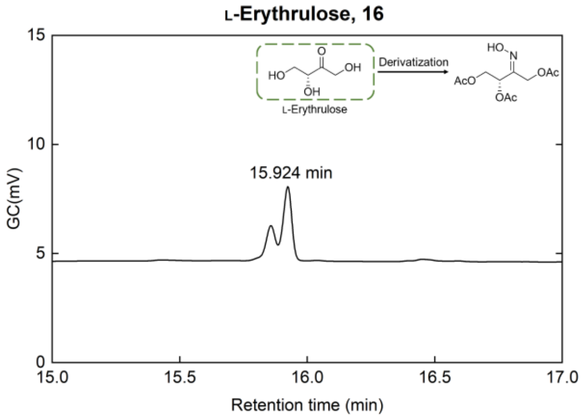




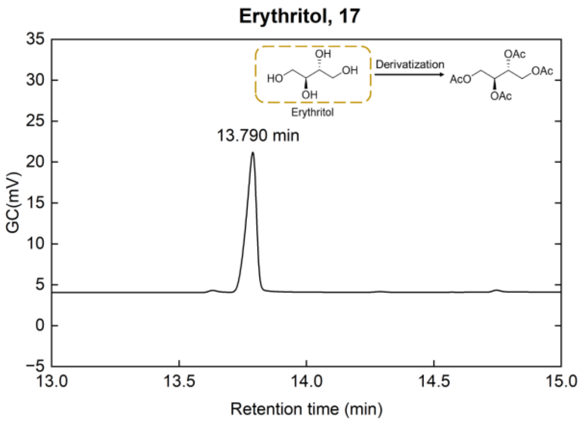


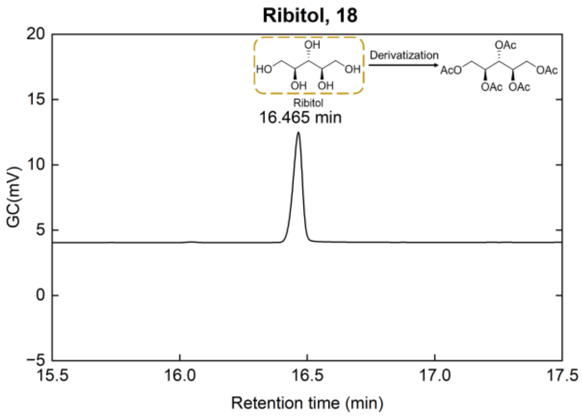
(2) Derivatized ketoses





(3) Derivatized sugar alcohols





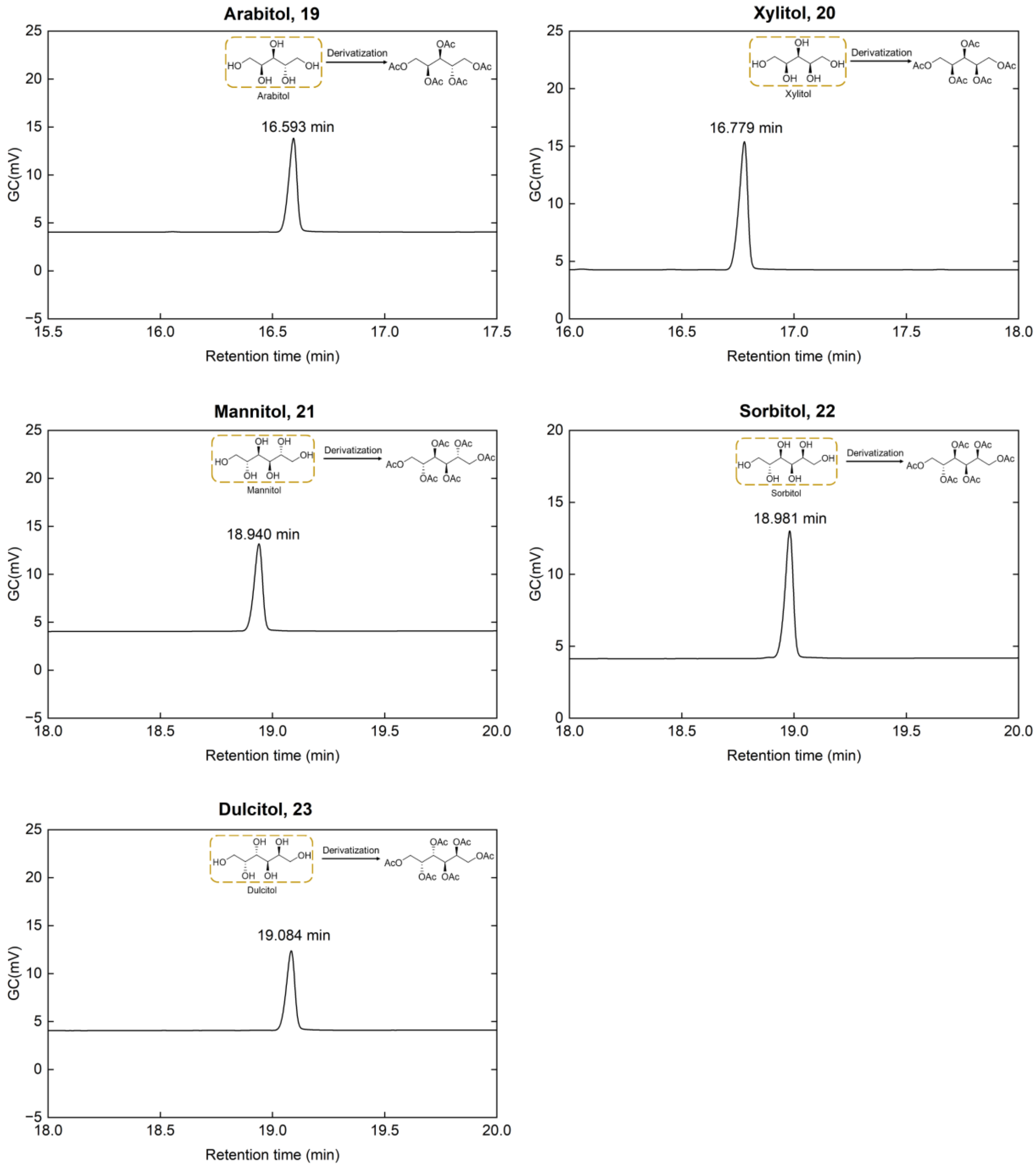
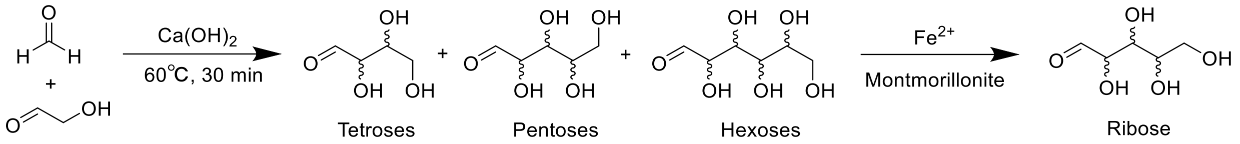


Fig. S2. GC traces of derivatized commercial samples: (1) D-erythrose, (2) L-threose, (3) D-ribose, (4) D-lyxose, (5) L-arabinose, (6) D-xylose, (7) D-allose, (8) D-talose, (9) D-mannose, (10) D-altrose, (11) D-glucose, (12) L-gulose, (13) D-idose, (14) D-galactose, (15)1,3-Dihydroxyacetone, (16) L-erythrulose, (17) erythritol, (18) adonitol, (19) arabitol, (20) xylitol, (21) mannitol, (22) sorbitol, (23) dulcitol.

Procedures for the formose reaction and subsequent selection of ribose with Fe^{2+}-montmorillonite:



Original mixture: To a mixture of $Ca(OH)_2$ (0.1 M) in water (300 mL) was added formaldehyde (4463 µL, 60 mmol, 0.2 M) and glycolaldehyde dimer (3.60 mg, 0.03 mmol, 0.1 mM), and stirred at 60 °C for 0.5 h under nitrogen atmosphere. The mixture was filtered and neutralized to pH 7 with aqueous HCl (as "the original mixture").

Derivatization of original mixture: 20 mL of the original mixture was removed solvent by rotary evaporator to give a yellow oily residue. To the residue was added a solution of hydroxylamine hydrochloride in pyridine (0.58 M, 4 mL) and stirred at 90 °C for 0.5 h. After cooling to room temperature, acetic anhydride (42.6 mmol, 4 mL) was added to the mixture for acetylation in an ice bath. The mixture was again stirred at 90 °C for 0.5 h, and then cooled to room temperature. The mixture was filtered or decanted into sample vials for analysis by GC.

Adsorption experiment: The adsorption was performed under nitrogen atmosphere. In a Schlenk flask, montmorillonite (2.8 g) was added to the original mixture (280 mL). The prepared mixture was degassed by vacuum pump and filled with nitrogen. To degassed water (1 mL) was added $FeCl_2 \cdot 4H_2O$ (280 mg) under nitrogen atmosphere. The prepared $FeCl_2$ solution was injected into the Schlenk flask. The mixture in Schlenk flask was again vacuumed and filled with nitrogen. The pH of the mixture was adjusted to approximately 7 with sodium hydroxide solution added via syringe. The mixture was stirred at 1000 rpm at room temperature for 4 h. The residual solid was washed 3 times with H_2O followed by centrifugation (3–5 min, 7000 r.p.m.), and atmospheric dried overnight to be used for the desorption experiment.

Desorption experiment: To the solid sample was added H_2O (20 mL) and the pH was adjusted to approximately 3 with aqueous HCl. The mixture was stirred at 60 °C for 15 min, then cooled to room temperature and centrifuged (3–5 min, 7000 r.p.m.). The supernatant was removed solvent by rotary evaporator to give a yellow oily residue. To the residue was added a solution of hydroxylamine hydrochloride in pyridine (0.58 M, 1 mL) and stirred at 90 °C for 0.5 h. After cooling to room temperature, acetic anhydride (10.6 mmol, 1 mL) was added to the mixture for acetylation in an ice bath. The mixture was again stirred at 90 °C for 0.5 h, then cooled to room temperature. The mixture was filtered or decanted into sample vials for analysis by GC and GC-MS.

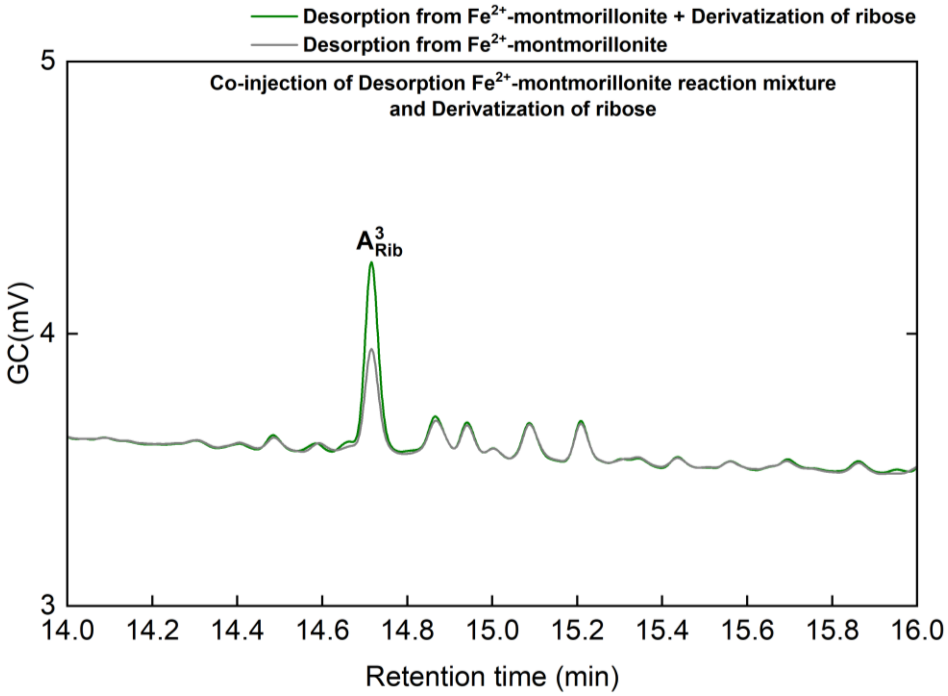


Fig. S3. GC traces of the co-injection of derivatized ribose (green) and the desorbed reaction mixture (from Fe^{2+}-montmorillonite, grey)

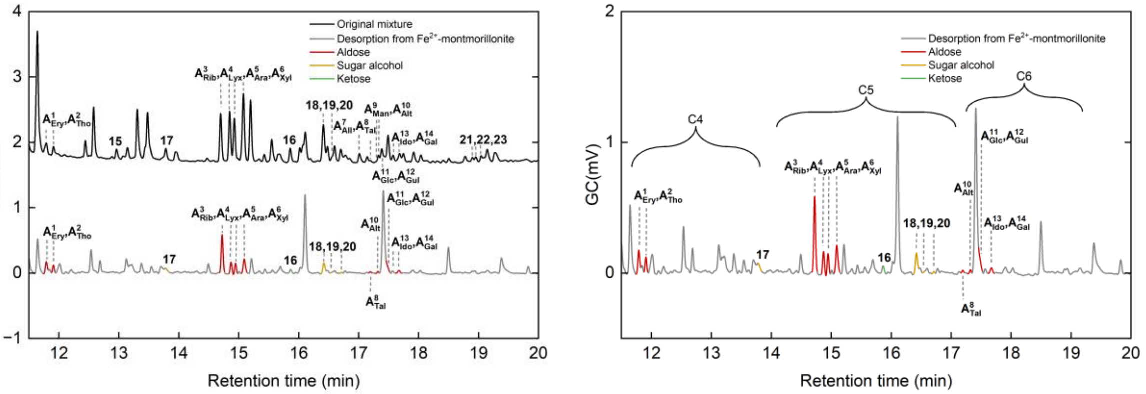
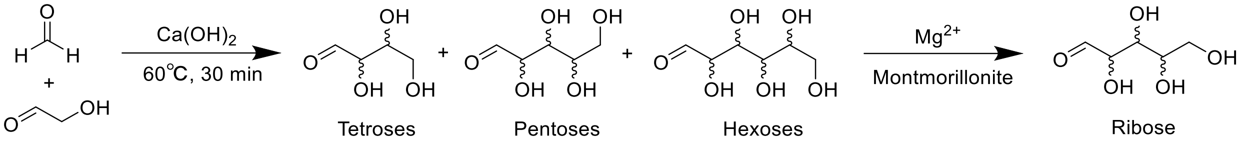


Fig. S4. (A) Comparison of the GC traces of the derivatized formose mixture and desorbed sugars from Fe^{2+}-montmorillonite; (B) GC trace of desorbed sugars from Fe^{2+}-montmorillonite. (**A^1_{Ery}**, erythrose; **A^2_{Tho}**, threose; **A^3_{Rib}**, ribose; **A^4_{Lyx}**, lyxose; **A^5_{Ara}**, arabinose; **A^6_{Xyl}**, xylose; **A^7_{All}**, allose; **A^8_{Tal}**, talose; **A^9_{Man}**, mannose; **A^{10}_{Alt}**, altrose; **A^{11}_{Glc}**, glucose; **A^{12}_{Gul}**, gulose; **A^{13}_{Ido}**, idose; **A^{14}_{Gal}**, galactose; **15**, 1,3-dihydroxyacetone; **16**, L-erythrulose; **17**, erythritol; **18**, adonitol; **19**, Arabitol; **20**, xylitol; **21**, mannitol; **22**, sorbitol; **23**, dulcitol). It is noteworthy that some peaks in the GC trace are partially colored and uncolored for two reasons: 1) For peaks assigned by the retention times of authentic samples, the signal intensities of the major ion fragments were low, indicating the presence of sugars and sugar alcohols at low concentrations which led us to partially colored the corresponding peaks in the GC trace. 2) For peaks not assigned by the retention times of authentic samples, the intensities of the major ion fragments were low and lacked characteristic fragment ions, suggesting they were not sugars or sugar alcohols, thus they were uncolored.

Procedures for the formose reaction and subsequent selection of ribose with Mg^{2+}-montmorillonite:



Original mixture: To a mixture of $Ca(OH)_2$ (0.1 M) in water (300 mL) was added formaldehyde (4463 µL, 60 mmol, 0.2 M) and glycolaldehyde dimer (3.60 mg, 0.03 mmol, 0.1 mM), and stirred at 60 °C for 0.5 h under nitrogen atmosphere. The mixture was filtered and neutralized to pH 7 with aqueous HCl (as "the original mixture").

Derivatization of original mixture: 20 mL of the original mixture was removed solvent by rotary evaporator to give a yellow oily residue. To the residue was added a solution of hydroxylamine hydrochloride in pyridine (0.58 M, 4 mL) and stirred at 90 °C for 0.5 h. After cooling to room temperature, acetic anhydride (42.6 mmol, 4 mL) was added to the mixture for acetylation in an ice bath. The mixture was again stirred at 90 °C for 0.5 h, then cooled to room temperature. The mixture was filtered or decanted into sample vials for analysis by GC.

Adsorption experiment: To original mixture was added montmorillonite (2.8 g) and $MgCl_2$ (280 mg). The pH of the mixture was adjusted to approximately 7 with sodium hydroxide solution added via syringe. The mixture was stirred at 1000 rpm at room temperature for 4 h. The residual solid was washed 3 times with H_2O followed by centrifugation (3–5 min, 7000 r.p.m.), and atmospheric dried overnight to be used for the desorption experiment.

Desorption experiment: To the solid sample was added H_2O (20 mL) and the pH was adjusted to approximately 3 with aqueous HCl. The mixture was stirred at 60 °C for 15 min, then cooled to room temperature and centrifuged (3–5 min, 7000 r.p.m.). The supernatant was removed solvent by rotary evaporator to give a yellow oily residue. To the residue was added a solution of hydroxylamine hydrochloride in pyridine (0.58 M, 1 mL) and stirred at 90 °C for 0.5 h. After cooling to room temperature, acetic anhydride (10.6 mmol, 1 mL) was added to the mixture for acetylation in an ice bath. The mixture was again stirred at 90 °C for 0.5 h, then cooled to room temperature. The mixture was filtered or decanted into sample vials for analysis by GC and GC-MS.

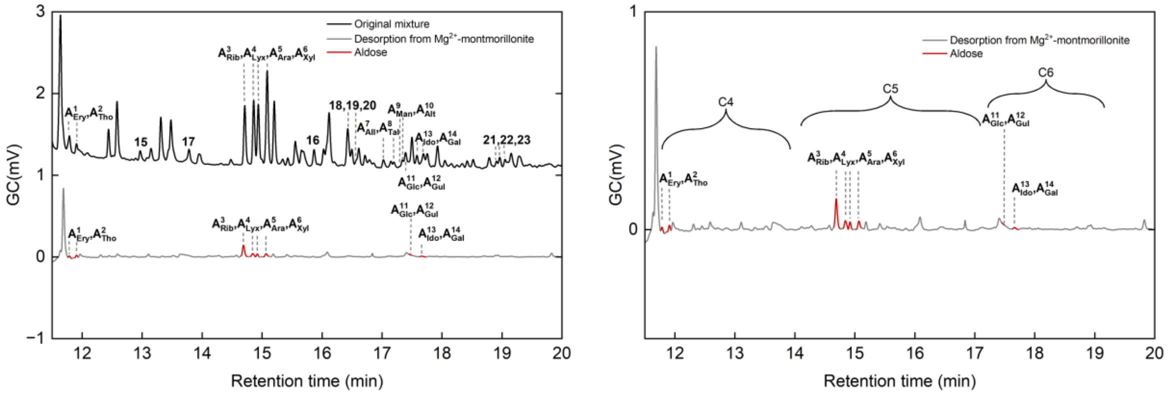
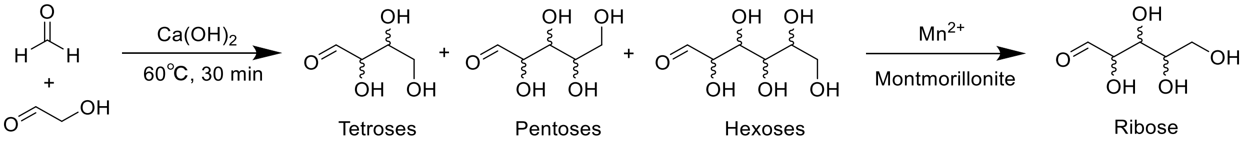


Fig. S5. (A) Comparison of the GC traces of the derivatized formose mixture and desorbed sugars from Mg^{2+}-montmorillonite; (B) GC trace of the desorbed sugars from Mg^{2+}-montmorillonite. (**A^1_{Ery}**, erythrose; **A^2_{Tho}**, threose; **A^3_{Rib}**, ribose; **A^4_{Lyx}**, lyxose; **A^5_{Ara}**, arabinose; **A^6_{Xyl}**, xylose; **A^7_{All}**, allose; **A^8_{Tal}**, talose; **A^9_{Man}**, mannose; **A^{10}_{Alt}**, altrose; **A^{11}_{Glc}**, glucose; **A^{12}_{Gul}**, gulose; **A^{13}_{Ido}**, idose; **A^{14}_{Gal}**, galactose; **15**, 1,3-dihydroxyacetone; **16**, L-erythrulose; **17**, erythritol; **18**, adonitol; **19**, arabitol; **20**, xylitol; **21**, mannitol; **22**, sorbitol; **23**, dulcitol)

Procedures for the formose reaction and subsequent selection of ribose with Mn^{2+}-montmorillonite:



Original mixture: To a mixture of $Ca(OH)_2$ (0.1 M) in water (300 mL) was added formaldehyde (4463 µL, 60 mmol, 0.2 M) and glycolaldehyde dimer (3.60 mg, 0.03 mmol, 0.1 mM), and stirred at 60 °C for 0.5 h under nitrogen atmosphere. The mixture was filtered and neutralized to pH 7 with aqueous HCl (as "the original mixture").

Derivatization of original mixture: 20 mL of the original mixture was removed solvent by rotary evaporator to give a yellow oily residue. To the residue was added a solution of hydroxylamine hydrochloride in pyridine (0.58 M, 4 mL) and stirred at 90 °C for 0.5 h. After cooling to room temperature, acetic anhydride (42.6 mmol, 4 mL) was added to the mixture for acetylation in an ice bath. The mixture was again stirred at 90 °C for 0.5 h, then cooled to room temperature. The mixture was filtered or decanted into sample vials for analysis by GC.

Adsorption experiment: To original mixture was added montmorillonite (2.8 g) and $MnCl_2•4H_2O$ (280 mg). The pH of the mixture was adjusted to approximately 7 with sodium hydroxide solution added via syringe. The mixture was stirred at 1000 rpm at room temperature for 4 h. The residual solid was washed 3 times with H_2O followed by centrifugation (3–5 min, 7000 r.p.m.), and atmospheric dried overnight to be used for the desorption experiment.

Desorption experiment: To the solid sample was added H_2O (20 mL) and the pH was adjusted to approximately 3 with HCl. The mixture was stirred at 60 °C for 15 min, then cooled to room temperature and centrifuged (3–5 min, 7000 r.p.m.). The supernatant was removed solvent by rotary evaporator to give a yellow oily residue. To the residue was added a solution of hydroxylamine hydrochloride in pyridine (0.58 M, 1 mL) and stirred at 90 °C for 0.5 h. After cooling to room temperature, acetic anhydride (10.6 mmol, 1 mL) was added to the mixture for acetylation in an ice bath. The mixture was again stirred at 90 °C for 0.5 h, then cooled to room temperature. The mixture was filtered or decanted into sample vials for analysis by GC and GC-MS.

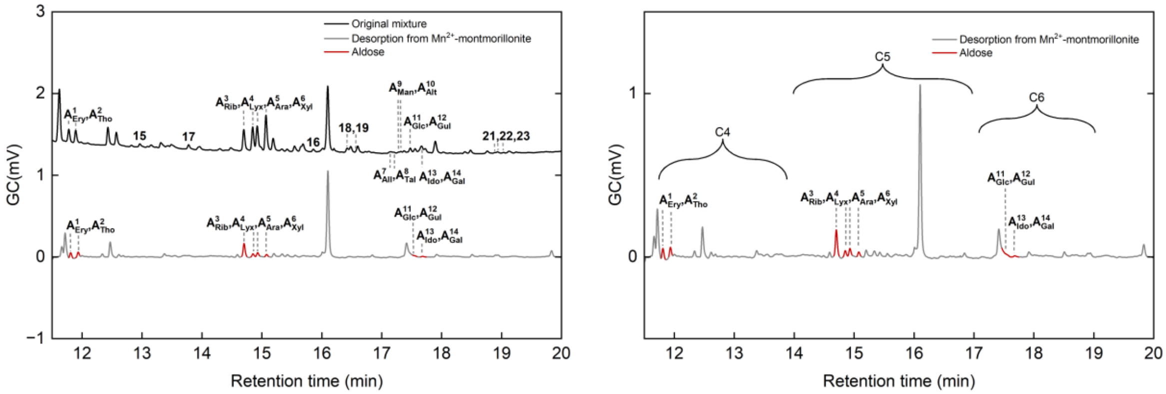
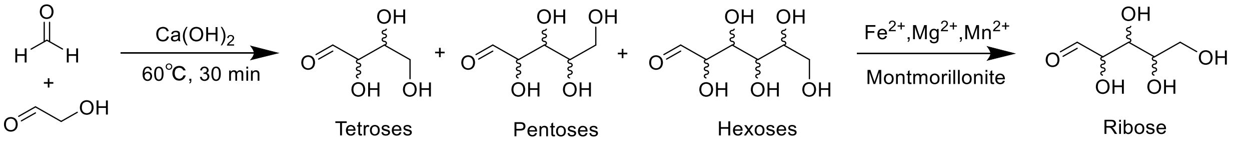


Fig. S6. (A) Comparison of the GC traces of the derivatized formose mixture and desorbed sugars from Mn^{2+}-montmorillonite; (B) GC trace of the desorbed sugars from Mn^{2+}-montmorillonite. (**A^1$_{Ery}$**, erythrose; **A^2$_{Tho}$**, threose; **A^3$_{Rib}$**, ribose; **A^4$_{Lyx}$**, lyxose; **A^5$_{Ara}$**, arabinose; **A^6$_{Xyl}$**, xylose; **A^7$_{All}$**, allose; **A^8$_{Tal}$**, talose; **A^9$_{Man}$**, mannose; **A^{10}$_{Alt}$**, altrose; **A^{11}$_{Glc}$**, glucose; **A^{12}$_{Gul}$**, gulose; **A^{13}$_{Ido}$**, idose; **A^{14}$_{Gal}$**, galactose; **15**, 1,3-dihydroxyacetone; **16**, L-erythrulose; **17**, erythritol; **18**, adonitol; **19**, arabitol; **20**, xylitol; **21**, mannitol; **22**, sorbitol; **23**, dulcitol)

Procedures for the formose reaction and subsequent selection of ribose with multimetal-montmorillonite:



Original mixture: To a mixture of Ca(OH)$_2$ (0.1 M) in water (300 mL) was added formaldehyde (4463 μL, 60 mmol, 0.2 M) and glycolaldehyde dimer (3.60 mg, 0.03 mmol, 0.1 mM), and stirred at 60 °C for 0.5 h under nitrogen atmosphere. The mixture was filtered and neutralized to pH 7 with aqueous HCl (as “the original mixture”).

Derivatization of original mixture: 20 mL of the original mixture was removed solvent by rotary evaporator to give a yellow oily residue. To the residue was added a solution of hydroxylamine hydrochloride acid in pyridine (0.58 M, 4 mL) and stirred at 90 °C for 0.5 h. After cooling to room temperature, acetic anhydride (42.6 mmol, 4 mL) was added to the mixture for acetylation in an ice bath. The mixture was again stirred at 90 °C for 0.5 h, then cooled to room temperature. The mixture was filtered or decanted into sample vials for analysis by GC.

Adsorption experiment: The adsorption was performed under nitrogen atmosphere. In a Schlenk flask, to the original mixture (280 mL) was added montmorillonite (2.8 g), $MgCl_2$ (280 mg), and $MnCl_2 \cdot 4H_2O$ (280 mg). The prepared mixture was degassed by vacuum pump and filled with nitrogen. To degassed water (1 mL) was added $FeCl_2 \cdot 4H_2O$ (280 mg) under nitrogen atmosphere and ultrasound. The prepared $FeCl_2$ solution was injected into the Schlenk flask. The mixture in Schlenk flask was again vacuumed and filled with nitrogen. The pH of the mixture was adjusted to approximately 7 with sodium hydroxide solution added via syringe. The mixture was stirred at 1000 rpm at room temperature for 4 h. The residual solid was washed 3 times with H_2O followed by centrifugation (3–5 min, 7000 r.p.m.), and atmospheric dried overnight to be used for the desorption experiment.

Desorption experiment: To the solid sample was added H_2O (20 mL) and the pH was adjusted to approximately 3 with aqueous HCl. The mixture was stirred at 60 °C for 15 min, then cooled to room temperature and centrifuged (3–5 min, 7000 r.p.m.). The supernatant was removed solvent by rotary evaporator to give a yellow oily residue. To the residue was added a solution of hydroxylamine hydrochloride acid in pyridine (0.58 M, 1 mL) and stirred at 90 °C for 0.5 h. After cooling to room temperature, acetic anhydride (10.6 mmol, 1 mL) was added to the mixture for acetylation in an ice bath. The mixture was again stirred at 90 °C for 0.5 h, then cooled to room temperature. The mixture was filtered or decanted into sample vials for analysis by GC and GC-MS.

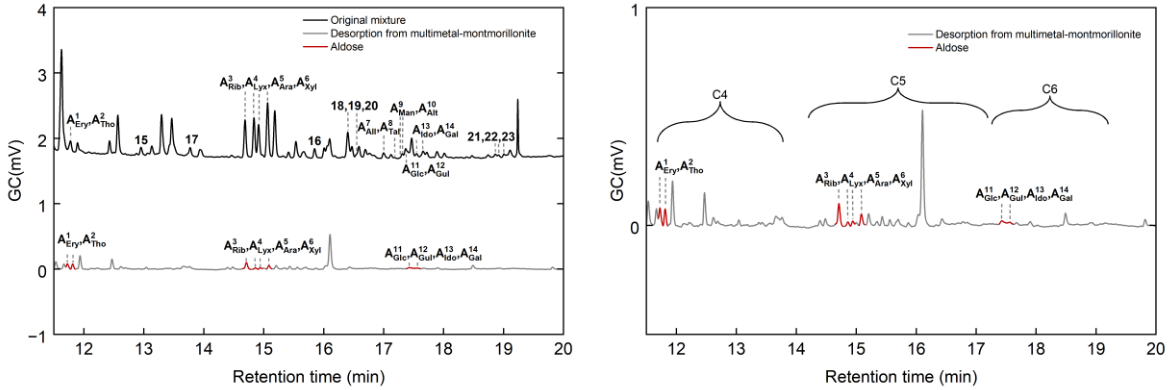


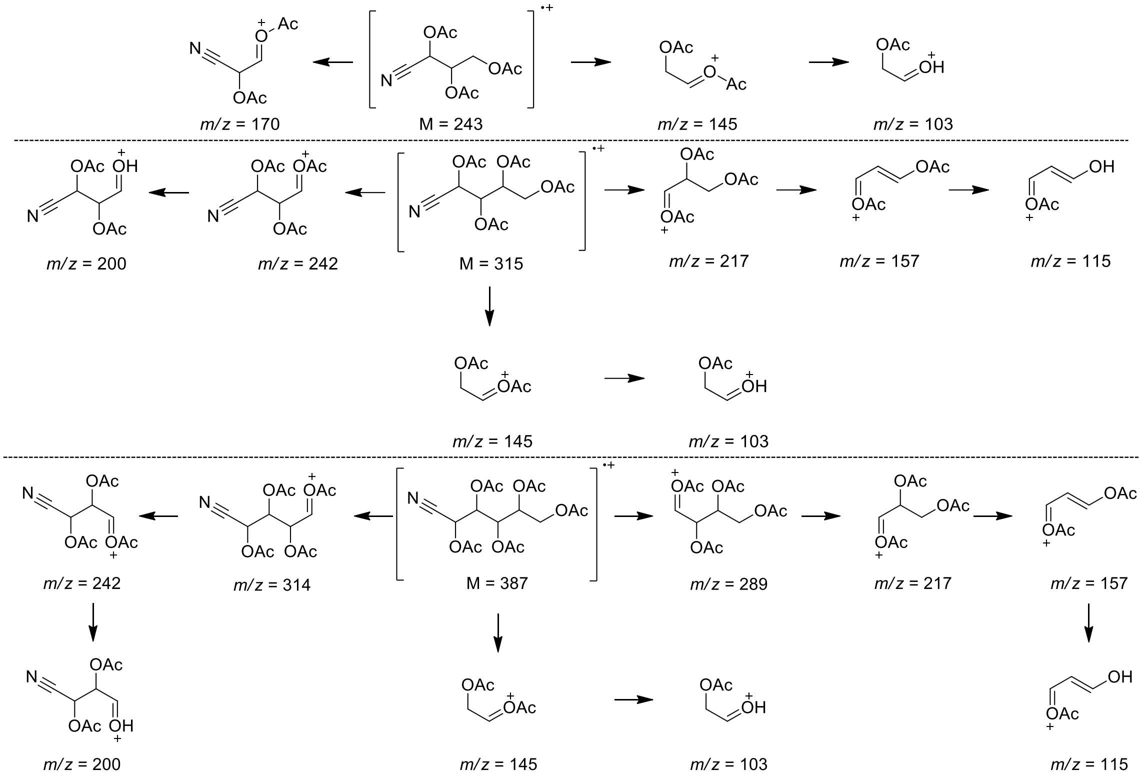
Fig. S7. (A) Comparison of the GC traces of the derivatized formose mixture and desorbed sugars from multimetal-montmorillonite; (B) GC trace of the desorbed sugars from multimetal-montmorillonite. ($\mathbf{A^1_{Ery}}$, erythrose; $\mathbf{A^2_{Tho}}$, threose; $\mathbf{A^3_{Rib}}$, ribose; $\mathbf{A^4_{Lyx}}$, lyxose; $\mathbf{A^5_{Ara}}$, arabinose; $\mathbf{A^6_{Xyl}}$, xylose; $\mathbf{A^7_{All}}$, allose; $\mathbf{A^8_{Tal}}$, talose; $\mathbf{A^9_{Man}}$, mannose; $\mathbf{A^{10}_{Alt}}$, altrose; $\mathbf{A^{11}_{Glc}}$, glucose; $\mathbf{A^{12}_{Gul}}$, gulose; $\mathbf{A^{13}_{Ido}}$, idose; $\mathbf{A^{14}_{Gal}}$, galactose; **15**, 1,3-dihydroxyacetone; **16**, L-erythrulose; **17**, erythritol; **18**, adonitol; **19**, arabitol; **20**, xylitol; **21**, mannitol; **22**, sorbitol; **23**, dulcitol)

Table S1. GC-MS fragmentation patterns and retention times of monosaccharide derivatives: (i) Derivatized using hydroxylamine hydrochloride, pyridine and acetic anhydride; (ii) Target ions are shown in bold, and the two reference ions are shown in italics.

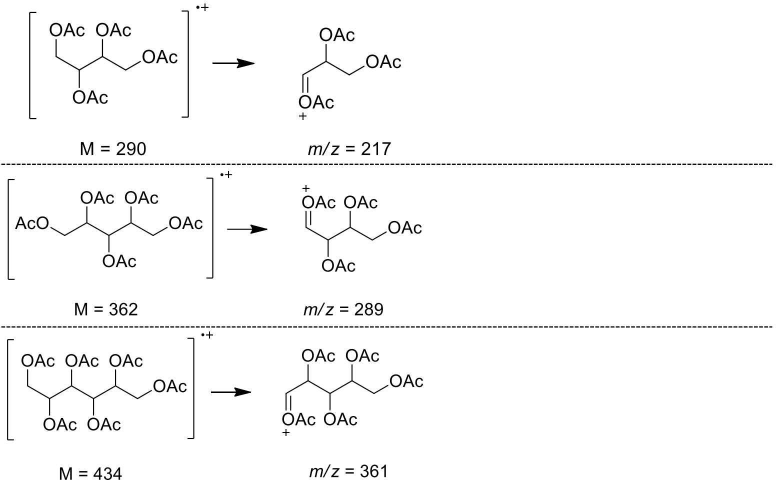
Name	Entry	Monosaccharide	R.T. (min)	Major ion fragments (*m/z*)
Aldose	1	Erythrose	11.76	**103**,**145**,**141**,*170*,*184*
	2	Threose	11.89	**103**,**145**,**141**,*171*,*184*
	3	Ribose	14.69	**115**,**103**,**145**,*157*,*175*
	4	Lyxose	14.83	**115**,**103**,**145**,*157*,*175*
	5	Arabinoses	14.90	**103**,**145**,**115**,*157*,*200*
	6	Xylose	15.07	**103**,**145**,**115**,*157*,*200*
	7	Allose	17.11	**145**,**103**,**115**,*187*,*217*
	8	Talose	17.30	**145**,**103**,**115**,*187*,*127*
	9	Mannose	17.35	**145**,**103**,**115**,*212*,*187*
	10	Altrose	17.40	**145**,**103**,**115**,*217*,*157*
	11	Glucose	17.46	**145**,**103**,**115**,*212*,*187*
	12	Gulose	17.46	**145**,**103**,**115**,*212*,*187*
	13	Idose	17.64	**145**,**103**,**115**,*127*,*157*
	14	Galactose	17.70	**145**,**103**,**115**,*212*,*157*
Ketose	15	1,3-Dihydroxyacetone	13.01	**129**,**99**,**130**,*100*,*189*
	16	Erythrulose	15.92	**111**,**99**,**201**,*69*,*141*
Sugar Alcohol	17	Erythritol	13.79	**145**,**115**,**103**,*128*,*217*
	18	Ribitol	16.47	**115**,**145**,**103**,*158*,*217*
	19	Arabitol	16.59	**115**,**145**,**103**,*127*,*187*
	20	Xylitol	16.78	**115**,**145**,**103**,*217*,*127*
	21	Mannitol	18.94	**115**,**139**,**145**,*103*,*187*
	22	Sorbitol	18.98	**115**,**145**,**103**,*139*,*187*
	23	Dulcitol	19.08	**115**,**145**,**139**,*103*,*187*

Table S2. MS fragmentation patterns[1–4]

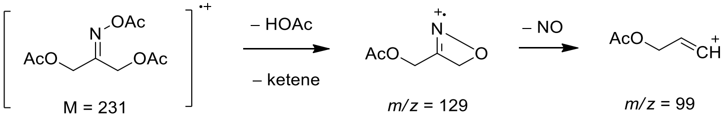
Aldose

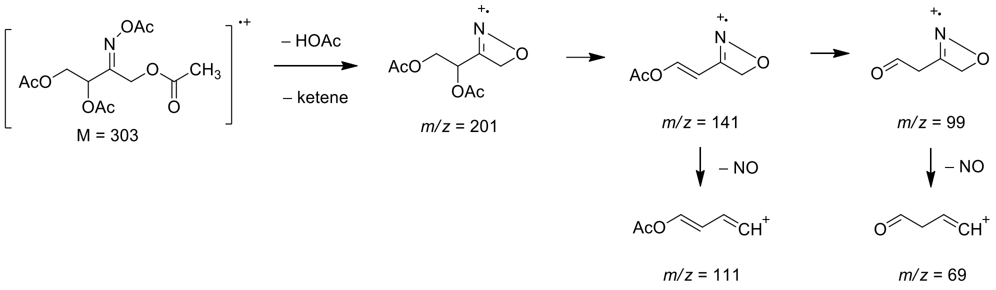


Sugar alcohol



Ketose





C5 and C6 ketoses were not detected.

TEM and EDS Mapping of Aldoses Adsorption on Fe^{2+}-montmorillonite

To visualize the selective adsorption of ribose, the structure and surface characteristics of metal-doped-clay were analysed using transmission electron microscope (TEM) coupled with energy dispersive X-ray spectroscopy (EDS) mapping. The TEM image and the corresponding element mappings are shown in Fig S8.

To eliminate the impact of possible carbonates in montmorillonite, an initial characterization of montmorillonite was conducted before the adsorption of sugar (Fig S8A). The TEM image in Fig S8A displays the stacked layered structure of montmorillonite. No distribution of Fe in montmorillonite was observed after excluding the background. A trace amount of carbon (C) was detected, suggesting that montmorillonite could have adsorbed a tiny quantity of atmospheric carbon dioxide, resulting in the formation of carbonate.

Next, TEM coupled with EDS-Mapping were performed on montmorillonite adsorbed with ribose (Fig S8B–E) and a representative set of aldoses: threose (C4), lyxose (C5) and mannose (C6), respectively (Fig S8F–H). To minimize potential biases arising from differences in purity or composition, ribose samples produced by different manufacturers (Sigma-Aldrich, TCI and Aladdin) were mixed and used for the experiments. TEM images were taken at four different positions (Fig S8B–E) on the sample to confirm its representativeness and ensure consistent analysis across regions.

Within the montmorillonite region, it could be observed that the C content in ribose-Fe^{2+}-montmorillonite experiment (Fig S8B–E) was much higher than that in the other three sugar adsorption experiments (Fig S8F–H). The difference of Fe content between samples also existed. These results suggested that ribose exhibits a higher affinity to Fe^{2+}-montmorillonite than the other three aldoses, as a complement to the indirect, desorption experiment. The high-affinity binding between divalent metal cations and ribose on the clay surface likely stems from ribose's unique molecular structure of having two hydroxyl groups facing the same direction[5].

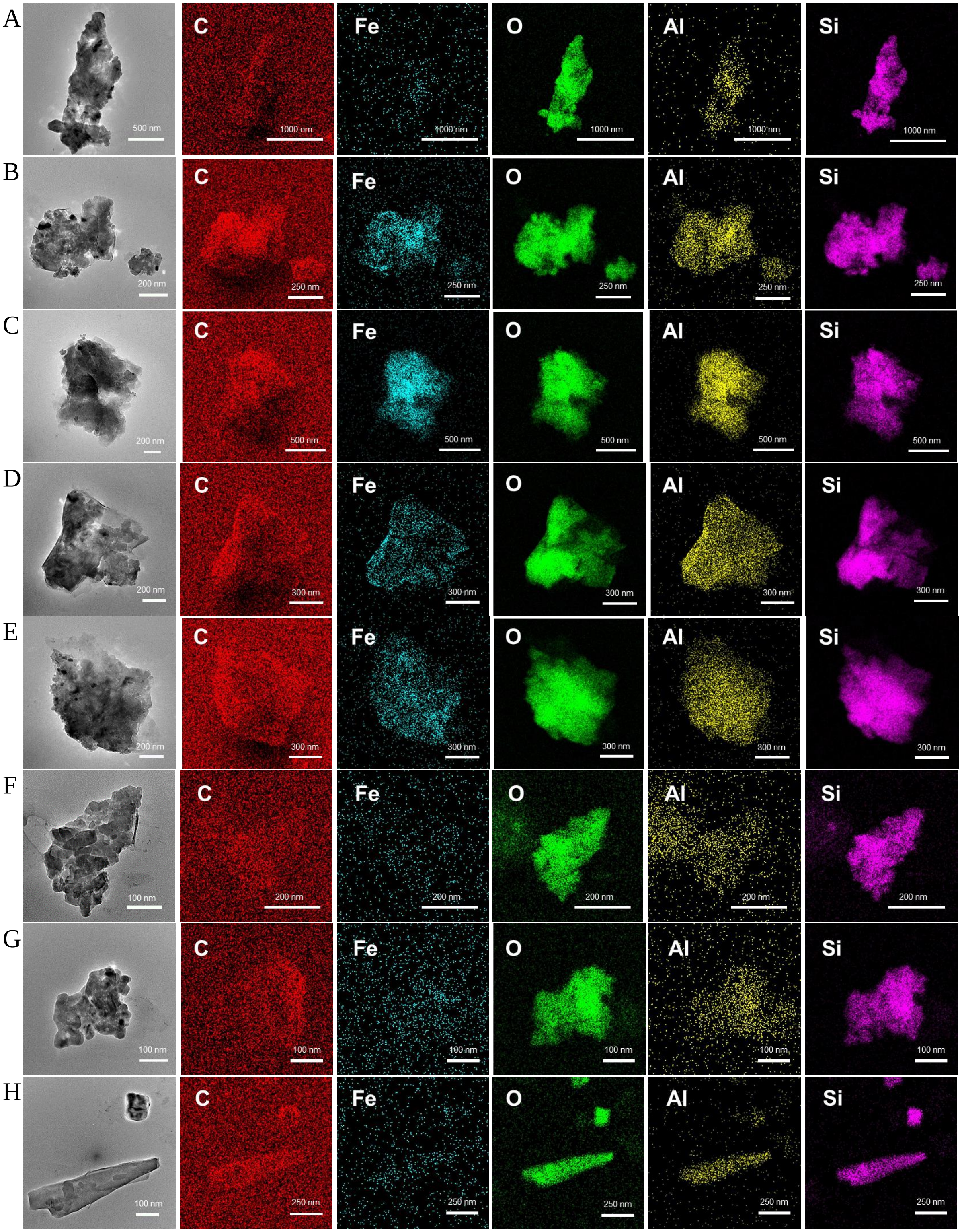
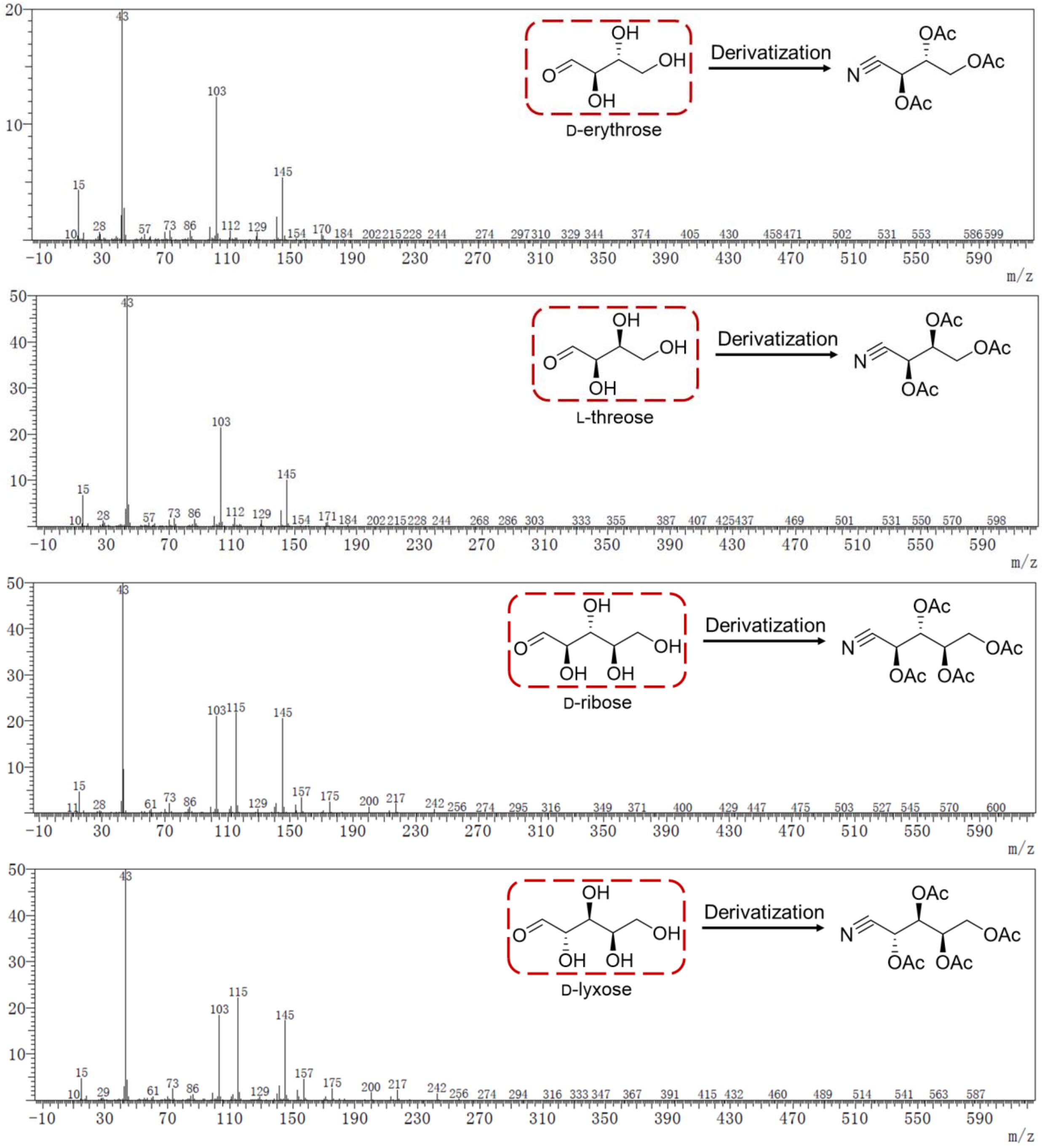
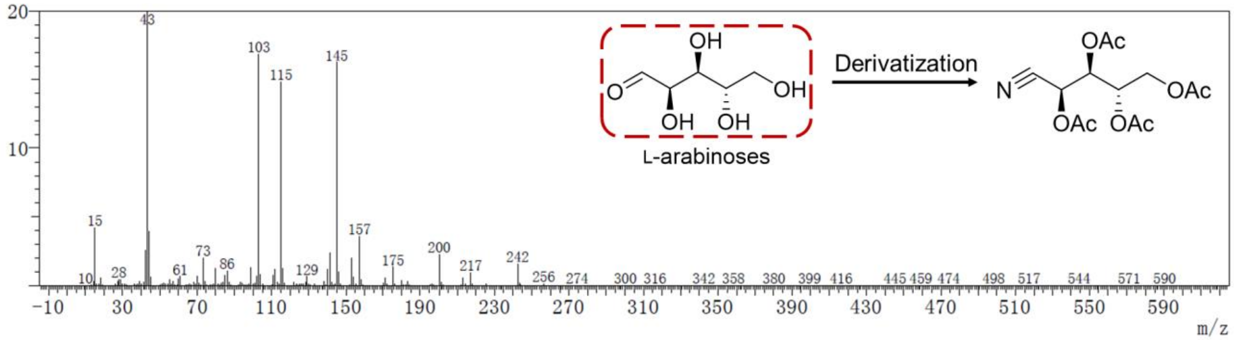
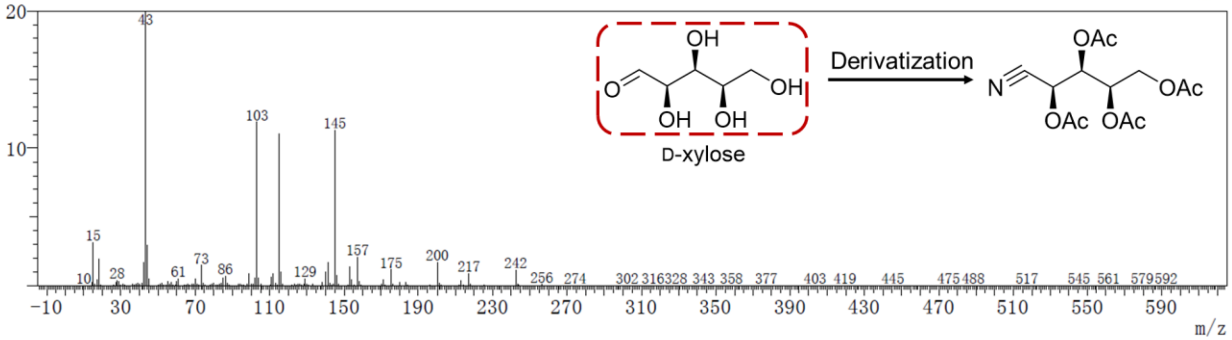


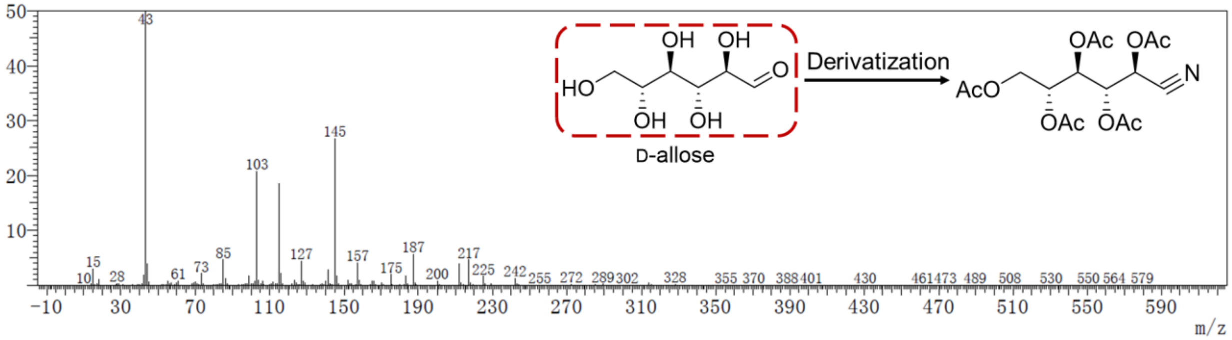
Fig. S8 TEM image and the corresponding element mappings of: (A) montmorillonite; (B–E) Fe^{2+}-ribose-montmorillonite; (F) Fe^{2+}-threose-montmorillonite; (G) Fe^{2+}-lyxose-montmorillonite; (H) Fe^{2+}-mannose-montmorillonite.

Data S1. MS data (by GC-MS, EI source) of each derivatized authentic sample.




20
10
43
103
115
145
15
157
73
200
86
175
217
242
61
129
28
10
256 274 300 316 342 358 380 399 416 445 459 474 498 517 544 571 590
−10 30 70 110 150 190 230 270 310 350 390 430 470 510 550 590
m/z
OH
O
OH
OH OH
L-arabinoses
Derivatization
OAc
N
OAc
OAc OAc


20
10
43
103
145
15
157
73
200
175
217
242
61
86
129
28
10
256 274 302 316328 343 358 377 403 419 445 475488 517 545 561 579592
−10 30 70 110 150 190 230 270 310 350 390 430 470 510 550 590
m/z
OH
O
OH
OH OH
D-xylose
Derivatization
OAc
N
OAc
OAc OAc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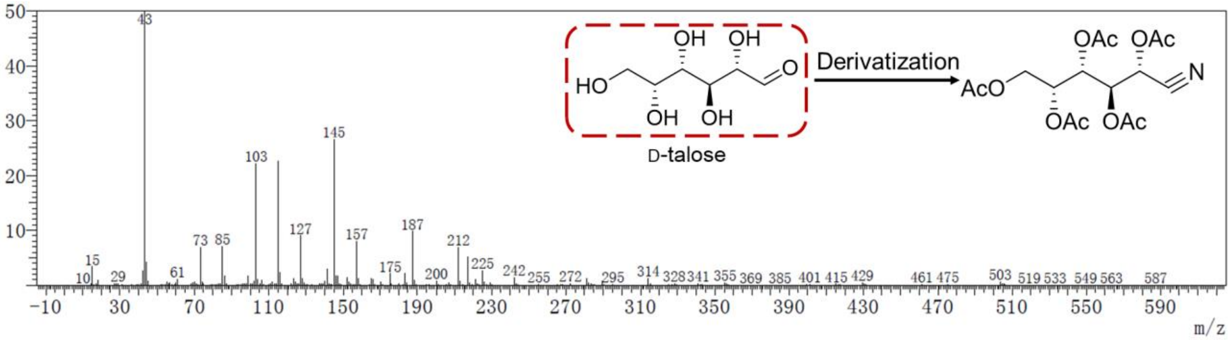
30
20
10
43
145
103
187
217
85
127
157
15
73
175
225
61
200
242
28
10
255 272 289302 328 355 370 388401 430 461473 489 508 530 550 564 579
−10 30 70 110 150 190 230 270 310 350 390 430 470 510 550 590
m/z
OH OH
HO
O
OH OH
D-allose
Derivatization
OAc OAc
AcO
N
OAc OAc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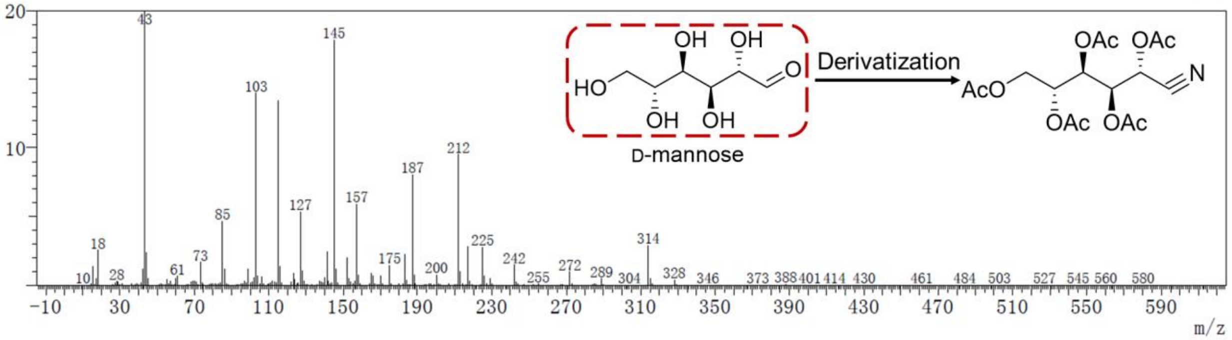
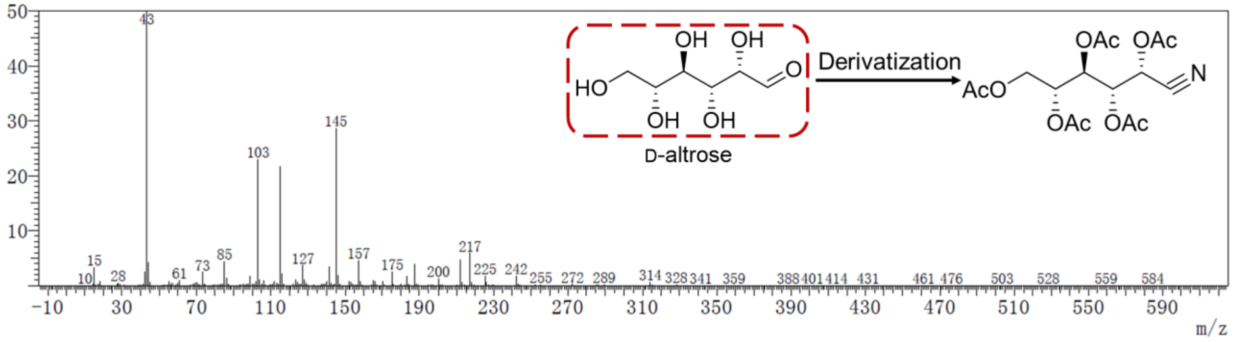
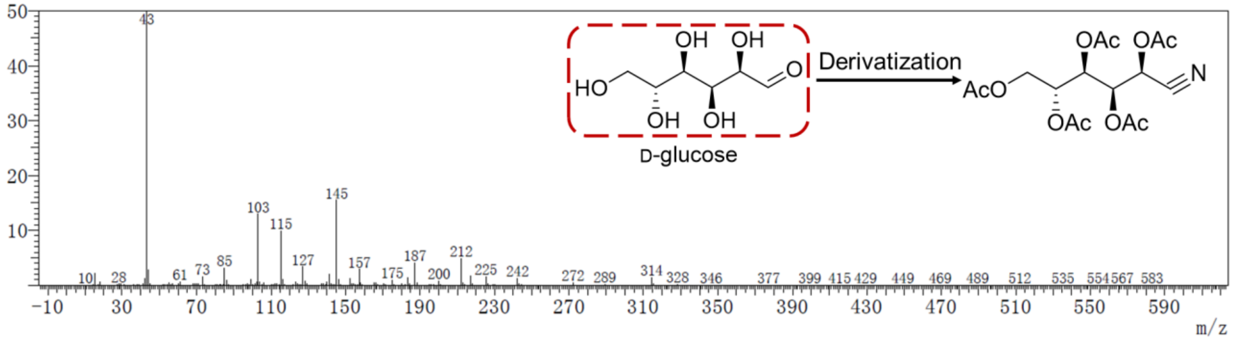
40
30
20
10
43
145
103
187
127
212
73 85
157
225
175
15
242
61
200
29
10
255 272 295 314 328341 355 369 385 401 415 429 461 475 503 519 533 549 563 587
−10 30 70 110 150 190 230 270 310 350 390 430 470 510 550 590
m/z
OH OH
HO
O
OH OH
D-talose
Derivatization
OAc OAc
AcO
N
OAc OAc

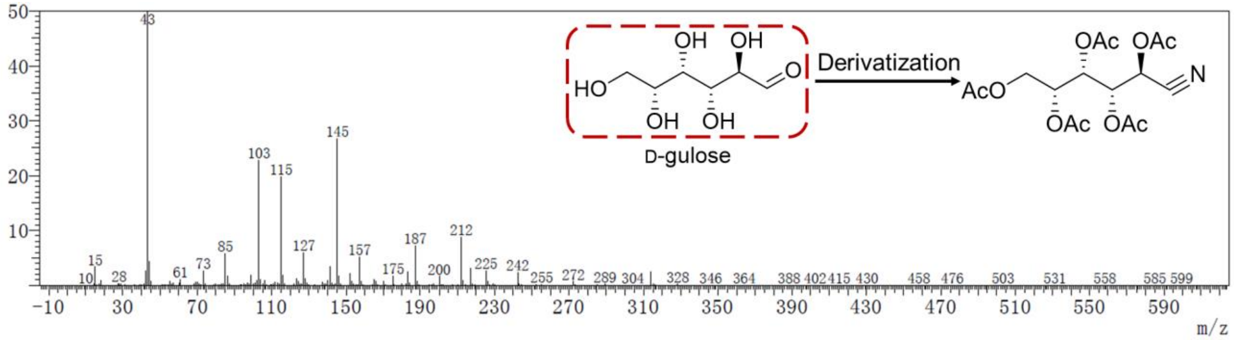

20
10
43
145
103
212
187
157
127
85
314
225
18
73
175
242
272
61
200
289
328
28
10
255 304 346 373 388401414 430 461 484 503 527 545 560 580
−10 30 70 110 150 190 230 270 310 350 390 430 470 510 550 590
m/z
OH OH
HO
O
OH OH
D-mannose
Derivatization
OAc OAc
AcO
N
OAc OAc



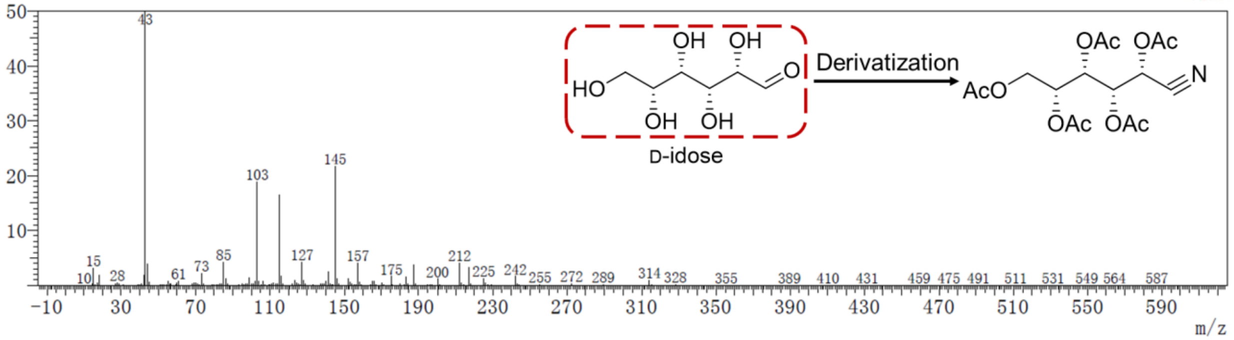
D-altrose
Derivatization
HO
OH
O
AcO
OAc
N
m/z
43
145
103
217
157
175
127
85
73
61
15
28
10
200
225
242
255 272 289 314 328 341 359 388 401 414 431 461 476 503 528 559 584



D-glucose
Derivatization
HO
OH
O
AcO
OAc
N
m/z
43
145
103
115
212
187
157
175
127
85
73
61
28
10
200
225
242
272 289 314 328 346 377 399 415 429 449 469 489 512 535 554 567 583



D-gulose
Derivatization
HO
OH
O
AcO
OAc
N
m/z
43
145
103
115
212
187
157
175
127
85
73
61
15
28
10
200
225
242
255 272 289 304 328 346 364 388 402 415 430 458 476 503 531 558 585 599



D-idose
Derivatization
HO
OH
O
AcO
OAc
N
m/z
43
145
103
212
157
175
127
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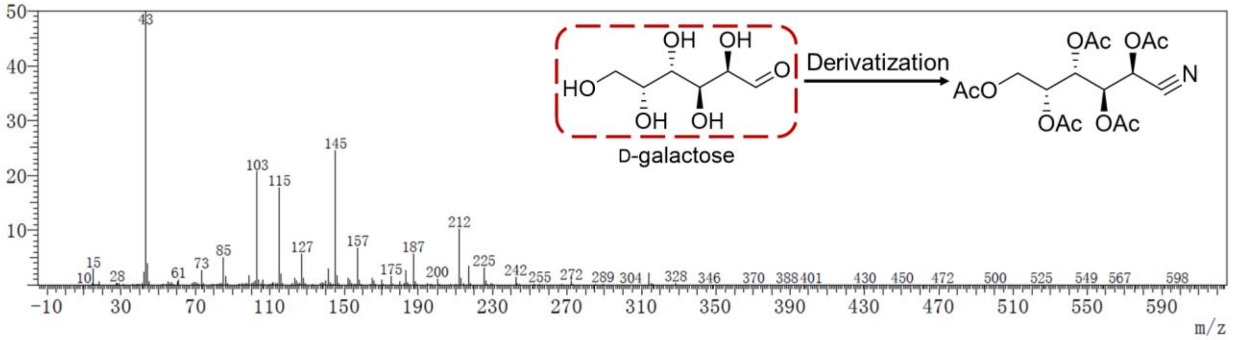
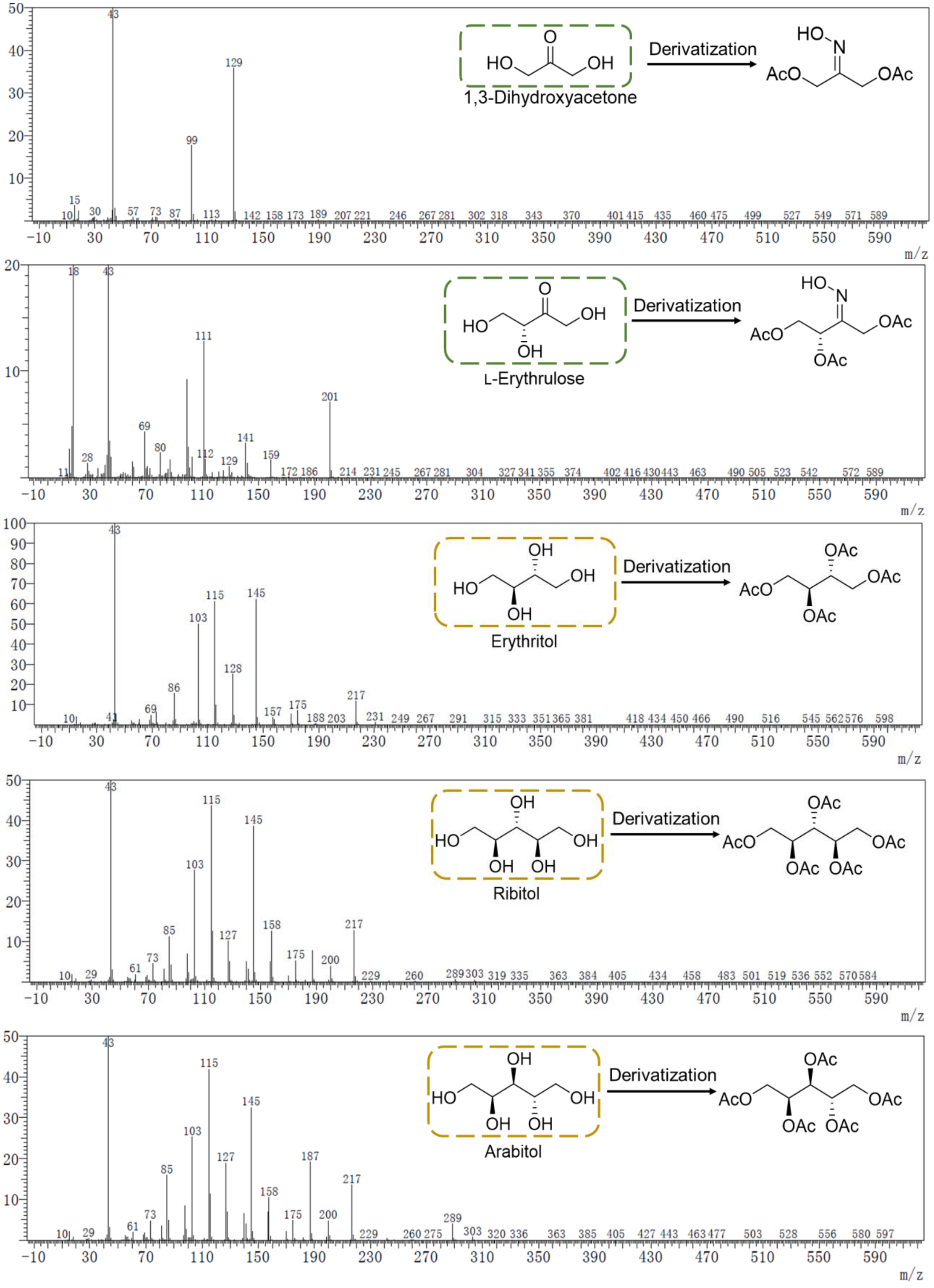
255 272 289 314 328 355 389 410 431 459 475 491 511 531 549 564 587



D-galactose
Derivatization
HO
OH
O
AcO
OAc
N
m/z
43
145
103
115
212
187
157
175
127
85
73
61
15
28
10
200
225
242
255 272 289 304 328 346 370 388 401 430 450 472 500 525 549 567 598


1,3-Dihydroxyacetone
HO
O
OH
Derivatization
HO
N
AcO
OAc
43
129
99
15
30
57
73
87
113
m/z
L-Erythrulose
18
43
111
201
69
80
141
159
112
129
28
Erythritol
OAc
43
115
145
103
128
86
217
175
157
69
Ribitol
43
115
145
103
158
217
85
127
175
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73
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Arabitol
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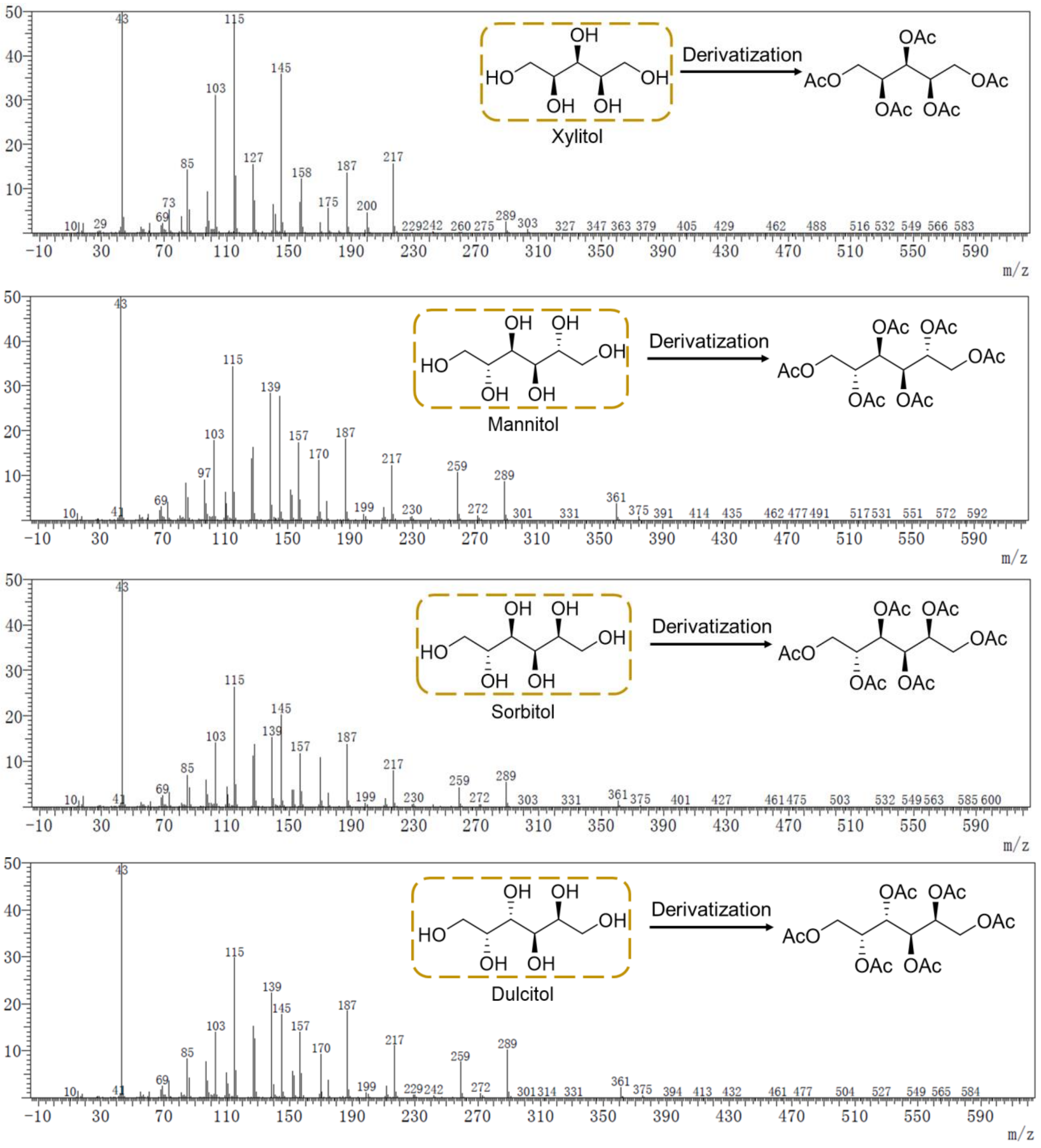
289
73
61
29


Xylitol
Derivatization
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OH
OH
OH
OH
AcO
OAc
OAc
OAc
OAc
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145
103
127
217
187
158
85
175
200
73
69
29
10
229 242 260 275 289 303 327 347 363 379 405 429 462 488 516 532 549 566 583
Mannitol
Derivatization
43
115
139
187
103
157
217
170
259
289
97
69
41
361
10 199 230 272 301 331 375 391 414 435 462 477 491 517 531 551 572 592
Sorbitol
Derivatization
43
115
145
139
103
187
157
217
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259
289
69
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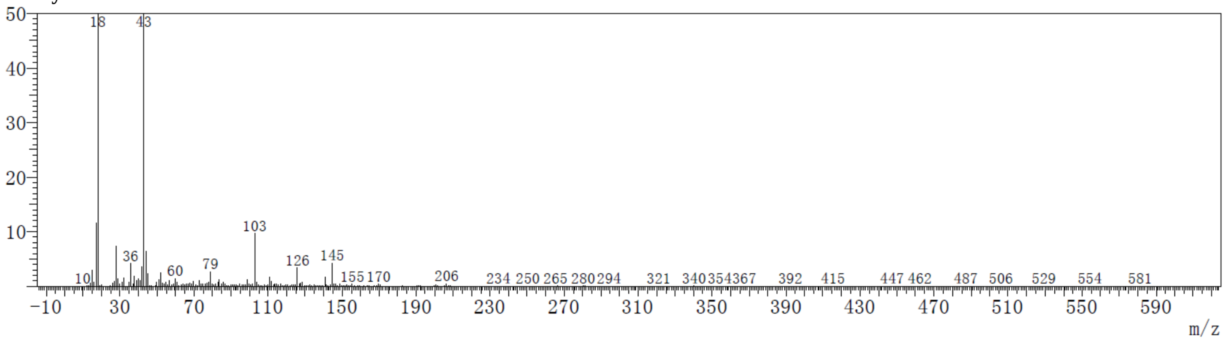
361
10 199 230 272 303 331 375 401 427 461 475 503 532 549 563 585 600
Dulcitol
Derivatization
43
115
139
145
187
103
157
170
217
85
289
259
69
41
361
10 199 229 242 272 301 314 331 375 394 413 432 461 477 504 527 549 565 584
50
40
30
20
10
-10 30 70 110 150 190 230 270 310 350 390 430 470 510 550 590
m/z

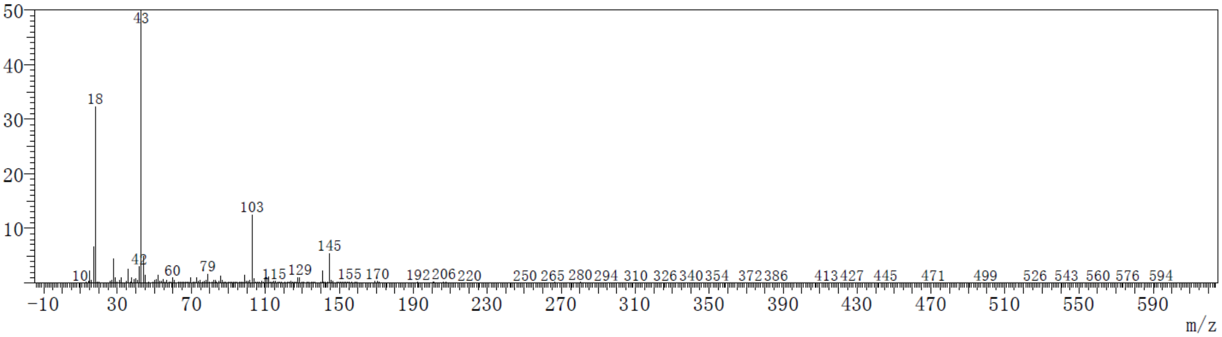
Data S2. MS spectra (by GC-MS, EI source) of the products from the reaction mixture

(1) From the Fe^{2+}-montmorillonite reaction:

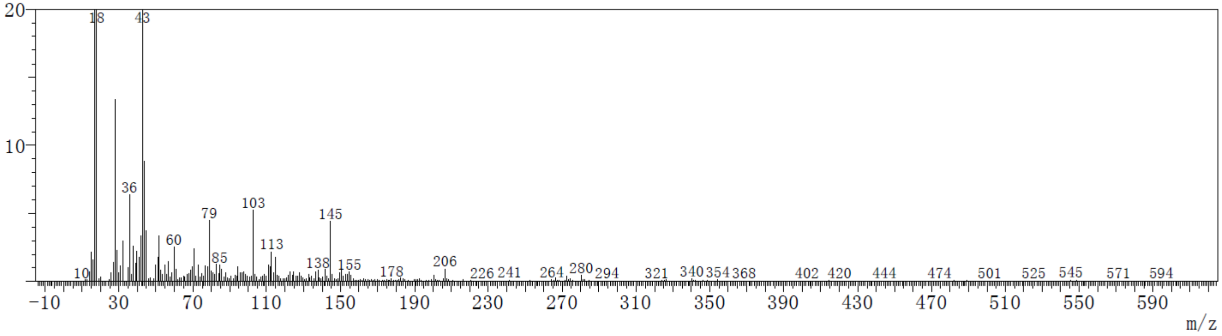
A^1_{Ery}:



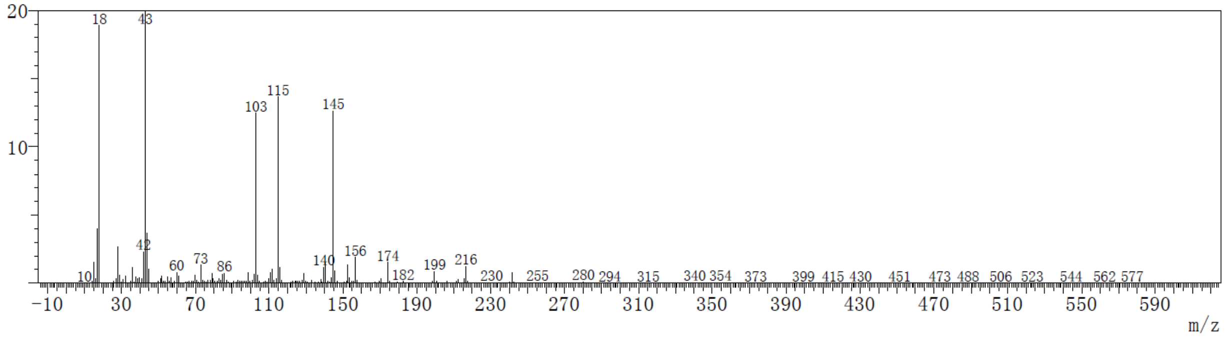
A^2_{Tho}:



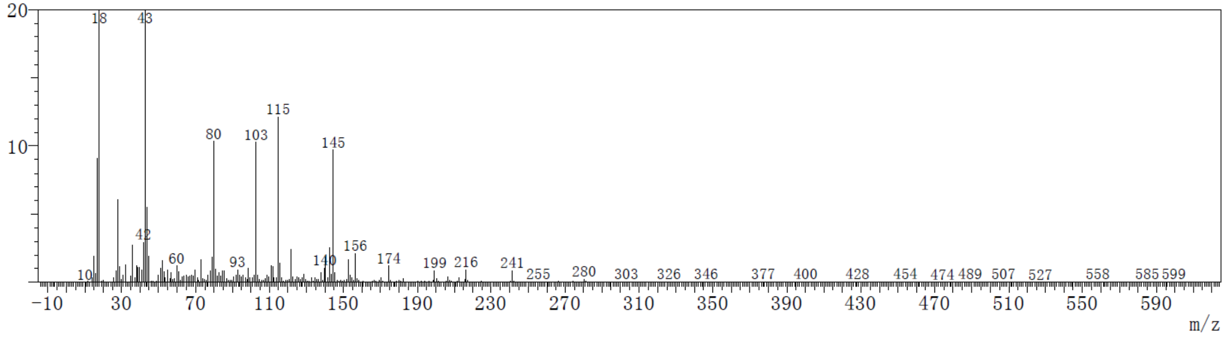
Compound 17:



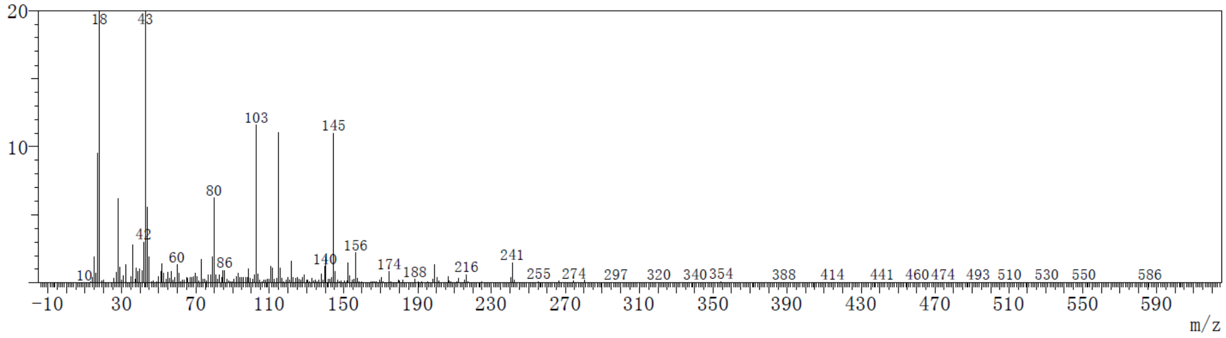
A^3_{Rib}:



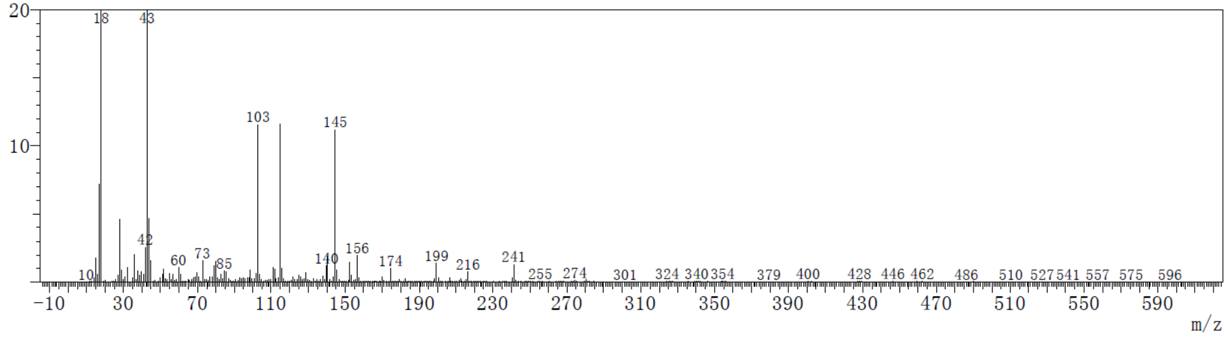
A$^{4}_{\text{Lyx}}$:



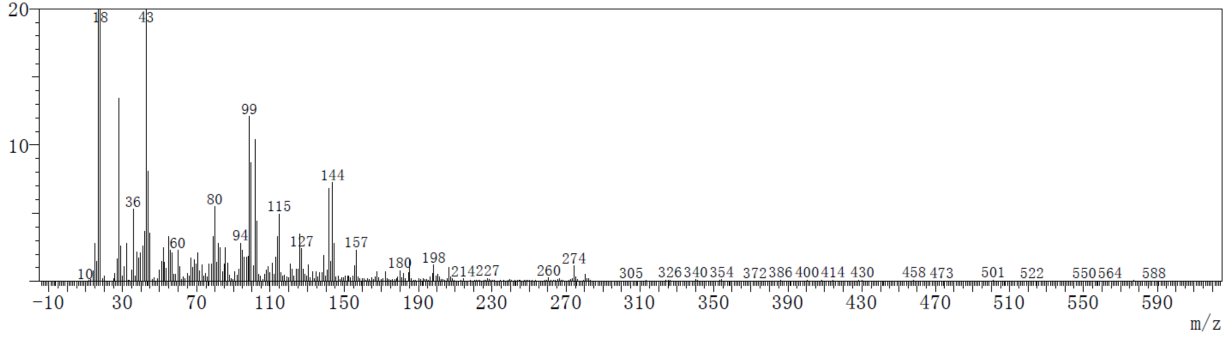
A$^{5}_{\text{Ara}}$:



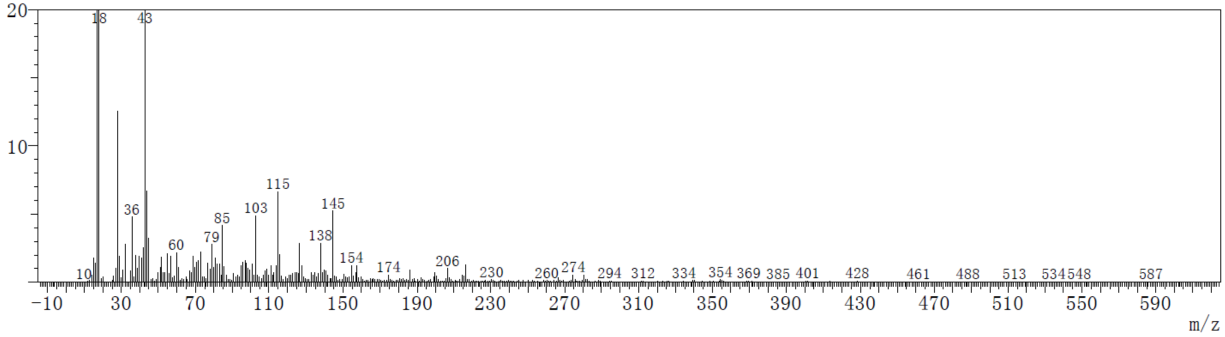
A$^{6}_{\text{Xyl}}$:



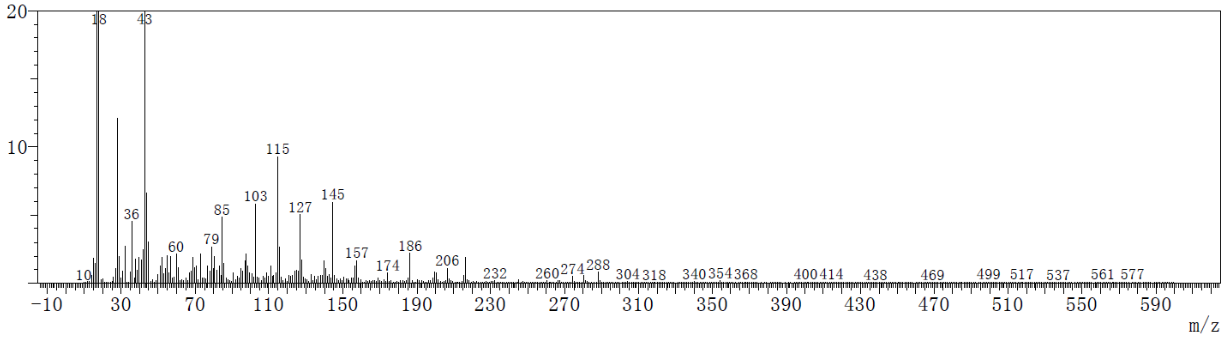
Compound 16:



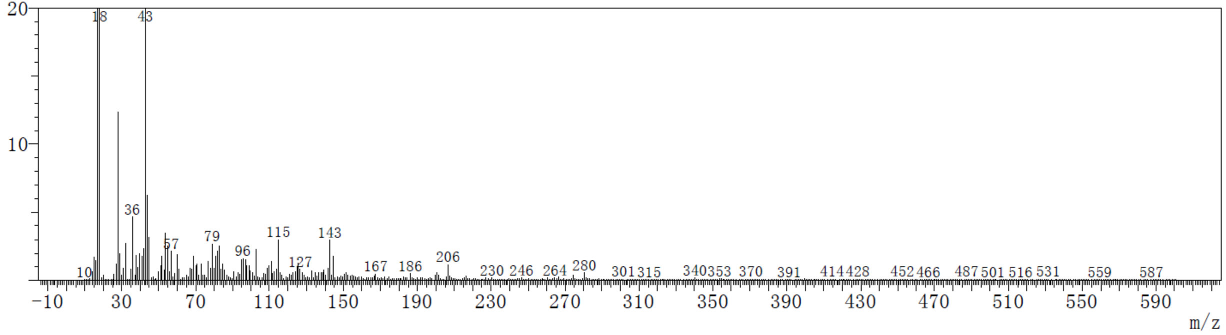
Compound 18:



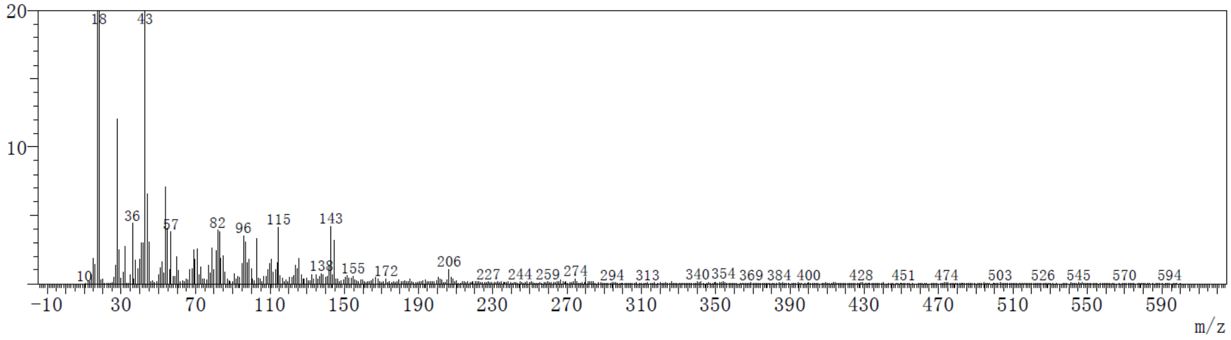
Compound 19:



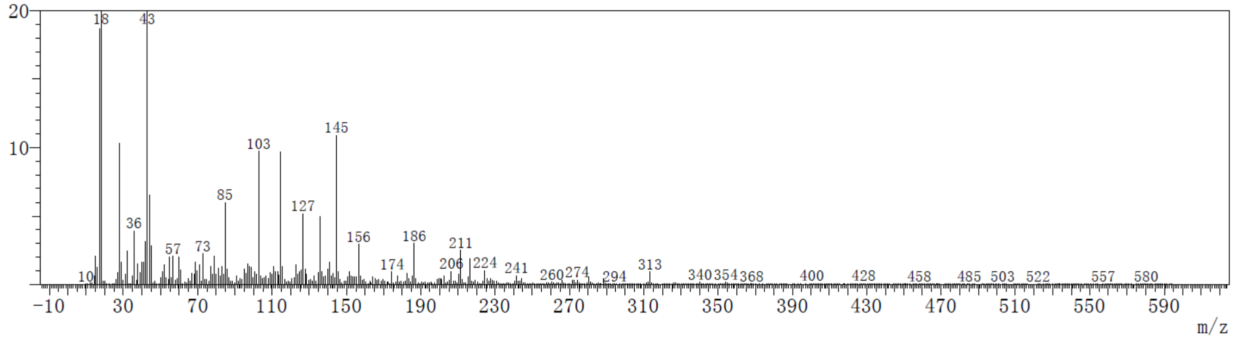
Compound 20:



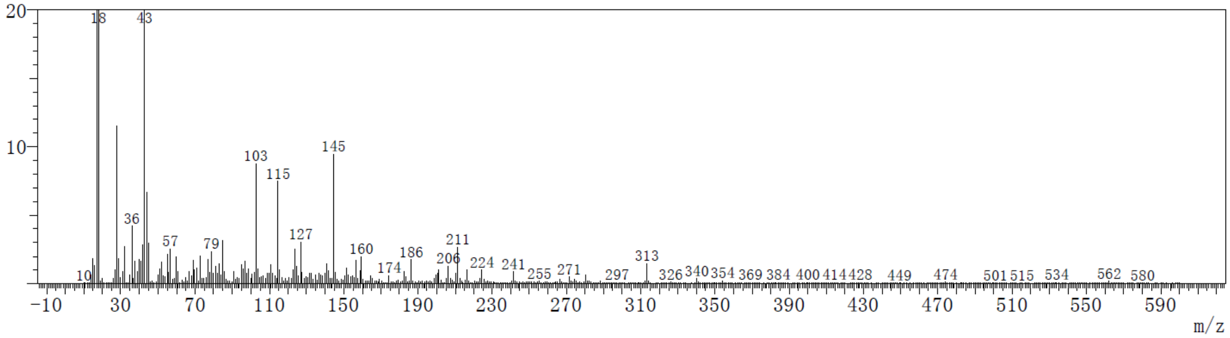
A^{8}_{Tal}:



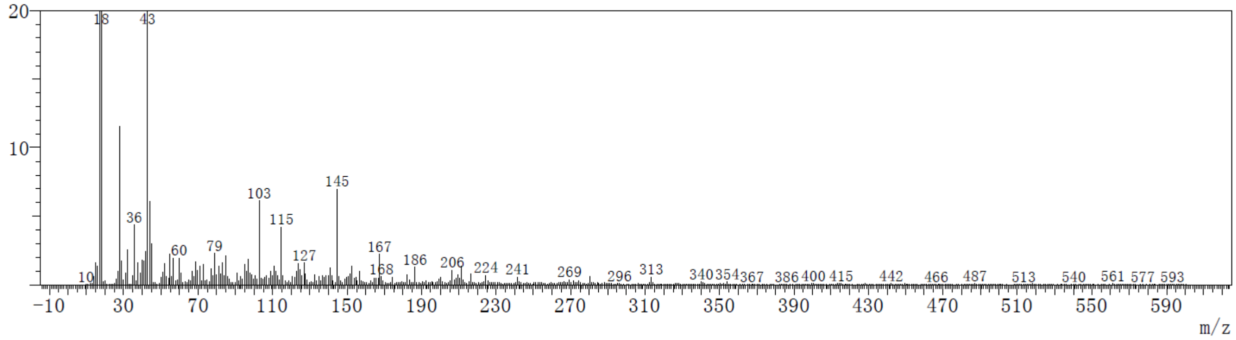
A^{10}_{Alt}:



A^{11}_{Glc}, A^{12}_{Gul}:



A^{13}_{Ido}, A^{14}_{Gal}:



(2) From the Mg^{2+}-montmorillonite reaction:

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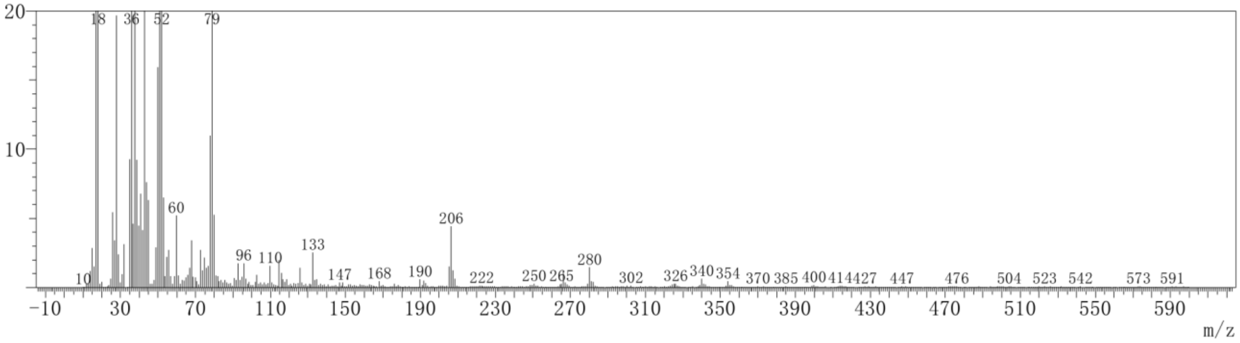
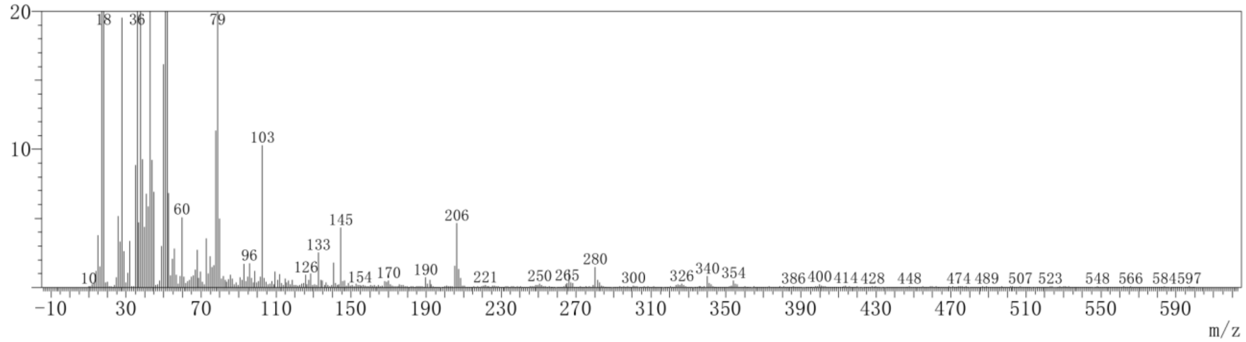
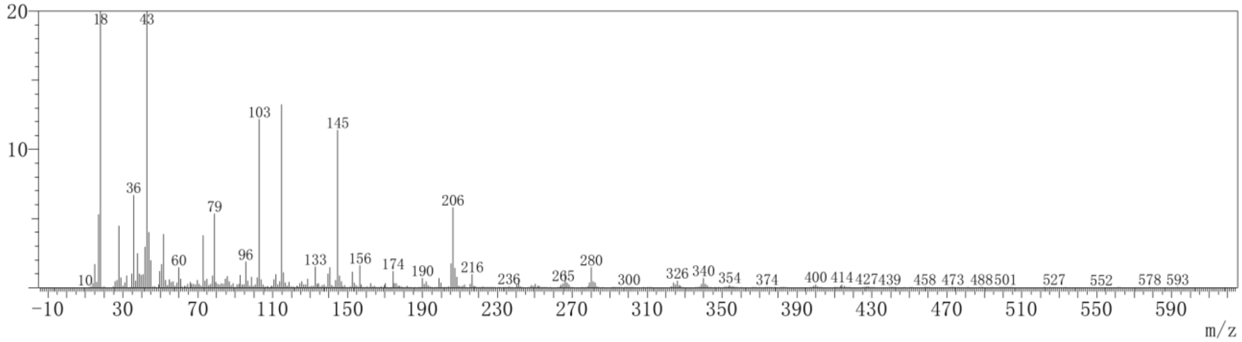


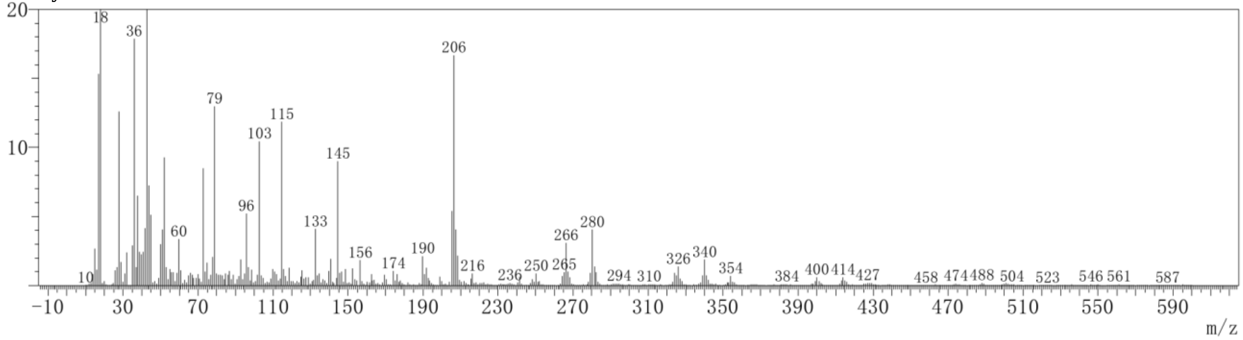
A^2_{Tho}:



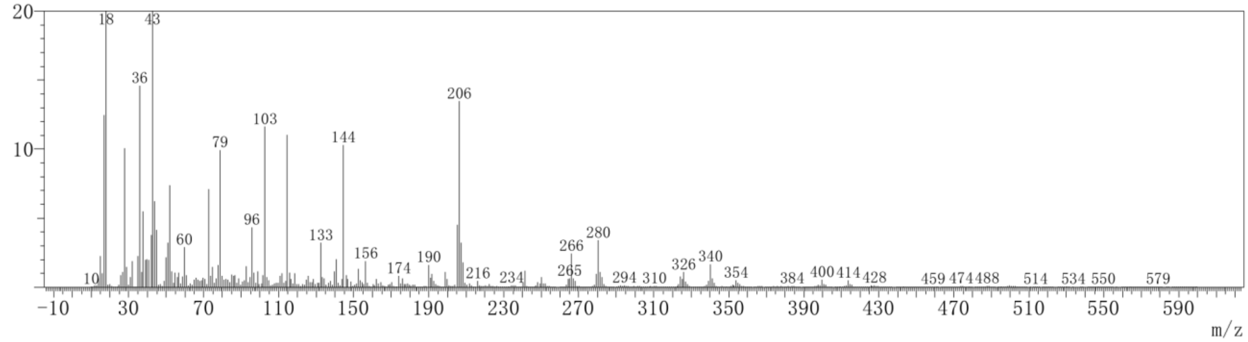
A^3_{Rib}:



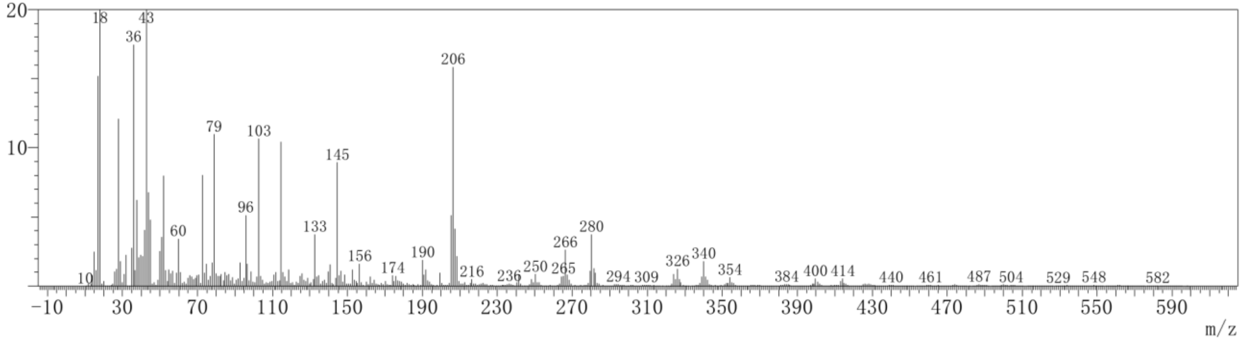
A^4_{Lyx}:



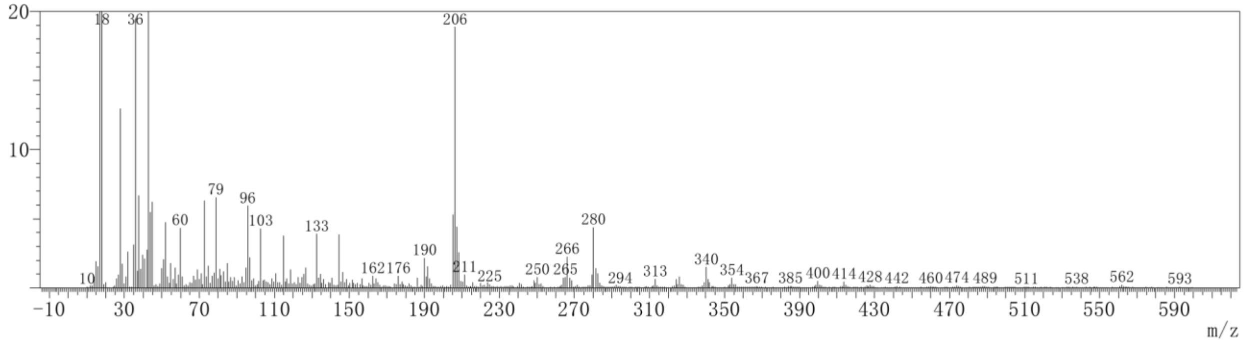
A^5_{Ara}:



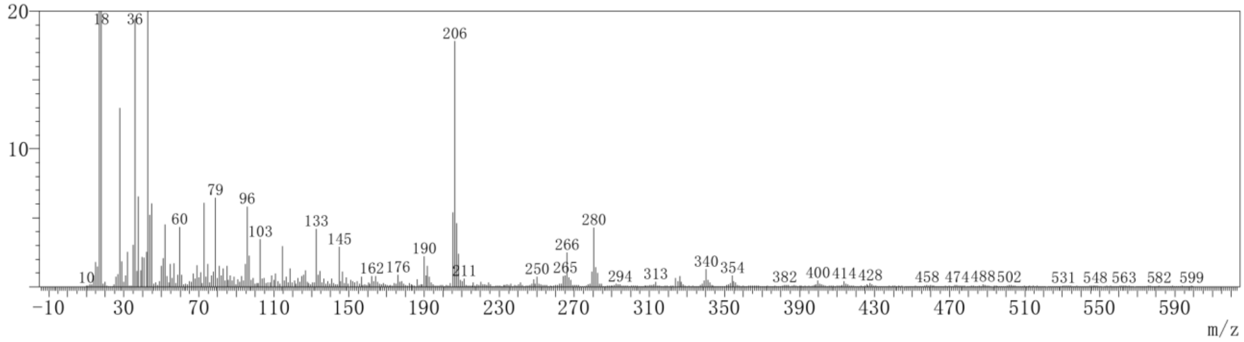
A^{6}_{Xyl}:



A^{11}_{Glc}, A^{12}_{Gul}:

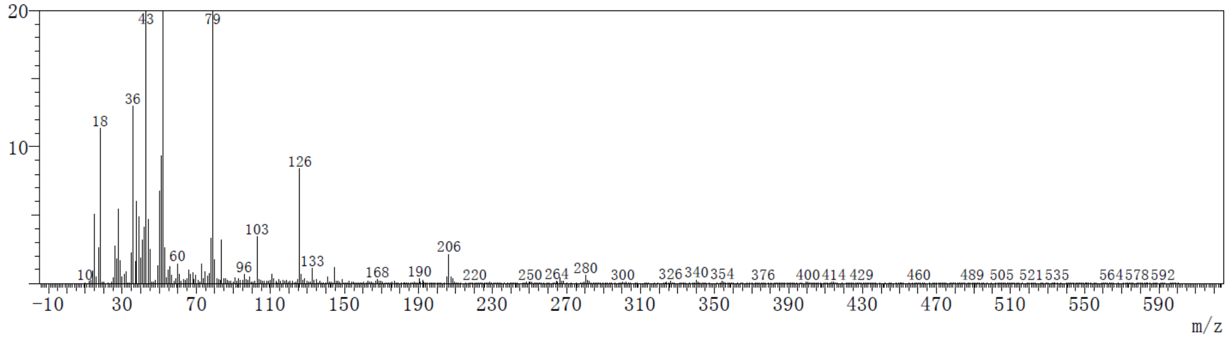


A^{13}_{Ido}, A^{14}_{Gal}:

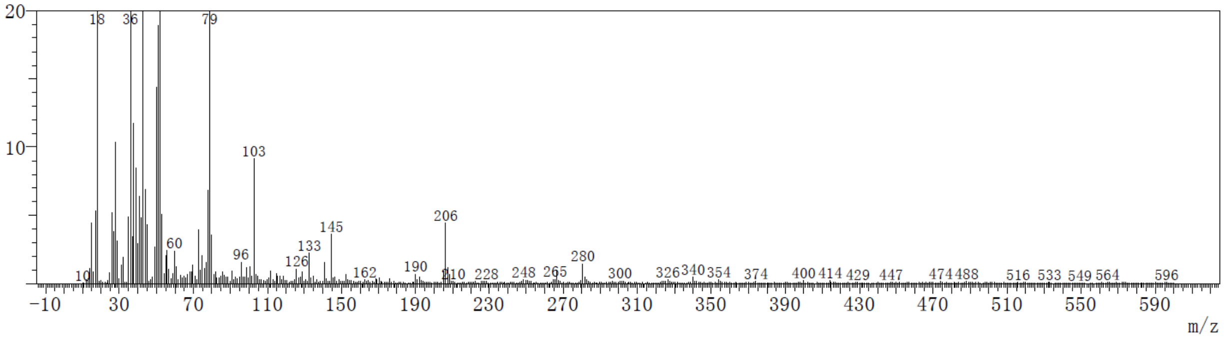


(3) From the Mn^{2+}-montmorillonite reaction:

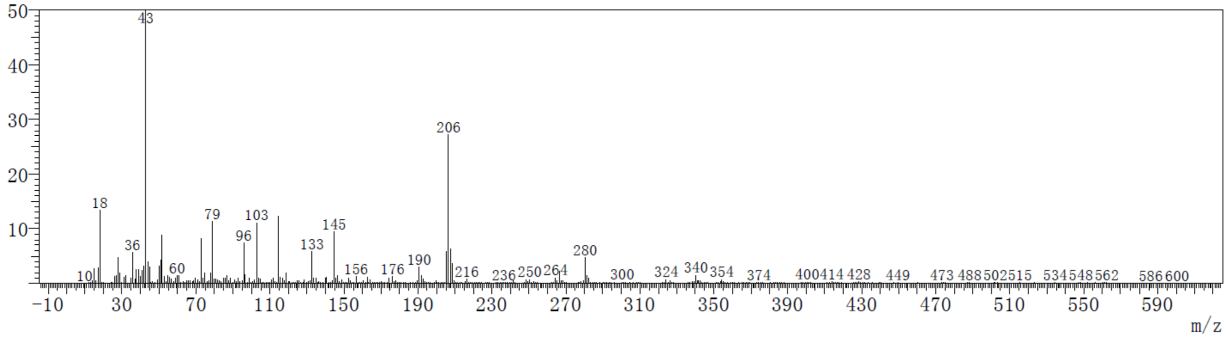
A^{1}_{Ery}:



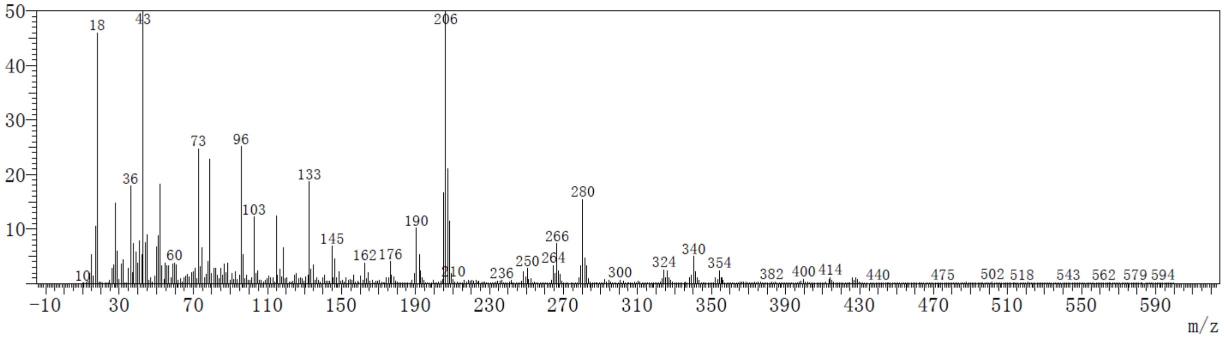
A^2_{Tho}:



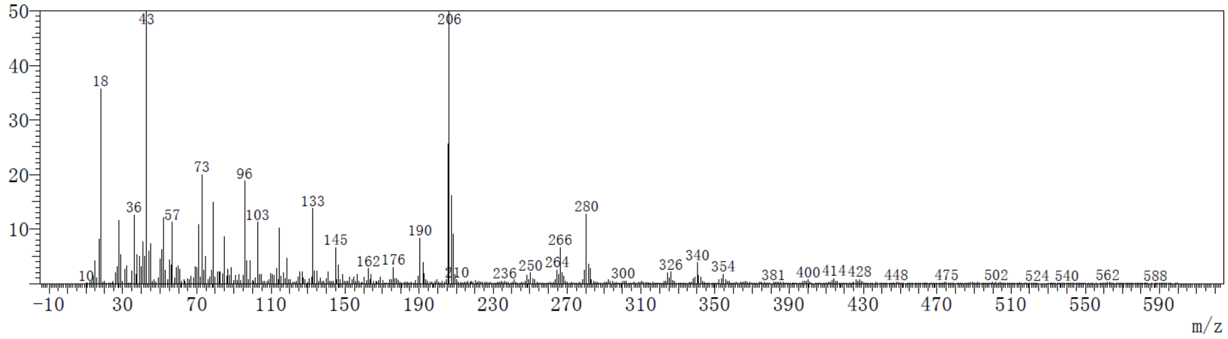
A^3_{Rib}:



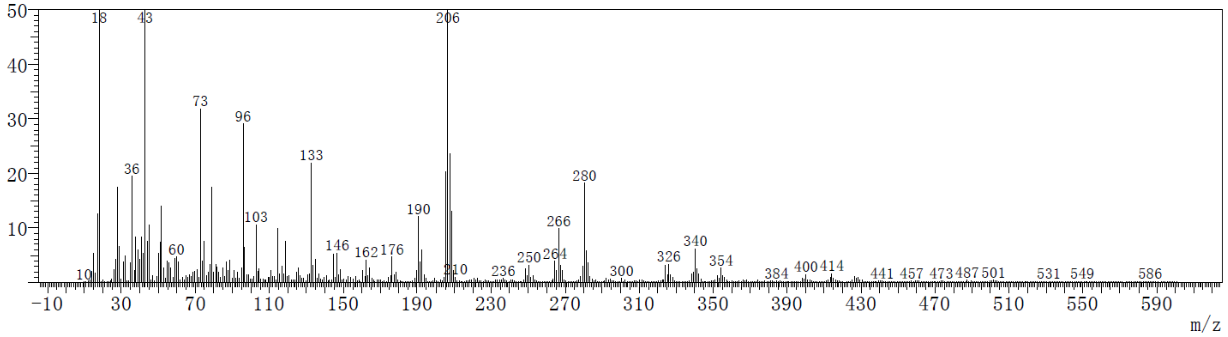
A^4_{Lyx}:



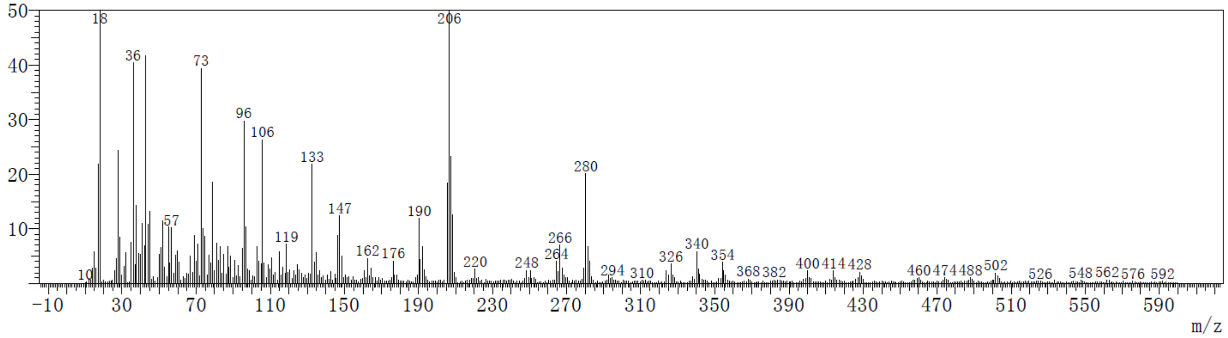
A^5_{Ara}:



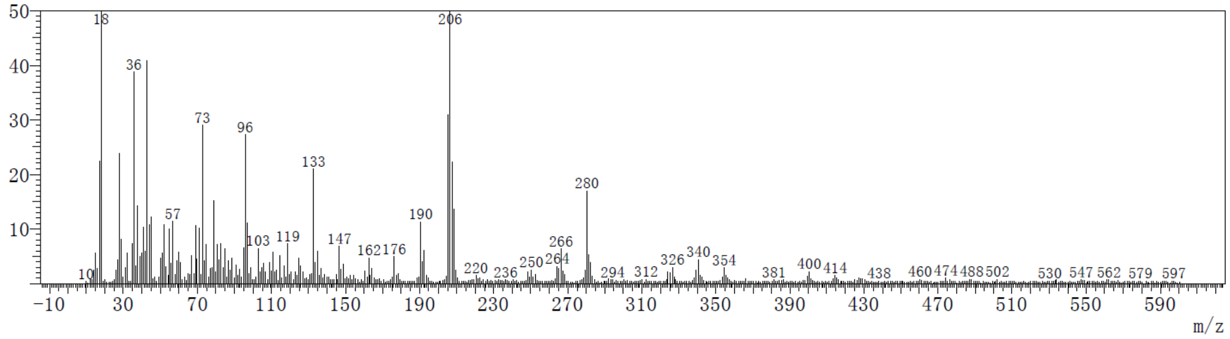
A^{6}_{Xyl}:



A^{11}_{Glc}, A^{12}_{Gul}:

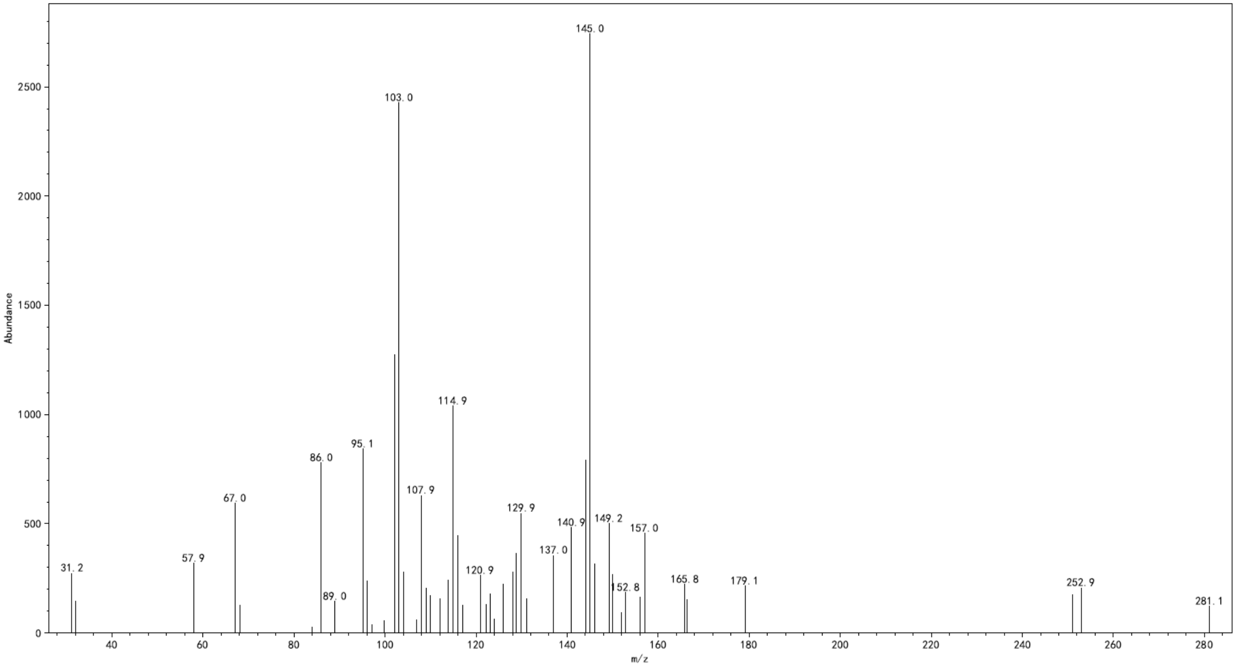


A^{13}_{Ido}, A^{14}_{Gal}:

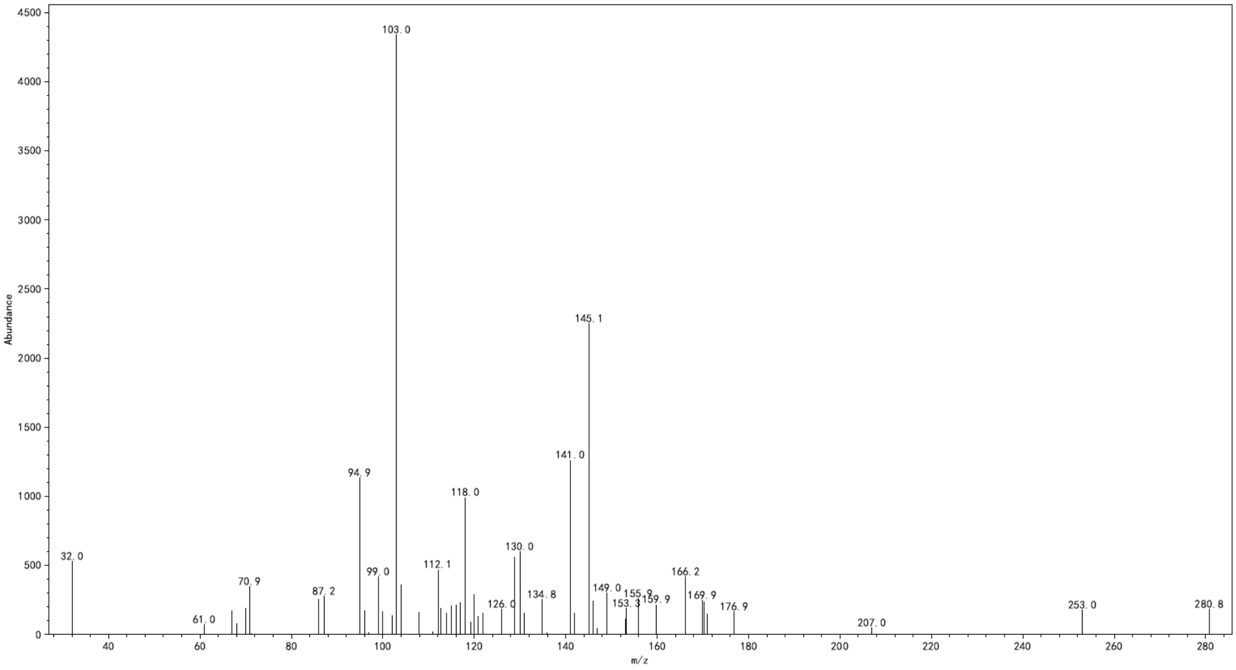


(4) From the multimetal-montmorillonite reaction:

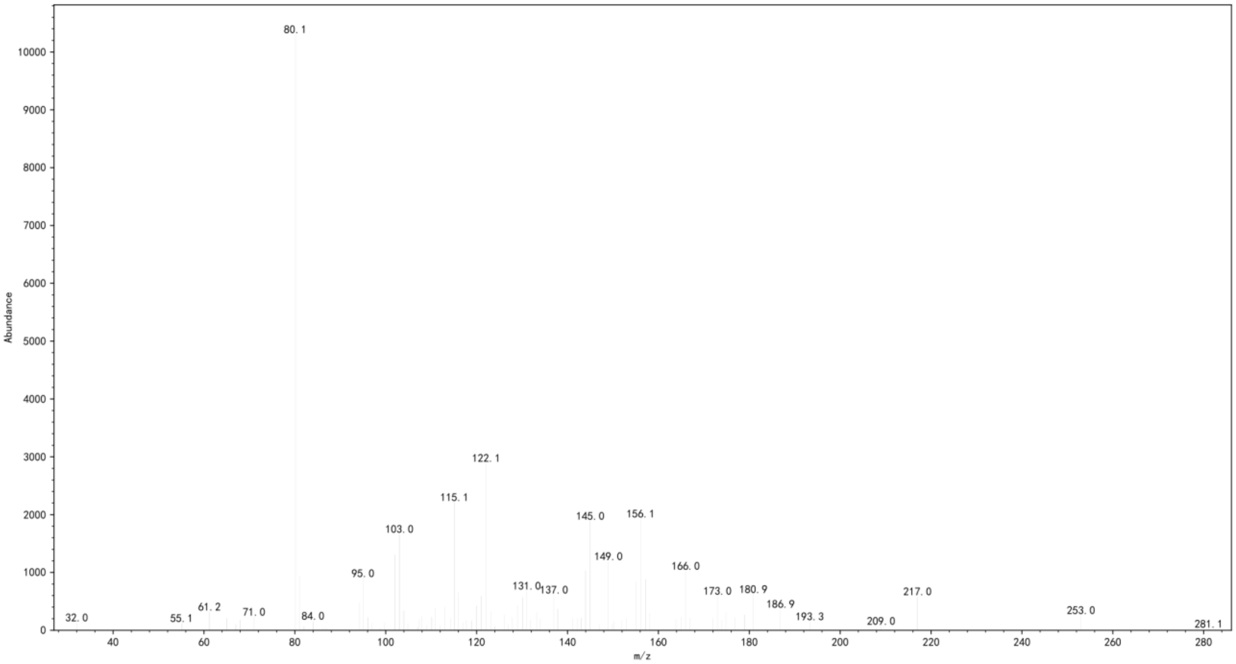
A^1_{Ery}:



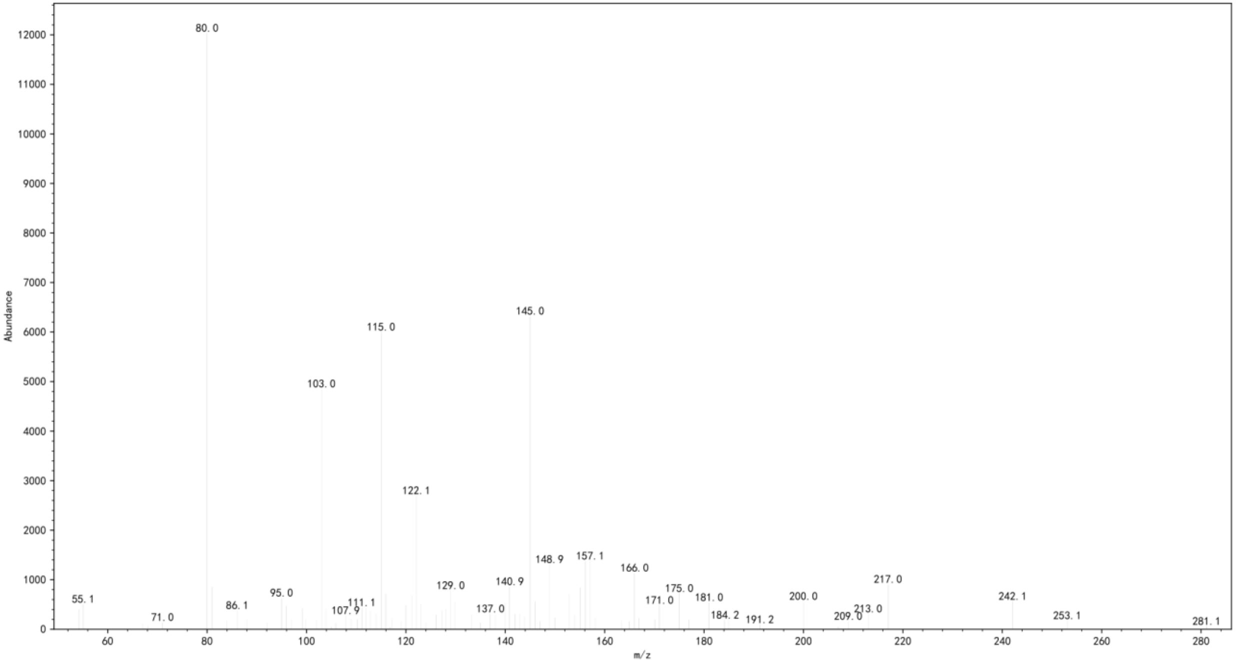
A^2_{Tho}:



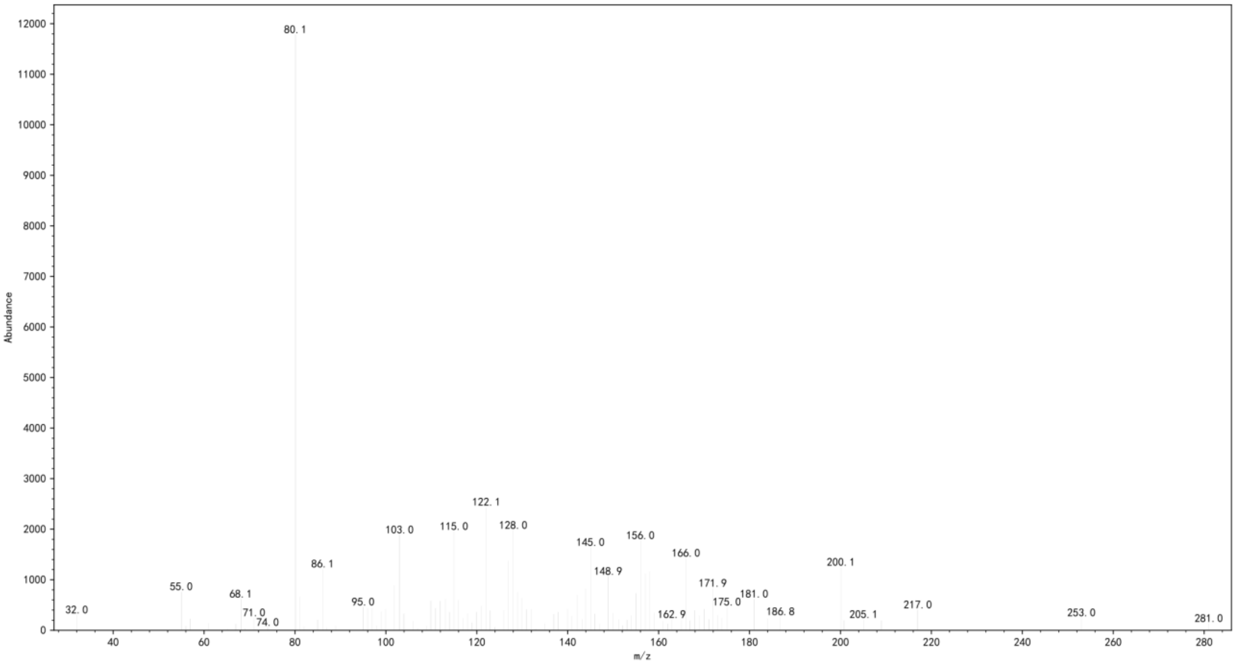
A^{3}_{Rib}:



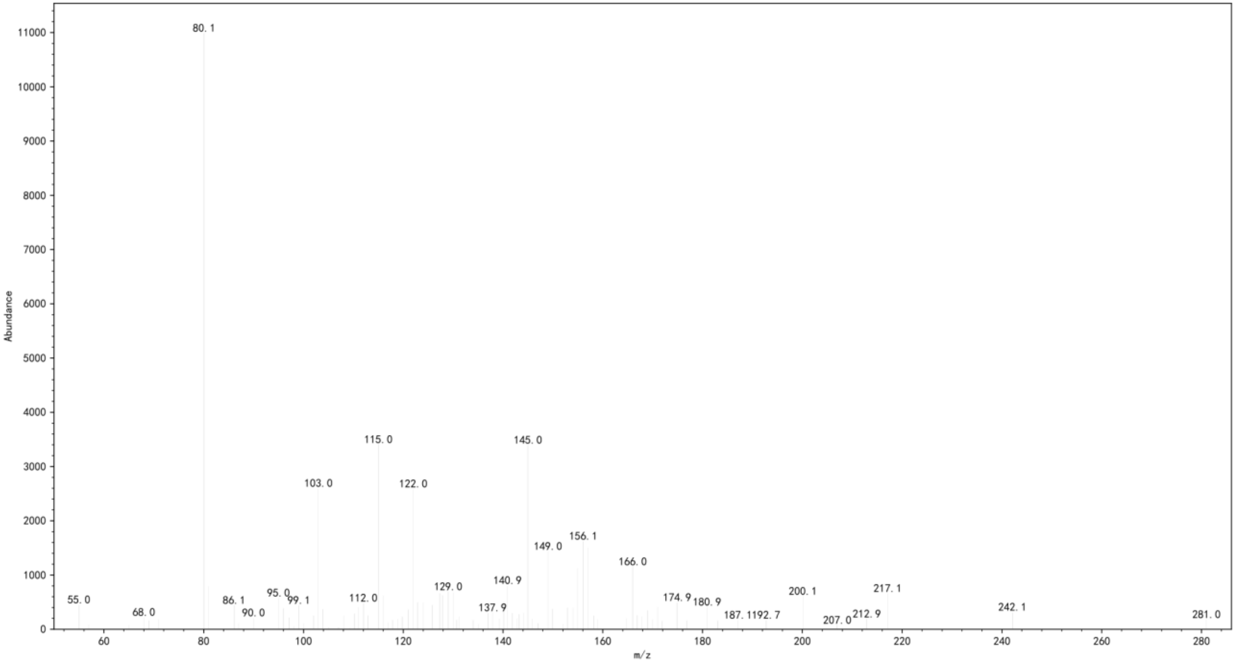
A^{4}_{Lyx}:



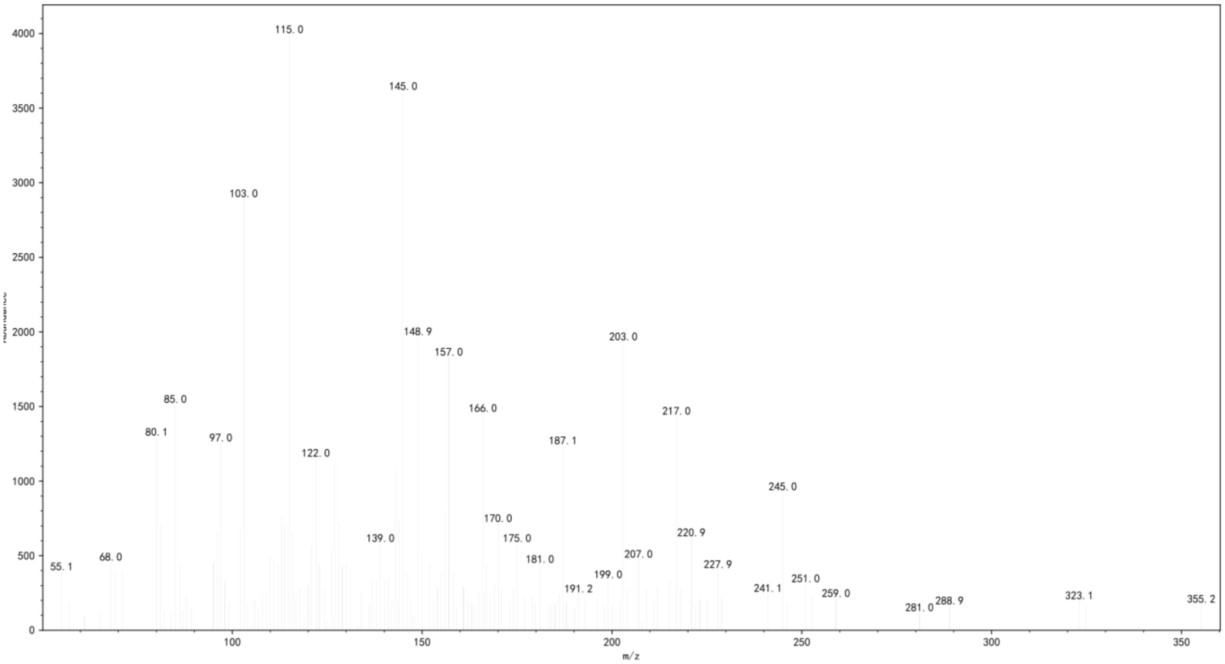
A$^{5}_{\text{Ara}}$:



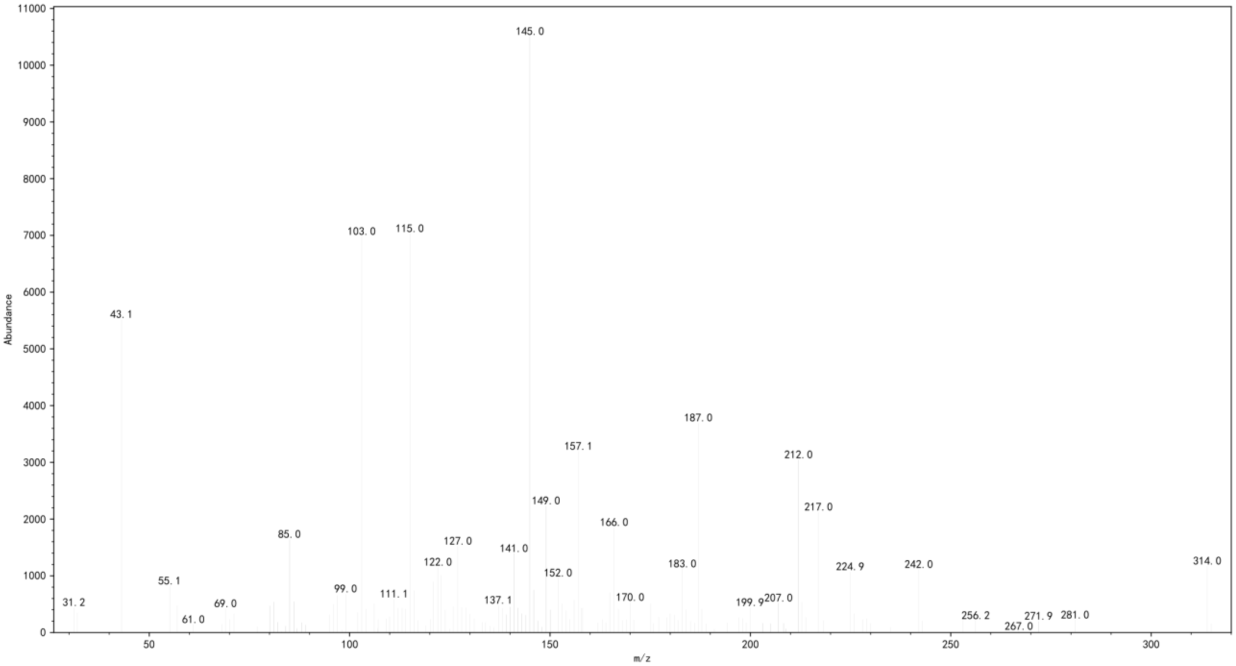
A$^{6}_{\text{Xyl}}$:



A^{11}_{Glc}, A^{12}_{Gul}:



A^{13}_{Ido}, A^{14}_{Gal}:



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