Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

- Supporting Information-

Probing the Effects of Fructose Concentration on the Evolution of Humins during Fructose Dehydration

Yexin Hu, Hui Li, Ping Hu, Linzhen Li, Di Wu, Zhidan Xue, Liangfang Zhu,* and Changwei Hu*

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, P. R. China.

**E-mail: zhulf@scu.edu.cn and changweihu@scu.edu.cn; Fax: +86 28 85411105; Tel: +86 28 85411105.*

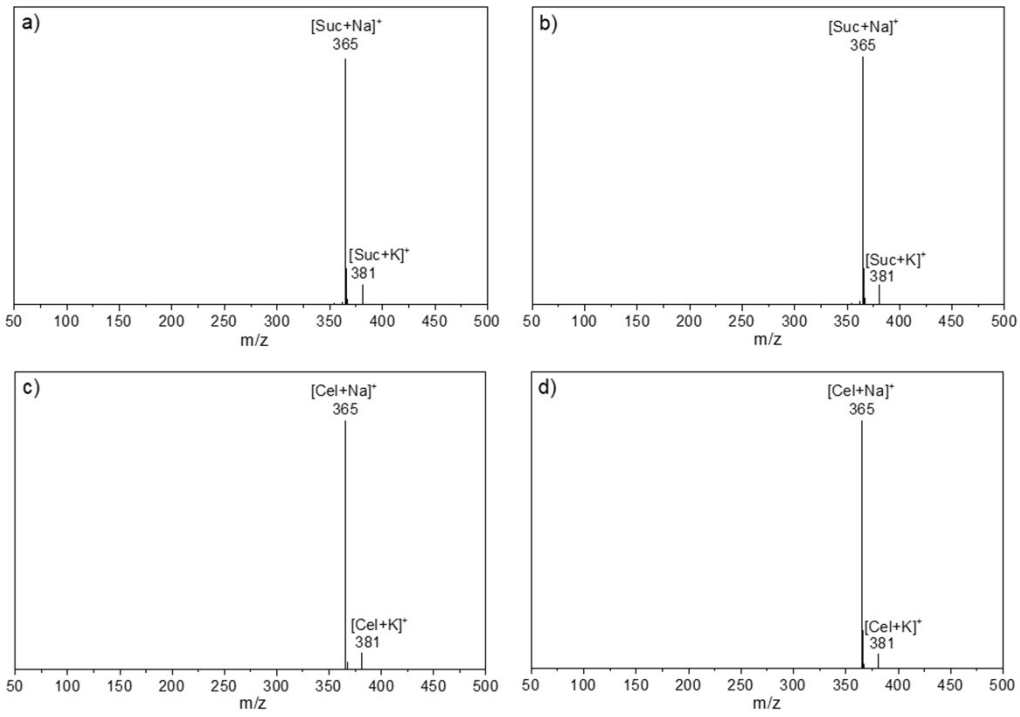

Fig. S1 ESI-MS spectra of the aqueous solutions of a) 0.5 M sucrose, b) 2.0 M sucrose, c) 0.5 M cellobiose, and d) 2.0 M cellobiose.

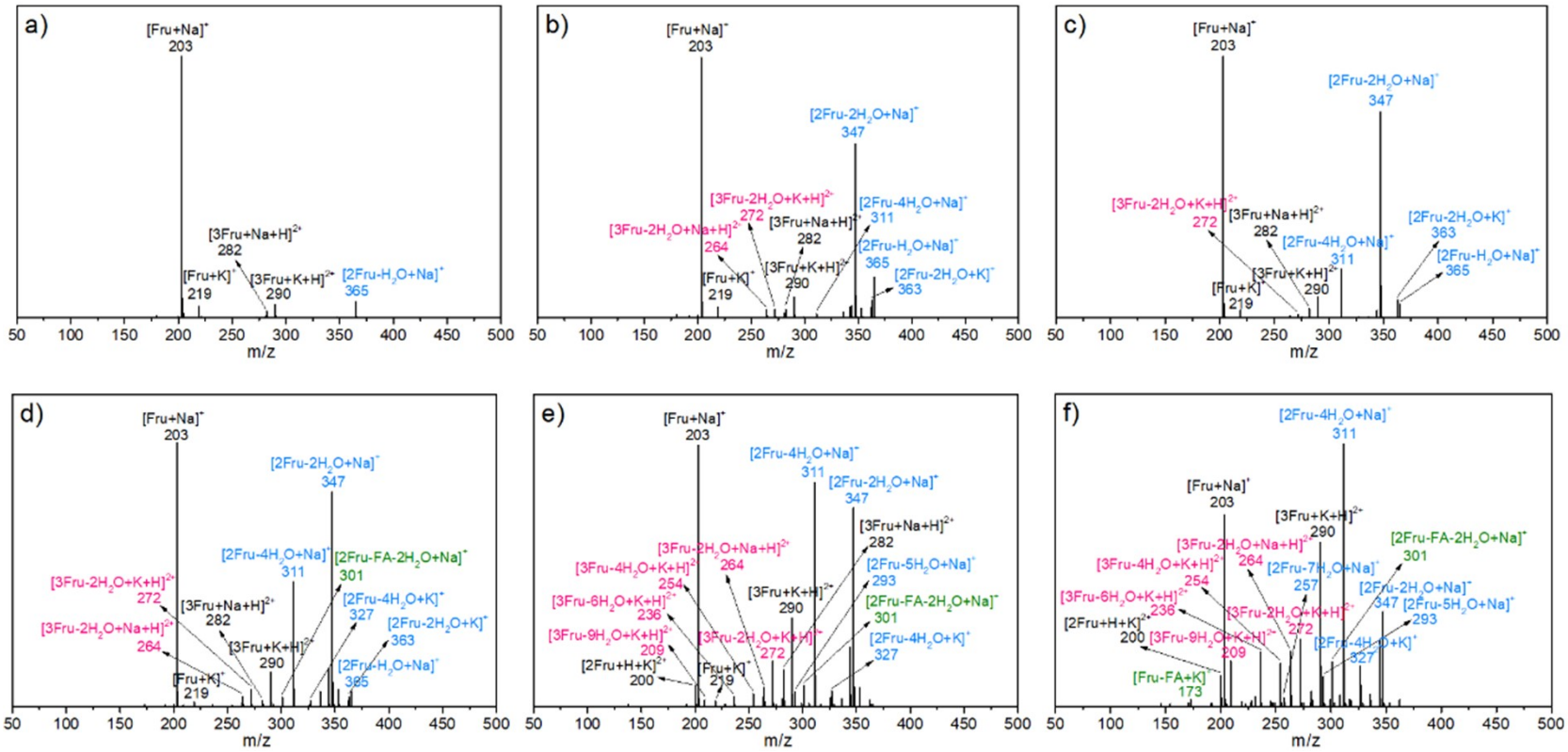

Fig. S2 The ESI-MS spectra of the reaction mixture before (a) and after (b ~ f) reacting fructose (18.0 *wt.*%) at 140 °C for different reaction time. b) 15 min, c) 30 min, d) 60 min, e) 90 min, and f) 120 min. Note: the peak with m/z of 209 could also be assigned to $[2Fru+HMF-6H_2O+H+K]^{2+}$, $[Fru+2HMF-3H_2O+H+K]^{2+}$, or $[3HMF+H+K]^{2+}$; the peak with m/z of 236 could also be assigned to $[2Fru+HMF-3H_2O+H+K]^{2+}$ or $[Fru+2HMF+H+K]^{2+}$; the peak with m/z of 254 could also be assigned to $[2Fru+HMF-H_2O+H+K]^{2+}$; the peak with m/z of 264 could also be assigned to $[2Fru+HMF+H_2O+H+Na]^{2+}$; the peak with m/z of 272 could also be assigned to $[2Fru+HMF+H_2O+H+K]^{2+}$; the peak with m/z of 301 could also be assigned to $[2Fru-FA+HMF+H_2O+Na]^{+}$.

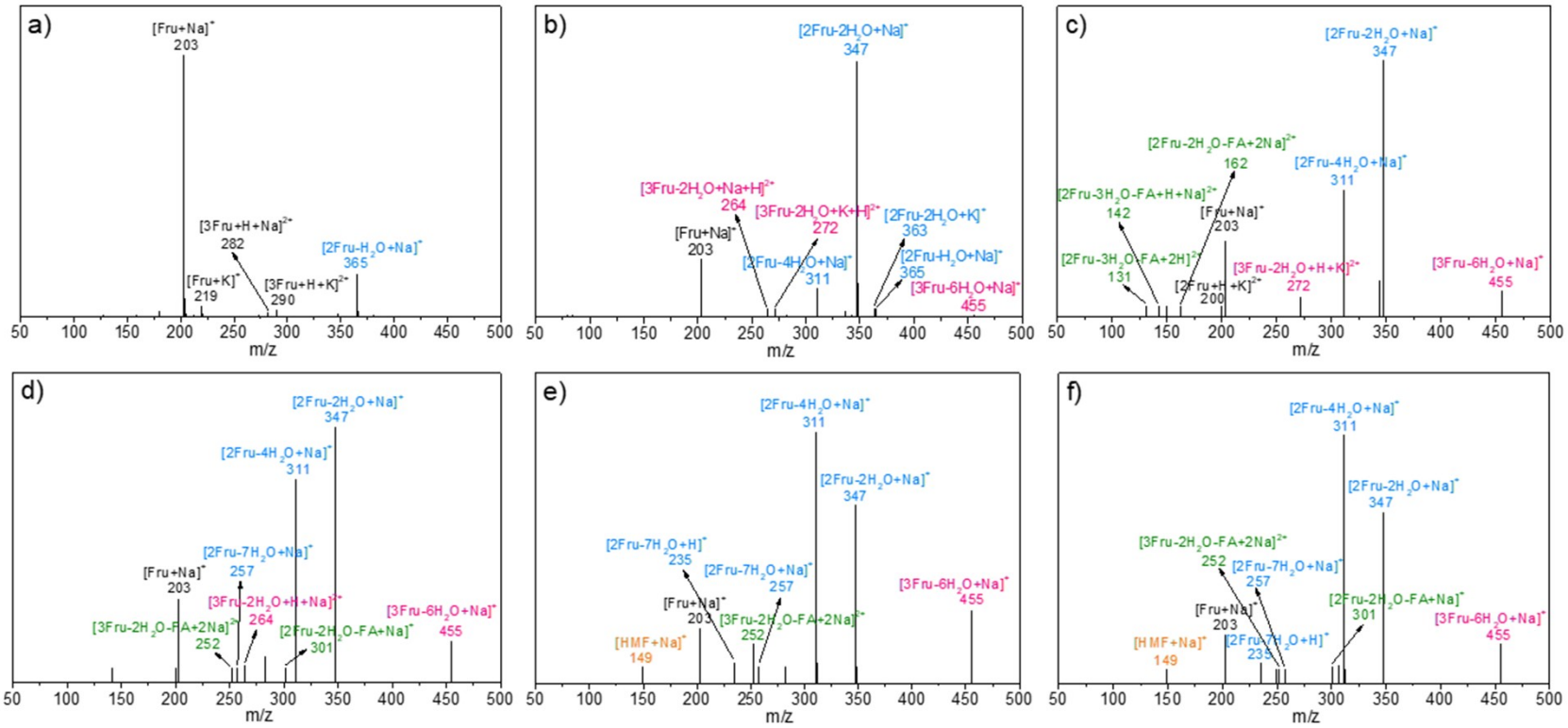

Fig. S3 The ESI-MS spectra of the reaction mixture before (a) and after (b ~ f) reacting fructose (270.0 *wt.*%) at 140 °C for different reaction time. b) 15 min, c) 30 min, d) 60 min, e) 90 min, and f) 120 min. Note: the peak with m/z of 131 could also be assigned to $[Fru\text{-}FA+HMF+2H]^{2+}$; the peak with m/z of 142 could also be assigned to $[Fru\text{-}FA+HMF+H+Na]^{2+}$; the peak with m/z of 162 could also be assigned to $[Fru\text{-}FA+HMF+H_2O+2Na]^{2+}$; the peak with m/z of 252 could also be assigned to $[2Fru\text{-}FA+HMF+H_2O+2Na]^{2+}$; the peak with m/z of 264 could also be assigned to $[2Fru+HMF+H_2O+H+Na]^{2+}$; the peak with m/z of 272 could also be assigned to $[2Fru+HMF+H_2O+H+K]^{2+}$; the peak with m/z of 301 could also be assigned to $[2Fru\text{-}FA+HMF+H_2O+Na]^{+}$; the peak with m/z of 455 could also be assigned to $[2Fru+HMF-3H_2O+Na]^{+}$ or $[Fru+2HMF+Na]^{+}$.

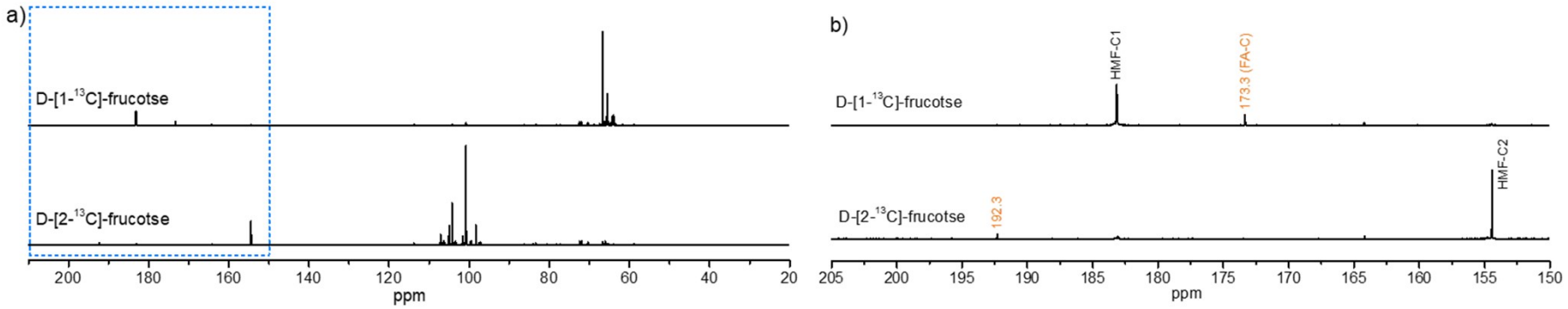

Fig. S4 ^{13}C NMR spectra of the reaction mixture after reacting fructose or isotopically labelled fructose at 140 °C for 0.5 h. Reaction conditions: 720 mg substrate, 1 mL H_2O, 0.05 M H_2SO_4, under a N_2 atmosphere. b) represented the enlarged spectra in the dotted regions of a).

The peaks in the range of 60 ~ 110 ppm were assigned to isotope-labelled fructose (Fig. S4a). The peak at 173.3 ppm in Fig. 4b was ascribed to carbon of FA formed by the C1-C2 cleavage of D-[1-^{13}C]-fructose. The peak at 192.3 ppm was assigned to the C11 species formed by condensation of degradative D-[2-^{13}C]-fructose with another fructose molecule.

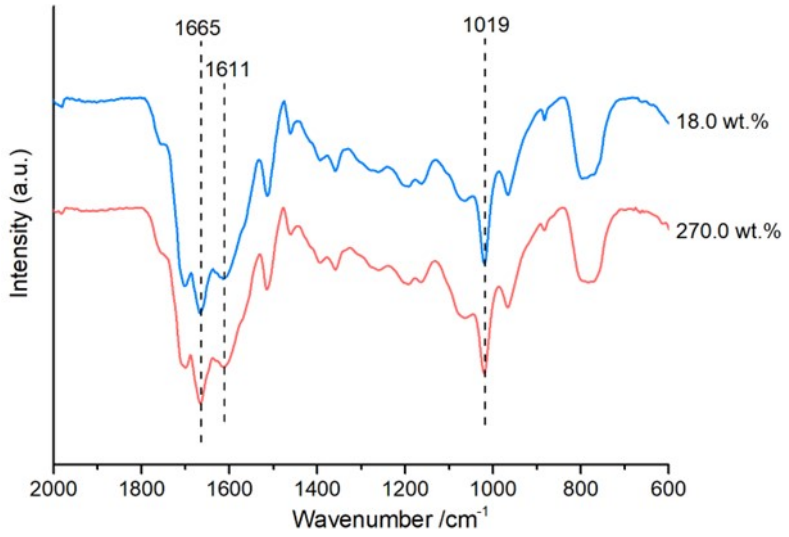

Figure S5 FT-IR spectra of the solid humins obtained after reacting fructose with different concentrations for a long reaction time. Reaction conditions: 1 mL of H_2O, 0.05 M of H_2SO_4, 140 °C, 2 h, under a N_2 atmosphere.

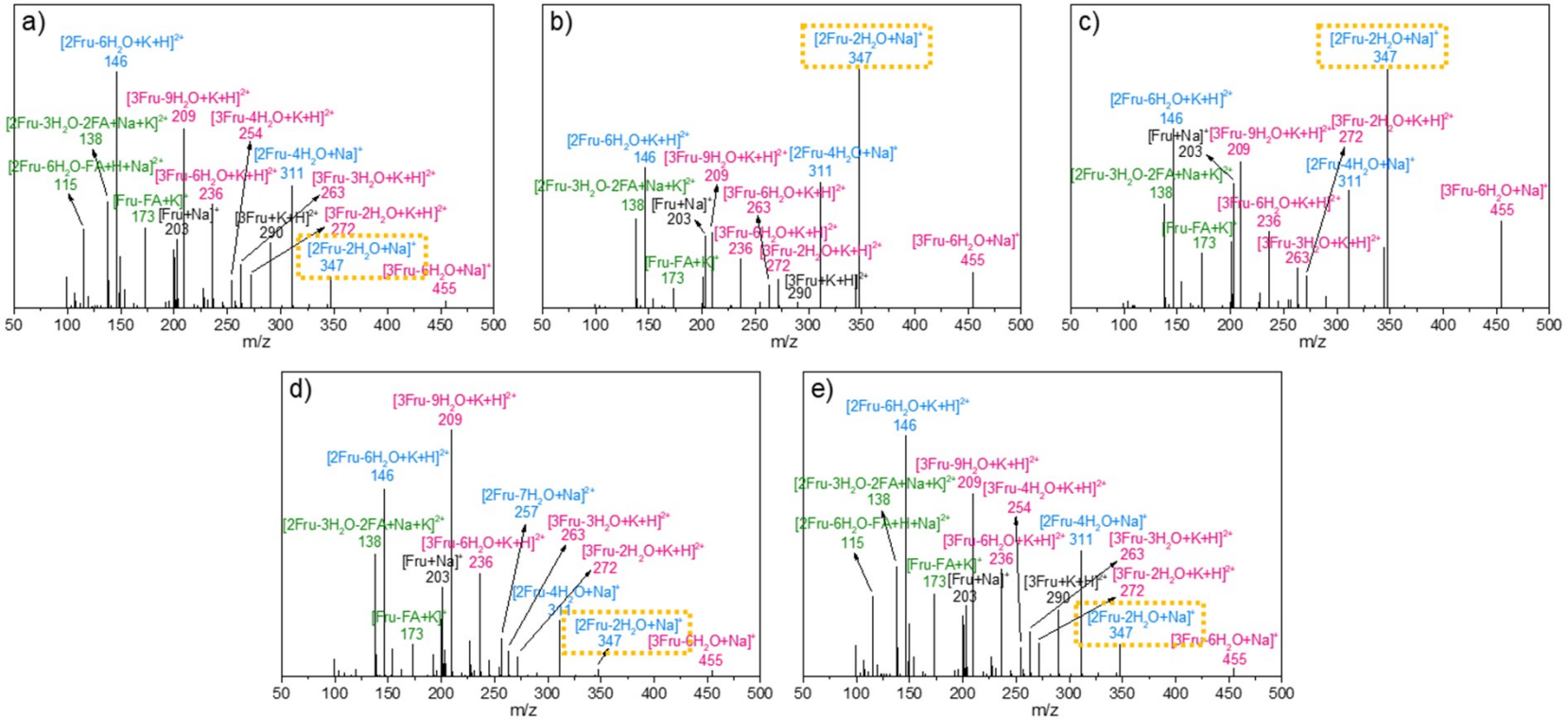

Fig. S6 ESI-MS spectra of the reaction mixture after reacting fructose (72.0 *wt*.%) at 140 °C in various solvents for different reaction time. a) H_2O, 90 min, b) THF-H_2O (*V/V*=7/3), 15 min, c) DIO-H_2O (*V/V*=7/3), 15 min, d) THF-H_2O (*V/V*=7/3), 30 min, and e) DIO-H_2O (*V/V*=7/3), 30 min. The yellow dotted squares label the signal of DFAs. Note: the peak with m/z of 115 could also be assigned to [Fru-FA-3H_2O+HMF+H+Na]$^{2+}$ or [2HMF-FA+H+Na]$^{2+}$; the peak with m/z of 138 could also be assigned to [Fru+HMF-2FA+Na+K]$^{2+}$; the peak with m/z of 209 could also be assigned to [2Fru+HMF-6H_2O+H+K]$^{2+}$, [Fru+2HMF-3H_2O+H+K]$^{2+}$, or [3HMF+H+K]$^{2+}$; the peak with m/z of 236 could also be assigned to [2Fru+HMF-3H_2O+H+K]$^{2+}$ or [Fru+2HMF+H+K]$^{2+}$; the peak with m/z of 254 could also be assigned to [2Fru+HMF-H_2O+H+K]$^{2+}$; the peak with m/z of 263 could also be assigned to [2Fru+HMF+H+K]$^{2+}$; the peak with m/z of 272 could also be assigned to [2Fru+HMF+H_2O+H+K]$^{2+}$;the peak with m/z of 455 could also be assigned to [2Fru+HMF-3H_2O+Na]$^{+}$ or [Fru+2HMF+Na]$^{+}$.

Table S1. The pH values of aqueous fructose solutions with various concentrations.[a]

Fructose concentration (wt.%)	pH value
-	7.01
4.5	6.99
18.0	6.94
72.0	6.87
180.0	6.72
270.0	6.58
360.0	6.56

[a] Different amount of fructose was dissolved in water and kept static for 5 h to ensure stable. The pH value was detected by a pen type pH meter (SX-620, Sanxin) at room temperature (20 °C).

Table S2. The attribution of characteristic ATR-IR peaks in this study.[1]

v (cm^{-1})	Assignments[a]
781	deformation vibrations of skeleton & δ(C1-O-H) c
811	υ(O-C2-C3) of β-1,3-difuranose
821	deformation vibrations of skeleton & δ(C6-O-H) c; υ(C2-C3-C4) & δ(C3-O-H) f; stretch vibrations of skeleton & δ(C5-O-H) p
870	δ(C2-O-H) & υ(C2-C3) c
921	δ(C1H2) & υ(C2-O) p
968	deformation vibrations of skeleton &δ(C6-O-H) c; stretch vibrations of skeleton & δ(C2-O-H) & δ(C4-O-H) f; δ(C2-O-H) & δ(C1H2OH) & υ(C5-C6-O) p υ(C1-O-H&C6-O) c;
981	stretch vibrations of skeleton & δ(C6-O-H) & δ(C4-O-H) f; υ(C3-C4) & v(C4-O-H) p
1017	υ(C5-O-C2) & δ(C6-O-H) & δ((C1)-O-H) f; υ(C1-O) p δ(C5-O-H) c;
1036	υ(C1-O) & δ(C6)-O-H) f; υ(C5-O) p
1064	υ(C1-O) & υ(C3-O) & δ(C6)-O-H) c; υ(C5-O-C2) & δ(C5)-O-H) & δ(C1)-O-H) p
1085	υ(C4-C5) & δ(C5-O-H) & δ((C1)-O-H) p
1105	υ(C1-O) & υ(C3-O-H) & δ(C4)-O-H) c; υ(C3-C4) & δ(C4)-O-H) & δ(C2)-O-H) f; δ(C1)-O-H) p
1158	δ(C6)-O-H) c; υ(C1-C2) & δ(C1-H) p
1183	δ(C2)-O-H) c; δ(C6)-O-H) f; δ(C3)-O-H) & δ(C2)-O-H) p
1252	δ(C3)-O-H) c; δ(C4-O-H) f; δ(C1-H) & ω(CH2) & ω(C4H) p;

[a] f = fructofuranose, p = fructopyranose, c = fructoketose, υ = stretching vibration, δ = deformation vibrations, ω = wagging vibrations.

References

1. X. Fu, Y. Hu, Y. Zhang, Y. Zhang, D. Tang, L. Zhu and C. Hu, ChemSusChem, 2020, 13, 501-512.