Electronic Supplementary Material (ESI) for Analyst.

SUPPLEMENTARY MATERIAL

for

Characterization of Glycosphingolipid Epimers by Radical-Directed Dissociation Mass Spectrometry

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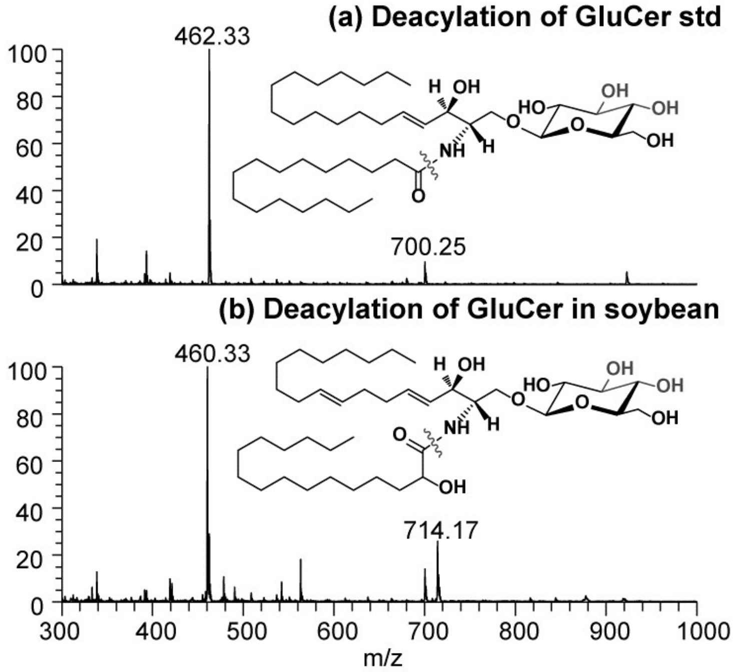
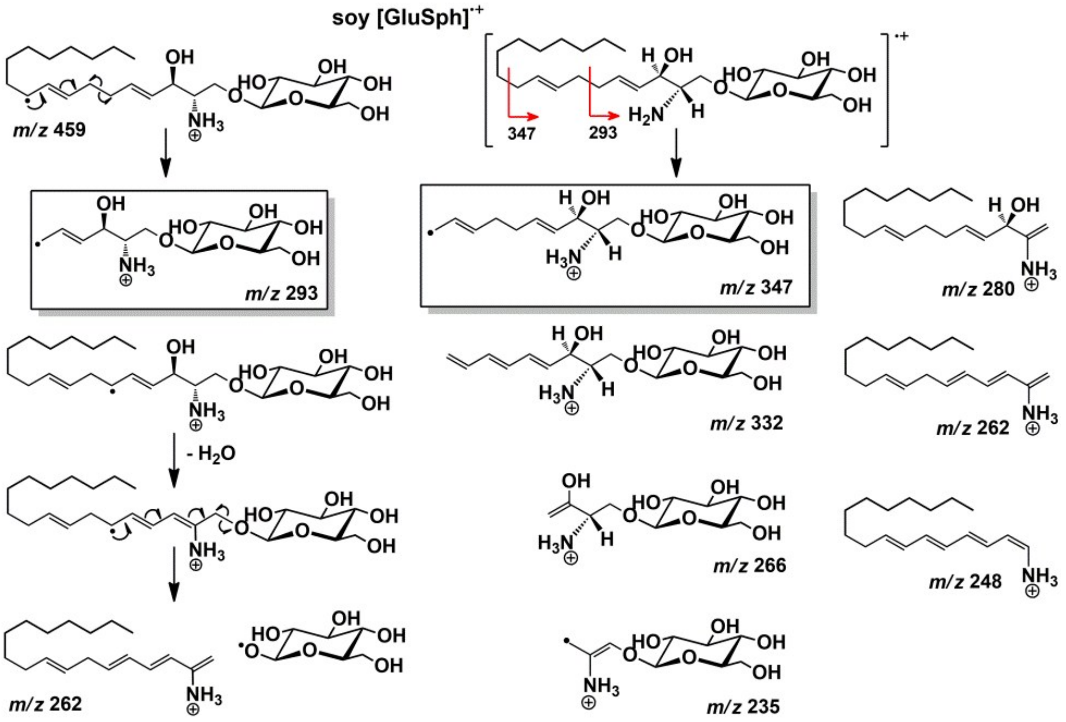


(a) Deacylation of GluCer std

(b) Deacylation of GluCer in soybean

Figure S-1. Full mass spectra acquired from deacylation reaction of (a) GluCer synthetic standard and (b) GluCer in soybean. Structures of the initial GSL are inserted with the likely side of bond cleavage in the associated condition (i.e. KOH 0.01 M, pH 12).

Scheme S-1. Proposed mechanism for some characteristic RDD product ions generated from soy $[\mathrm{GluSph}]^{+\bullet}$ m/z 459.



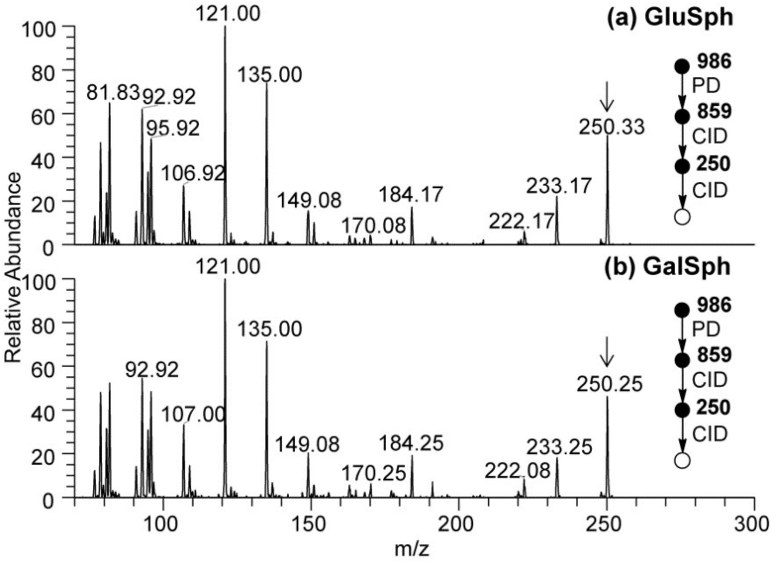


Figure S-2. MS^4 acquired on *m/z* 250 product ion generated in PD/CID of the noncovalent complexes (a) $[GluSph+H+IB18C6]^+$ and (b) $[GalSph+H+IB18C6]^+$, respectively.

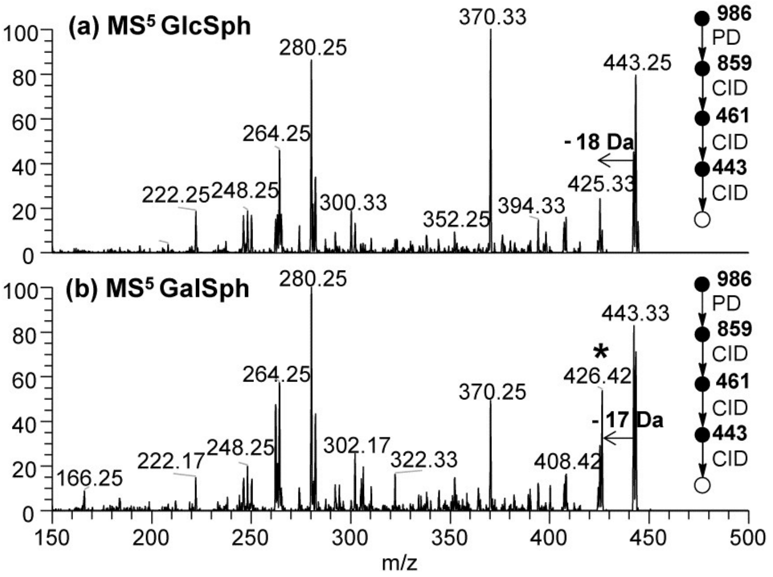


Figure S-3. MS^5 acquired on *m/z* 443 product ion generated in RDD spectra from (a) $[GluSph]^{+\bullet}$ and (b) $[GalSph]^{+\bullet}$, respectively.

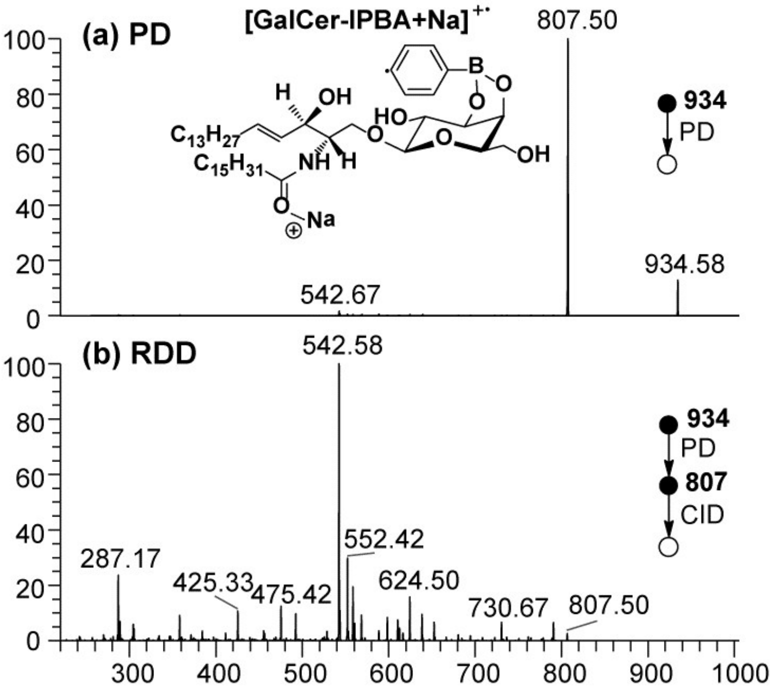


Figure S-4. (a) PD spectrum and (d) RDD spectrum obtained from $[\text{GalCer–IPBA+Na}]^+$ precursor ion resulted from addition of IPBA and NaOAc to the solution of GalCer.