



Figure S3. Structural analysis and fragmentation pattern of *N. benthamiana* acyl sugars. A, Proposed fragmentation pathways of the major acyl sugar species (MW 636) corresponding to $[M+NH_4]^+$ at m/z 654, on the basis of positive ion APCI. R1 corresponding to the only acyl group proposed to be esterified with glucose (GLU: A) is shown in position 4 but X and Y are also possible positions (the method did not provide any relevant positional information). In the fructose (FRU: B) ring R2 and R3 correspond to one acetyl and one acyl group, in either position. B, Fragmentation and structure elucidation based on MS2 spectral information of $[M]^+$ and MS3 for $[M-GLU-n \text{ acyl}]^+$.