Supporting Information

Analysis of Carbohydrates and Steroids by Desorption Electrospray Ionization Mass Spectrometry

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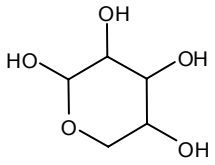
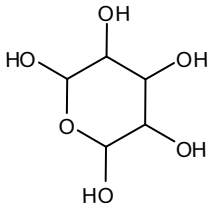
Abstract: Additional information is provided including a table of solvent systems studied, tables of the ions observed in the xylose and cortisone spectra with the different spray solvent systems, structures of the compounds studied and graphs illustrating the optimization of the solvent system in the positive and negative ion modes.

Table S1 Solvent systems studied.

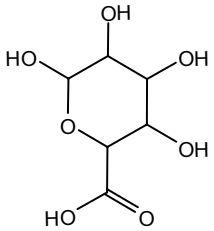
	Solvent	Salt Concentration	Monitored Ion
Positive ion mode			
1	water/methanol/formic acid	0.1%	$[M+H]^+$
2	water/methanol/lithium chloride	100 μM	$[M+Li]^+$
3	water/methanol/sodium chloride	100 μM	$[M+Na]^+$
4	water/methanol/potassium chloride	100 μM	$[M+K]^+$
5	water/methanol/silver nitrate	100 μM	$[M+Ag]^+$
6	water/methanol/ammonium acetate	100 μM	$[M+NH_4]^+$
Negative ion mode			
1	water/methanol/ammonium hydroxide	0.1%	$[M-H]^-$
2	water/methanol/chloroform	3/6/1	$[M+Cl]^-$
3	water/methanol/ammonium chloride	10 μM	$[M+Cl]^-$
4	water/methanol/ammonium bromide	10 μM	$[M+Br]^-$
5	water/methanol/formic acid	0.01%	$[M+CHOO]^-$
6	water/methanol/acetic acid	0.01%	$[M+CH_3COO]^-$
7	water/methanol/sulfuric acid	10 μM	$[M+HSO_4]^-$, $[M+SO_4]^{2-}$
8	water/methanol/ammonium nitrate	100 μM	$[M+NO_3]^-$



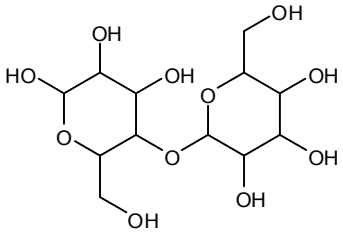
Xylose
MW = 150



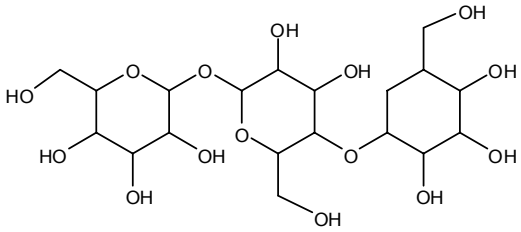
Glucose
MW = 180



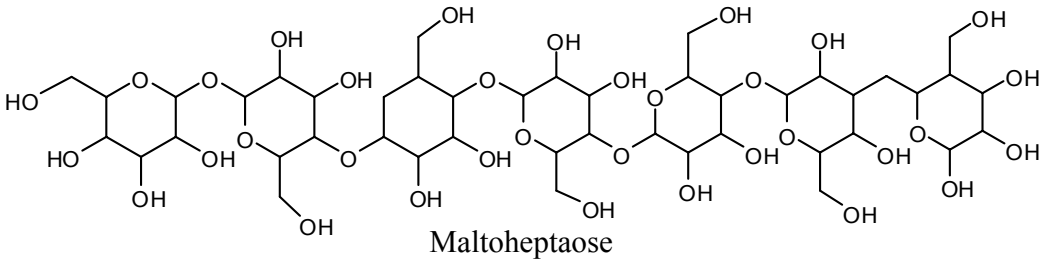
Glucuronic Acid
MW = 194



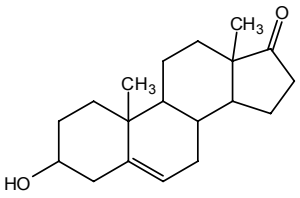
Maltose
MW = 342



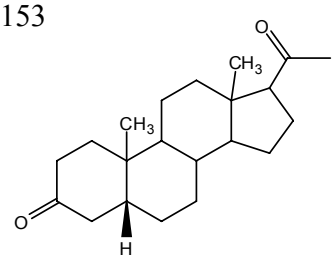
Maltotriose
MW = 504



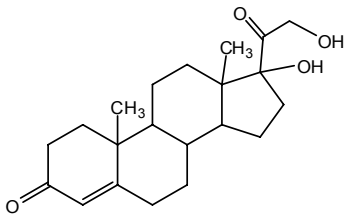
Maltoheptaose
MW = 1153



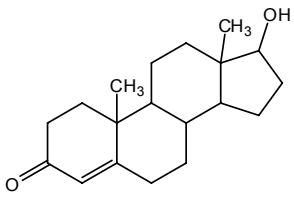
Dehydroepianderosterone
MW = 288



5β-pregnan-3,20-dione
MW = 316



Cortisone
MW = 360



Testosterone
MW = 288

Figure S1 Structures of the compounds studied

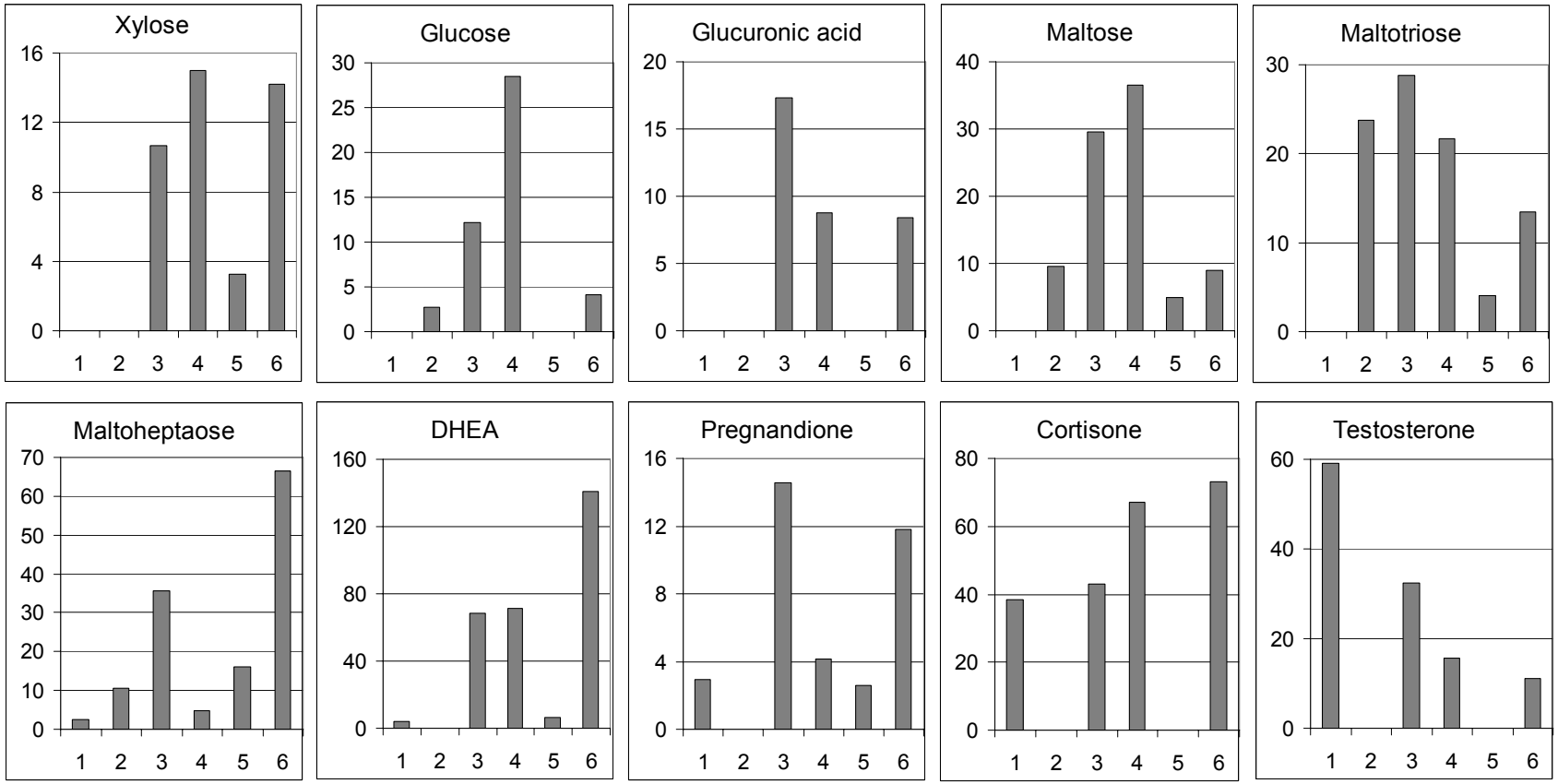


Figure S2 Positive ion mode DESI signal-to-noise ratios of the analyte ions using different spray solvents. Solvents: 1. H_2O/MeOH/HCOOH (0.1%), 2. H_2O/MeOH/LiCl (100 μM), 3. H_2O/MeOH/NaCl (100 μM), 4. H_2O/MeOH/KCl (100 μM), 5. H_2O/MeOH/$AgNO_3$ (100 μM), 6. H_2O/MeOH/CH_3COONH_4 (100 μM). DESI analysis of 0.5 μL of analyte (10 μM – 10 mM depending on ionization efficiency) from a teflon substrate

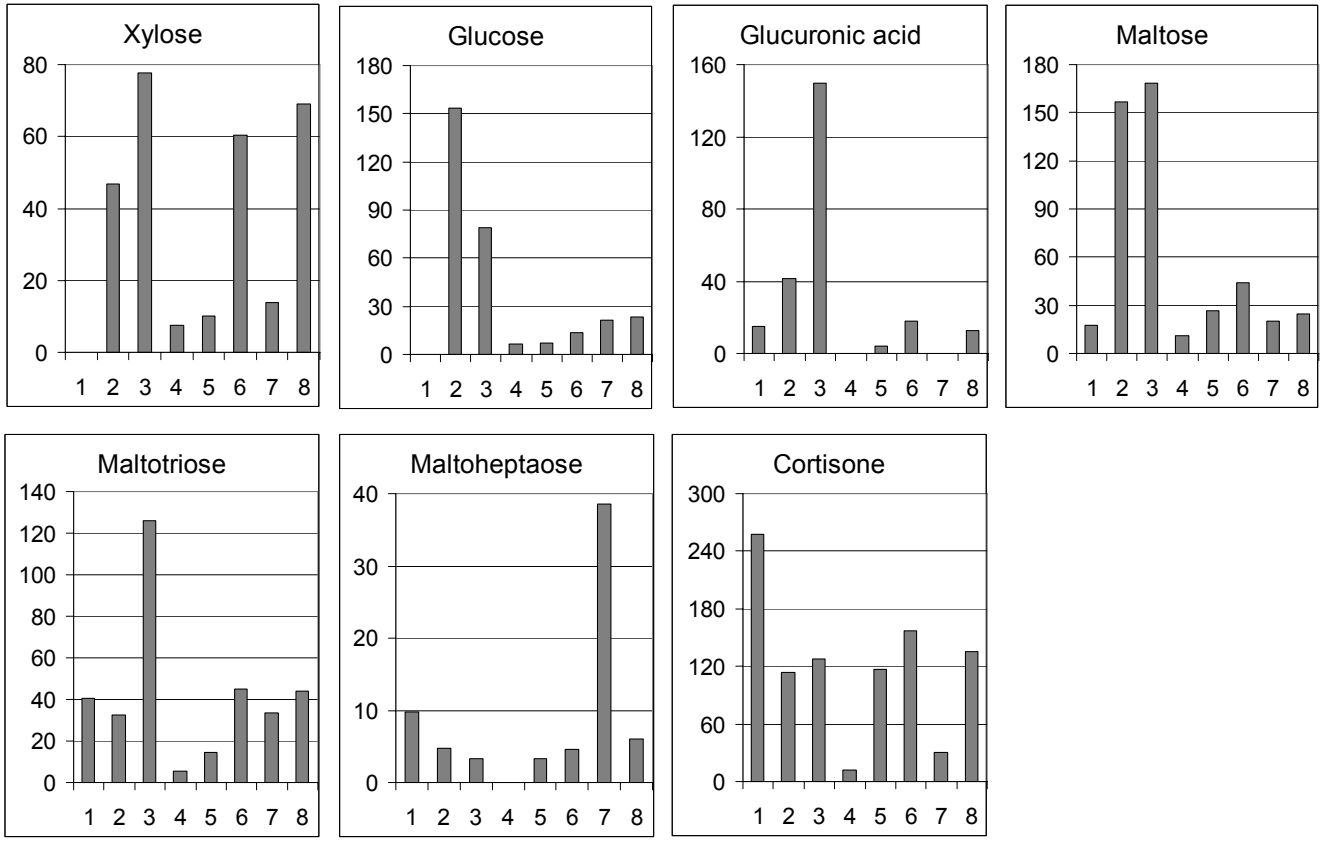


Figure S3 Negative ion mode DESI signal-to-noise ratios of the analyte ions using different spray solvents. Solvents: 1. H_2O/MeOH/NH_4OH (0.1%), 2. H_2O/MeOH/$CHCl_3$ (3/6/1), 3. H_2O/MeOH/NH_4Cl (10 μM), 4. H_2O/MeOH/NH_4Br (10 μM), 5. H_2O/MeOH/CHOOH (0.01%), 6. H_2O/MeOH/CH_3COOH (0.01%), 7. H_2O/MeOH/H_2SO_4 (10 μM), 8. H_2O/MeOH/NH_4NO_3 (100 μM). DESI analysis of 0.5 μL of analyte (10 μM – 10 mM depending on ionization efficiency) from a teflon substrate

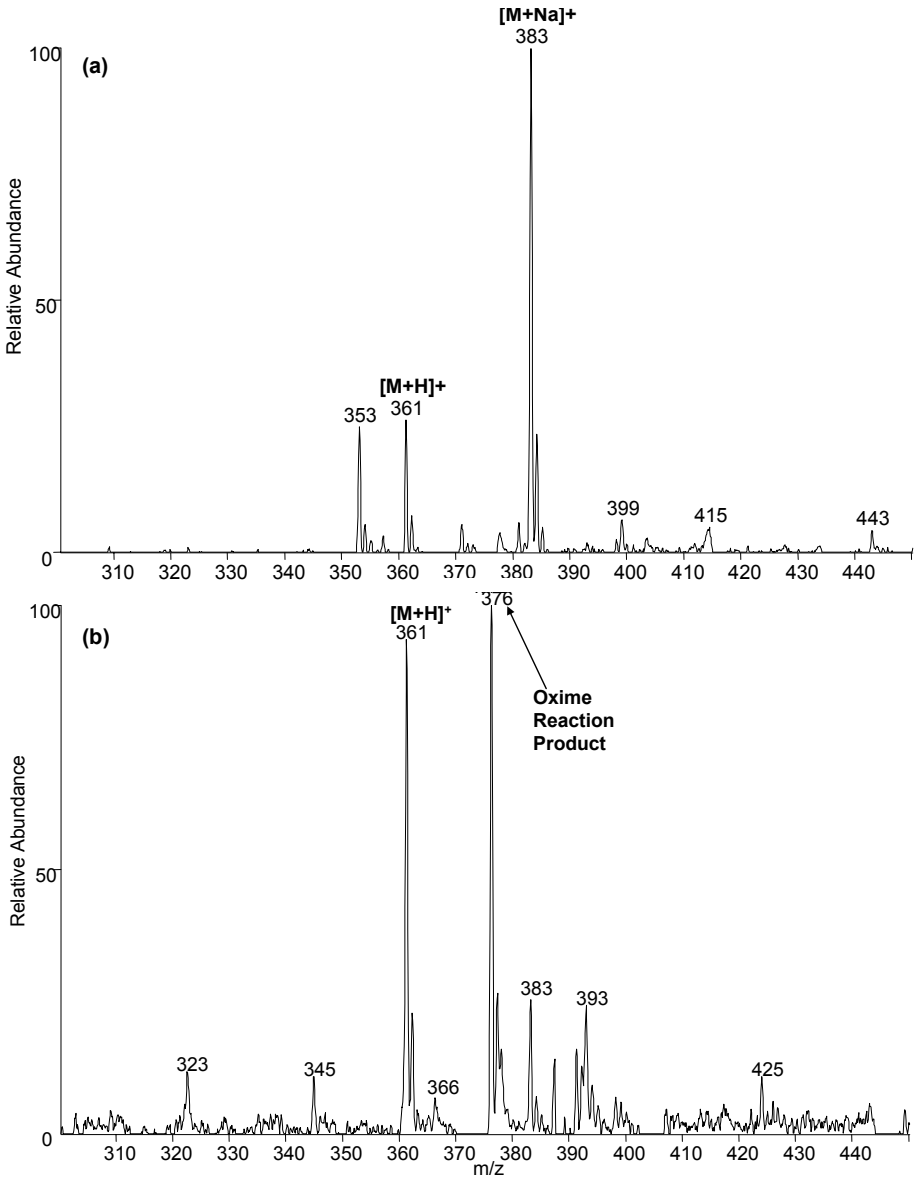


Figure S4 Comparison of **(a)** adduct formation using MeOH/H_2O/NaCl (10 μM) and **(b)** reactive DESI using MeOH/H_2O/CH_3COOH (0.05%)/NH_2OH (5%) in the direct analysis of cortisone (1 mM) in positive ion mode from teflon. Simple salt adduct formation resulted in a higher signal intensity and somewhat better signal to noise ratios than did reaction to form the oxime product. Both spectra have been background subtracted for comparison