Table S2. Peak annotation details of Figure 2.

Compound name	Fragment	Hydrogen rearrangement	Rule	Annotation	Theoretical *m/z*	Error (mDa)	Enthalpy change (kcal/mol)
Reserpine	a	C 0	P1	[M-H]+	577.2550	3.391	-117.5
	b	C 0, C -1	P1, P4	[M-3H]+	448.1971	2.042	-122.9
	c	N +2, C -1 or C 0, N +1	P2, P4 or P1, P3	[M-H]+	436.1971	1.542	-105.3
	d	C 0	P1	[M-H]+	397.2127	2.332	-115.8
	e	C 0, C -1, C -1, C -1	P1, P4, P4, P4	[M-7H]+	368.1498	1.898	-135.8
	f	C 0, C -1	P1, P4	[M-3H]+	365.1865	1.518	-116.4
	g	C 0, C -1, C -1	P1, P4, P4, P4	[M-5H]+	236.1287	1.968	-117.7
	h	C 0	P1	[M-H]+	195.0657	0.834	-136.0
2'-deoxycytidine 5'-diphosphate	a	P -2	N2	[M-3H]-	368.0049	1.877	-59.3
	b	C -2	N2	[M-3H]-	274.9722	0.920	-49.8
	c	C -2, P -1 or P -2, C -1	N2, N5	[M-5H]-	256.9616	0.015	-30.0
	d	P -2	N2	[M-3H]-	158.9248	0.064	-47.9
	e	O 0	N1	[M-H]-	96.9691	0.230	-31.3
	f	P -2	N2	[M-3H]-	78.9585	1.195	-48.0
3-indoxyl sulfate	a	O 0	N1	[M-H]-	132.0449	1.061	-32.8
	b	S 0	N1	[M-H]-	80.9646	1.860	-37.4
	b'	S -1	N3	[M-2H]-	79.9568	1.985	-31.3

The alphabet for each fragment matches that of Figure 3. The enthalpy change from the precursor to the product ion fragment was calculated with the MOPAC package.