

Supplementary data:

Table 1. (M+H⁺) m/z, chemical formula, retention time (RT), MS fragments and delta m/z for 4-Cl-PVP and its metabolites according to (Pelletier et al., 2022). (NA: not applicable, ND: not detected)

Molecule	[M+H] ⁺ m/z	Chemical formula	RT (min)	Biotransformation reactions	Delta m/z	Main fragments m/z
M1	238.0992	C ₁₃ H ₁₆ ClNO	6.0	Demethylation x2	-28.0313	195.0577 152.0019 125.0157
M2	256.1106	C ₁₃ H ₁₈ ClNO ₂	5.9	Demethylation x2 + Oxidation + Dihydrogenation	-10.0211	195.0577 153.0101 125.0157
Parent	266.1312	C ₁₅ H ₂₀ ClNO	6.2	None	NA	195.0577 138.9949 125.0157
M3	268.1462	C ₁₅ H ₂₂ ClNO	NA	Dihydrogenation	+2.0157	ND
M4	280.1097	C ₁₅ H ₁₈ ClNO ₂	8.4	Oxidation + Dehydrogenation	+13.9792	195.0577 138.9949
M5	282.1254	C ₁₅ H ₂₀ ClNO ₂	7.0	Oxidation	+15.9949	179.0621 144.0933 98.0604 142.1233 153.0109
M6	284.1411	C ₁₅ H ₂₂ ClNO ₂	6.2	Oxidation + Dihydrogenation	+18.0106	194.0730 152.0261 125.0153
M7	296.1047	C ₁₅ H ₁₈ ClNO ₃	7.5	Oxidation x2 + Dehydrogenation	+29.9742	195.0577 138.9949 125.0157
M8	298.1204	C ₁₅ H ₂₀ ClNO ₃	6.2	Oxidation x2	+31.9899	280.1096 194.0730 125.0151 194.0730 125.0153
M9	300.1367	C ₁₅ H ₂₂ ClNO ₃	5.8	Oxidation x2 + Dihydrogenation	+34.0055	206.0728 194.0729 125.0152
M10	314.1153	C ₁₅ H ₂₀ ClNO ₄	6.0	Oxidation x3	+47.9848	296.1044 206.0729 125.0152
M11	456.1418	C ₂₁ H ₂₆ ClNO ₈	7.3	Oxidation + Dehydrogenation + Glucuronidation	+190.0113	280.1096 262.0999 179.0621
M12a	458.1574	C ₂₁ H ₂₈ ClNO ₈	5.7	Oxidation + Glucuronidation	+192,0269	282.1251 138.9942 125.0152 98.0603
M13	472.1366	C ₂₁ H ₂₆ ClNO ₉	5.6	Carboxylation + Glucuronidation	+206.0061	278.0940 195.0570 125.0153
M14	474.1524	C ₂₁ H ₂₈ ClNO ₉	5.3	Oxidation x2 + Glucuronidation	+208.0218	280.1098 195.0570 125.0154 196.0888 179.0612
M15	490.1472	C ₂₁ H ₂₈ ClNO ₁₀	6.6	Oxidation x3 + Glucuronidation	+224.0167	296.1046 196.0888 85.0289

Table 2. (M+H⁺) m/z, chemical formula, retention time (RT), delta m/z and MS fragments for eutylone and its metabolites according to (Pelletier et al., 2023). (NA: not applicable)

Molecule	[M+H] ⁺ m/z	Chemical formula	RT (min)	Biotransformation reactions	Delta m/z	Main fragments m/z
M1	190.0864	C ₁₁ H ₁₁ NO ₂	4.5	Demethylation x2 + Deshydroxylation + Dehydrogenation x2	-46.0419	161.0160 160.0759 132.0810
M2	208.0970	C ₁₁ H ₁₃ NO ₃	4.5	Demethylation x2	-28.0313	190.0860 160.0760 132.0810
M3	210.1126	C ₁₁ H ₁₅ NO ₃	3.8	Dihydrogenation + Demethylation x2	-26.0157	192.1020 161.0598 160.0758
M4	224.1283	C ₁₂ H ₁₇ NO ₃	3.2	O-demethylenation	-12.0000	206.1178 188.1072 177.0787
Parent	236.1283	C ₁₃ H ₁₇ NO ₃	4.9	None	NA	218.1179 189.0787 188.1072
M5	238.1440	C ₁₃ H ₁₉ NO ₃	4.2	Dihydrogenation	2.0157	220.1334 191.0944 188.1073
M6	250.1076	C ₁₃ H ₁₇ NO ₄	6.4	Oxidation + Dehydrogenation	13.9793	208.0970 190.0864 160.0758
M7	304.0851	C ₁₂ H ₁₇ NO ₆ S	3.6	Dihydrogenation + Sulfatation + Demethylation	67.9568	224.1281 206.1177 188.1071
M8	318.1006	C ₁₂ H ₁₉ NO ₅ S	3.9	Dihydrogenation + Sulfatation	81.9723	238.1437 220.1333 188.1071
M9	386.1444	C ₁₈ H ₂₇ NO ₈	1.2	Demethylation x2 + Glucuronidation	150.0161	210.1126 192.1020 160.0758
M10	400.1600	C ₁₈ H ₂₅ NO ₉	2.7	Dihydrogenation + Demethylation + Glucuronidation	164.0317	224.1282 206.1176 188.1071
M11	414.1760	C ₁₉ H ₂₇ NO ₉	2.3	Dihydrogenation + Glucuronidation	178.0477	238.1438 220.1333 188.1071