Supporting Information (SI) – Chemical Profiling and Classification of Cannabis through Electrospray ionization coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry and Chemometrics

Bruna T. Borille,[a] Rafael S. Ortiz,[b,c] Kristiane C. Mariotti,[a,c] Gabriela Vanini,[d] Lilian V. Tose,[d] Paulo R. Filgueiras,[c,d] Marcelo C. A. Marcelo,[e] Marco F. Ferrão,[e] Michel J. Anzanello,[c,f] Renata P. Limberger [a,c] and Wanderson Romão,[c,d]

[a] Laboratory of Analyses and Research in Toxicology, Federal University of Rio Grande do Sul, Department of Pharmacy, Porto Alegre, 90610000, RS, Brazil.

[b] Technical and Scientific Police Superintendent of Rio Grande do Sul, Brazilian Federal Police, Porto Alegre, 90160092, RS, Brazil.

[c] National Institute of Forensic Science and Technology (INCT Forensic), Porto Alegre (RS), and Vila Velha (IFES, ES), Brazil.

[d] Petroleomic and Forensic Laboratory, Federal University of Espírito Santo, Department of Chemistry, Vitória, 29075910, ES, Brazil.

[e] Chemistry Institute, Federal University of Rio Grande do Sul, Porto Alegre, 91501970, RS, Brazil.

[f] Department of Industrial Engineering, Federal University of Rio Grande do Sul, Porto Alegre, 90035190, RS, Brazil.
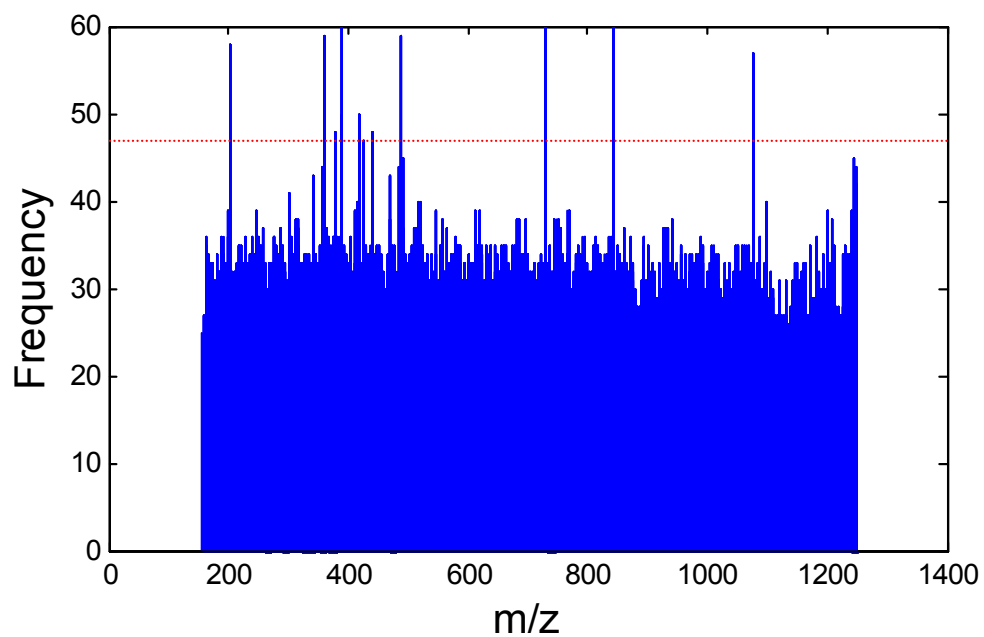
Figure S-1. Frequency of variable selection by the genetic algorithm using the negative mode. The dashed red line represents the frequency selection limit of the variable to be used in the final molding.
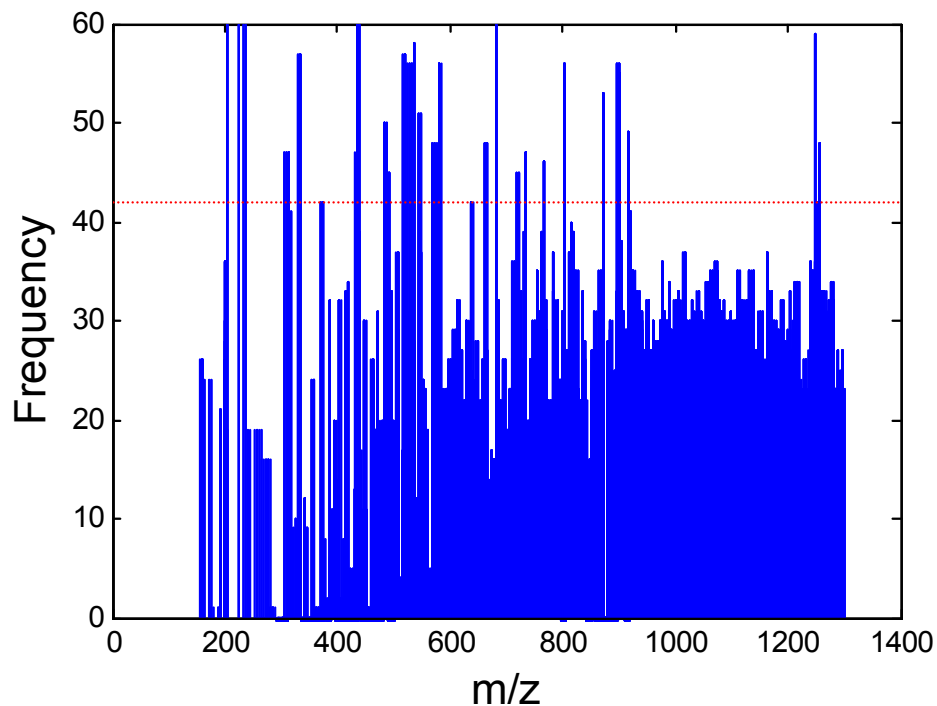
Figure S-2. Frequency of variable selection by the genetic algorithm using the positive mode. The dashed red line represents the frequency selection limit of the variable to be used in the final molding.
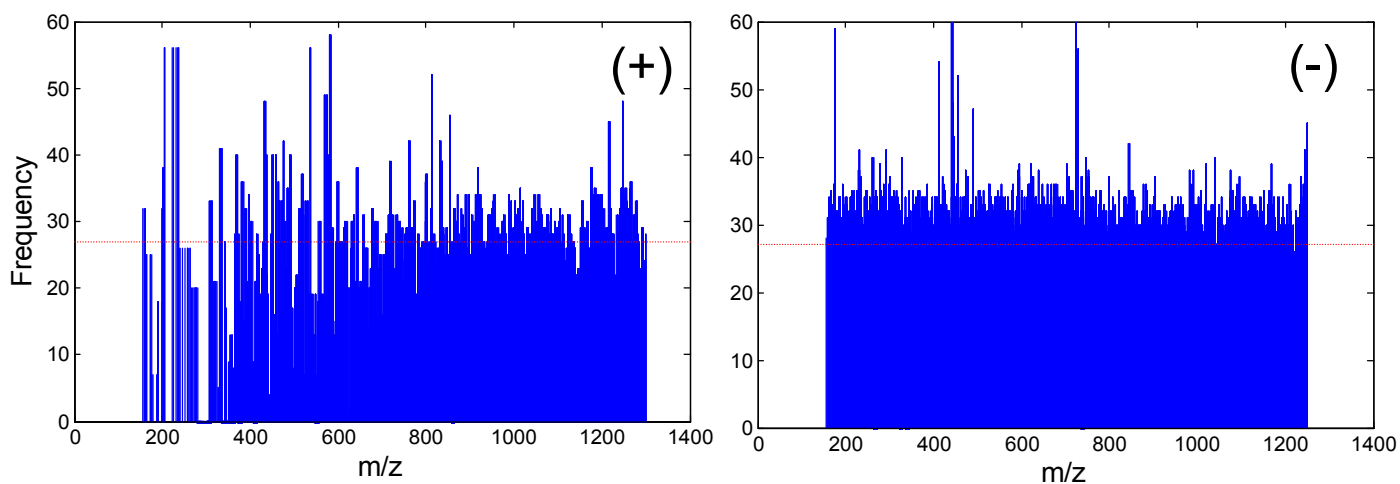

Figure S-3. Frequency of variable selection by the genetic algorithm using the positive and negative modes. The dashed red line represents the frequency selection limit of the variable to be used in the final molding.
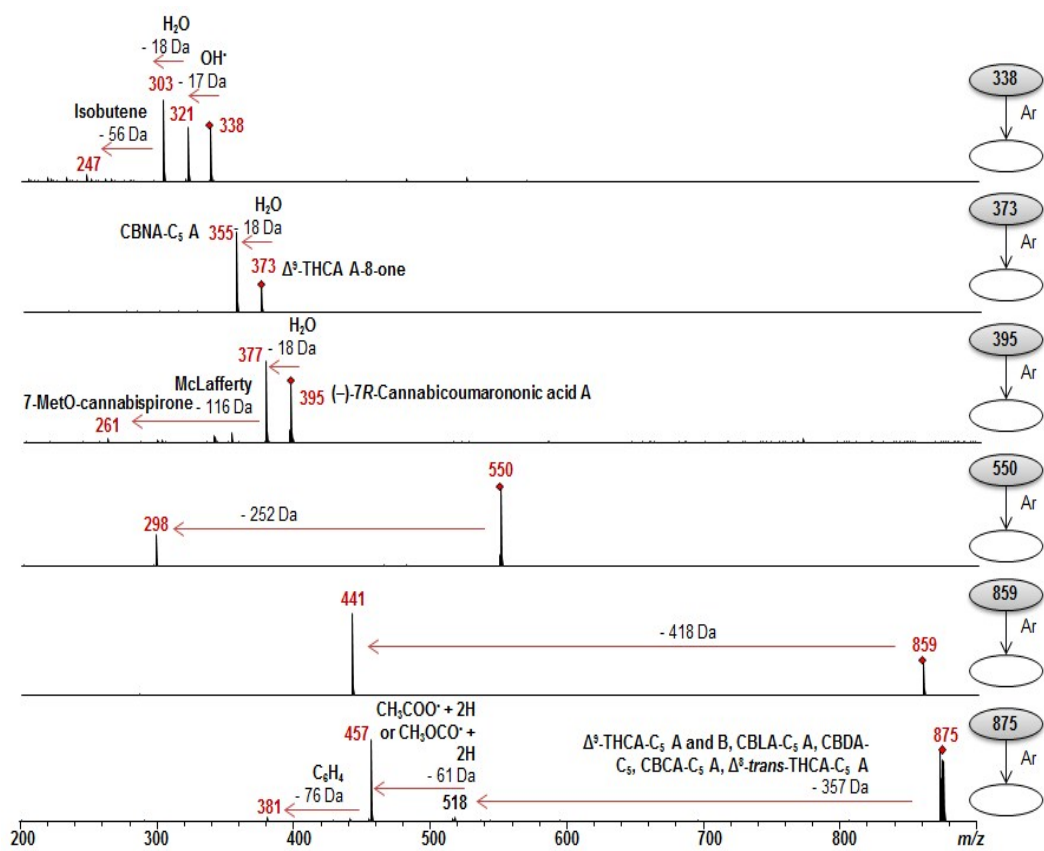
Figure S-4. ESI(+)-FT-ICR MS/MS for the following precursor ions: *m/z* 338, 373, 395, 550, 859 and 875.

Table S-1. Formula, DBE, measured and theoretical mass values of the compounds identified from cannabis samples analysed by ESI(−)-FT-ICR MS.

	Formula	$m/z_{measured}$	$m/z_{theoretical}$	Error (ppm)	DBE	Proposed Compound
1	$[C_{21}H_{26}O_2 - H]^-$	309.18593	309.18600	0.25	9	Cannabinol (CBN-C$_5$),[1,8,29]Cannabinodiol (CBND-C$_5$),[1,8,29]Cannabifuran (CBF-C$_5$)[1,29]
2	$[C_{21}H_{30}O_2 - H]^-$	313.21726	313.21730	0.13	7	(−)-Δ^9-*cis*-(6a*R*,10a*R*)-Tetrahydrocannabinol [(−)-Δ^9-*cis*-THC-C$_5$],[1,29] (−)-Δ^9-*trans*-(6a*R*,10a*R*)-Tetrahydrocannabinol (Δ^9-*trans*-THC-C$_5$),[1,29] (±)-Cannabichromene (CBC-C$_5$),[1,29](−)-Cannabidiol (CBD-C$_5$),[1,8,29](−)-Δ^8-*trans*-(6a*R*,10a*R*)-Tetrahydrocannabinol (Δ^8-*trans*-THC-C$_5$),[1,8,29] (±)-(1a*S*,3a*R*,8b*R*,8c*R*)-Cannabicyclol (CBL-C$_5$),[1,29](−)-Δ^7-*trans*-(1*R*,3*R*,6*R*)-Isotetrahydrocannabinol-C$_5$ [(−)-Δ^7-*trans*-(1*R*,3*R*,6*R*)-*iso*-THC-C$_5$][1]
3	$[C_{21}H_{26}O_3 - H]^-$	325.18093	325.18092	-0.05	9	(*S*)-1'-Hydroxycannabinol [(*S*)-1'-OH-CBN][37]
4	$[C_{21}H_{28}O_3 - H]^-$	327.19657	327.19657	0.01	8	10-*Oxo*-Δ$^{6a(10a)}$-Tetrahydrocannabinol (OTHC),[1,8,29] 8-*Oxo*-Δ^9-Tetrahydrocannabinol (8-*Oxo*-Δ^9-THC),[37] Cannabicoumaronone-C$_5$ (CBCON-C$_5$)[1]
5	$[C_{20}H_{26}O_4 - H]^-$	329.17581	329.17583	0.02	8	Cannabidivarinic acid (CBDVA-C$_3$),[1,29]Δ^9-Tetrahydrocannabivarinic acid A (Δ^9-THCVA-C$_3$ A),[1,29] (±)-Cannabichromevarinic acid A (CBCVA-C$_3$ A)[1]
6	$[C_{21}H_{30}O_3 - H]^-$	329.21228	329.21222	-0.20	7	(5a*S*,6*S*,9*R*,9a*R*)-Cannabielsoin (CBE-C$_5$),[1,29] 8α-hydroxy-Δ^9-tetrahydrocannabinol (8α-OH-Δ^9-THC),[41] 8β-hydroxy-Δ^9-tetrahydrocannabinol (8β-OH-Δ^9-THC),[41] 10α-hydroxy-Δ^8-tetrahydrocannabinol (10α-OH-Δ^8-THC),[41] 10β-hydroxy-Δ^8-tetrahydrocannabinol (10β-OH-Δ^8-THC), [41] 10α-hydroxy-Δ^{9,11}-hexahydrocannabinol (10α-OH-Δ^{9,11}-hexahydrocannabinol), [41] 9β,10β-epoxyhexahydrocannabinol (9β,10β-EtO-hexahydrocannabinol), [41] (±)-3''-hydroxy-Δ$^{(4''5'')}$-

#	Formula	Calc.	Exp.	Δ (ppm)	DBE	Compounds
						cannabichromene [(±)-3''-OH-Δ$^{(4''5'')}$-CBC-C$_5$] [42]
7	[C$_{20}$H$_{28}$O$_4$ – H]$^-$	331.19145	331.19148	0.11	7	Cannabigerovarinic acid A (trans-CBGVA-C$_3$A),[1]Cannabichromanone (CBCN-C$_5$)[1,29]
8	[C$_{21}$H$_{32}$O$_3$ – H]$^-$	331.22779	331.22789	0.24	6	9α-Hydroxyhexahydrocannabinol (9α-OH-hexahydrocannabinol),[38] 10α-Hydroxyhexahydrocannabinol (10α-OH-hexahydrocannabinol),[38] 10aR-Hydroxyhexahydrocannabinol (10aR-OH-hexahydrocannabinol),[38] (±)-6,7-cis-Epoxycannabigerol [(±)-6,7-cis-EtO-CBG-C$_5$],[37] (±)-6,7-trans-Epoxycannabigerol [(±)-6,7-trans-EtO-CBG-C$_5$],[37] (–)-7-Hydroxycannabichromane [(–)-7-OH-CBC-C$_5$][42]
9	[C$_{22}$H$_{28}$O$_3$ – H]$^-$	339.19993	339.19992	-0.02	9	Cannabidiolic acid (CBDA-C$_5$) – Water (H$_2$O)[3]
10	[C$_{21}$H$_{28}$O$_4$ – H]$^-$	343.19145	343.19148	0.08	8	Δ^9-Tetrahydrocannabinolic acid-C$_4$ A and B (Δ^9-THCA-C$_4$ A and B),[1,8,29] 10aα-Hydroxy-10-oxo-Δ^8-Tetrahydrocannabinol (10aα-OH-10-oxo-Δ^8-THC),[38] 9α-Hydroxy-10-oxo-Δ^{6a,10a}-Tetrahydrocannabinol (9α-OH-10-oxo-Δ^{6a,10a}-THC)[38]
11	[C$_{21}$H$_{30}$O$_4$ – H]$^-$	345.20711	345.20713	0.06	7	(–)-trans-Cannabitriol [(–)-trans-CBT-C$_5$],[1] (+)-trans-Cannabitriol [(+)-trans-CBT-C$_5$],[1] (±)-cis-Cannabitriol [(±)-cis-CBT-C$_5$],[1] trans-10-Ethoxy-9-hydroxy-Δ$^{6a(10a)}$-tetrahydrocannabivarin-C$_3$ (trans-CBT-OEt-C$_3$),[1] 8,9-Dihydroxy-Δ$^{6a(10a)}$-tetrahydrocannabinol (8,9-Di-OH-CBT-C$_5$),[1] 7-Oxo-8α-hydroxyhexahydrocannabinol (7-Oxo-8α-OH-hexahydrocannabinol)[38]
12	[C$_{22}$H$_{26}$O$_4$ – H]$^-$	353.17586	353.17583	-0.07	10	Cannabinolic acid A (CBNA-C$_5$ A)[1,29]
13	[C$_{22}$H$_{30}$O$_4$ – H]$^-$	357.20714	357.20713	-0.01	8	Δ^9-Tetrahydrocannabinolic acid A and B (Δ^9-THCA-C$_5$ A and B),[1,29] (±)-(1aS,3aR,8bR,8cR)-Cannabicyclolic acid A (CBLA-C$_5$ A),[1,29] Cannabidiolic acid (CBDA-C$_5$),[1,29] (±)-Cannabichromenic acid A (CBCA-C$_5$ A),[10](–)-Δ^8-trans-(6aR,10aR)-Tetrahydrocannabinolic acid A

						(Δ^8-*trans*-THCA-C$_5$ A)[1]
14	[C$_{22}$H$_{32}$O$_4$ – H]$^-$	359.22280	359.22278	-0.04	7	Cannabigerolic acid A (*cis*-CBGA-C$_5$ A and *trans*-CBGA-C$_5$ A)[1,10,37]
15	[C$_{22}$H$_{24}$O$_5$ – H]$^-$	367.15570	367.15568	0.05	11	8-Hydroxycannabinolic acid A (8-OH-CBNA-C$_5$ A)[42]
16	[C$_{24}$H$_{32}$O$_3$ – H]$^-$	367.22801	367.22787	-0.39	9	Δ^9-Tetrahydrocannabinolic acid A and B (Δ^9-THCA-C$_5$ A and B) + Ethynol (C$_2$H$_2$O)[29] – Oxygen (O$_2$)
17	[C$_{22}$H$_{26}$O$_5$ – H]$^-$	369.17070	369.17075	0.12	10	Δ^9-Tetrahydrocannabinolic acid A-8-one (Δ^9-THCA A-8-one)[29] – Hydrogen (H$_2$), Cannabicoumaric acid[10] – Hydrogen (H$_2$), (±)-4-Acetoxycannabichromene [(±)-4-AcO-CBC-C$_5$][10,42] – Hydrogen (H$_2$)
18	[C$_{22}$H$_{28}$O$_5$ – H]$^-$	371.18641	371.18640	-0.03	9	Δ^9-Tetrahydrocannabinolic acid A-8-one (Δ^9-THCA A-8-one),[29,39]Cannabicoumaric acid[10]
19	[C$_{23}$H$_{32}$O$_4$ – H]$^-$	371.22279	371.22278	-0.01	8	5-Acetoxy-6-geranyl-3-*n*-pentyl-1,4-benzoquinone (5-AcO-6-C$_9$H$_{17}$-3-*n*-C$_5$H$_{11}$-1,4-C$_6$H$_4$O$_2$)*,[40] (±)-4-Acetoxycannabichromene [(±)-4-AcO-CBC-C$_5$][10,42]
20	[C$_{22}$H$_{30}$O$_5$ – H]$^-$	373.20202	373.20205	0.08	8	11-Hydroxy-Δ^9-Tetrahydrocannabinolic acid A (11-OH-Δ^9-THCA A),[29,39](±)-6,7-*cis*-Epoxycannabigerolic acid [(±)-6,7-*cis*-EtO-CBGA-C$_5$],[37] (5a*S*,6*S*,9*R*,9a*R*)-Cannabielsoic acid A and B (CBEA-C$_5$ A and B)[1]
21	[C$_{23}$H$_{34}$O$_4$ – H]$^-$	373.23845	373.23843	-0.05	7	Cannabigerolic acid A monomethyl ether (*trans*-CBGAM-C$_5$A),[1,10] 10-Ethoxy-9-hydroxy-Δ^{6a}-Tetrahydrocannabinol (10-EtO-9-OH-Δ^{6a}-THC)[10], 5-Acetyl-4-hydroxycannabigerol (5-COCH$_3$-4-OH-CBG-C$_5$),[42] 4-Acetoxy-2-geranyl-5-hydroxy-3-*n*-pentylphenol (4-AcO-2-C$_9$H$_{17}$-5-OH-3-*n*-C$_{11}$H$_{16}$O), [42] - 5'-Metoxycannabigerolic acid (5'-MetO-CBGA-C$_5$), [37] (−)-*trans*-10-Ethoxy-9-hydroxy- $\Delta^{6a(10a)}$-tetrahydrocannabinol [(−)-*trans*-CBT-OEt-C$_5$] [1]

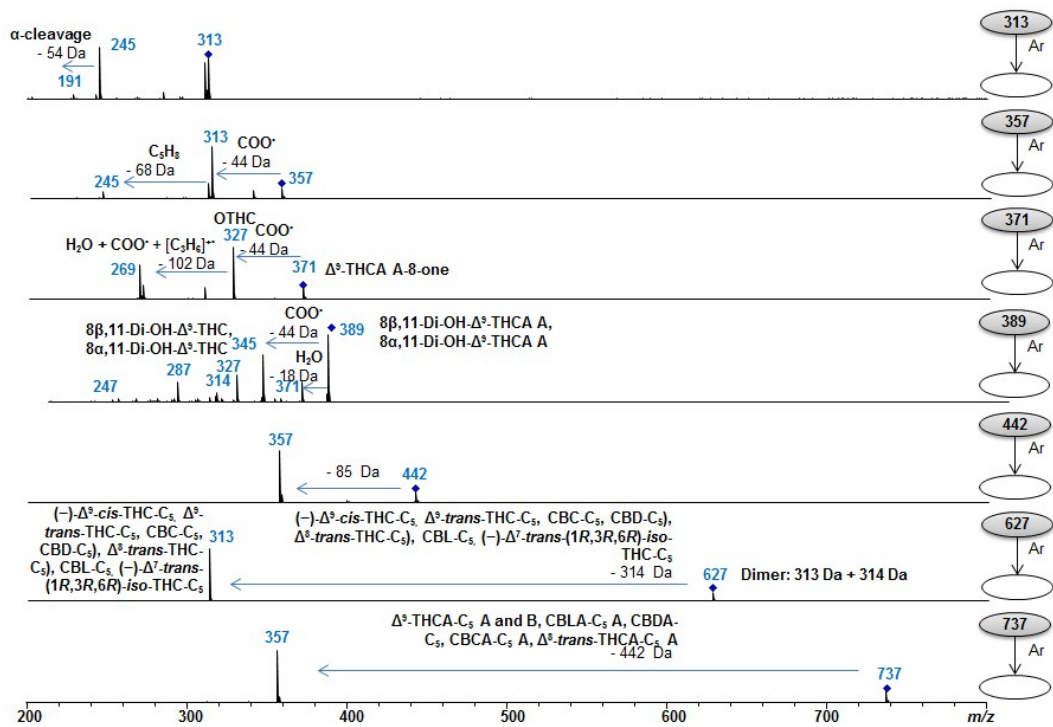| 22	$[C_{22}H_{28}O_6 - H]^-$	387.18133	387.18131	-0.05	9	11-nor-9-COOH-Δ^9-Tetrahydrocannabinolic acid A (Δ^9-THCA A-COOH)[29,39]
23	$[C_{22}H_{30}O_6 - H]^-$	389.19694	389.19696	0.06	8	8β,11-Dihydroxy-Δ^9-Tetrahydrocannabinolic acid (8β,11-Di-OH-Δ^9-THCA), [29,39] 8α,11-Dihydroxy-Δ^9-Tetrahydrocannabinolic acid (8α,11-Di-OH-Δ^9-THCA) [39]
24	$[C_{24}H_{32}O_5 - H]^-$	399.21777	399.21770	-0.18	9	Δ^9-Tetrahydrocannabinolic acid A and B (Δ^9-THCA-C_5 A and B) + Ethynol (C_2H_2O) [29]
25	$[C_{22}H_{33}NO_6 + Cl]^-$	442.18474	442.18472	-0.04	7	-
26	$[C_{42}H_{60}O_4 - H]^-$	627.44201	627.44188	-0.21	13	Dimer: 313 Da + 314 Da = ($[C_{21}H_{30}O_2 - H]^-$) + $[C_{21}H_{30}O_2]$
27	$[C_{40}H_{62}O_{10} + Cl]^-$	737.40355	737.40370	0.21	9	-

* Non-cannabinoid; - Unidentified compound

Figure S-5. ESI(−)-FT-ICR MS/MS for the following precursor ions: m/z 313, 357, 371, 389, 442, 627 and 737.