

Electronic Supplementary Material

Journal name

Molecules

Article title

UFLC-Q-TOF-MS/MS-based screening and identification of flavonoids and derived metabolites in human urine after oral administration of Exocarpium *Citri grandis* extract

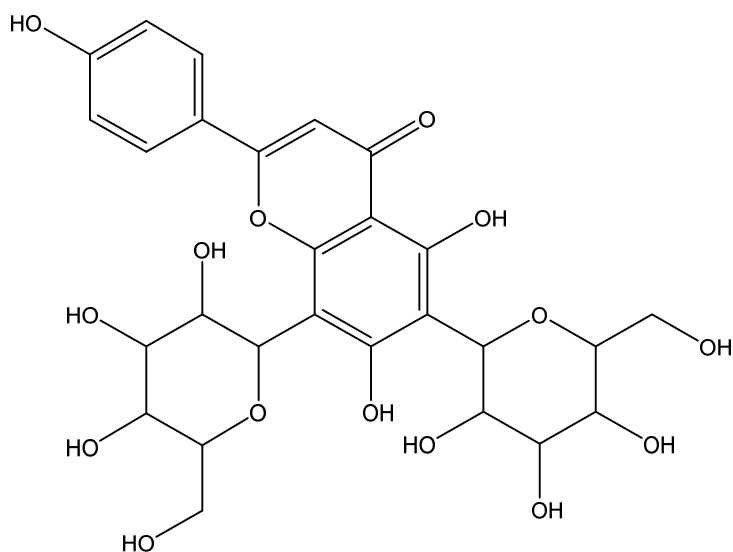
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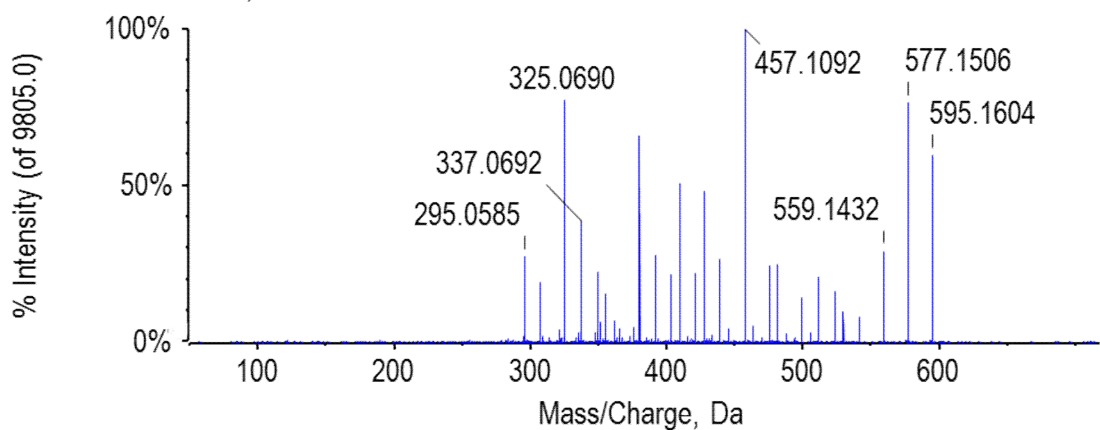
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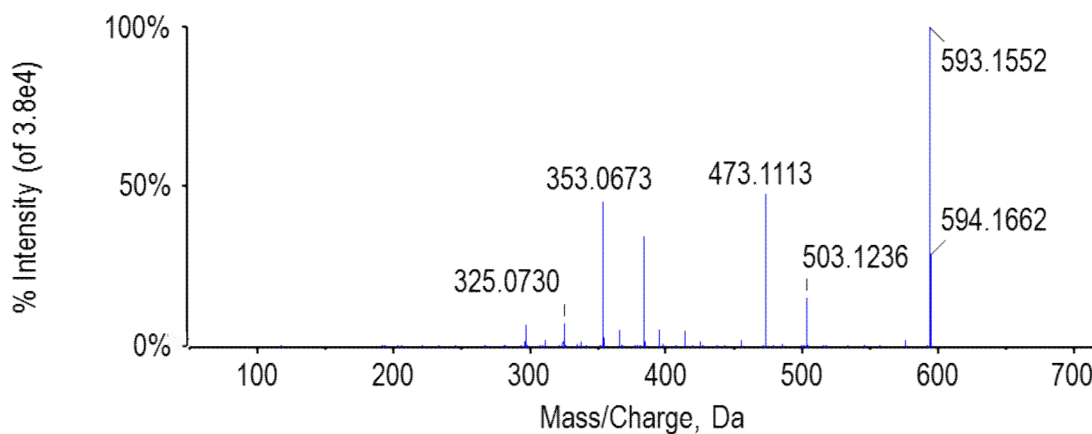
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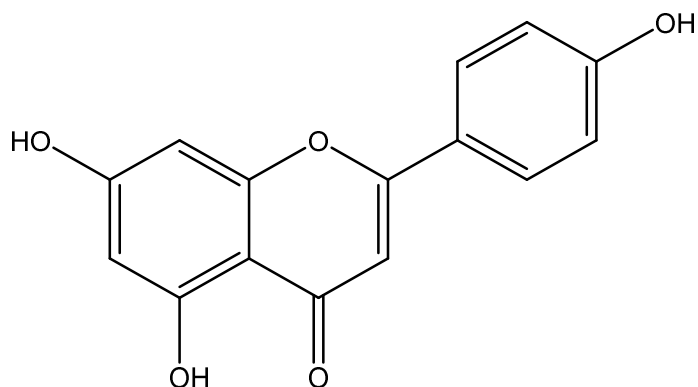
Part I. Structures and product ion spectra of identified flavonoids in *Exocarpium Citri grandis* extract**F1. Vicenin-2 (RT=9.5 min)**Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 9.555 min

Precursor: 595.2 Da, CE=35

Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 9.542 min

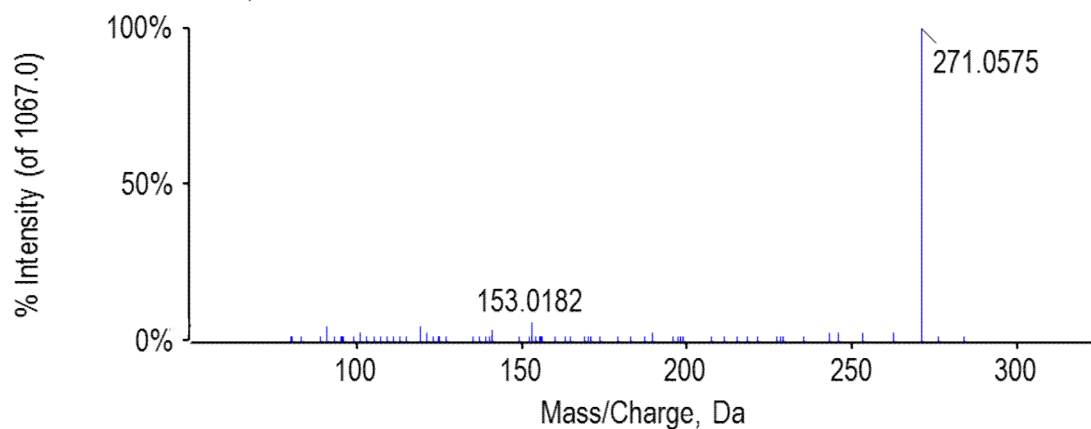
Precursor: 593.2 Da CE=-35



F3. Apigenin (RT=14.9 min)

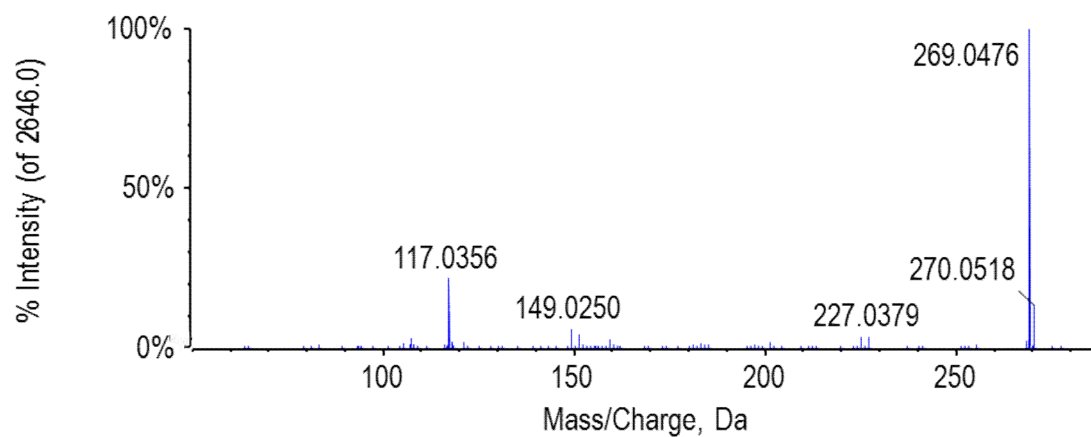
Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 14.899 min

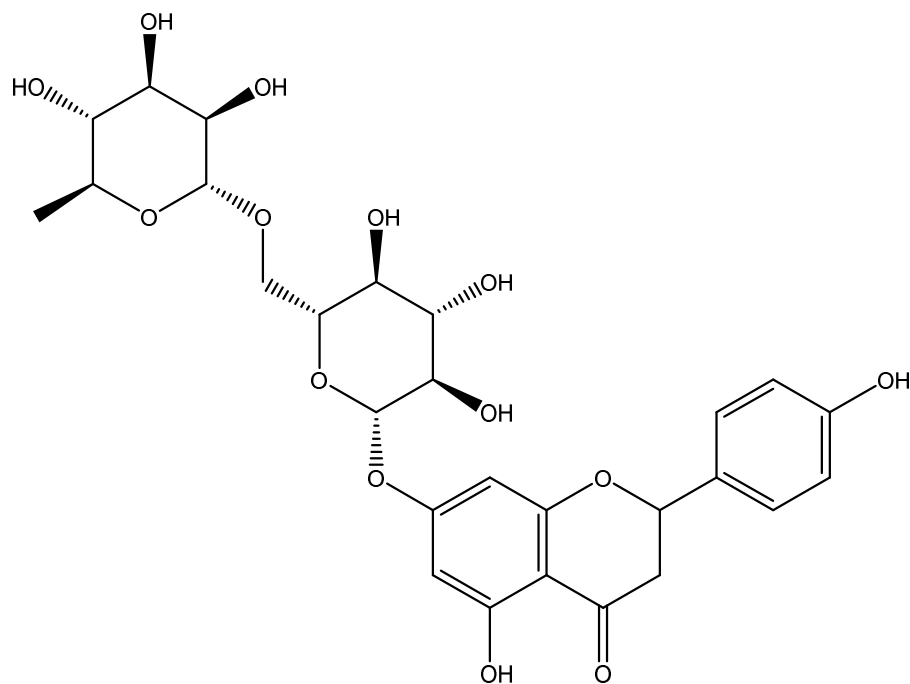
Precursor: 271.1 Da, CE=35



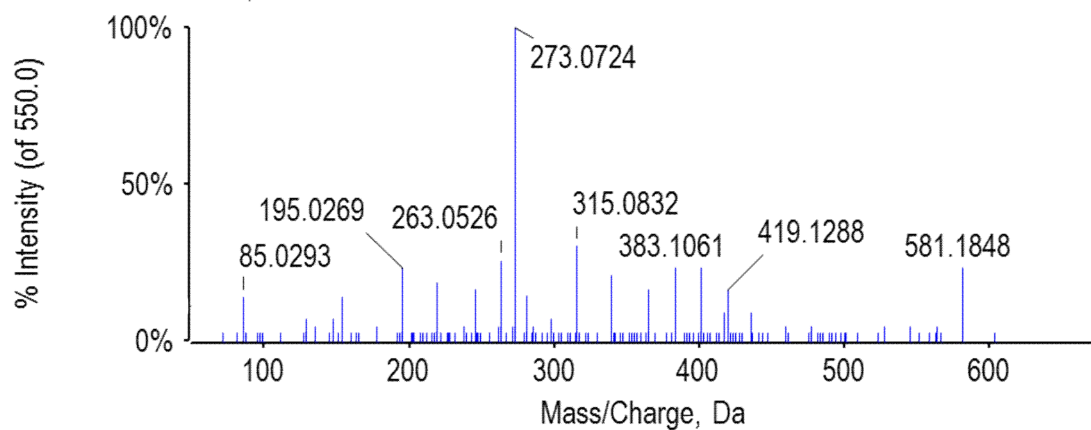
Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 14.934 min

Precursor: 269.0 Da CE=-35

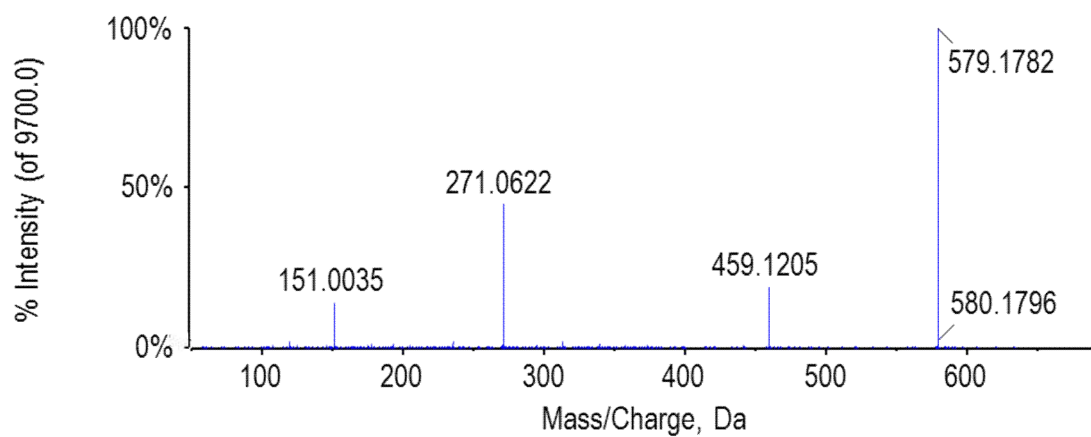


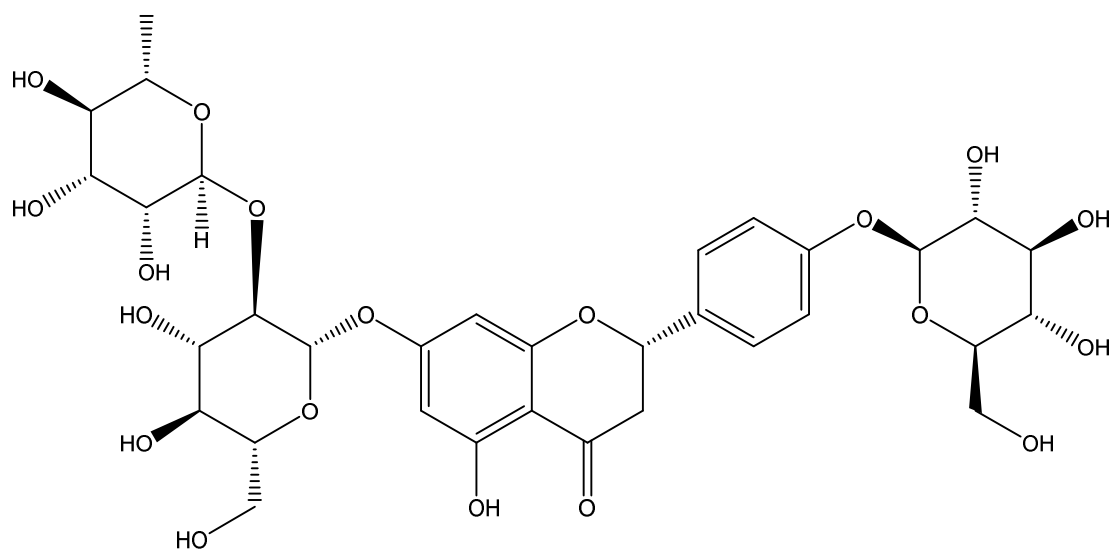
F4. Narirutin (RT=9.7 min)

Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 9.681 min
Precursor: 581.2 Da, CE=35

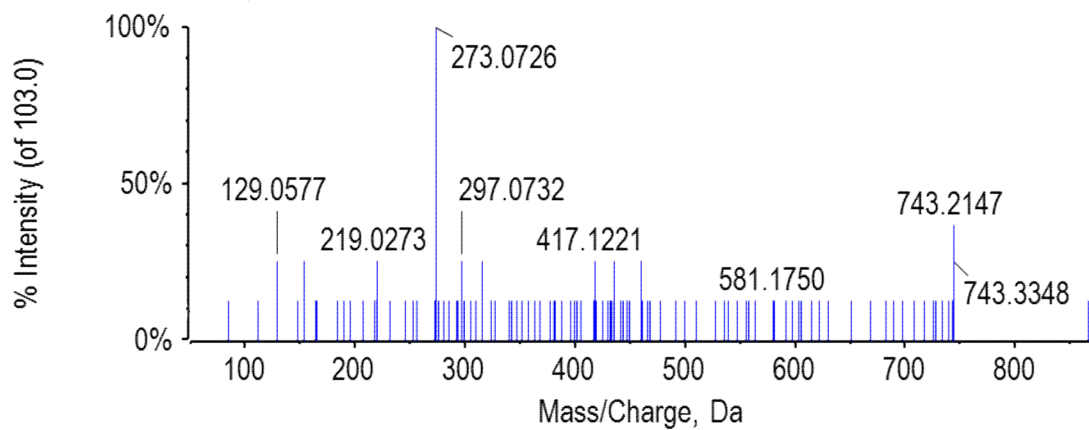


Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 9.684 min
Precursor: 579.2 Da CE=-35

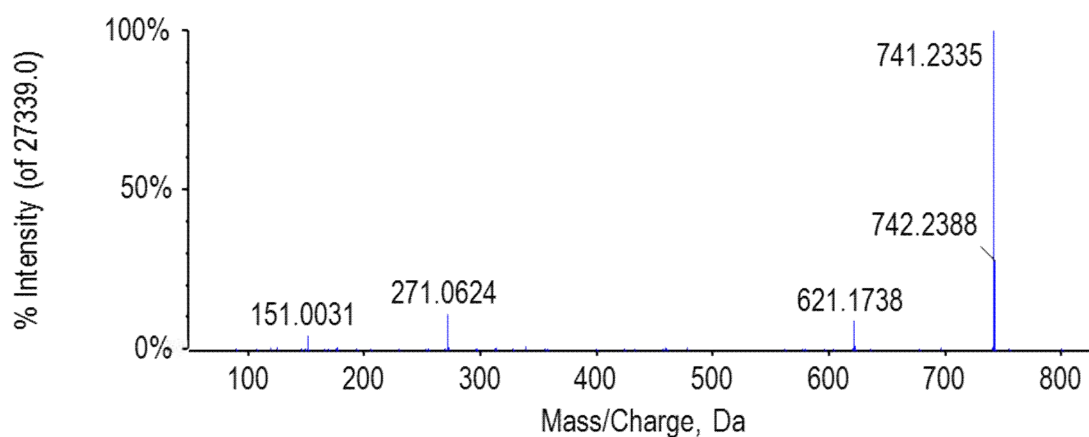


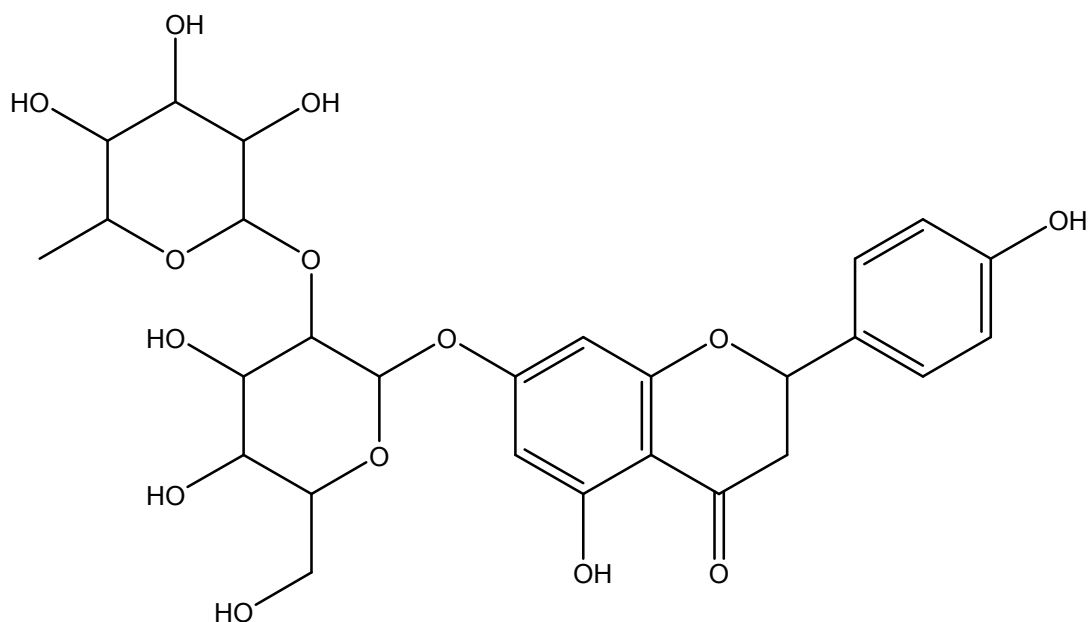
F6. Naringin-4'-O-glucoside (RT=10.4 min)Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 10.297 min

Precursor: 743.2 Da, CE=35

Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 10.365 min

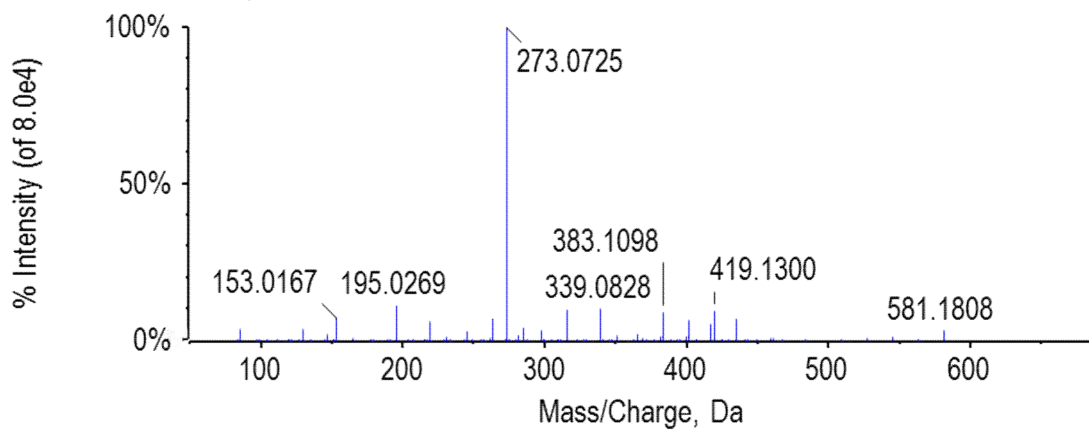
Precursor: 741.2 Da CE=-35



F7. Naringin (RT=11.4 min)

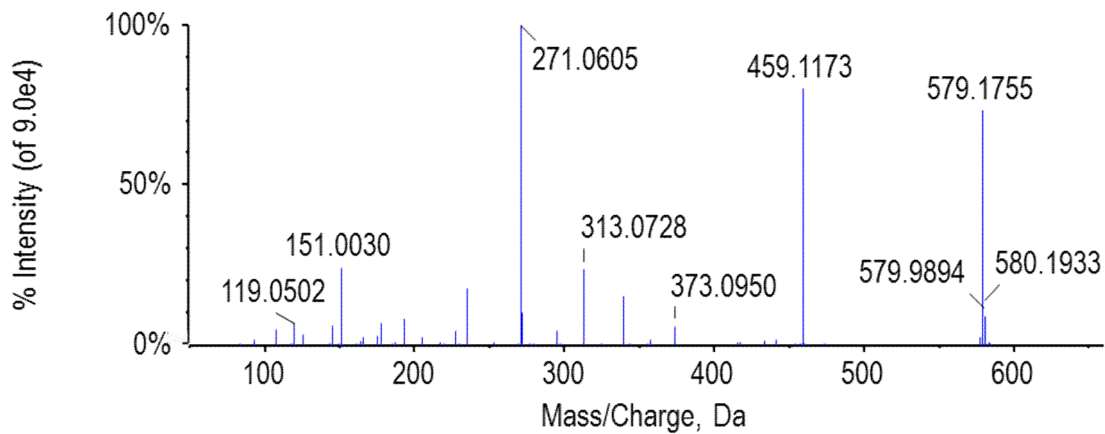
Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 11.436 min

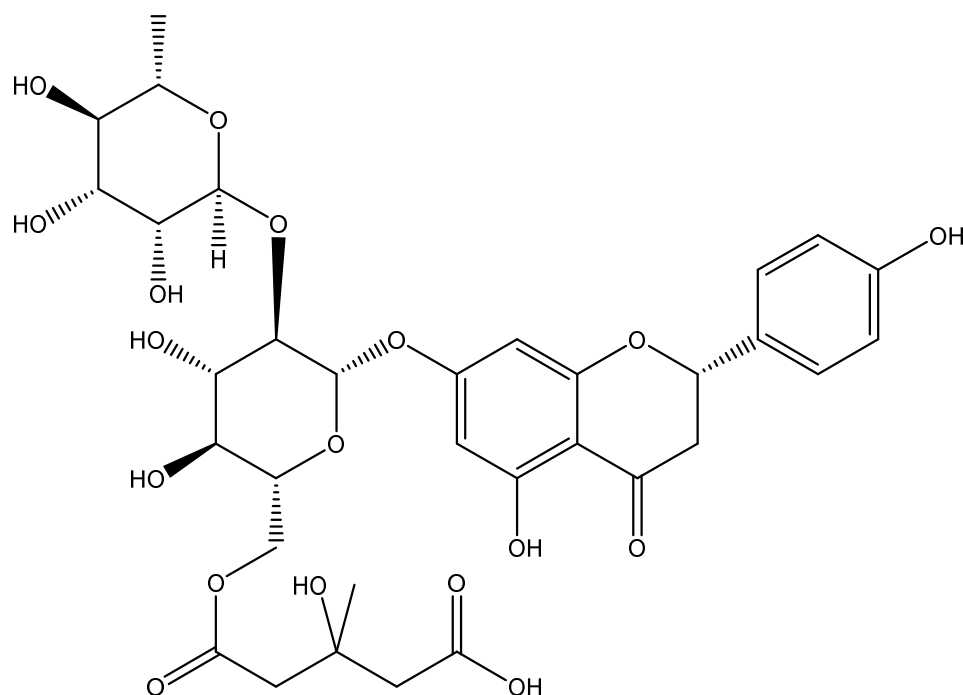
Precursor: 581.2 Da, CE=35



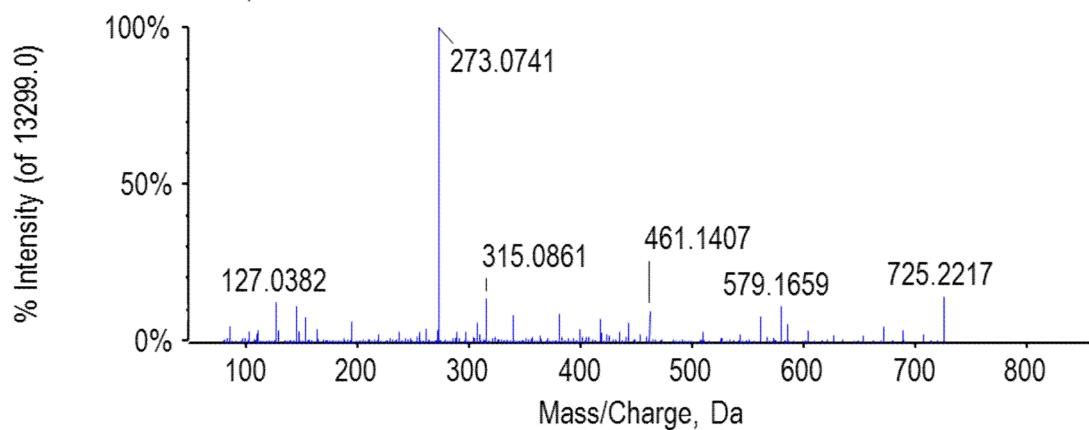
Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 11.399 min

Precursor: 579.2 Da CE=-35

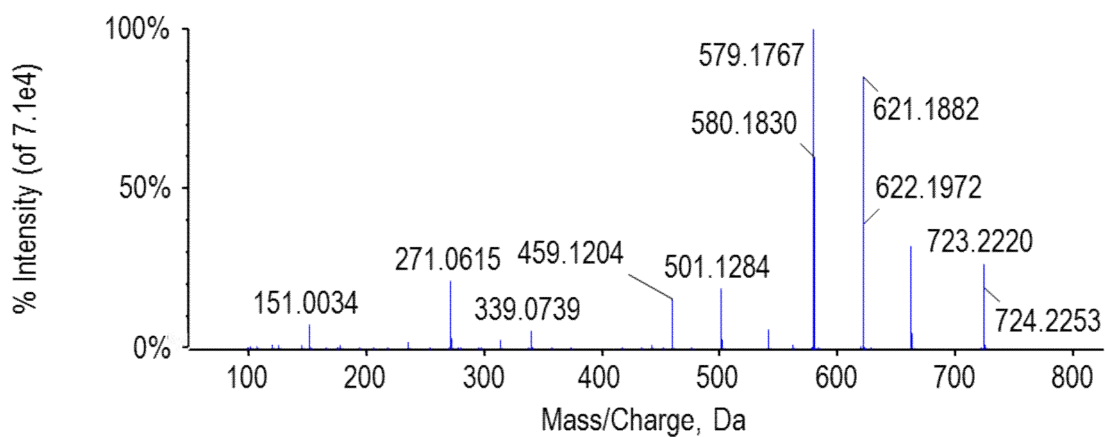


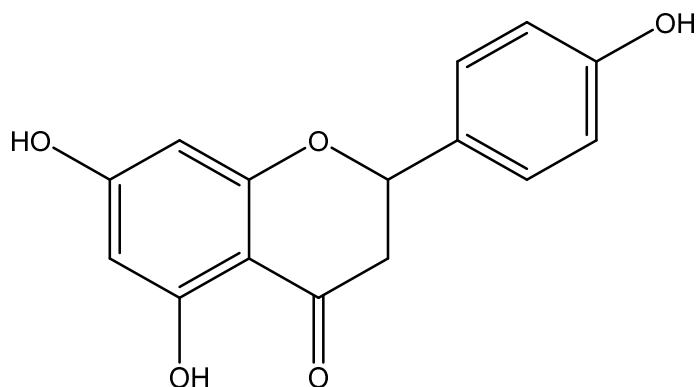
F8. Melitidin (RT=12.4 min)

Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 12.431 min
Precursor: 725.2 Da, CE=35



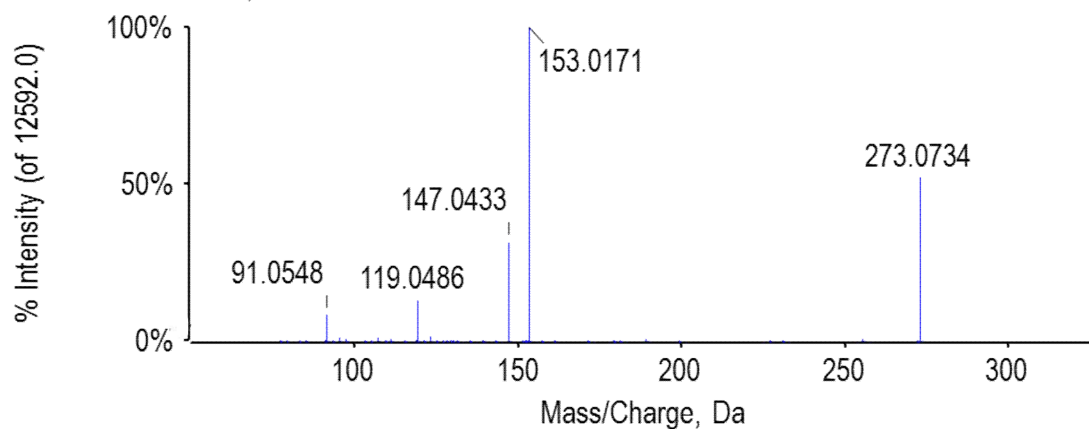
Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 12.402 min
Precursor: 723.2 Da CE=-35



F9. Naringenin (RT=13.7 min)

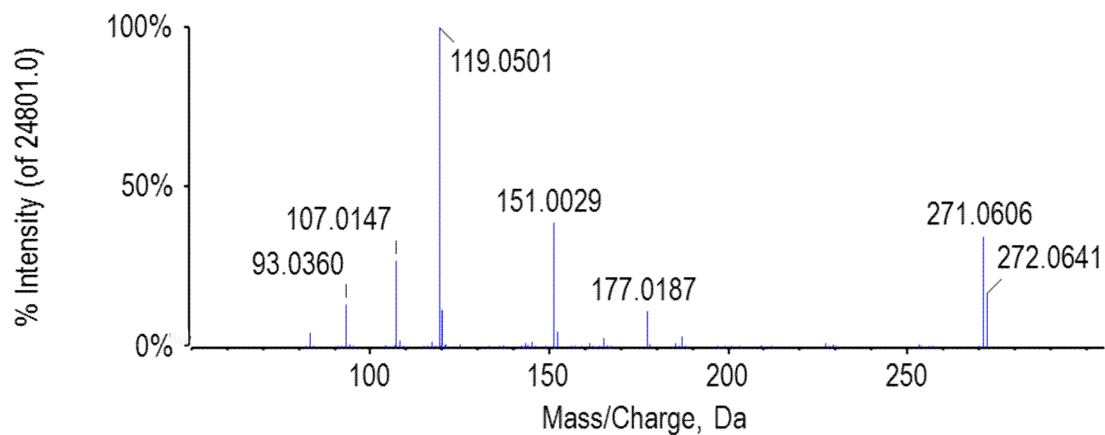
Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 13.650 min

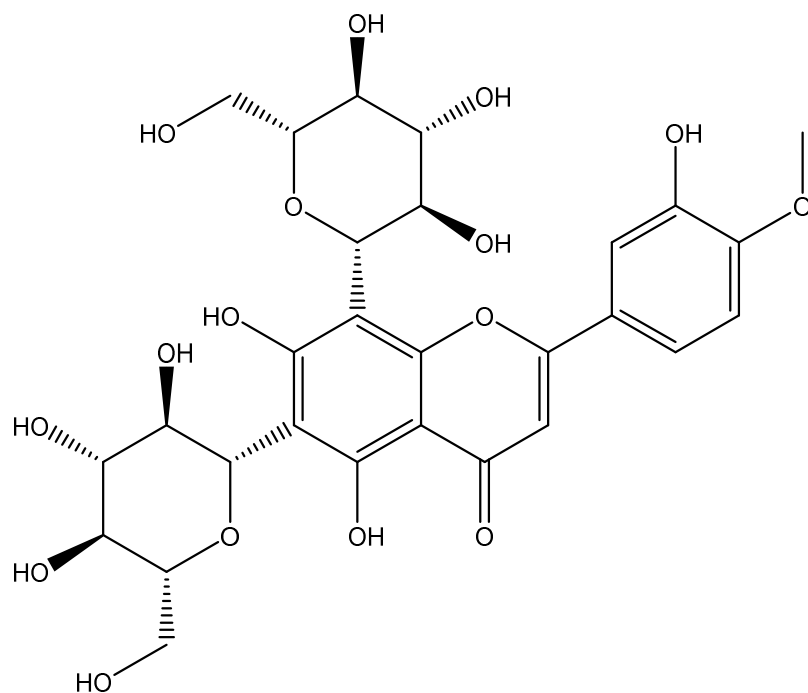
Precursor: 273.1 Da, CE=35



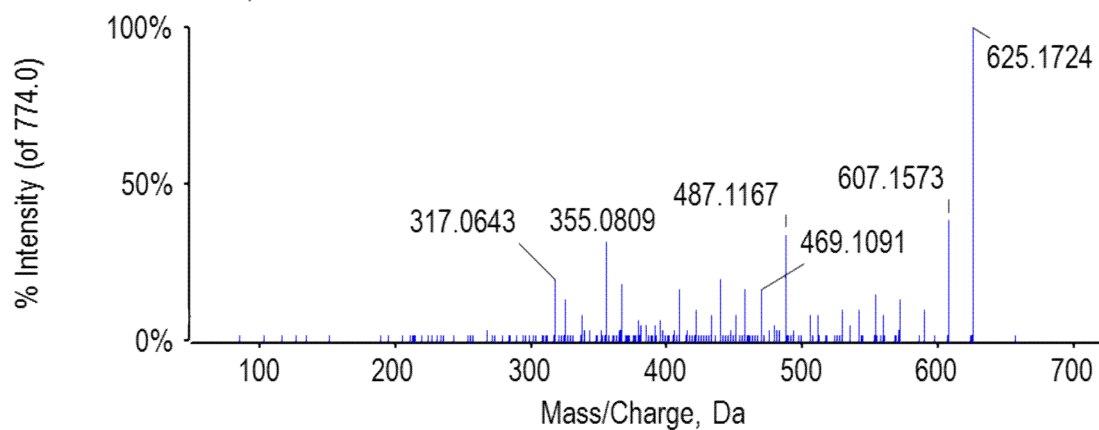
Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 13.660 min

Precursor: 271.1 Da CE=-35

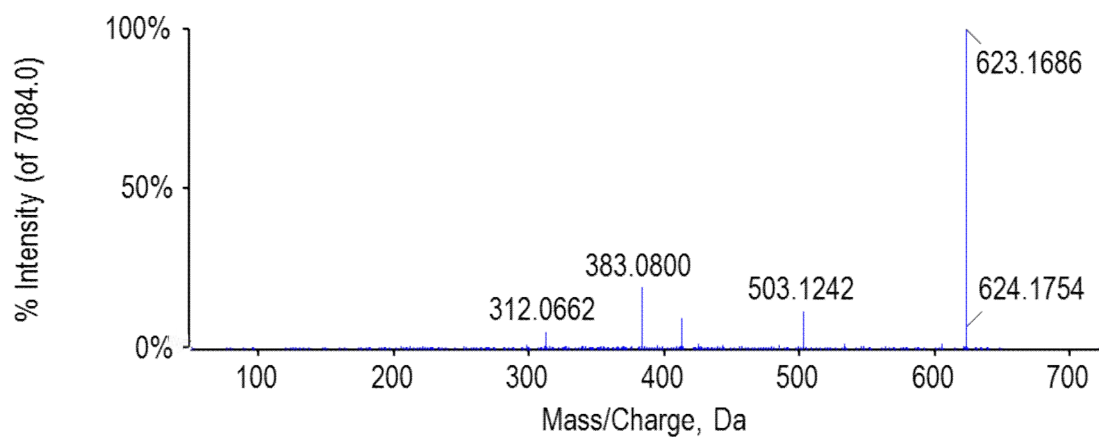


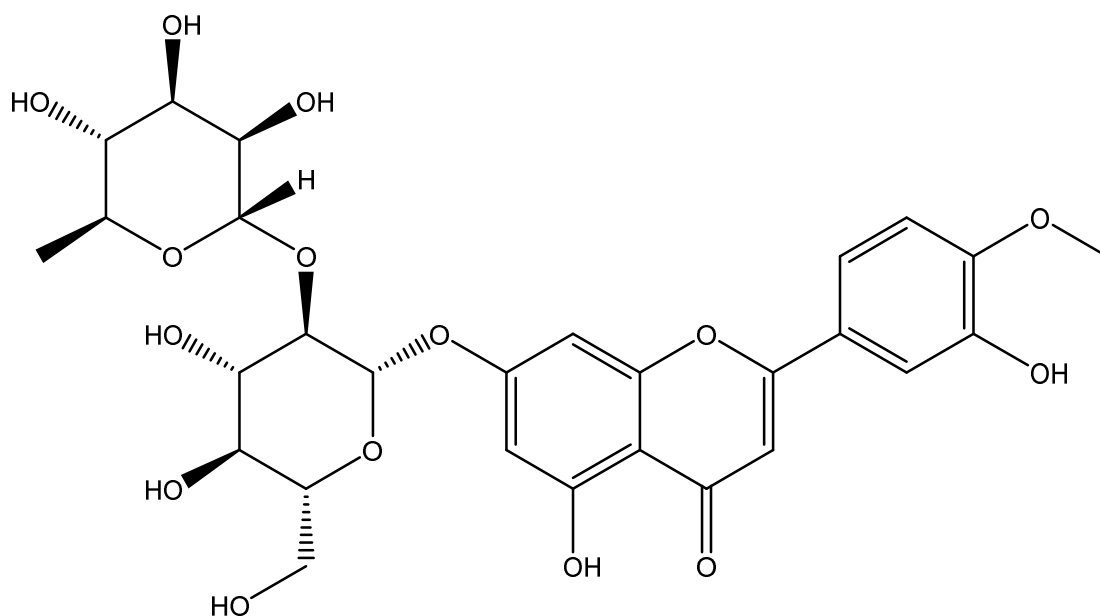
F10. Lucenin-2,4'-methyl ether (RT=9.8 min)

Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 9.752 min
Precursor: 625.2 Da, CE=35



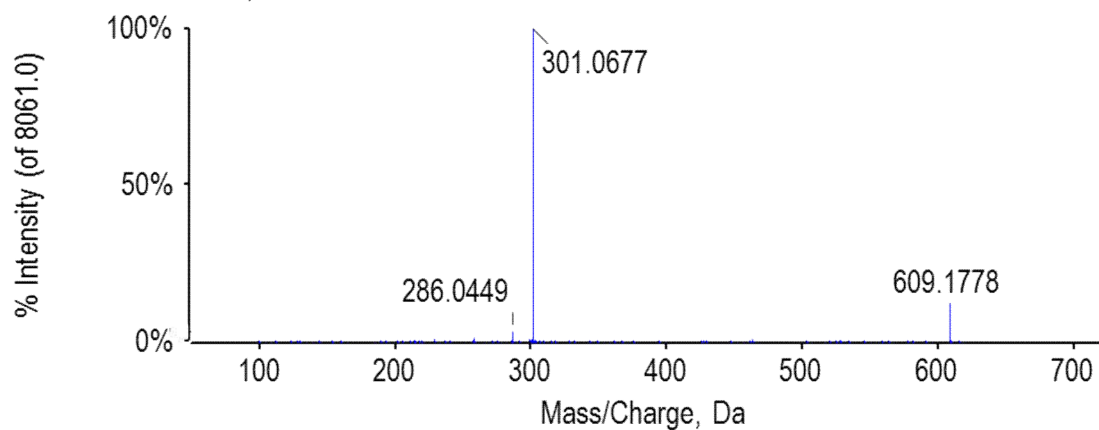
Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 9.791 min
Precursor: 623.2 Da CE=-35



F11. Neodiosmin (RT=12.2 min)

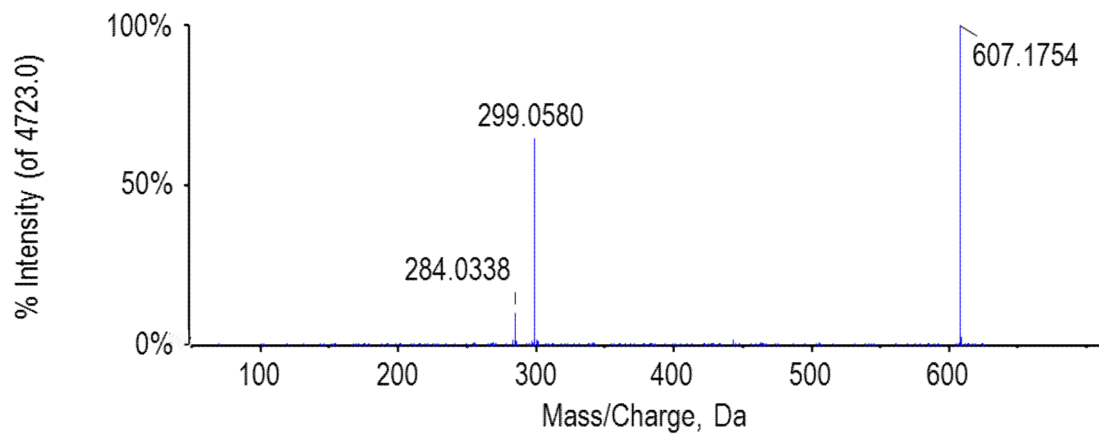
Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 12.236 min

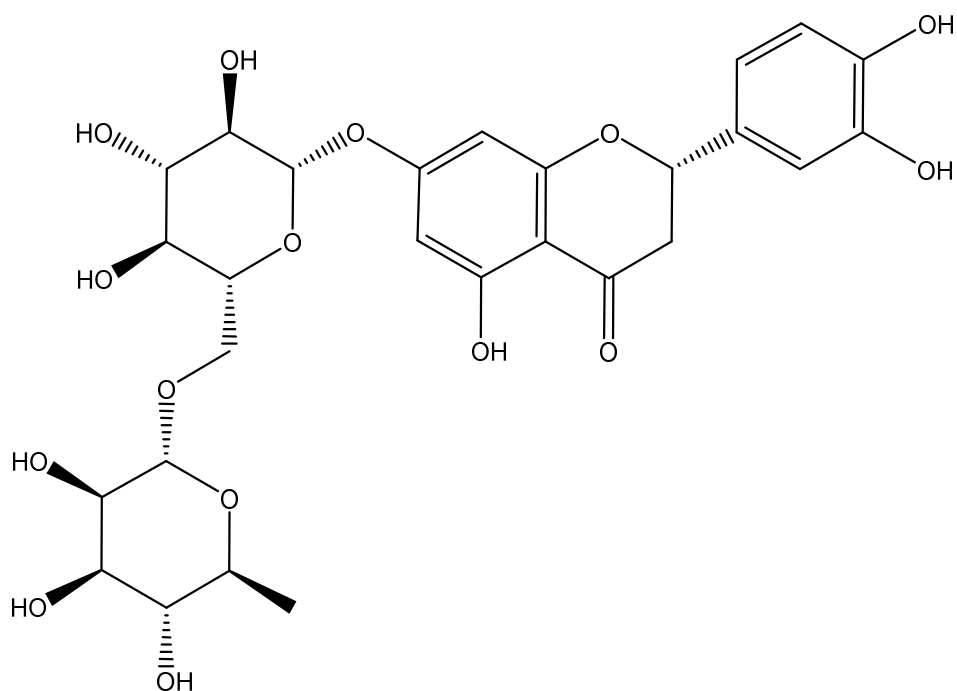
Precursor: 609.2 Da, CE=35



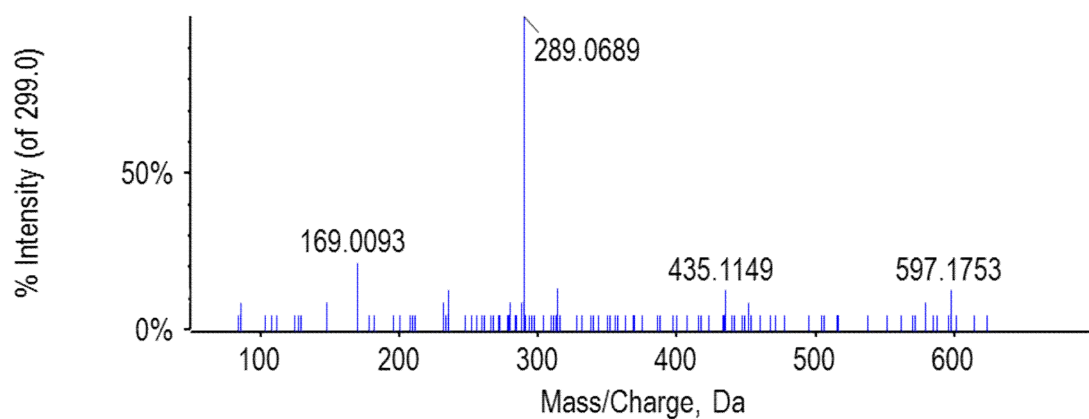
Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 12.210 min

Precursor: 607.2 Da CE=-35

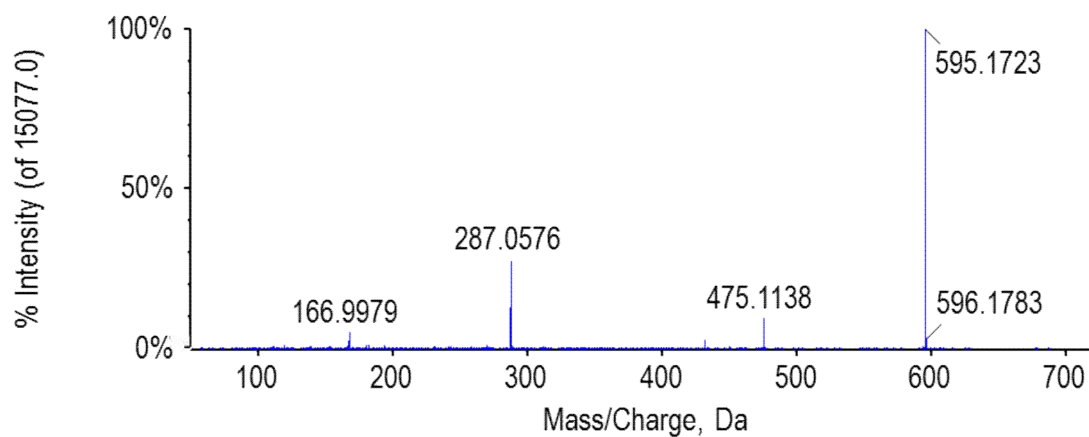


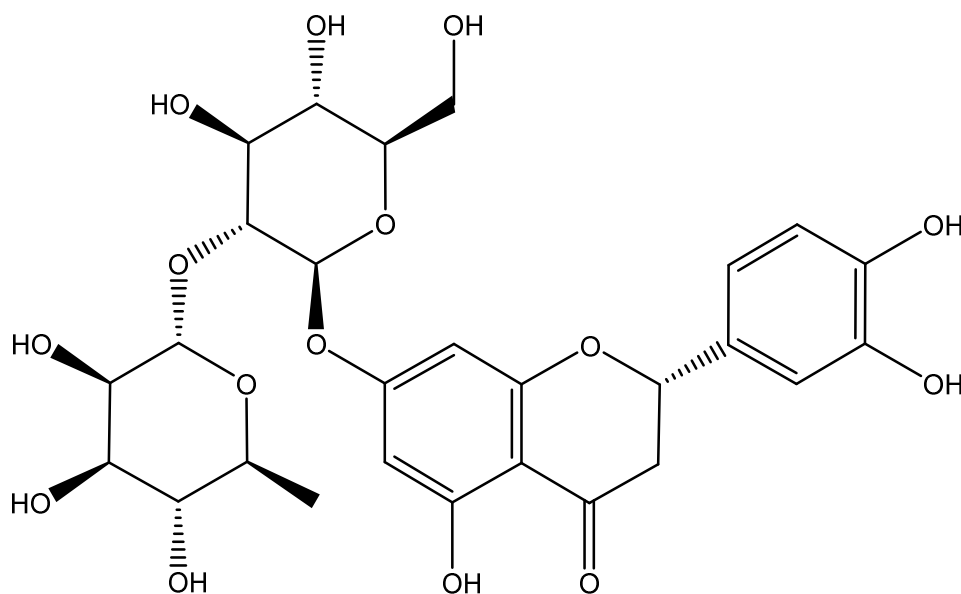
F12. Eriocitrin (RT=10.2 min)

Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 10.219 min
Precursor: 597.2 Da, CE=35

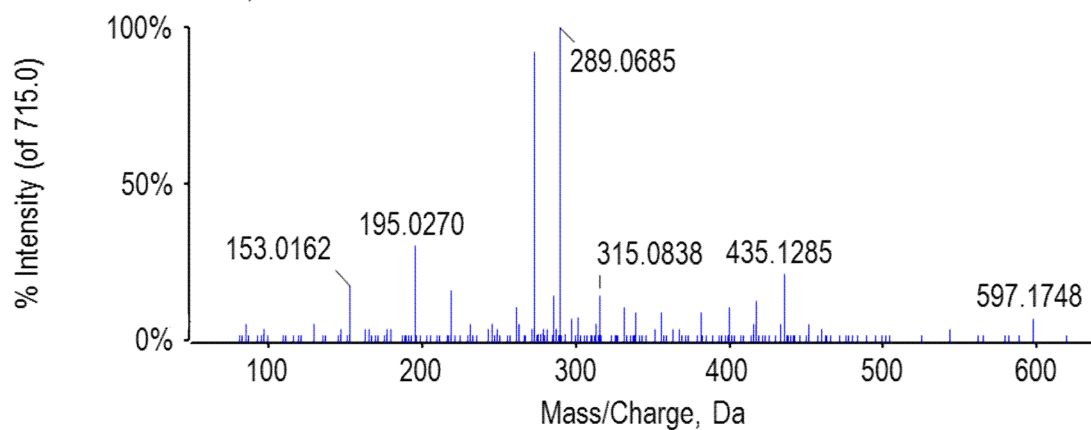


Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 10.230 min
Precursor: 595.2 Da CE=-35

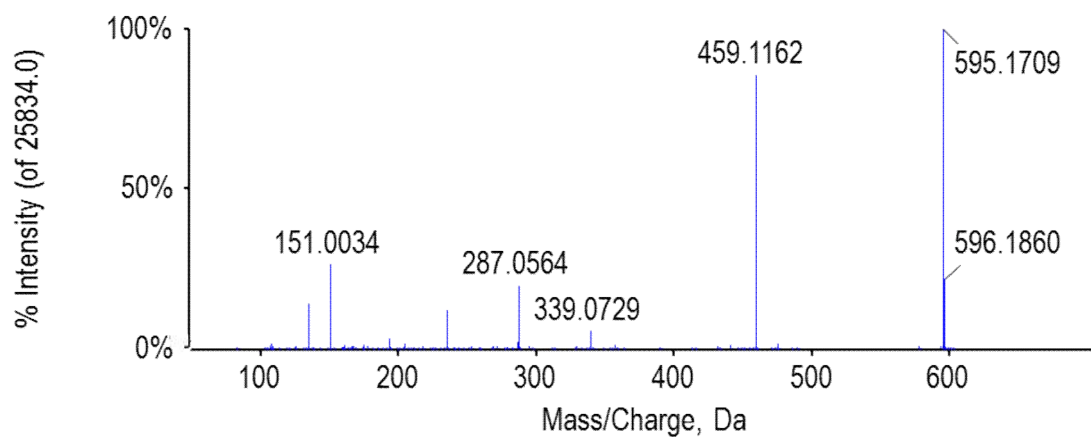


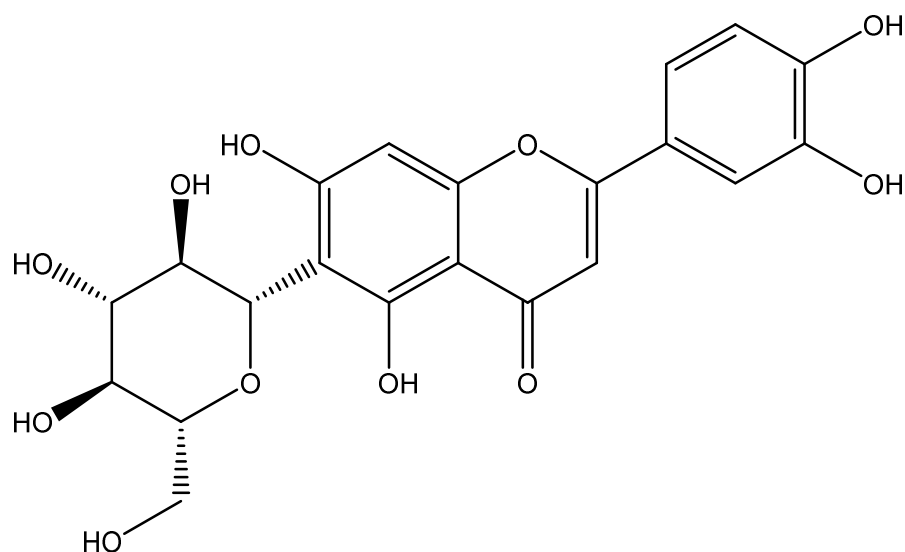
F13. Neeriocitrin (RT=10.7 min)

Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 10.659 min
Precursor: 597.2 Da, CE=35

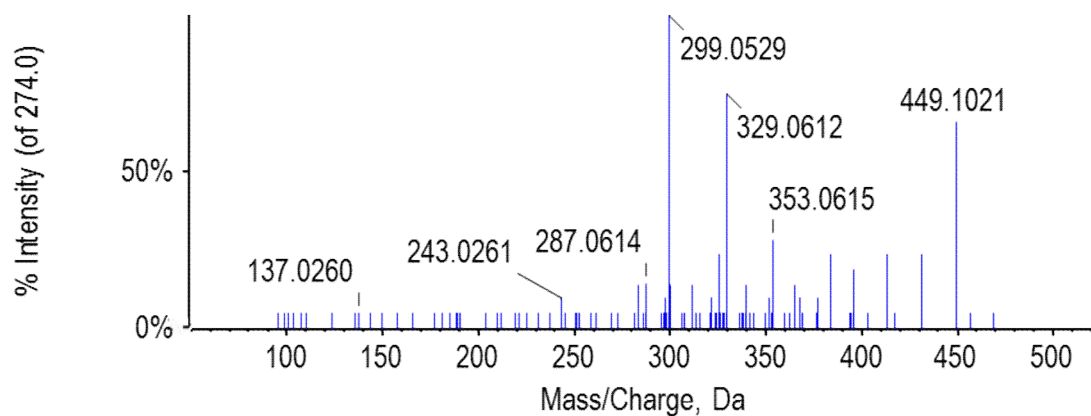


Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 10.627 min
Precursor: 595.2 Da CE=-35

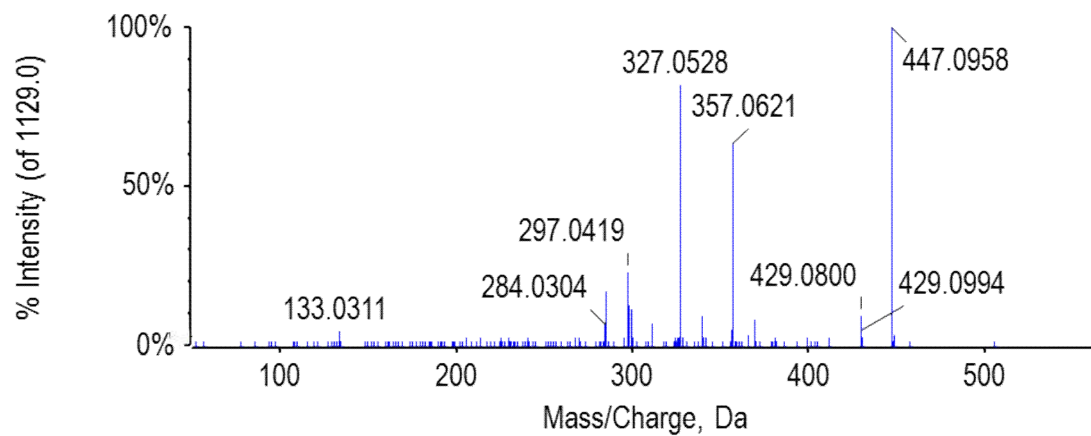


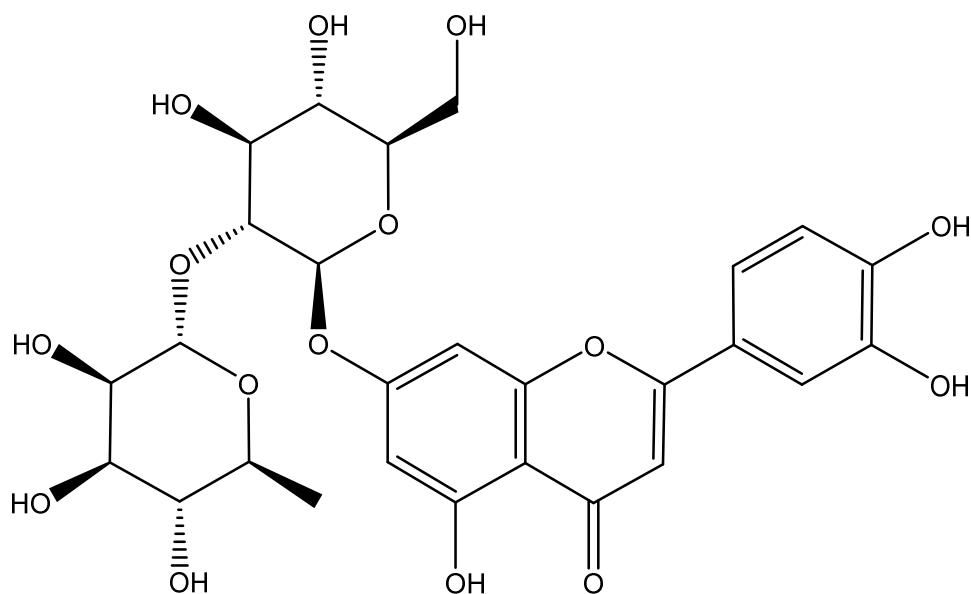
F14. Luteolin-6-C-glucoside (RT=10.5 min)

Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 10.487 min
Precursor: 449.1 Da, CE=35

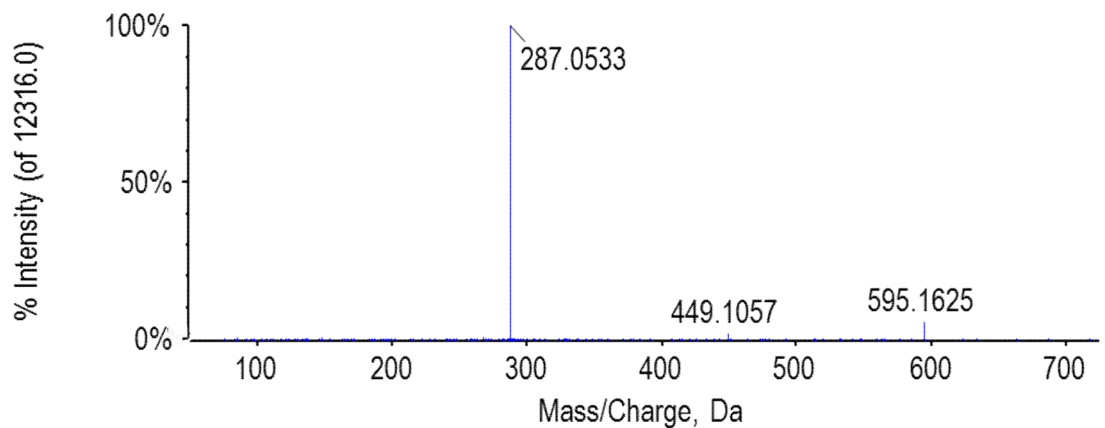


Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 10.493 min
Precursor: 447.1 Da CE=-35

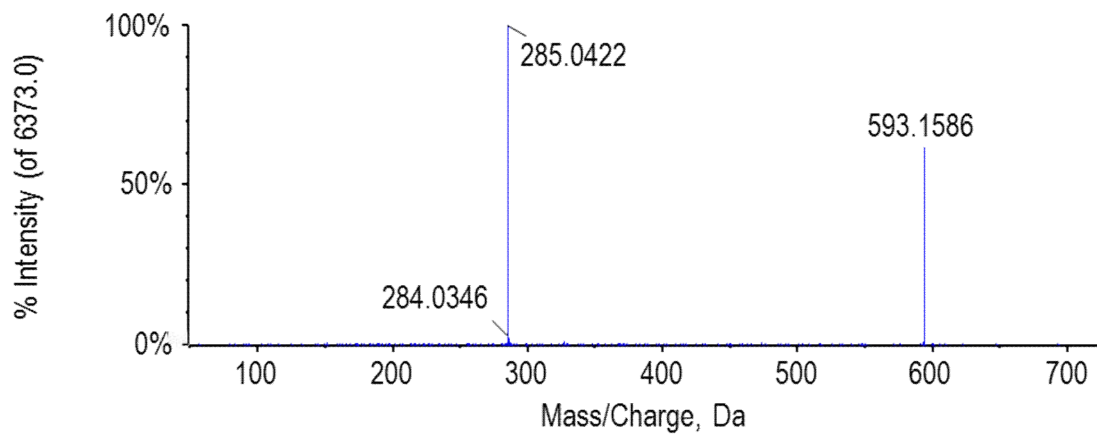


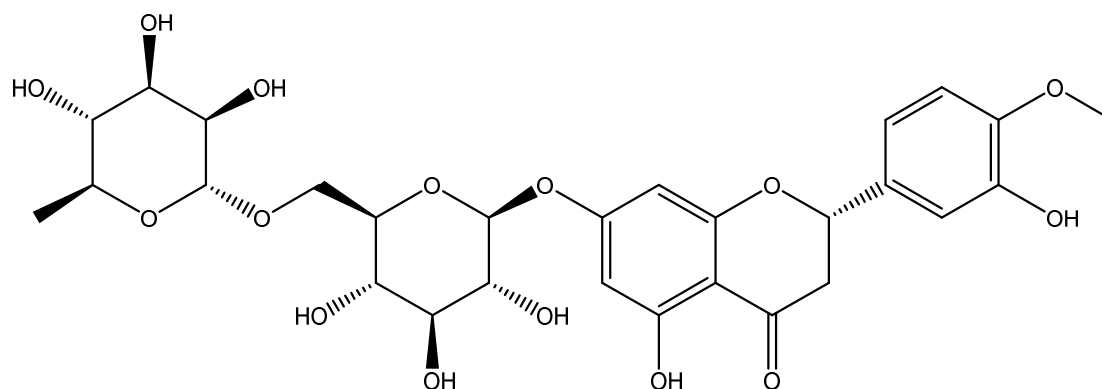
F15. Veronicastroside (RT=11.9 min)

Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 11.861 min
Precursor: 595.2 Da, CE=35

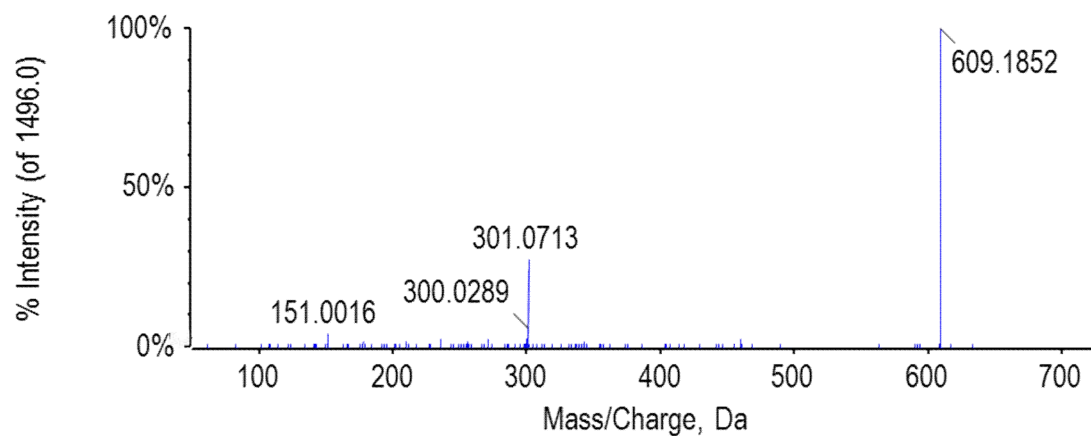


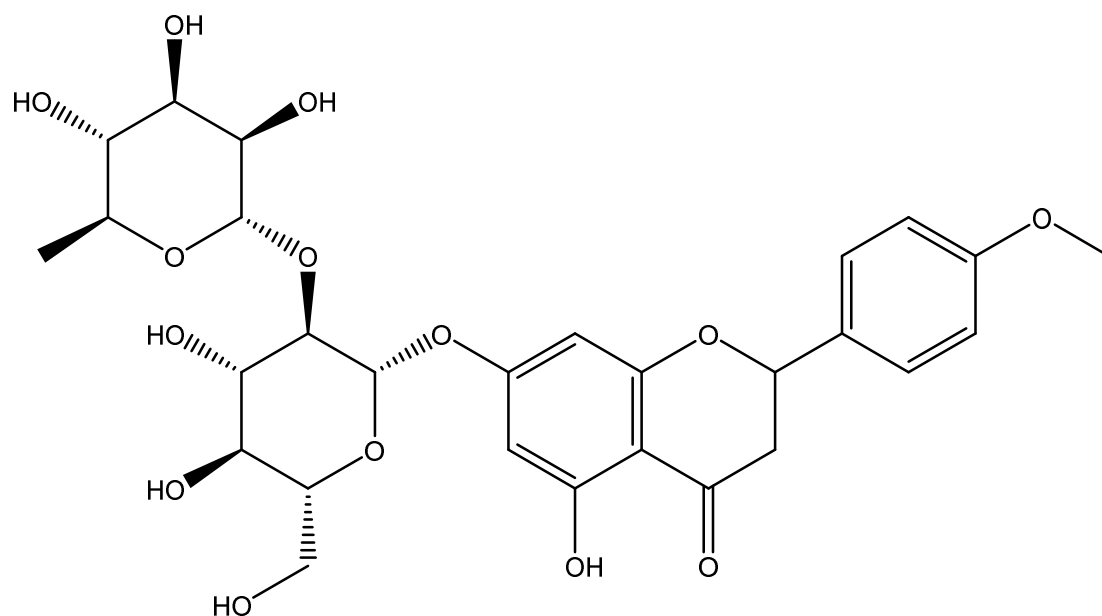
Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 11.887 min
Precursor: 593.2 Da CE=-35



F16. Hesperidin (RT=11.6 min)

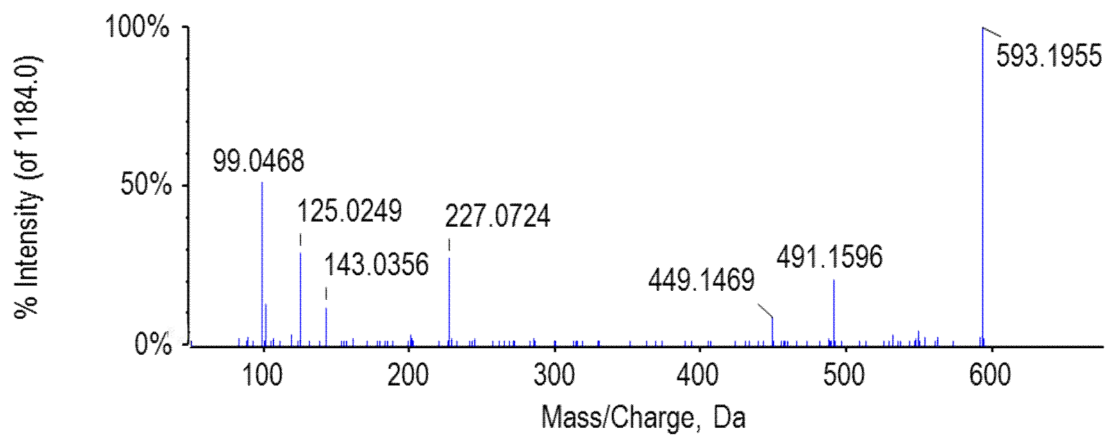
Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 11.550 min
Precursor: 609.2 Da CE=-35

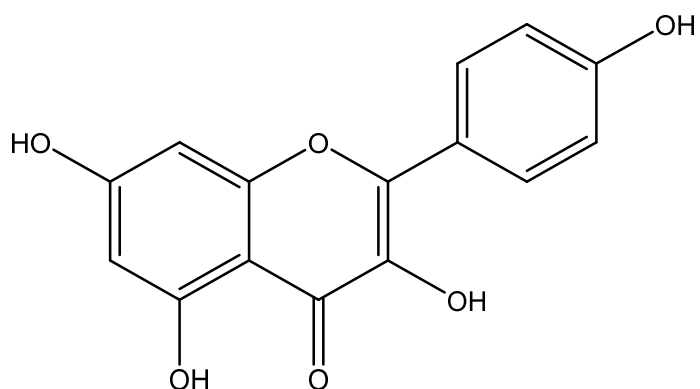


F17. Poncirin (RT=13.9 min)

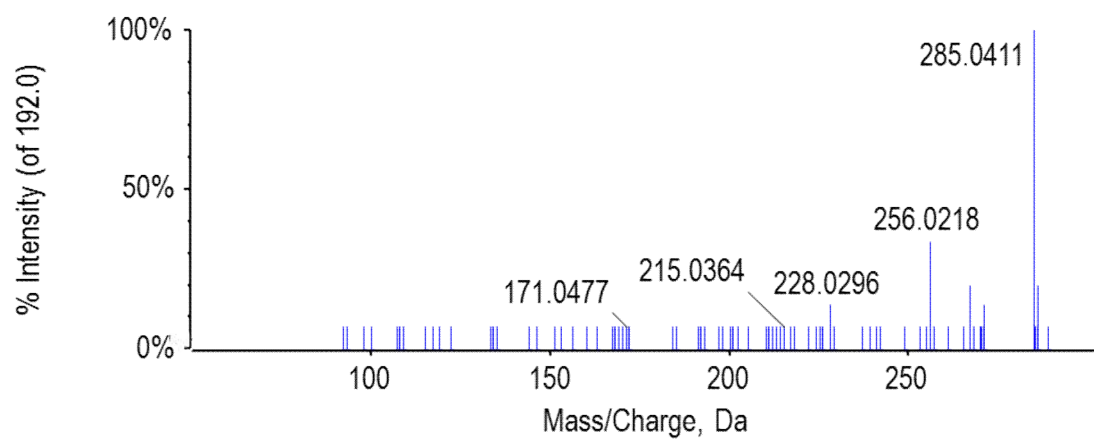
Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 13.901 min

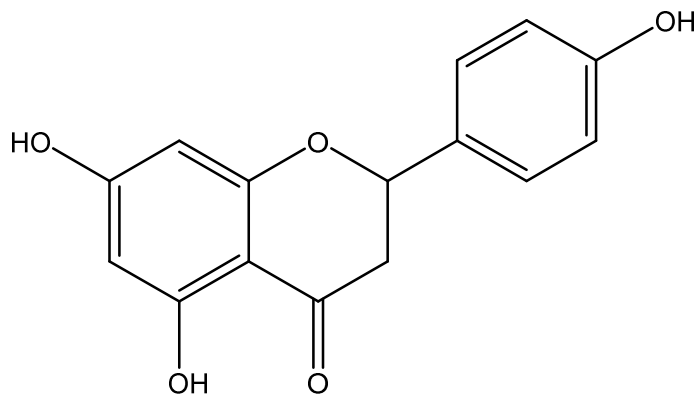
Precursor: 593.2 Da CE=-35



F18. Kaempferol (RT=14.7 min)

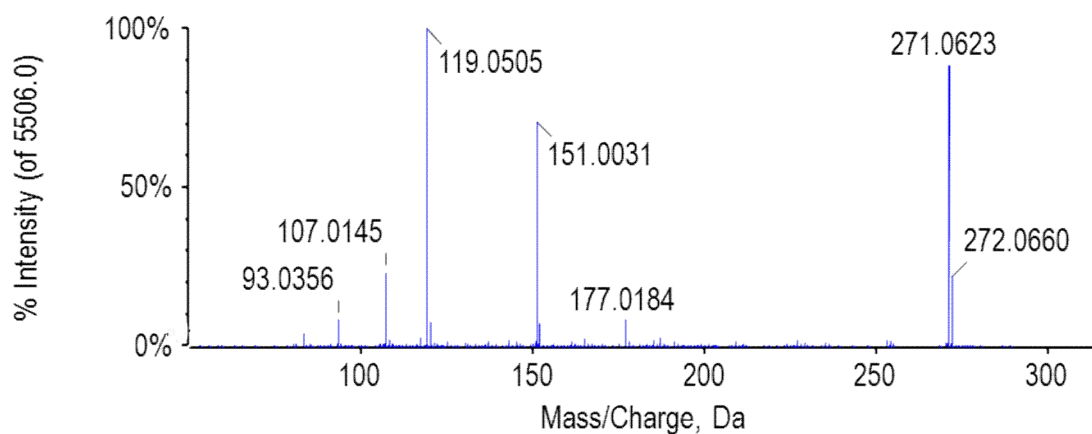
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Precursor: 285.0 Da CE=-35

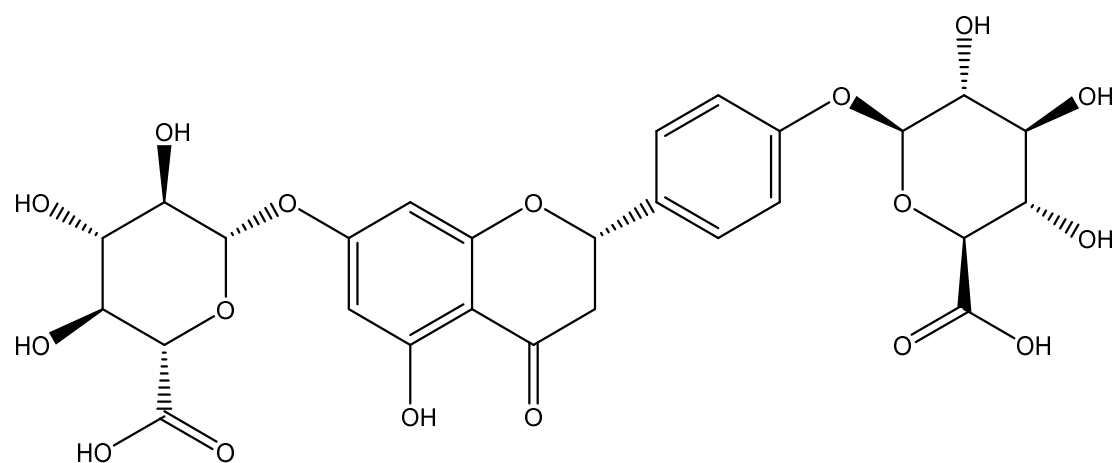


Part II. Structures and product ion spectra of identified metabolites in urine after the consumption of 250 mL Exocarpium *Citri grandis* extract**M1. Naringenin (RT=13.6 min)**

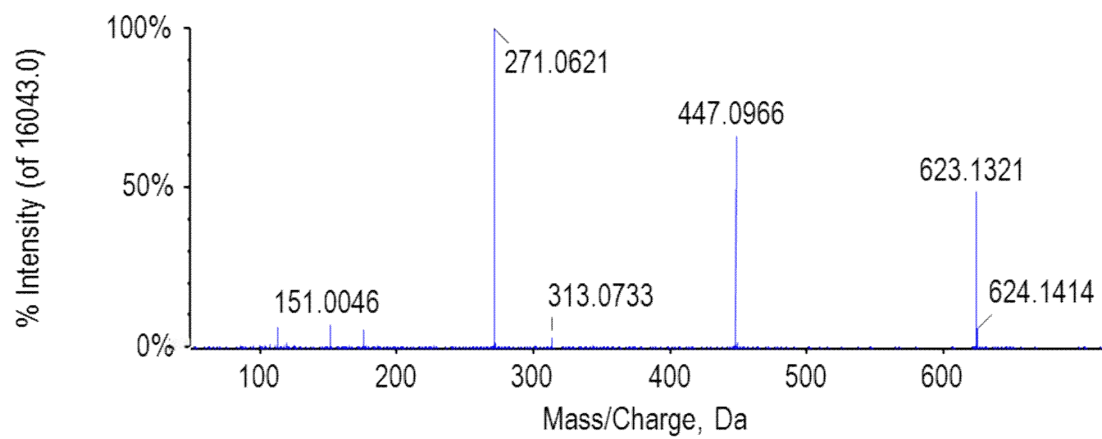
Spectrum from Urine_S4_3, -TOF MS² (50 - 1500) from 13.610 min

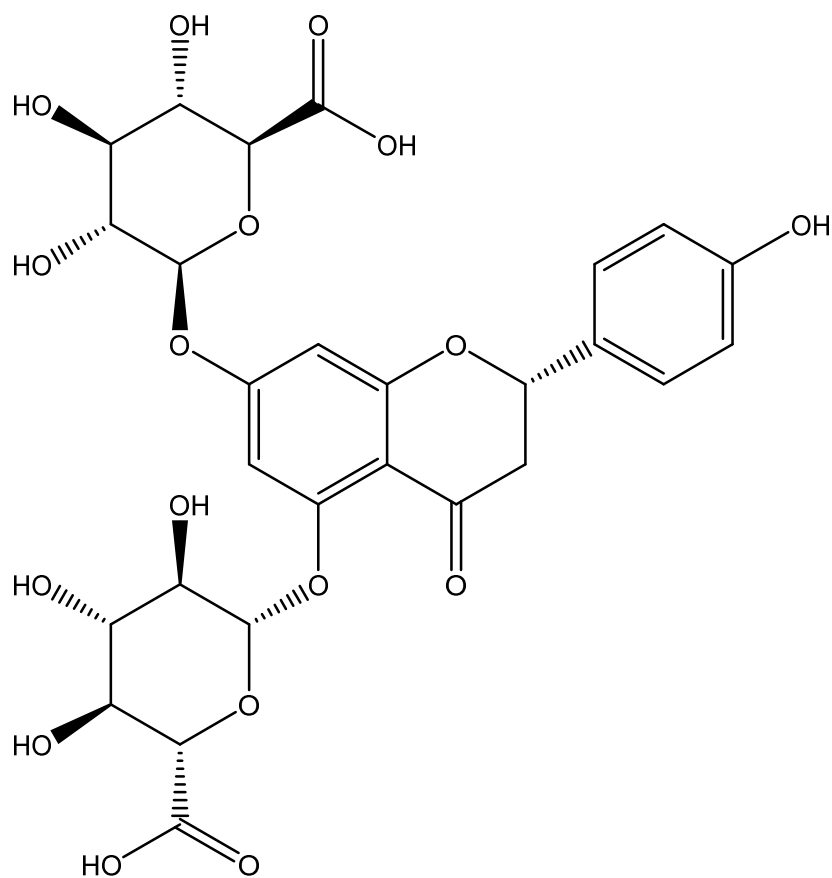
Precursor: 271.1 Da CE=-35



M2. Naringenin-4',7-O-diglucuronide (RT=8.8 min)

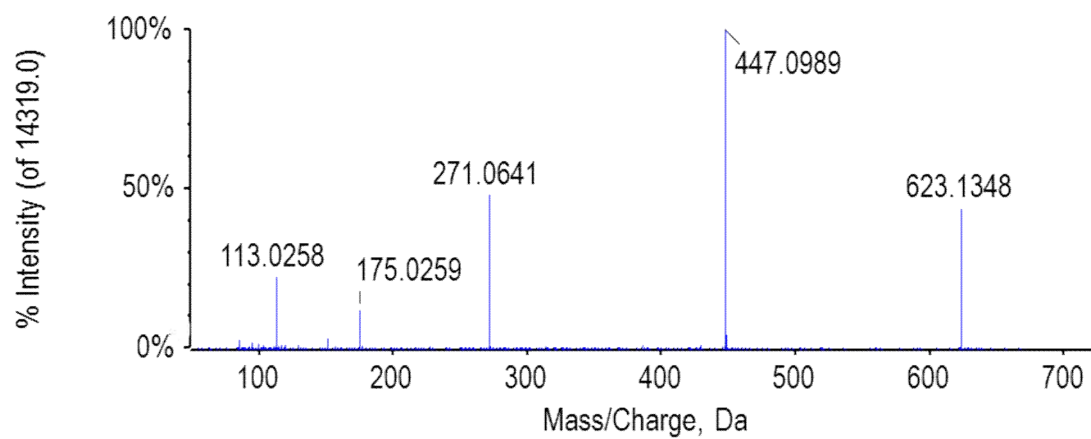
Spectrum from Urine_S1_3, -TOF MS² (50 - 1500) from 8.791 min
Precursor: 623.1 Da CE=-35

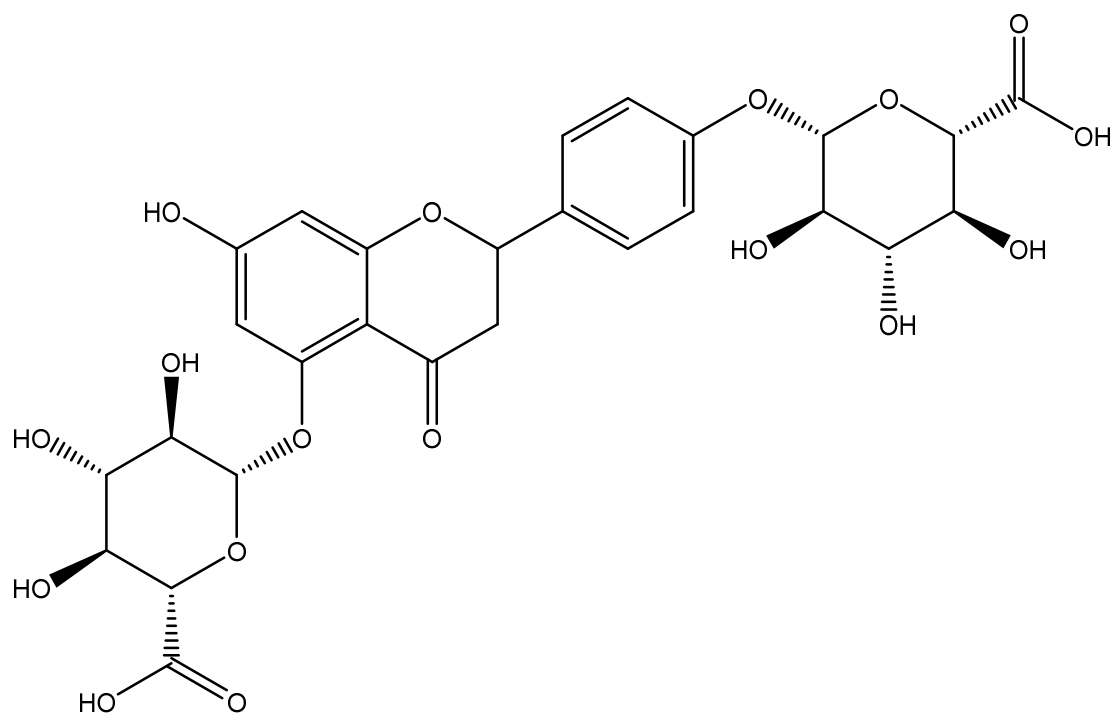


M3. Naringenin-5,7-O-diglucuronide (RT=9.4 min)

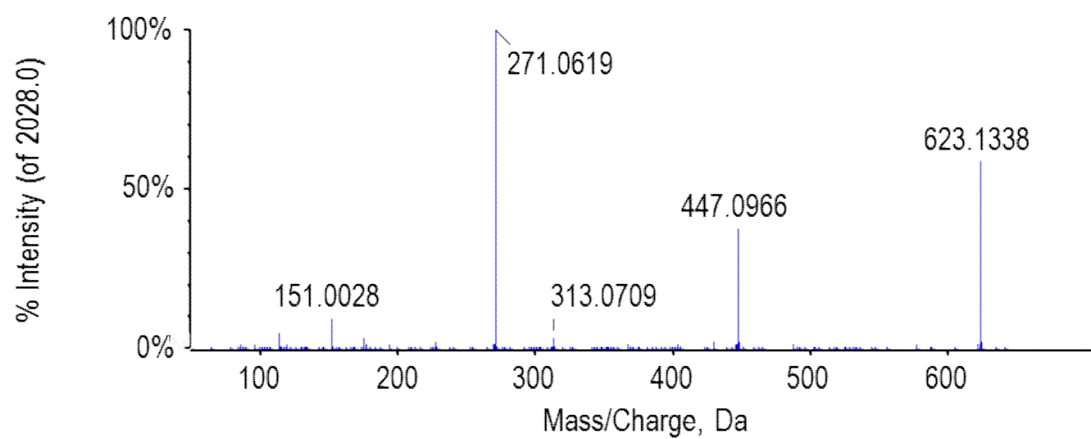
Spectrum from Urine_S1_3, -TOF MS² (50 - 1500) from 9.442 min

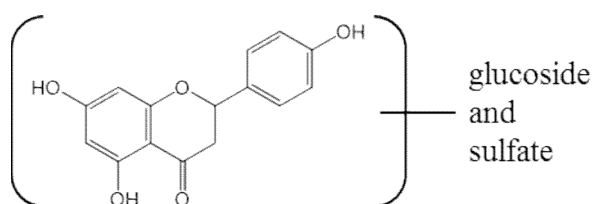
Precursor: 623.1 Da CE=-35



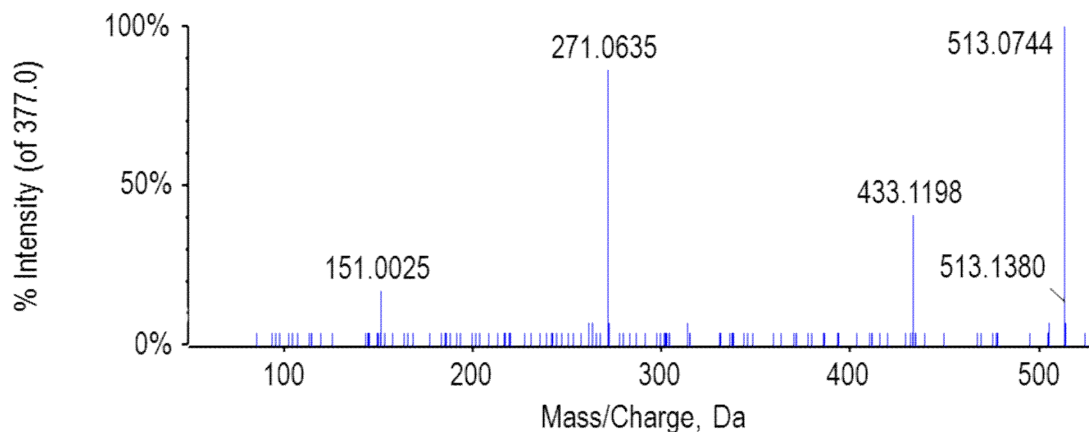
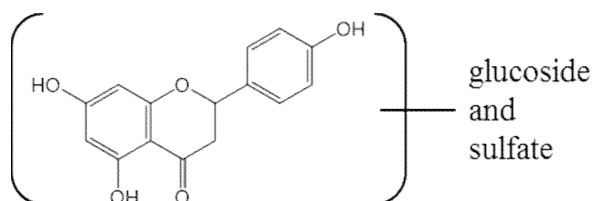
M4. Naringenin-4',5-O-diglucuronide (RT=10.7 min)

Spectrum from Urine_S1_3, -TOF MS² (50 - 1500) from 10.703 min
Precursor: 623.1 Da CE=-35

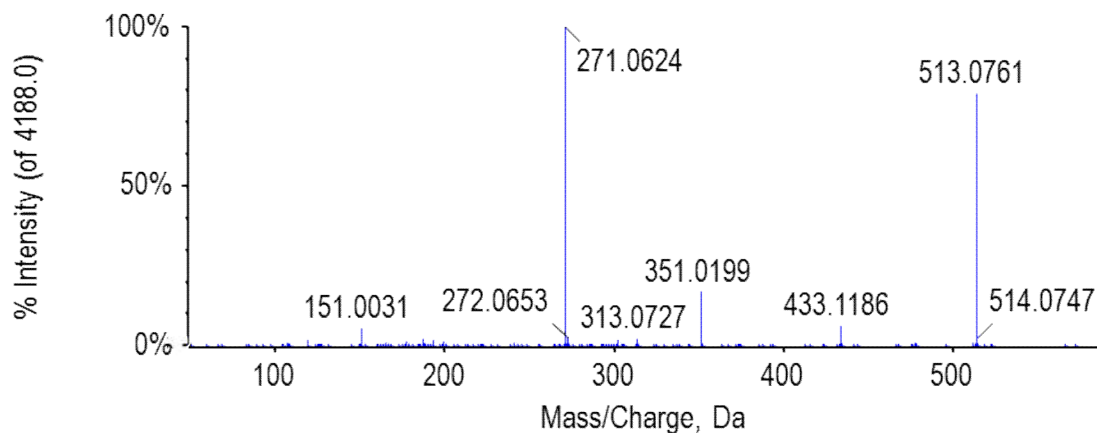


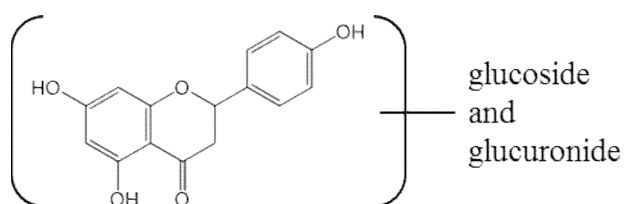
M5. Naringenin-O-glucoside-O-sulfate (RT=9.3 min)

Spectrum from Urine_S1_3, -TOF MS² (50 - 1500) from 9.205 min
Precursor: 513.1 Da CE=-35

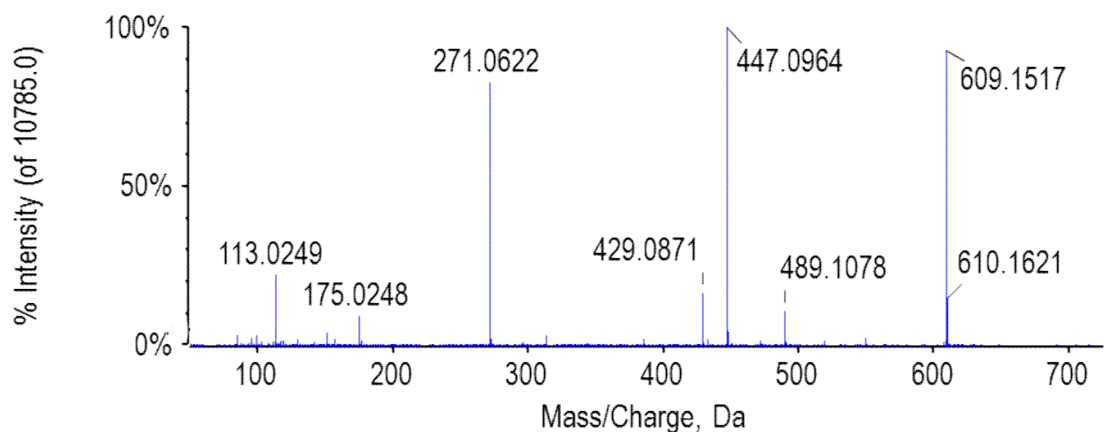
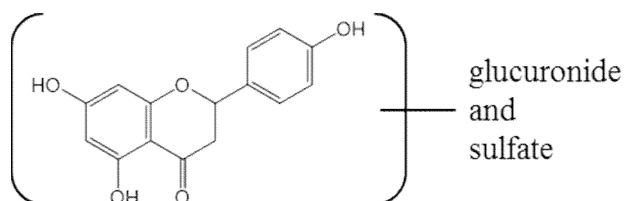
**M6. Naringenin-O-glucoside-O-sulfate (RT=9.9 min)**

Spectrum from Urine_S1_3, -TOF MS² (50 - 1500) from 9.719 min
Precursor: 513.1 Da CE=-35

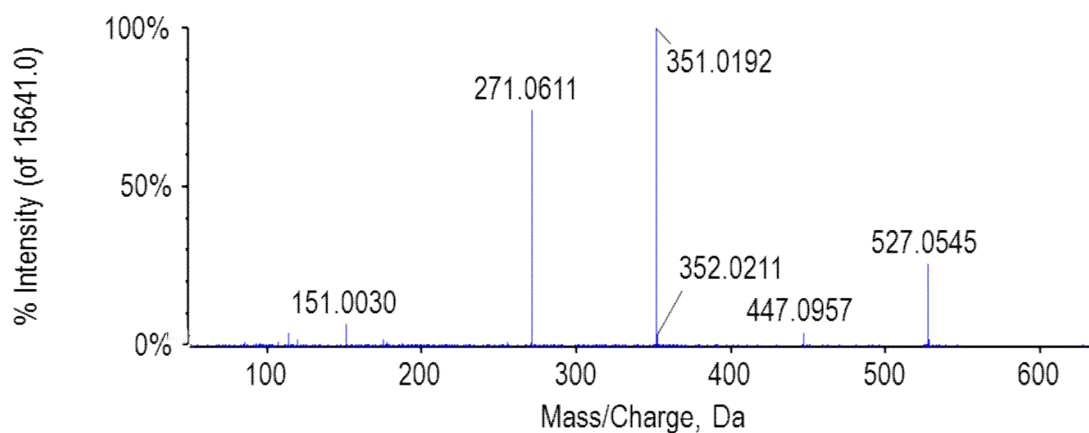


M7. Naringenin-O-glucoside-O-glucuronide (RT=9.4 min)Spectrum from Urine_S4_3, -TOF MS² (50 - 1500) from 9.407 min

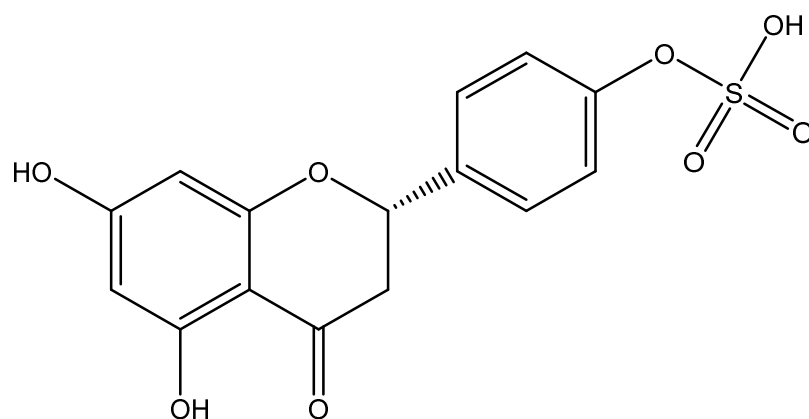
Precursor: 609.1 Da CE=-35

**M8. Naringenin-O-glucuronide-O-sulfate (RT=10.1 min)**Spectrum from Urine_S4_3, -TOF MS² (50 - 1500) from 10.099 min

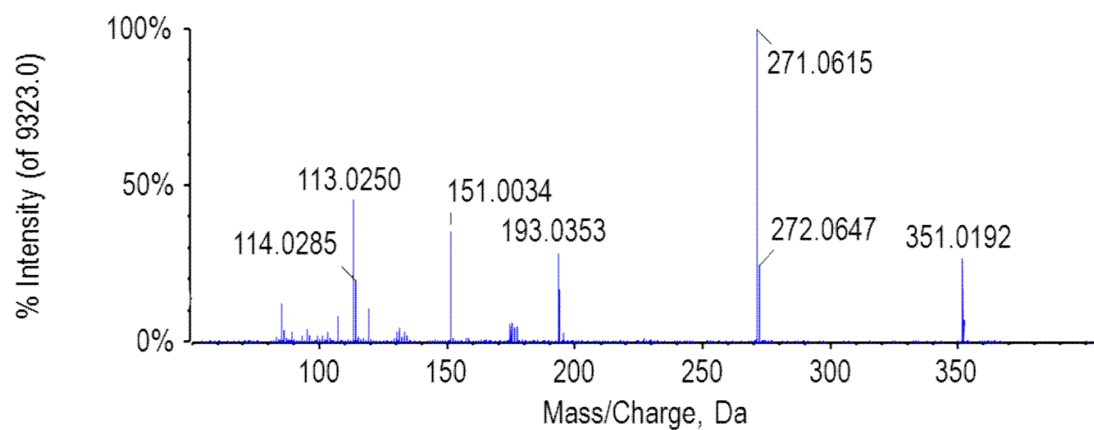
Precursor: 527.1 Da CE=-35

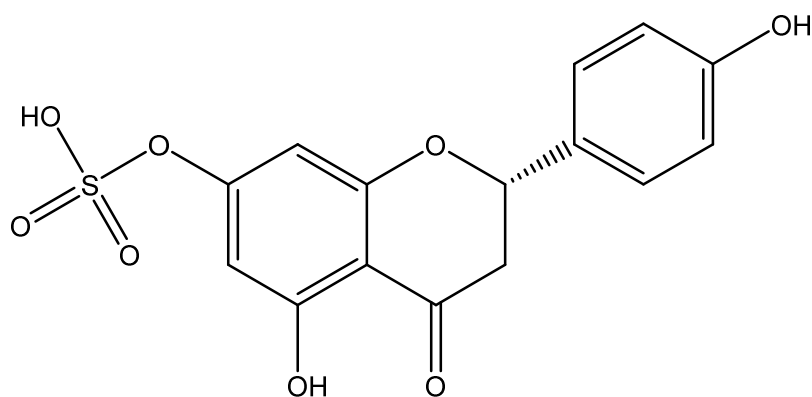


M9. Naringenin-4'-O-sulfate (RT=10.3 min)

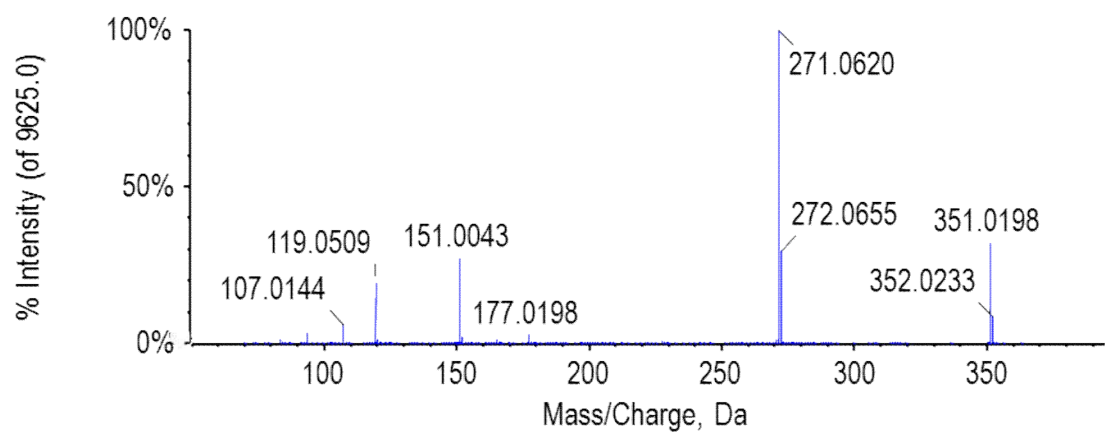


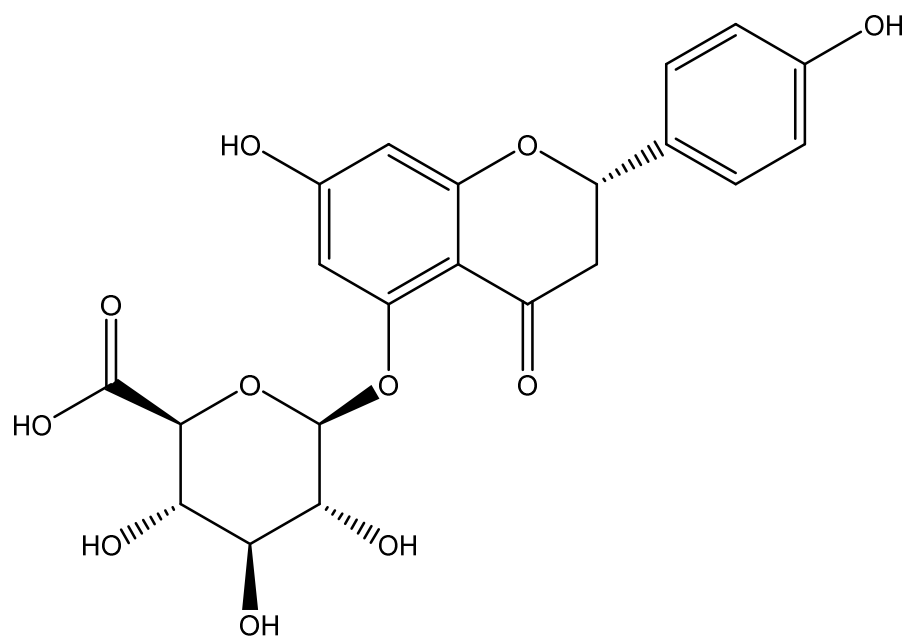
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 10.462 min
Precursor: 351.0 Da CE=-35



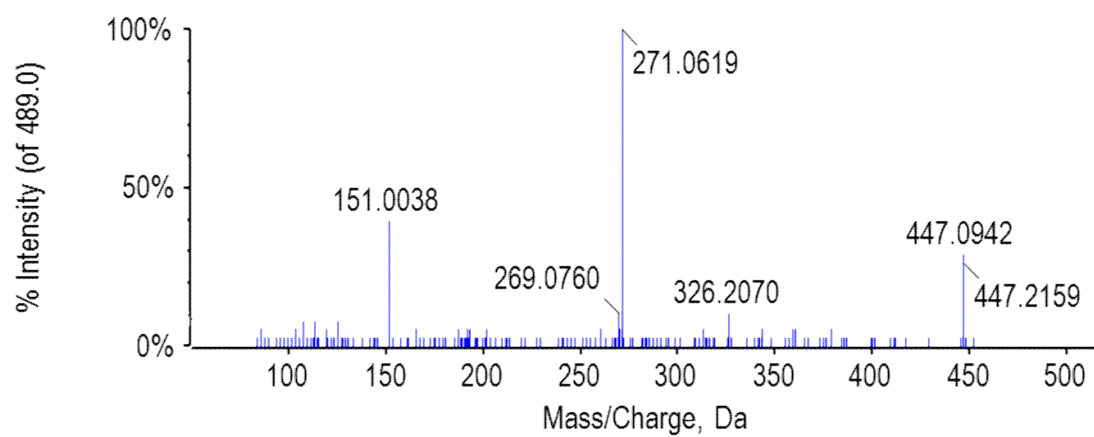
M10. Naringenin-7-O-sulfate (RT=12.3 min)Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 12.327 min

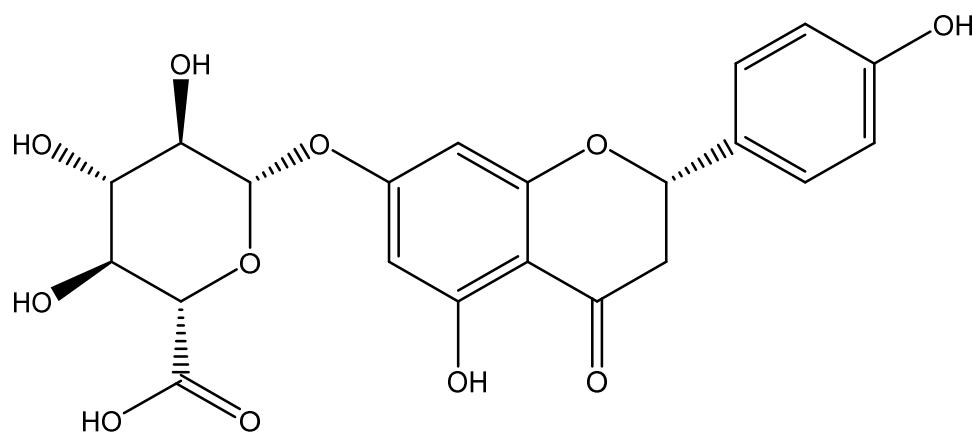
Precursor: 351.0 Da CE=-35



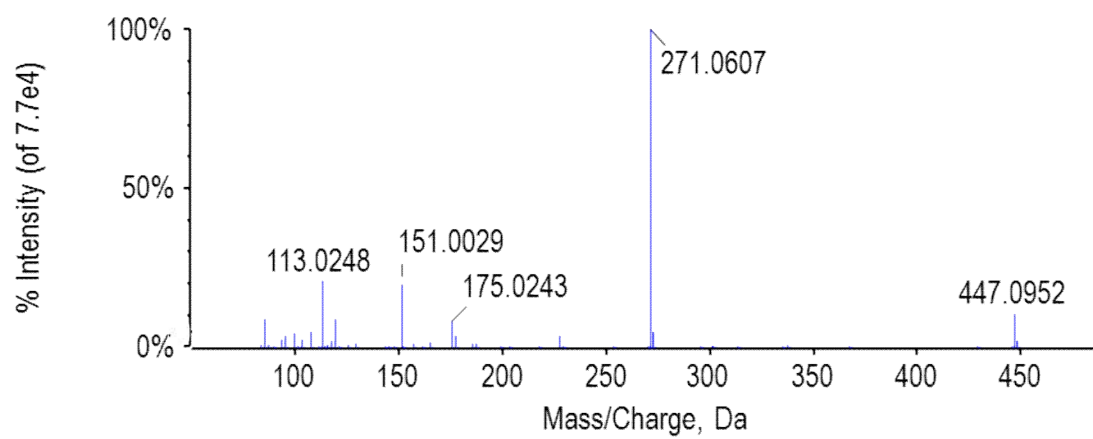
M11. Naringenin-5-O-glucuronide (RT=10.7 min)

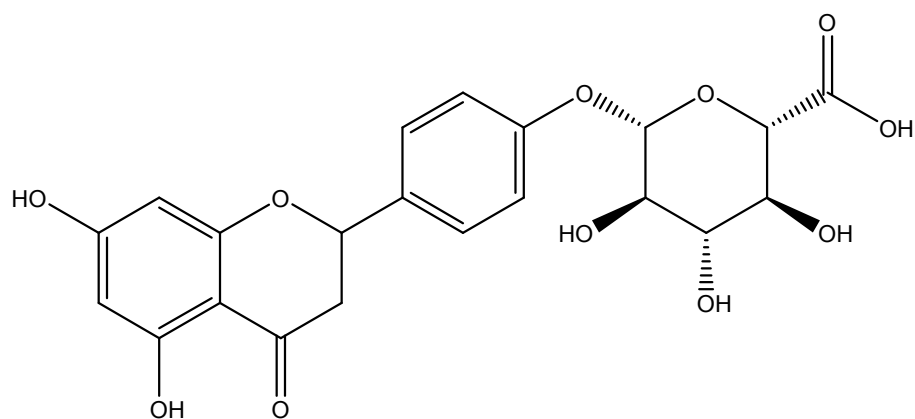
Spectrum from Urine_S4_3, -TOF MS² (50 - 1500) from 10.725 min
Precursor: 447.1 Da CE=-35



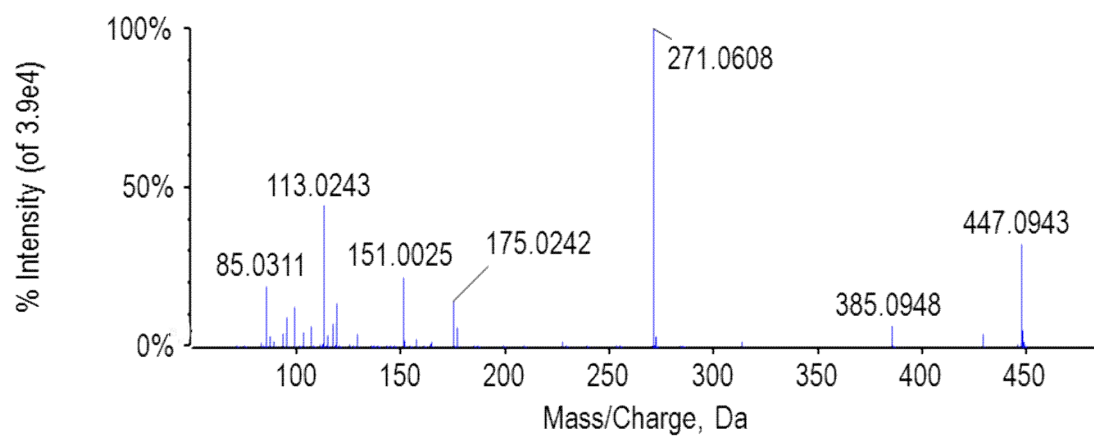
M12. Naringenin-7-O-glucuronide (RT=11.4 min)

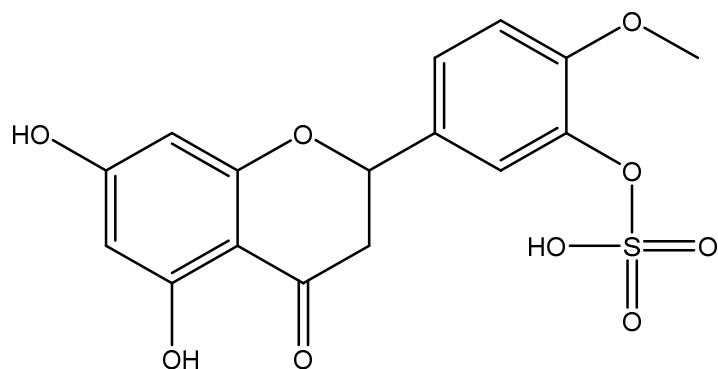
Spectrum from Urine_S4_3, -TOF MS² (50 - 1500) from 11.453 min
Precursor: 447.1 Da CE=-35



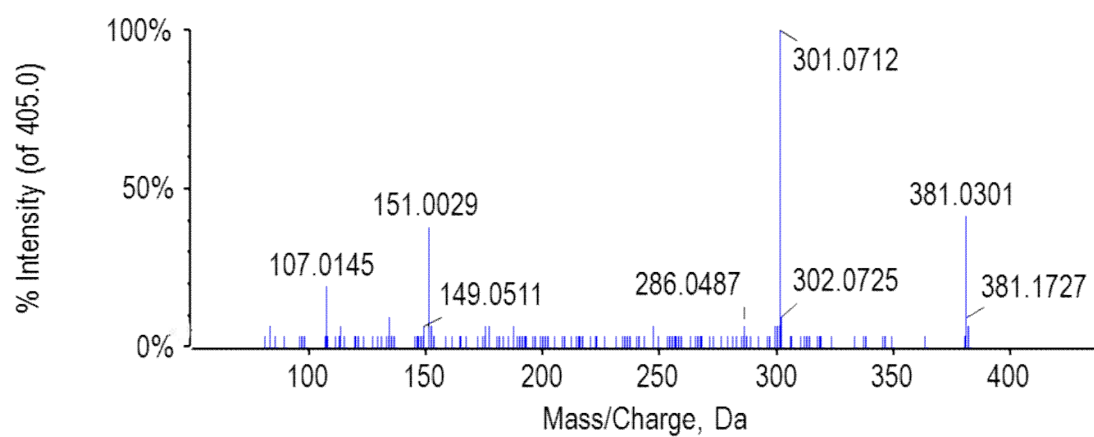
M13. Naringenin-4'-O-glucuronide (RT=11.7 min)

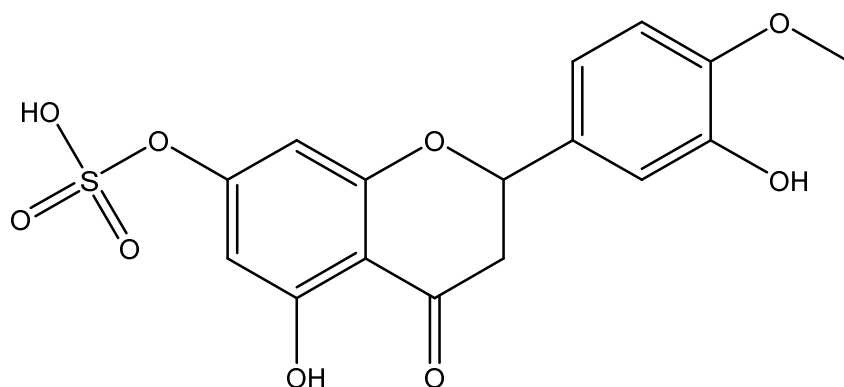
Spectrum from Urine_S4_3, -TOF MS² (50 - 1500) from 11.705 min
Precursor: 447.1 Da CE=-35



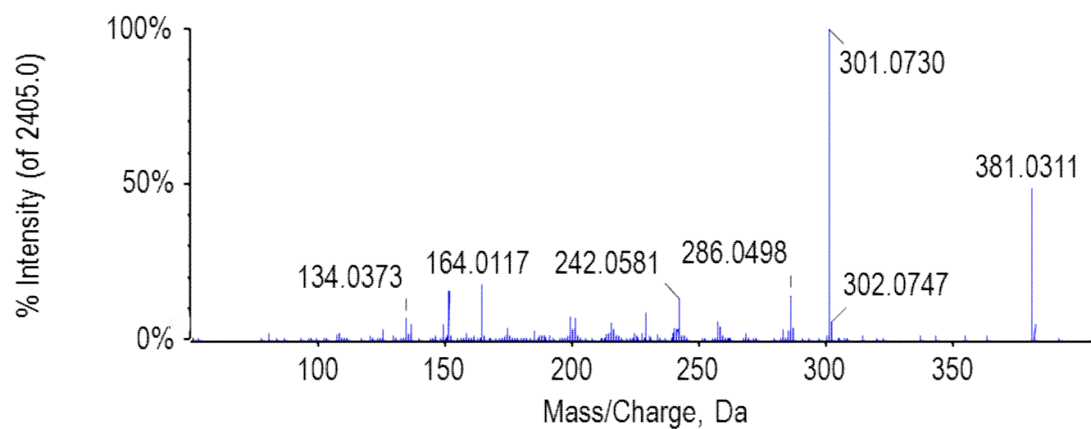
M14. Hesperetin-3'-O-sulfate (RT=10.4 min)

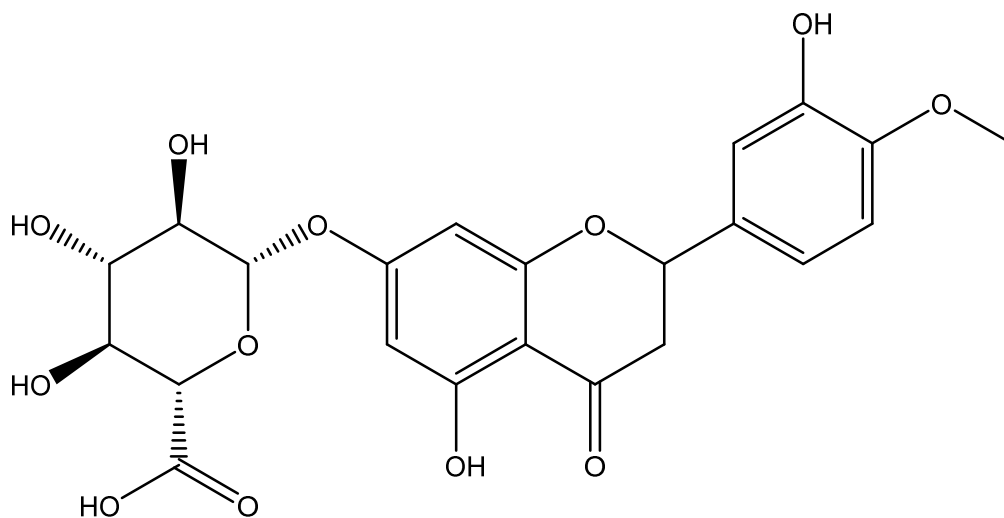
Spectrum from Urine_S4_3, -TOF MS² (50 - 1500) from 10.427 min
Precursor: 381.0 Da CE=-35



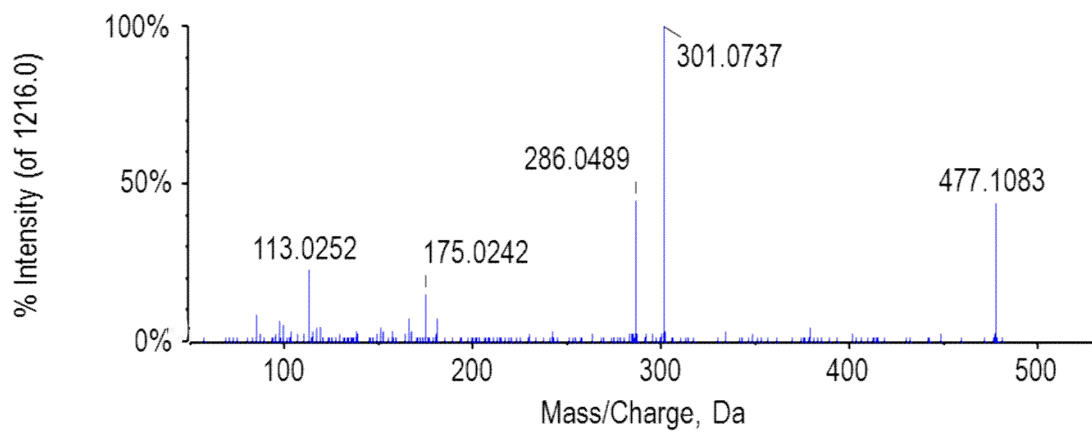
M15. Hesperetin-7-O-sulfate (RT=12.6 min)

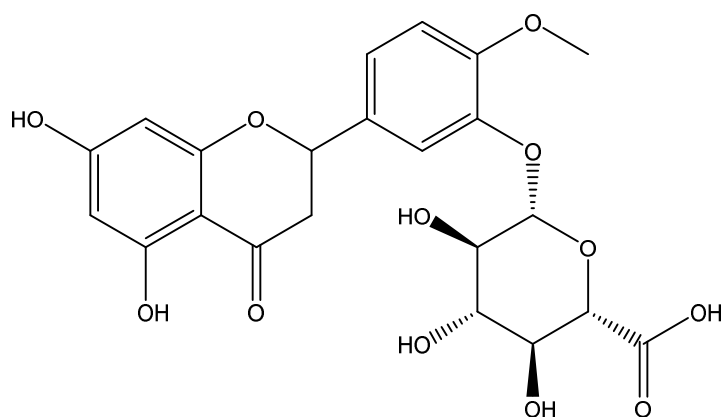
Spectrum from Urine_S3_1, -TOF MS² (50 - 1500) from 12.482 min
Precursor: 381.0 Da CE=-35



M16. Hesperetin-7-O-glucuronide (RT=11.8 min)

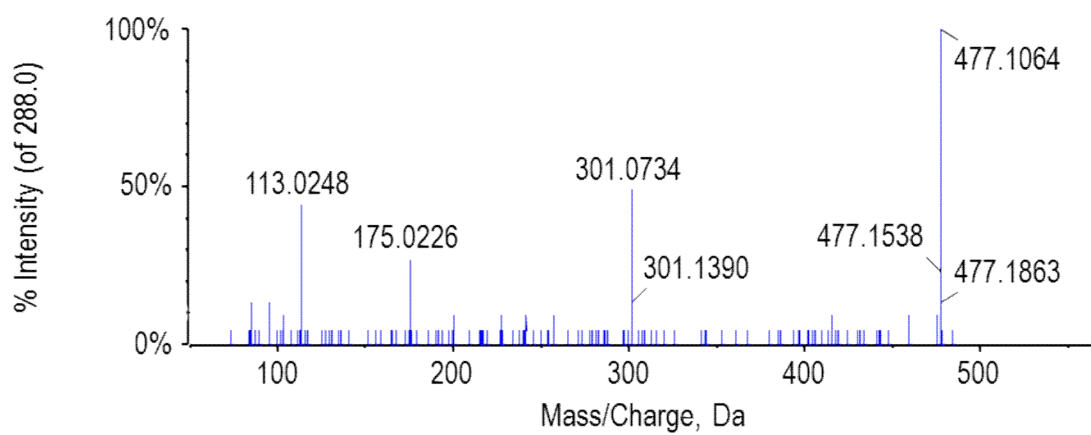
Spectrum from Urine_S5_3, -TOF MS² (50 - 1500) from 11.804 min
Precursor: 477.1 Da CE=-35

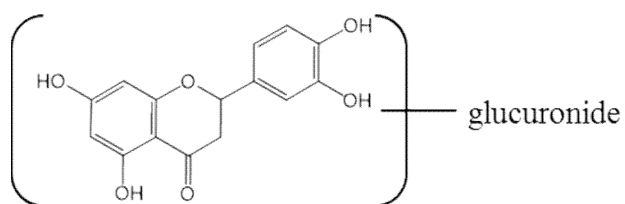


M17. Hesperetin-3'-O-glucuronide (RT=12.3 min)

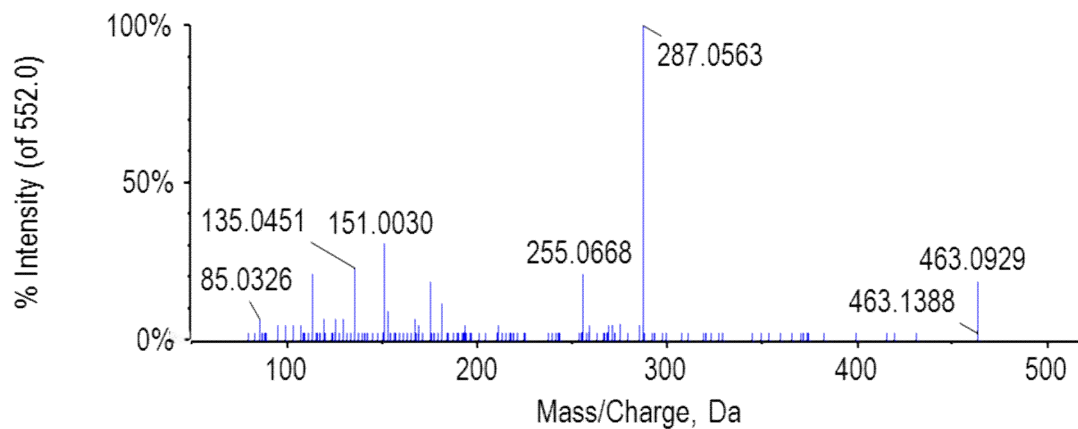
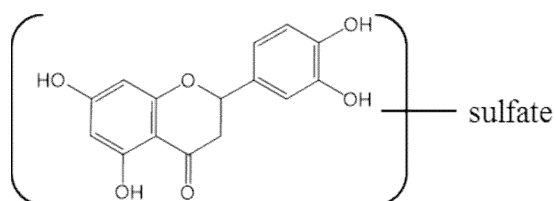
Spectrum from Urine_S3_2, -TOF MS² (50 - 1500) from 12.328 min

Precursor: 477.1 Da CE=-35

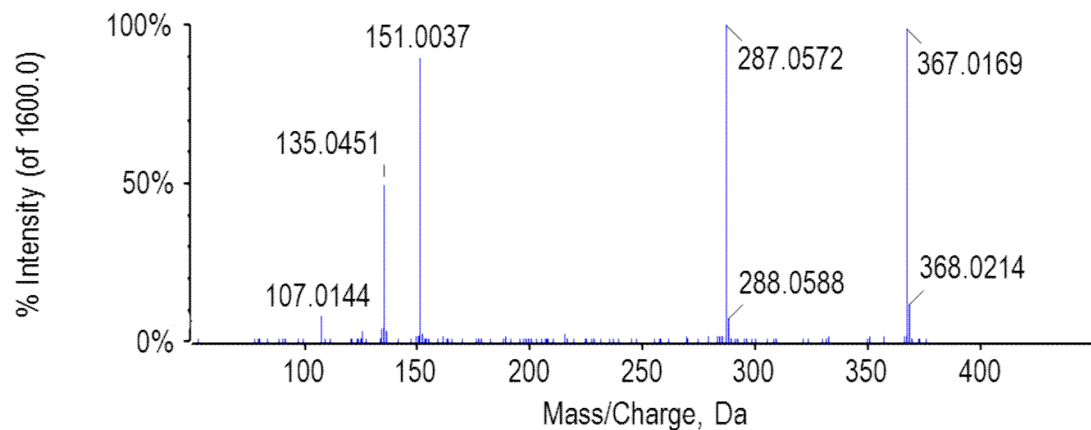


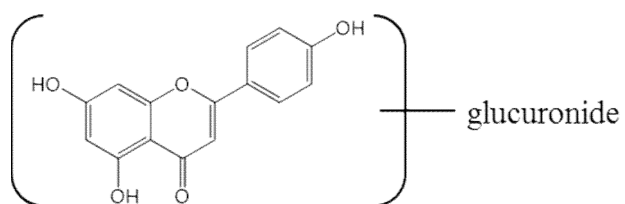
M18. Eriodictyol-O-glucuronide (RT=10.9 min)Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 10.880 min

Precursor: 463.1 Da CE=-35

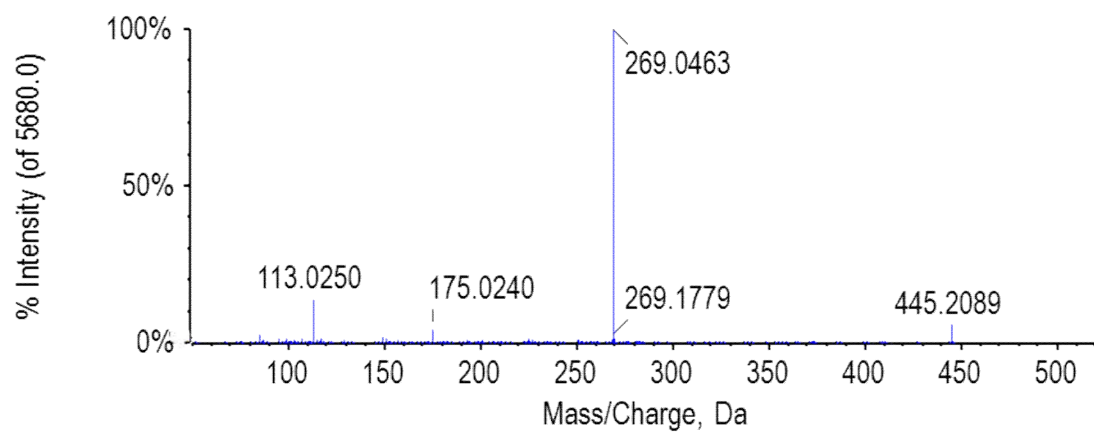
**M19. Eriodictyol-O-sulfate (RT=12.5 min)**Spectrum from Urine_S4_3, -TOF MS² (50 - 1500) from 12.509 min

Precursor: 367.0 Da CE=-35



M20. Apigenin-O-glucuronide (RT=12.6 min)

Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 12.537 min
Precursor: 445.1 Da CE=-35



Part III. Detailed information, structures, and product ion spectra of identified phenolic catabolites in urine after the consumption of 250 mL Exocarpium *Citri grandis* extract

Table 1. UFLC-Q-TOF-MS/MS based identifications of phenolic catabolites in human urine collected 0-48 h after 250 mL Exocarpium *Citri grandis* extract consumption.

No.	Identified metabolites	Formula	RT (min)	[M-H] ⁻	Fragment ions in negative (-) ion mode ^a
Phenylpropanoid acid derivatives					
C1	Ferulic acid or Isoferulic acid ^{b, c}	C ₁₀ H ₁₀ O ₄	8.7	193.0515	178.0279[M-H-CH ₃] ⁻ , 149.0617[M-H-CO ₂] ⁻ , 134.0375[M-H-CH ₃ -CO ₂] ⁻
C2	Ferulic acid-4'-O-glucuronide	C ₁₆ H ₁₈ O ₁₀	8.3	369.0865	193.0502[M-H-GlcUA] ⁻ , 178.0269[M-H-GlcUA-CH ₃] ⁻ , 175.0688[M-H-FC] ⁻ , 149.0058[M-H-GlcUA-CO ₂] ⁻ , 134.0377[M-H-GlcUA-CH ₃ -CO ₂] ⁻ , 113.0250[M-H-FC-CO ₂ -H ₂ O] ⁻ , 85.0308[M-H-FC-CO ₂ -H ₂ O-CO] ⁻
C3	Isoferulic acid-3'-O-glucuronide	C ₁₆ H ₁₈ O ₁₀	9.5	369.0862	193.0501[M-H-GlcUA] ⁻ , 178.0433[M-H-GlcUA-CH ₃] ⁻ , 175.0622[M-H-IFC] ⁻ , 134.0378[M-H-GlcUA-CH ₃ -CO ₂] ⁻ , 113.0240[M-H-IFC-CO ₂ -H ₂ O] ⁻ , 85.0303[M-H-IFC-CO ₂ -H ₂ O-CO] ⁻
C4	Ferulic acid-4'-sulfate or Isoferulic acid-3'-sulfate	C ₁₀ H ₁₀ O ₇ S	8.8	273.0072	193.0503[M-H-SO ₃] ⁻ , 178.0267[M-H-SO ₃ -CH ₃] ⁻ , 149.0605[M-H-SO ₃ -CO ₂] ⁻ , 134.0363[M-H-SO ₃ -CH ₃ -CO ₂] ⁻ , 96.9612

Supplementary material

C5	Caffeic acid-4'-sulfate or Caffeic acid-3'-sulfate	C ₉ H ₈ O ₇ S	8.6	259.1307	241.1221[M-H-H ₂ O] ⁻ , 179.0354[M-H-SO ₃] ⁻ , 135.0446[M-H-SO ₃ -CO ₂] ⁻
C6	Caffeic acid-4'-O-glucuronide or Caffeic acid-3'-O-glucuronide	C ₁₅ H ₁₆ O ₁₀	9.2	355.1042	179.0709[M-H-GlcUA] ⁻ , 175.0244[M-H-CA] ⁻ , 135.0422[M-H-GlcUA-CO ₂] ⁻ , 113.0250[M-H-CA-CO ₂ -H ₂ O] ⁻ , 85.0293[M-H-CA-CO ₂ -H ₂ O-CO] ⁻
C7	Feruloylglycine	C ₁₂ H ₁₃ NO ₅	9.5	250.0723	232.0604[M-H-H ₂ O] ⁻ , 206.0821[M-H-CO ₂] ⁻ , 191.0778[M-H-CO ₂ -CH ₃] ⁻ , 163.0625[M-H-CO ₂ -CH ₃ -CO] ⁻ , 149.0458[M-H-CO ₂ -C ₂ H ₃ NO] ⁻ , 134.0374[M-H-CO ₂ -C ₂ H ₃ NO-CH ₃] ⁻ , 100.0046
C8	3'-Hydroxycinnamic acid or 4'-Hydroxycinnamic acid	C ₉ H ₈ O ₃	10.7	163.0354	119.0487[M-H-CO ₂] ⁻ , 93.0362[M-H-CO-C ₂ H ₂] ⁻
Phenylpropionic acid derivatives					
C9	3-(3'-Hydroxy-4'-methoxyphenyl)hydracrylic acid	C ₁₀ H ₁₂ O ₅	11.6	211.0617	193.0494[M-H-H ₂ O] ⁻ , 167.0708[M-H-CO ₂] ⁻ , 149.0662[M-H-H ₂ O-CO ₂] ⁻ , 123.0809[M-H-H ₂ O-CO ₂ -C ₂ H ₂] ⁻ , 107.0514[M-H-H ₂ O-CO ₂ -C ₂ H ₂ -CH ₄] ⁻ , 95.0495
C10	3-(3'-Methoxyphenyl) propionic	C ₁₀ H ₁₂ O ₇ S	8.6	275.0248	195.0664[M-H-SO ₃] ⁻ , 151.0765[M-H-SO ₃ -CO ₂] ⁻ ,

	acid-4'-sulfate				136.0530[M-H-SO ₃ -CO ₂ -CH ₃] ⁻ , 108.0488[M-H-SO ₃ -CO ₂ -CH ₃ -C ₂ H ₄] ⁻ , 79.9596[M-H-SO ₃ -CO ₂ -CH ₃ -C ₂ H ₄ -CO] ⁻
C11	3-(4'-Methoxyphenyl) propionic acid-3'-sulfate	C ₁₀ H ₁₂ O ₇ S	9.0	275.0225	233.0966, 195.0656[M-H-SO ₃] ⁻ , 151.0755[M-H-SO ₃ -CO ₂] ⁻ , 149.0605[M-H-SO ₃ -HCOOH] ⁻ , 136.0521[M-H-SO ₃ -CO ₂ -CH ₃] ⁻ , 119.0504, 108.0420[M-H-SO ₃ -CO ₂ -CH ₃ -C ₂ H ₄] ⁻ , 79.9593[M-H-SO ₃ -CO ₂ -CH ₃ -C ₂ H ₄ -CO] ⁻
C12	3-(3'-Methoxyphenyl) propionic acid-4'-O-glucuronide	C ₁₆ H ₂₀ O ₁₀	8.7	371.1014	353.0888[M-H-H ₂ O] ⁻ , 223.0615, 195.0658[M-H-GlcUA] ⁻ , 175.0239[M-H-3MPPA] ⁻ , 151.0698[M-H-GlcUA-CO ₂] ⁻ , 136.0465[M-H-GlcUA-CO ₂ -CH ₃] ⁻ , 135.0429[M-H-GlcUA-CO ₂ -CH ₄] ⁻ , 113.0242[M-H-3MPPA-CO ₂ -H ₂ O] ⁻ , 85.0309[M-H-3MPPA-CO ₂ -H ₂ O-CO] ⁻
C13	3-(4'-Methoxyphenyl) propionic acid-3'-O-glucuronide	C ₁₆ H ₂₀ O ₁₀	9.4	371.0998	353.0871[M-H-H ₂ O] ⁻ , 195.0665[M-H-GlcUA] ⁻ , 175.0247[M-H-4MPPA] ⁻ , 151.0744[M-H-GlcUA-CO ₂] ⁻ , 136.0532[M-H-GlcUA-CO ₂ -CH ₃] ⁻ , 113.0251[M-H-4MPPA-CO ₂ -H ₂ O] ⁻

Supplementary material

					85.0312[M-H-4MPPA-CO ₂ -H ₂ O-CO] ⁻
C14	3-(4'-Hydroxyphenyl) propionic acid or 3-(3'-Hydroxyphenyl) propionic acid ^c	C ₉ H ₁₀ O ₃	11.5	165.0522	137.0217[M-H-CO] ⁻ , 93.0345[M-H-CO-C ₂ H ₄ O] ⁻
C15	3-(3',4'-Dihydroxyphenyl) propionic acid	C ₉ H ₁₀ O ₄	8.0	181.0467	163.0383[M-H-H ₂ O] ⁻ , 135.0438[M-H-HCOOH] ⁻ , 121.0288[M-H-HCOOH-CH ₂] ⁻ , 93.0346
C16	3-(3'-Hydroxyphenyl) propionic acid-4'-sulfate	C ₉ H ₁₀ O ₇ S	7.3	261.0080	217.0176[M-H-CO ₂] ⁻ , 181.0502[M-H-SO ₃] ⁻ , 137.0608[M-H-SO ₃ -CO ₂] ⁻ , 122.0374[M-H-SO ₃ -CO ₂ -CH ₂] ⁻ , 121.0299[M-H-SO ₃ -CO ₂ -CH ₃] ⁻ , 79.9594
C17	3-(4'-Hydroxyphenyl) propionic acid-3'-sulfate	C ₉ H ₁₀ O ₇ S	8.1	261.0080	181.0510[M-H-SO ₃] ⁻ , 137.0611[M-H-SO ₃ -CO ₂] ⁻ , 121.0300[M-H-SO ₃ -CO ₂ -CH ₃] ⁻ , 109.0255[M-H-SO ₃ -CO ₂ -C ₂ H ₄] ⁻ , 79.9591
C18	3-(Phenyl)-2-propenoic acid-4'-sulfate	C ₉ H ₈ O ₆ S	8.6	242.9963	163.0393[M-H-SO ₃] ⁻ , 119.0504[M-H-SO ₃ -CO ₂] ⁻
C19	3-(Phenyl) propionic acid-4'-O-glucuronide	C ₁₅ H ₁₈ O ₉	9.0	341.0890	323.0805[M-H-H ₂ O] ⁻ , 227.1384, 175.0242[M-H-3PPA] ⁻ , 165.0554[M-H-GlcUA] ⁻ , 121.0661[M-H-GlcUA-CO ₂] ⁻ , 113.0234[M-H-3PPA-CO ₂ -H ₂ O] ⁻ , 85.0312[M-H-3PPA-CO ₂ -H ₂ O-CO] ⁻
C20	3-(Phenyl) propionic	C ₁₅ H ₁₈ O ₉	10.9	341.0920	175.0252[M-H-3PPA] ⁻ , 165.0567[M-H-GlcUA] ⁻

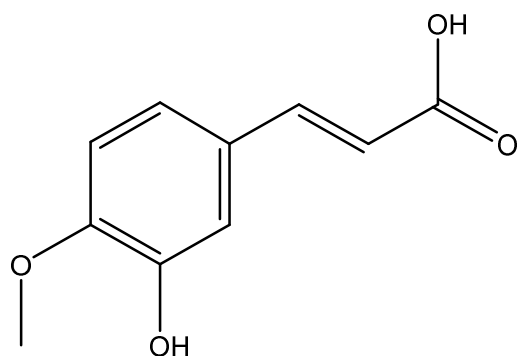
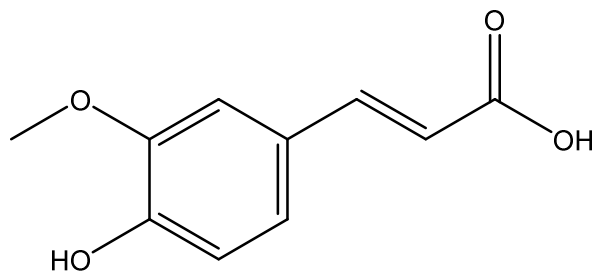
acid-3'-O-glucuronide					137.0230[M-H-GlcUA-CO] ⁻ , 113.0249[M-H-3PPA-CO ₂ -H ₂ O] ⁻ , 92.0285[M-H-GlcUA-CO C ₂ H ₅ O] ⁻ , 85.0322[M-H-3PPA-CO ₂ -H ₂ O-CO] ⁻
Benzoic acid derivatives					
C21	Benzoic acid-4-sulfate or Benzoic acid-3-sulfate	C ₇ H ₆ O ₆ S	6.6	216.9816	137.0243[M-H-SO ₃] ⁻ , 93.0360[M-H-SO ₃ -CO ₂] ⁻
C22	3-Hydroxybenzoic acid-4-sulfate	C ₇ H ₆ O ₇ S	6.7	233.0112	153.0201[M-H-SO ₃] ⁻ , 123.0544, 109.0307[M-H-SO ₃ -CO ₂] ⁻
C23	4-Hydroxybenzoic acid-3-sulfate	C ₇ H ₆ O ₇ S	7.2	232.9940	153.0195[M-H-SO ₃] ⁻ , 109.0302[M-H-SO ₃ -CO ₂] ⁻
Phenylacetic Acid Derivatives					
C24	Hydroxyphenylacetic acid-4'-sulfate or Hydroxyphenylacetic acid-3'-sulfate	C ₈ H ₈ O ₆ S	7.0	230.9968	151.0395[M-H-SO ₃] ⁻ , 107.0506[M-H-SO ₃ -CO ₂] ⁻
C25	3'-Methoxy-4'-hydroxyphenylacetic acid	C ₉ H ₁₀ O ₄	9.5	181.0501	137.0600[M-H-CO ₂] ⁻ , 122.0375[M-H-CO ₂ -CH ₃] ⁻ , 94.0423[M-H-CO ₂ -CH ₃ -CO] ⁻
Hydroxycarboxylic acid derivatives					

C26	3'-Methoxy-4'-hydroxymandelic acid	C ₉ H ₁₀ O ₅	5.8	197.0443	137.0244[M-H-HCOOH-CH ₂] ⁻ , 108.0211[M-H-HCOOH-CH ₂ -CHO] ⁻
Benzoylglycine Derivatives					
C27	Hippuric acid ^{b, c}	C ₉ H ₉ NO ₃	8.9	178.0511	134.0613[M-H-CO ₂] ⁻ , 102.0353[M-H-C ₆ H ₄] ⁻ , 77.0426[M-H-C ₃ H ₃ NO ₃] ⁻
C28	4'-Hydroxyhippuric acid	C ₉ H ₉ NO ₄	7.3	194.0418	150.0531[M-H-CO ₂] ⁻ , 121.0297[M-H-CO ₂ -CH ₃ N] ⁻ , 93.0348[M-H-CO ₂ -CH ₃ N-CO] ⁻
C29	3'-Hydroxyhippuric acid	C ₉ H ₉ NO ₄	10.3	194.0434	150.0543[M-H-CO ₂] ⁻ , 121.0290[M-H-CO ₂ -CH ₃ N] ⁻ , 93.0356[M-H-CO ₂ -CH ₃ N-CO] ⁻

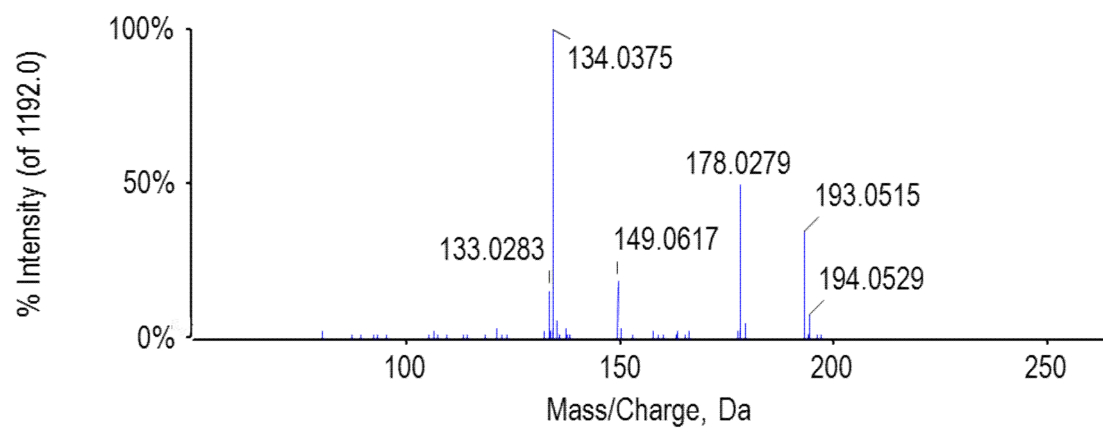
^a The losses are: FC=Ferulic acid; IFC= isoferulic acid; 3MPPA=3-(3'-methoxyphenyl) propionic acid; 4MPPA=3-(4'-methoxyphenyl) propionic acid; 3PPA=3-(phenyl) propionic acid, CA=caffeic acid.

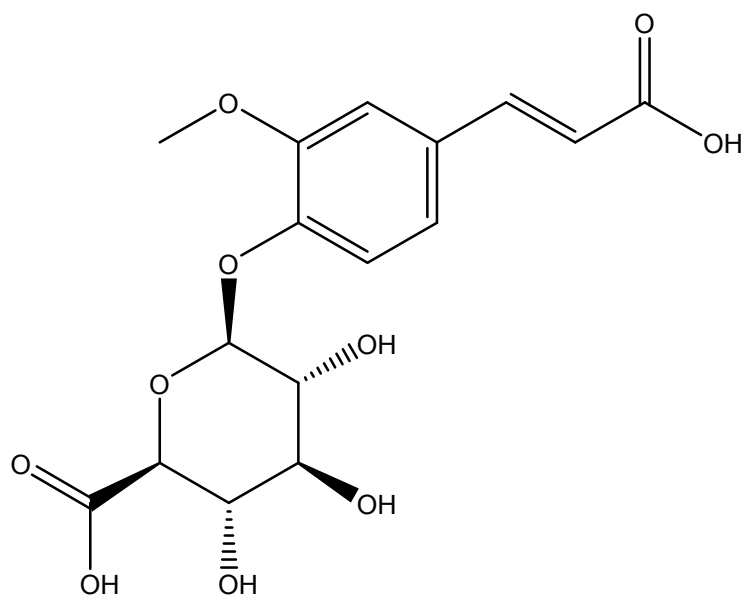
^b Confirmation in comparison with mass spectral library (Natural Products HR-MS/MS Spectral Library, Version 1.0, AB Sciex).

^c Confirmation in comparison with authentic standards.

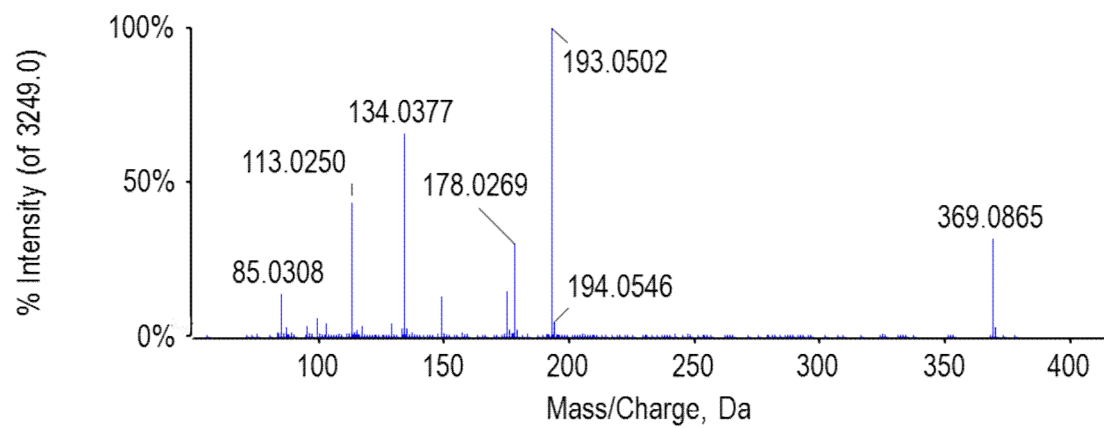
Structures, and product ion spectra of identified phenolic catabolites**C1. Ferulic acid or Isoferulic acid (RT=8.7 min)**

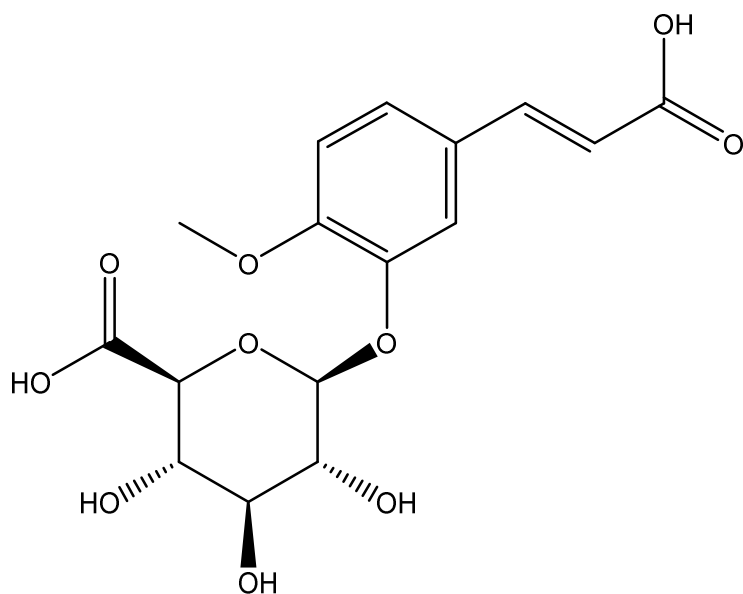
Spectrum from Urine_S3_1, -TOF MS² (50 - 1500) from 8.727 min
Precursor: 193.1 Da CE=-35



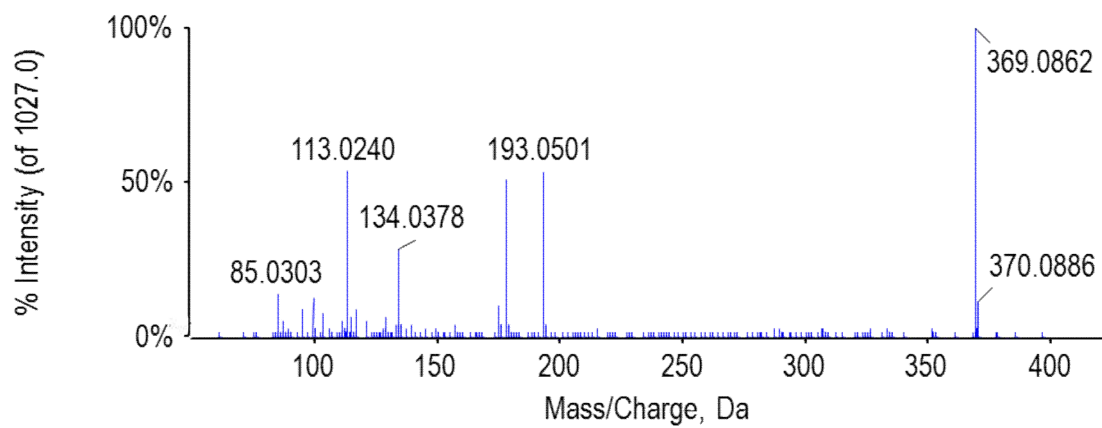
C2. Ferulic acid-4'-O-glucuronide (RT=8.3 min)

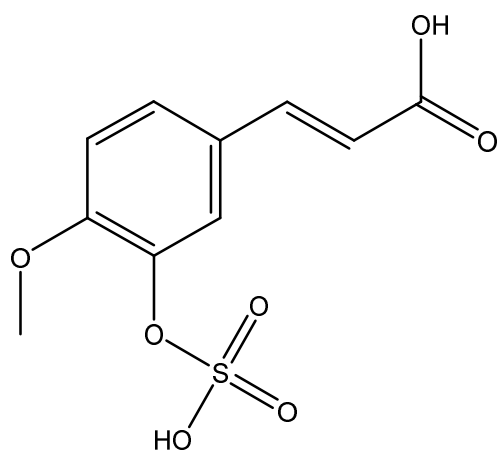
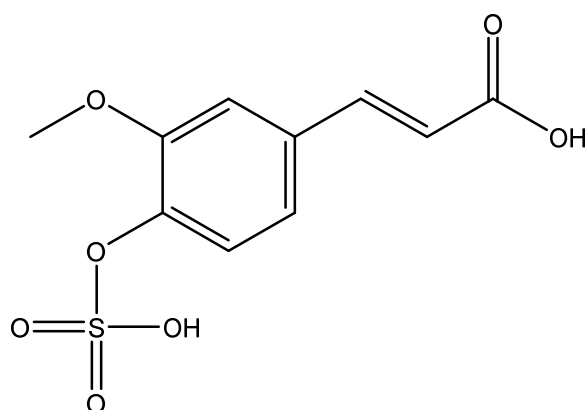
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 8.338 min
Precursor: 369.1 Da CE=-35



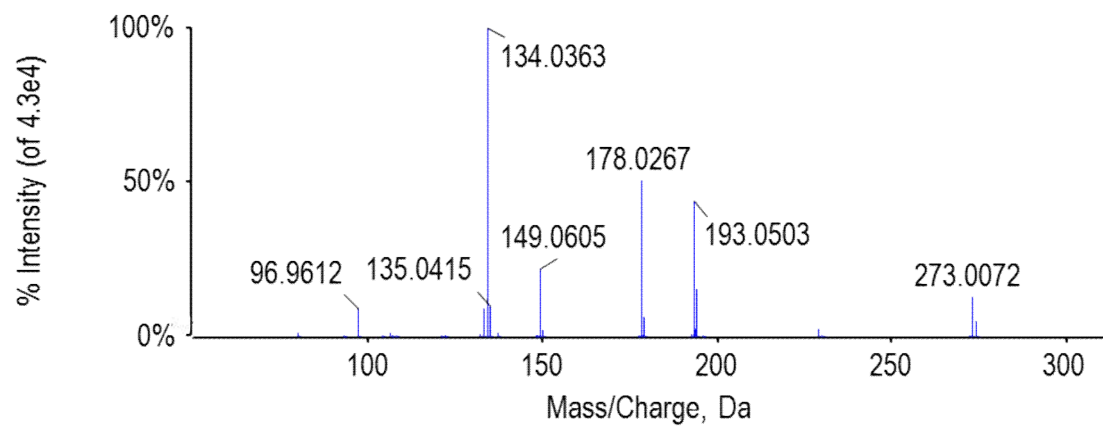
C3. Isoferulic acid-3'-O-glucuronide (RT=9.5 min)

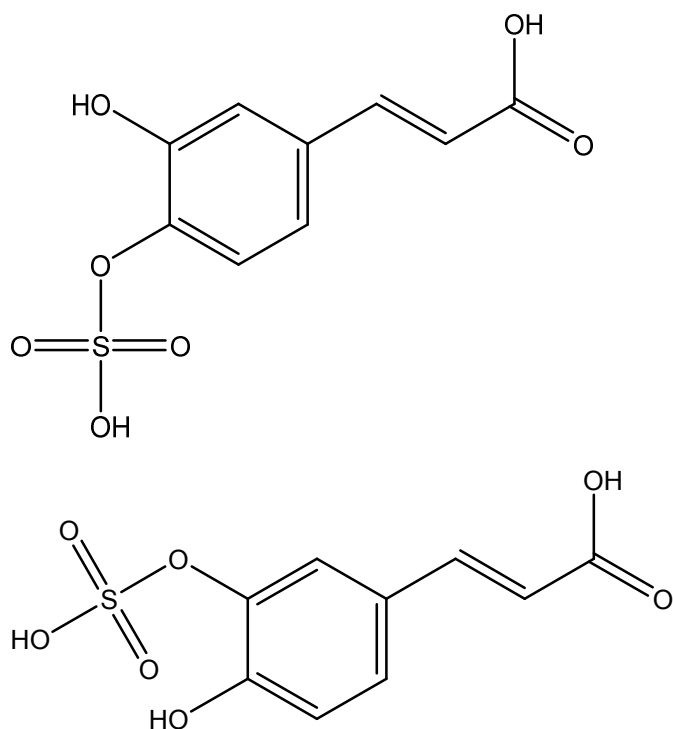
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 9.407 min
Precursor: 369.1 Da CE=-35



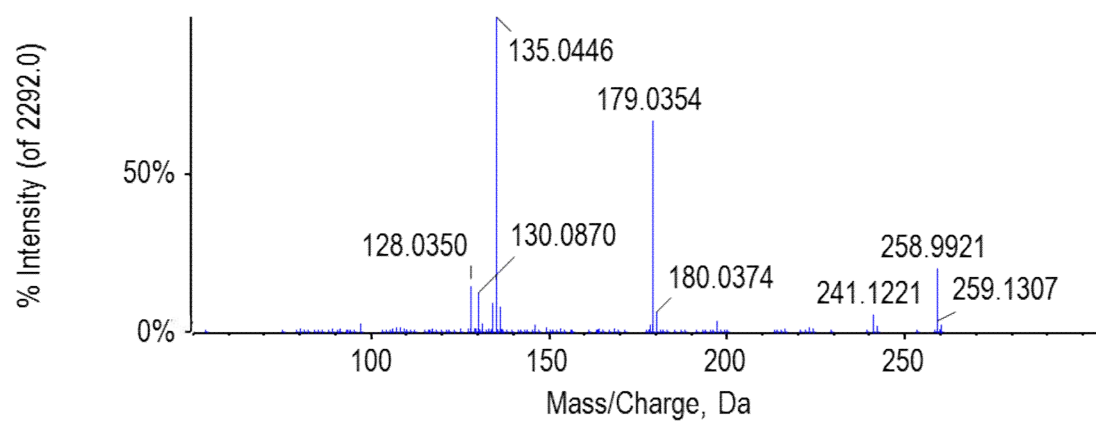
C4. Ferulic acid-4'-sulfate or Isoferulic acid-3'-sulfate (RT=8.8 min)

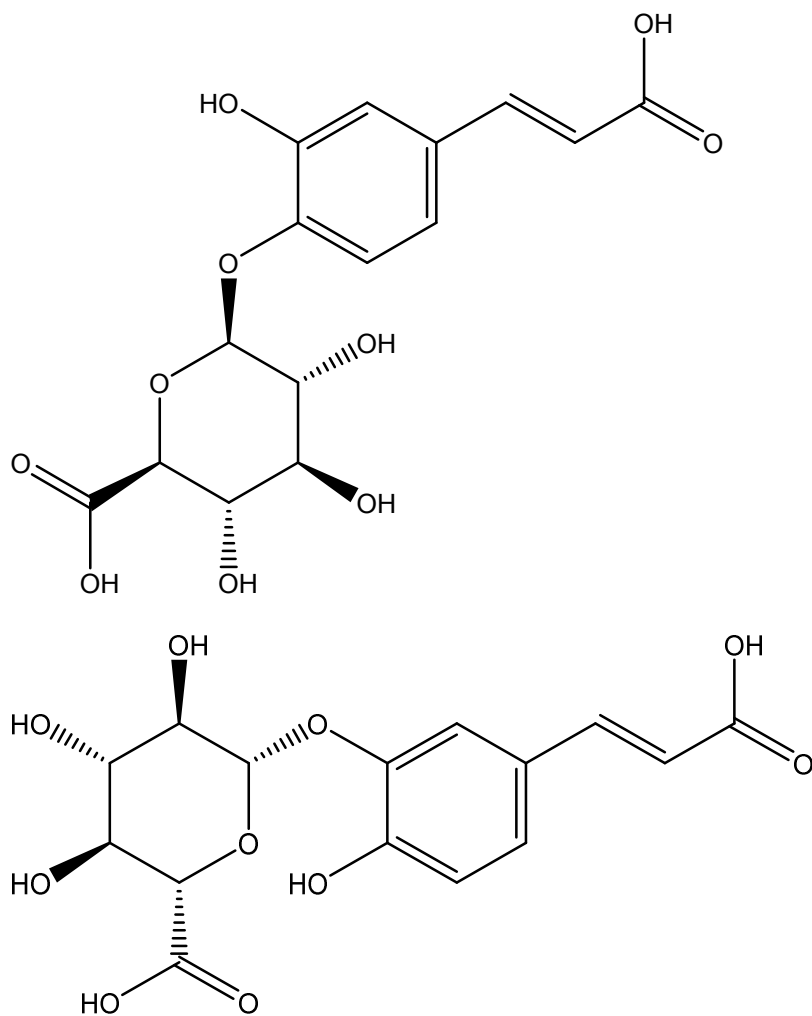
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 8.830 min
Precursor: 273.0 Da CE=35



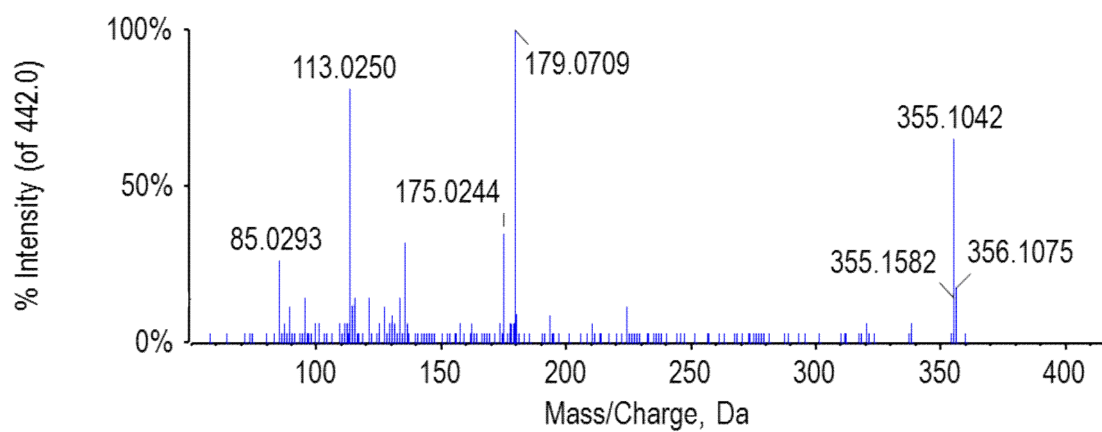
C5. Caffeic acid-4'-sulfate or Caffeic acid-3'-sulfate (RT=8.6 min)

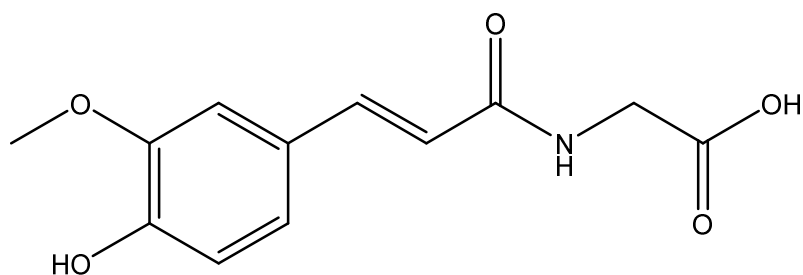
Spectrum from Urine_S2_2, -TOF MS² (50 - 1500) from 8.615 min
Precursor: 259.0 Da CE=35



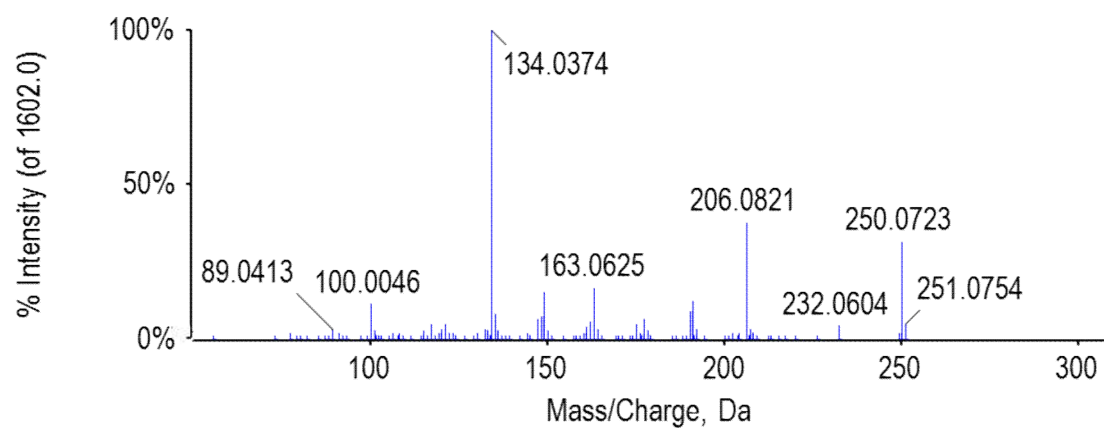
C6. Caffeic acid-4'-O-glucuronide or Caffeic acid-3'-O-glucuronide (RT=9.2 min)

Spectrum from Urine_S1_3, -TOF MS² (50 - 1500) from 9.154 min
Precursor: 355.1 Da CE=-35

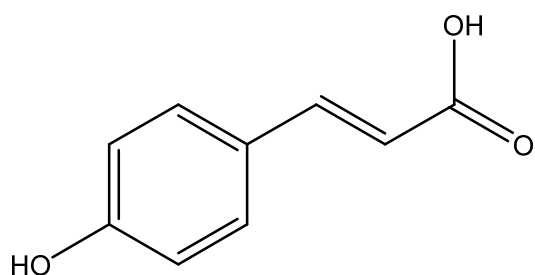
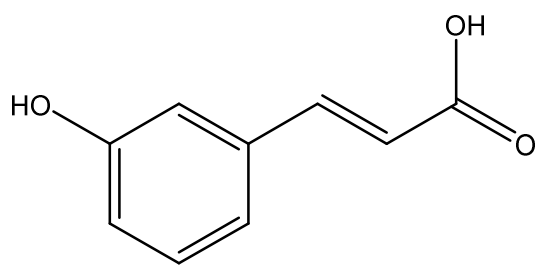


C7. Feruloylglycine (RT=9.5 min)

Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 9.523 min
Precursor: 250.1 Da CE=-35

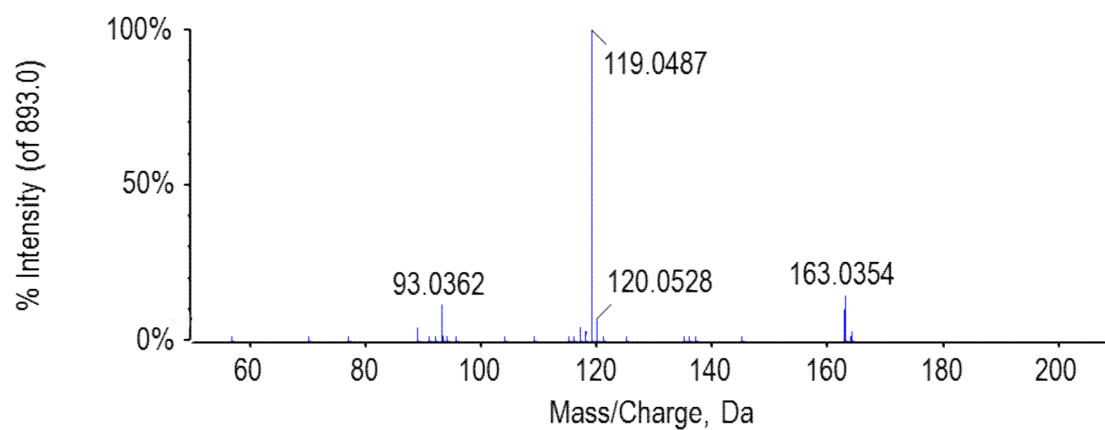


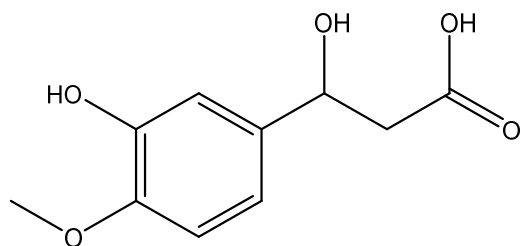
C8. 3'-Hydroxycinnamic acid or 4'-Hydroxycinnamic acid (RT=10.7 min)



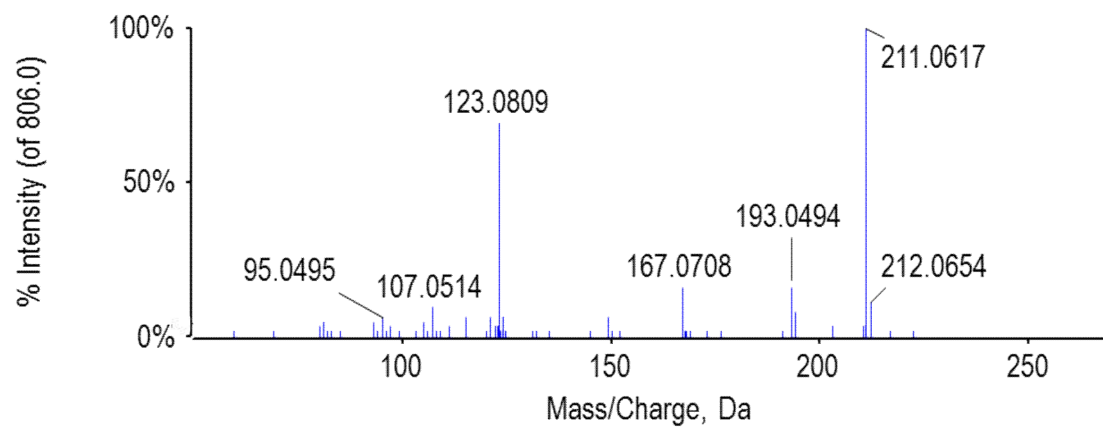
Spectrum from Urine_S2_3, -TOF MS² (50 - 1500) from 10.699 min

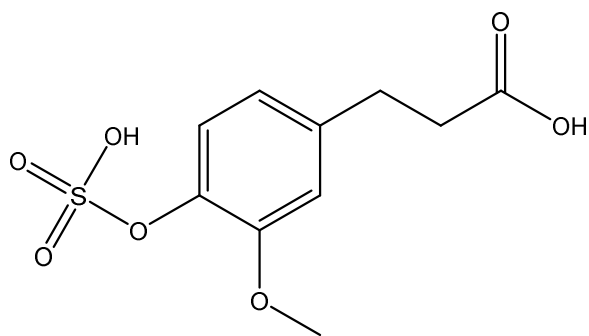
Precursor: 163.0 Da CE=-35



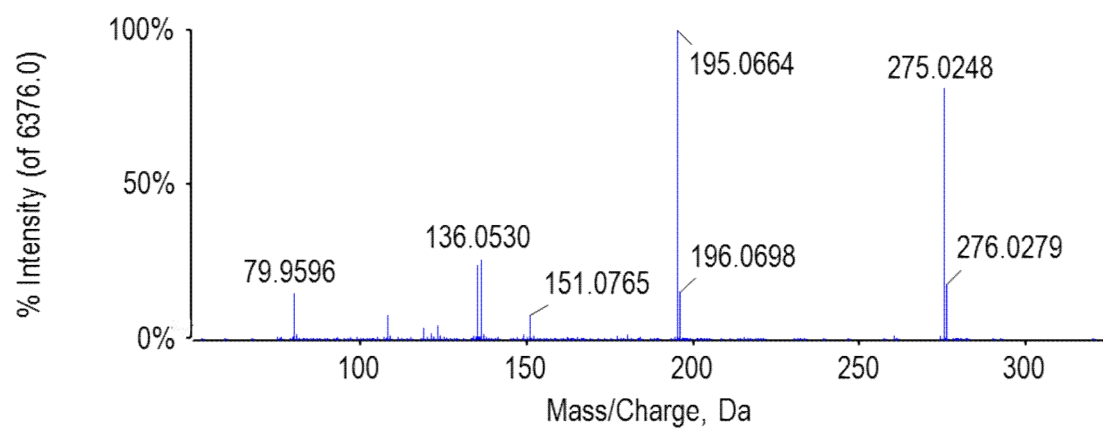
C9. 3-(3'-Hydroxy-4'-methoxyphenyl) hydracrylic acid (RT=11.6 min)

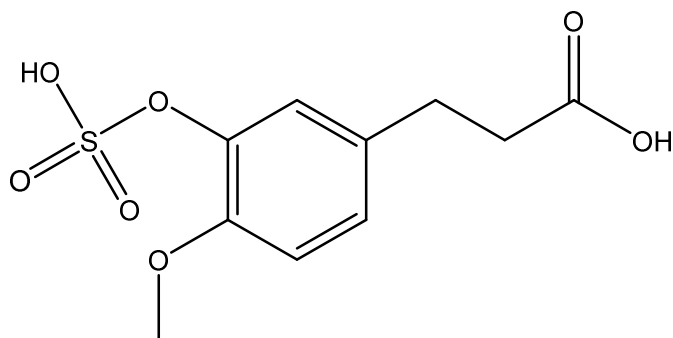
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 11.615 min
Precursor: 211.1 Da CE=-35



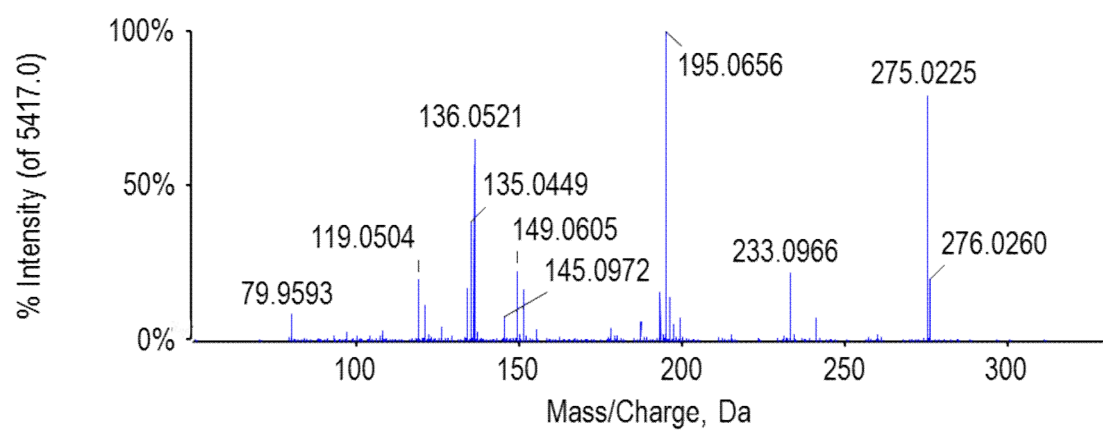
C10. 3-(3'-Methoxyphenyl) propionic acid-4'-sulfate (RT=8.6 min)Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 8.569 min

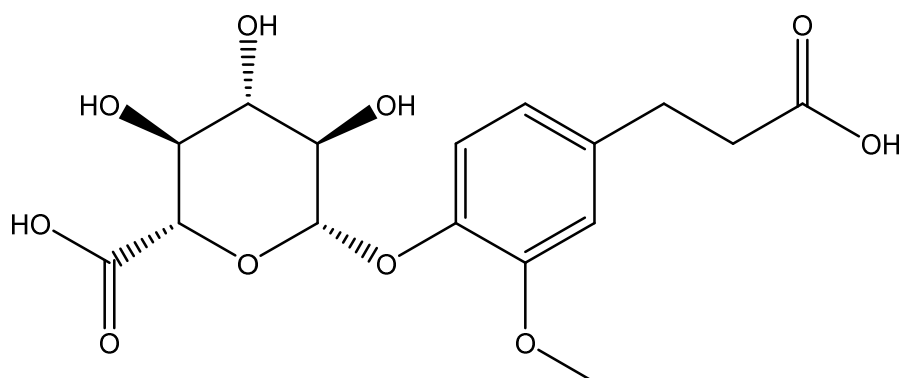
Precursor: 275.0 Da CE=-35



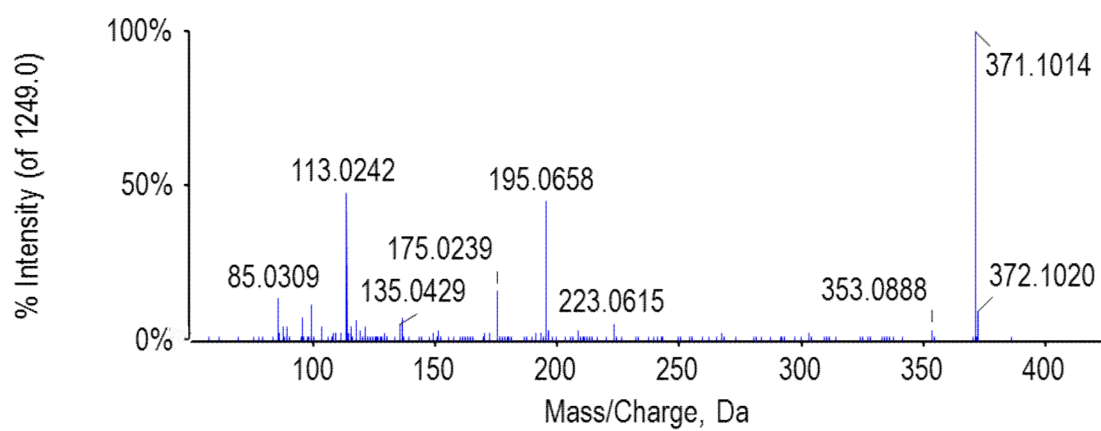
C11. 3-(4'-Methoxyphenyl) propionic acid-3'-sulfate (RT=9.0 min)Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 8.963 min

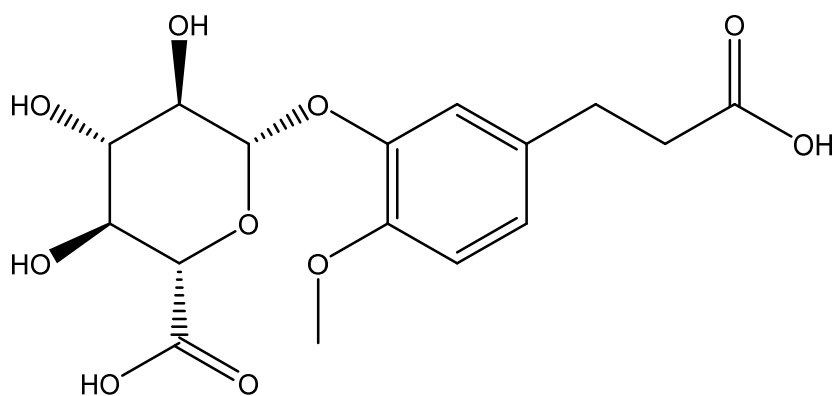
Precursor: 275.0 Da CE=-35



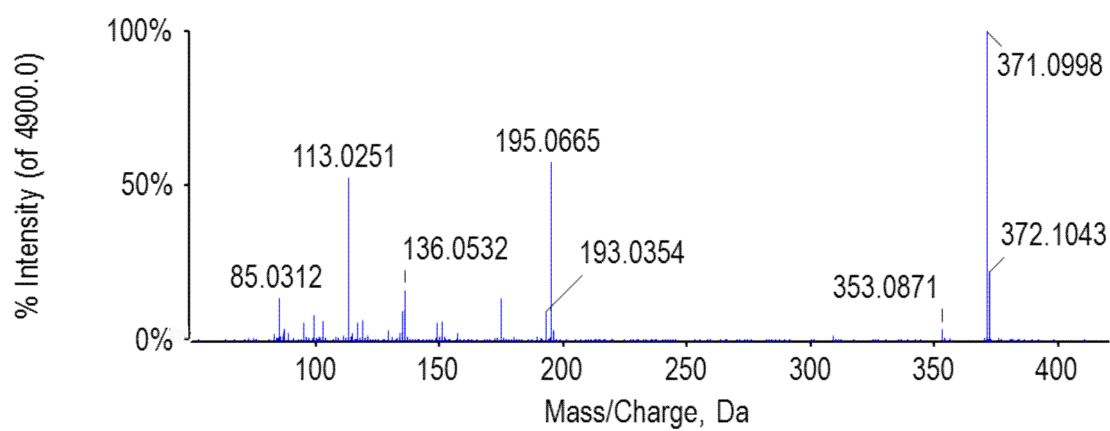
C12. 3-(3'-Methoxyphenyl) propionic acid-4'-O-glucuronide (RT=8.7 min)Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 8.624 min

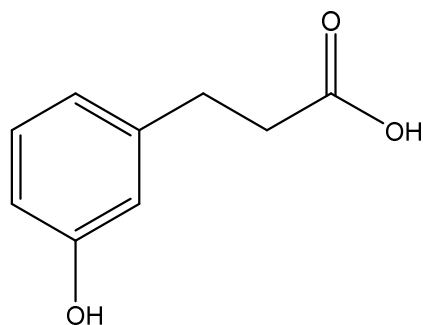
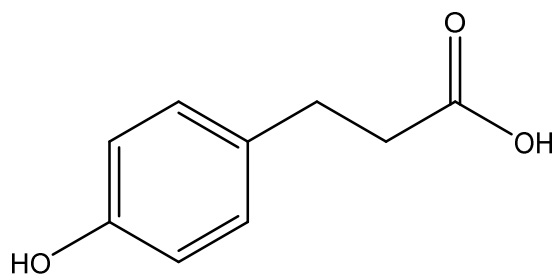
Precursor: 371.1 Da CE=-35



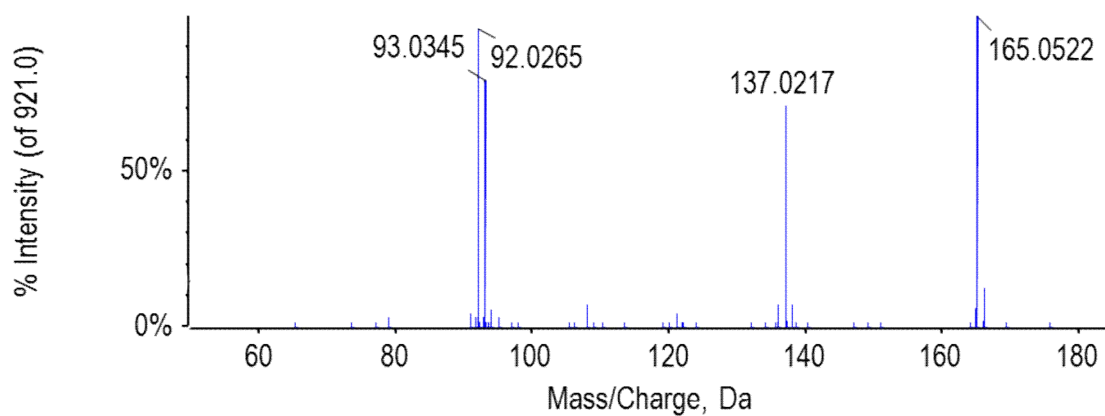
C13. 3-(4'-Methoxyphenyl) propionic acid-3'-O-glucuronide (RT=9.4 min)Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 9.440 min

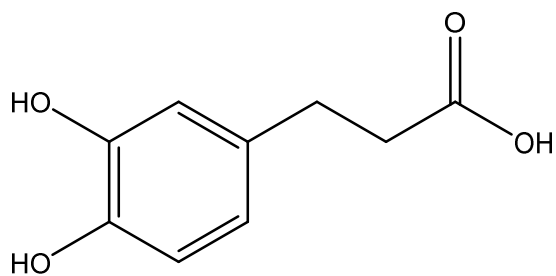
Precursor: 371.1 Da CE=-35



C14. 3-(4'-Hydroxyphenyl) propionic acid or 3-(3'-Hydroxyphenyl) propionic acid (RT=11.5 min)

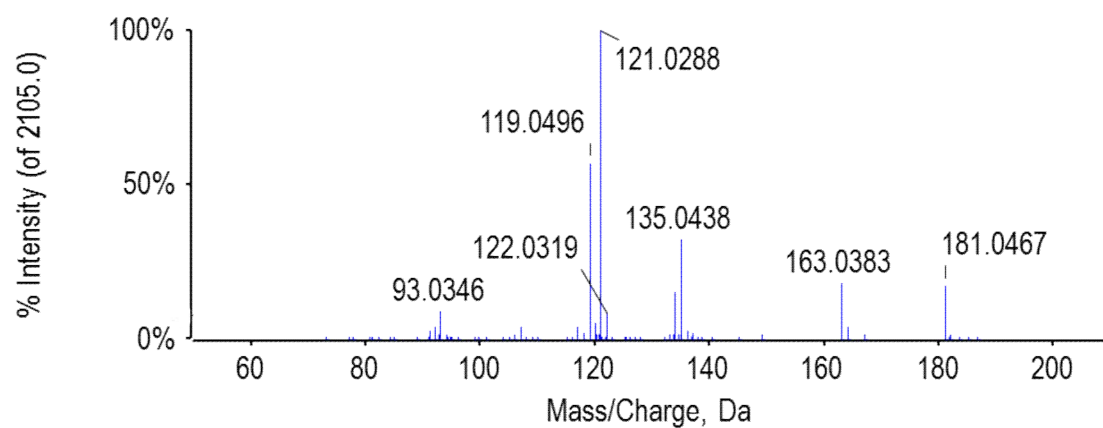
Spectrum from Urine_S2_3, -TOF MS² (50 - 1500) from 11.544 min
Precursor: 165.1 Da CE=-35

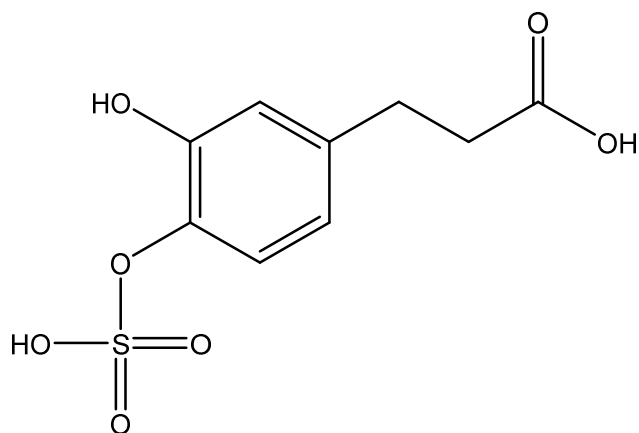


C15. 3-(3',4'-Dihydroxyphenyl) propionic acid (RT=8.0 min)

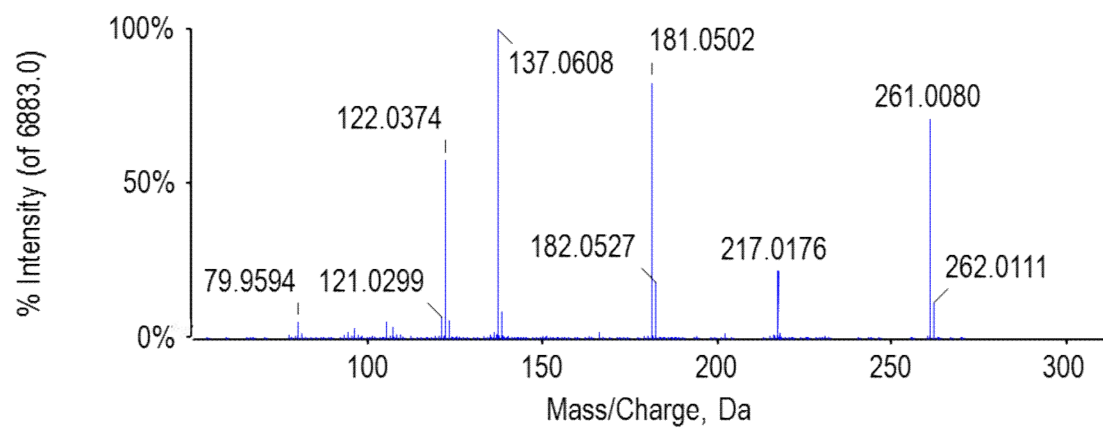
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 7.929 min

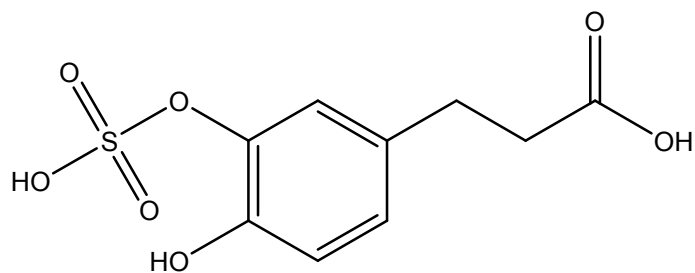
Precursor: 181.1 Da CE=-35



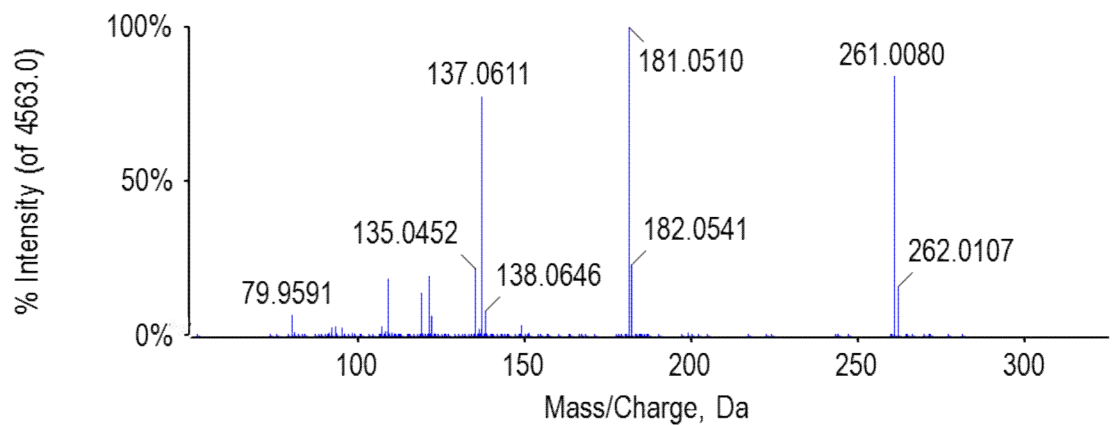
C16. 3-(3'-Hydroxyphenyl) propionic acid-4'-sulfate (RT=7.3 min)

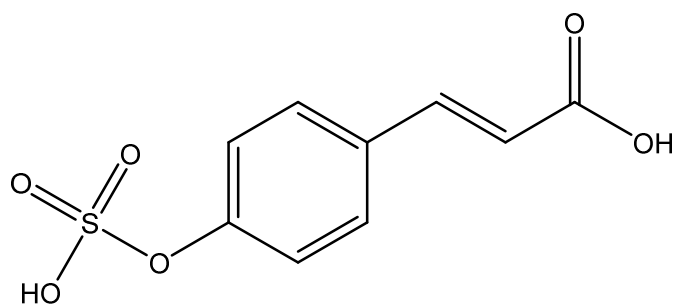
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 7.295 min
Precursor: 261.0 Da CE=35



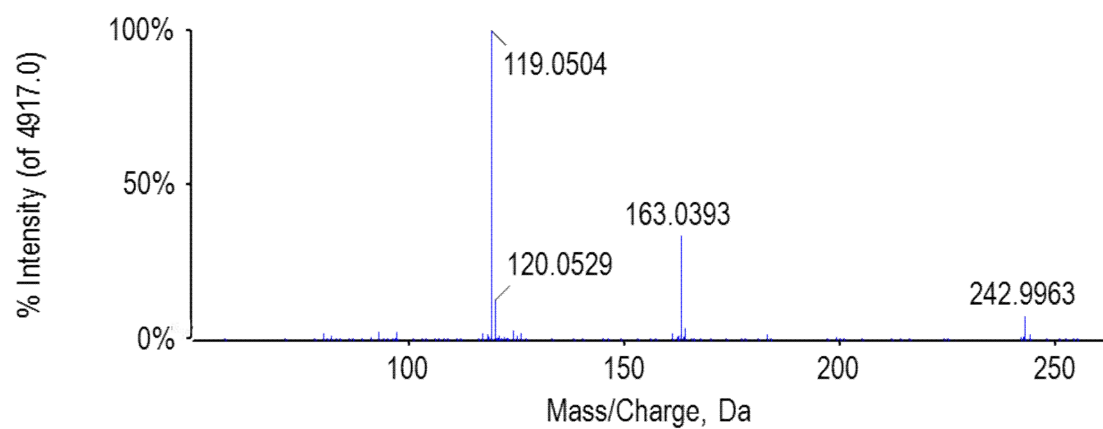
C17. 3-(4'-Hydroxyphenyl) propionic acid-3'-sulfate (RT=8.1 min)

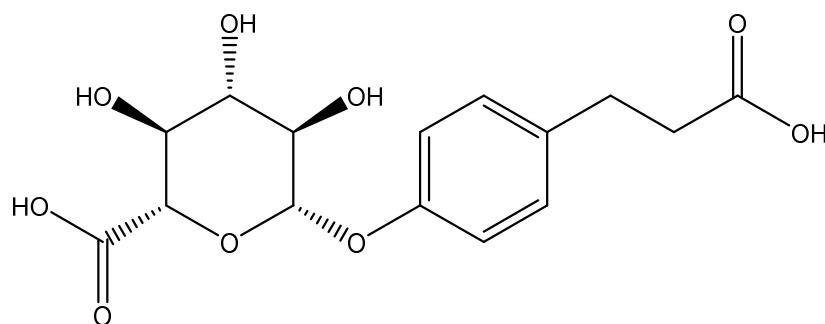
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 8.096 min
Precursor: 261.0 Da CE=-35



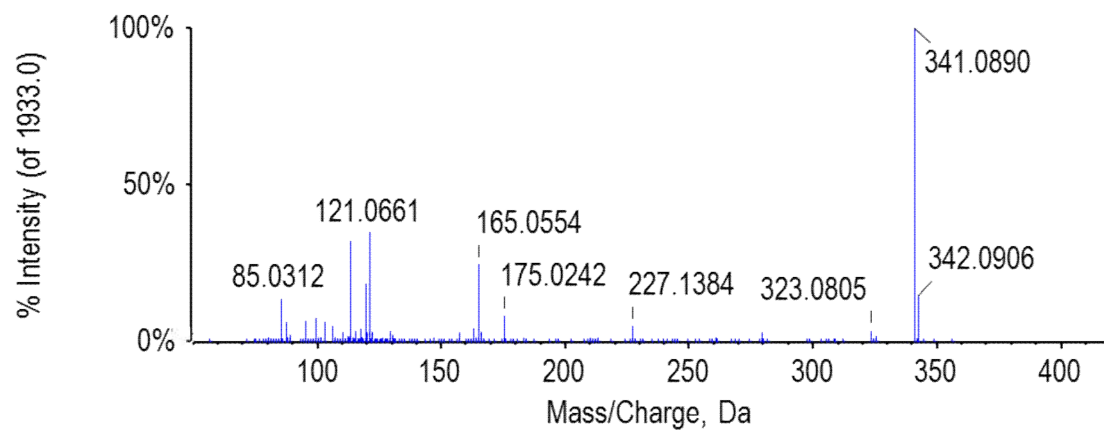
C18. 3-(Phenyl)-2-propenoic acid-4'-sulfate (RT=8.6 min)Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 8.617 min

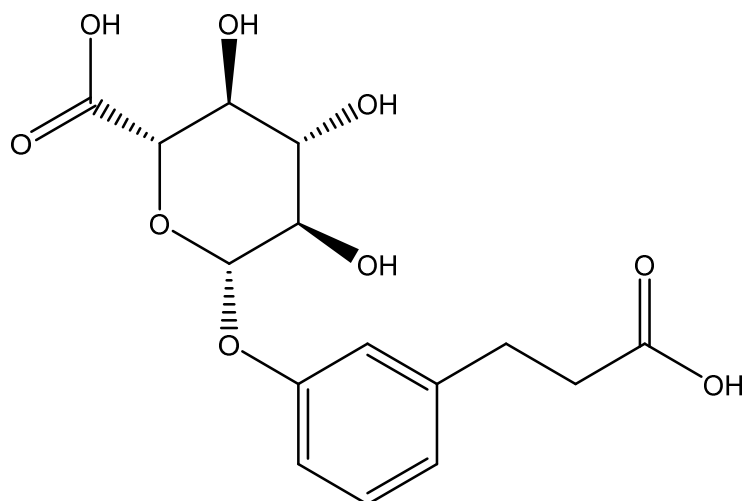
Precursor: 243.0 Da CE=-35



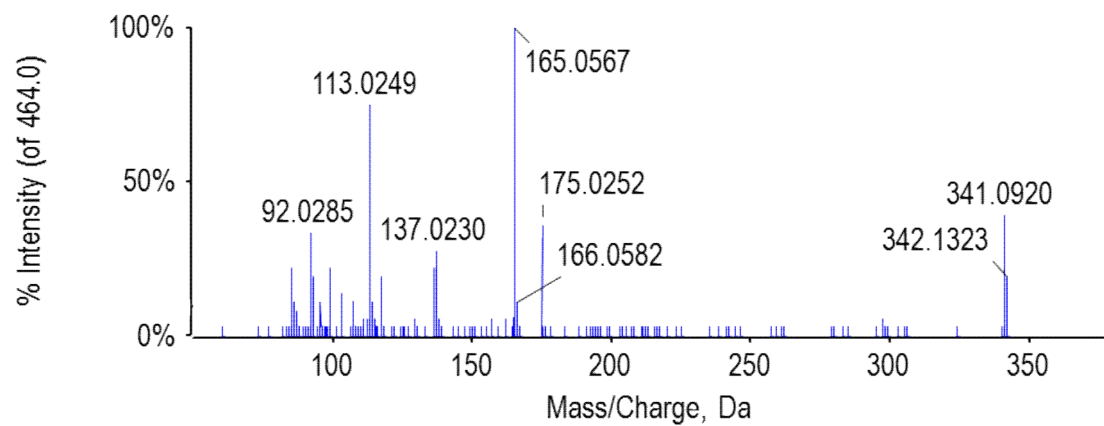
C19. 3-(Phenyl) propionic acid-4'-O-glucuronide (RT=9.0 min)Spectrum from Urine_S1_3, -TOF MS² (50 - 1500) from 8.929 min

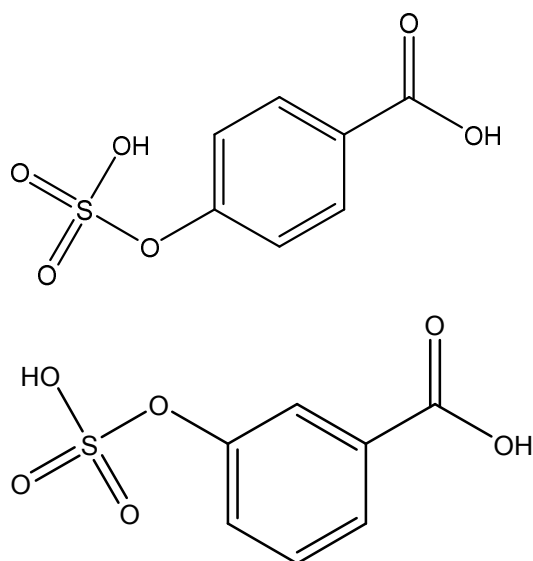
Precursor: 341.1 Da CE=-35



C20. 3-(Phenyl) propionic acid-3'-O-glucuronide (RT=10.9 min)

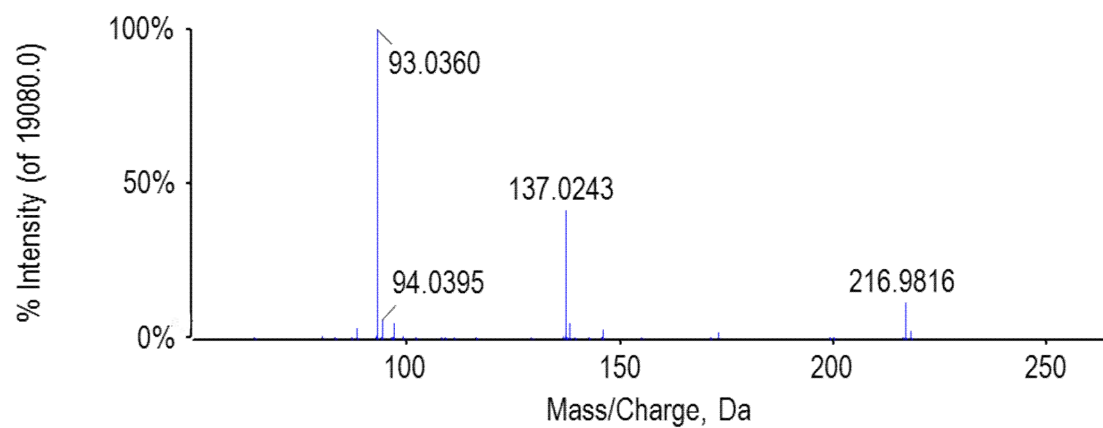
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 10.917 min
Precursor: 341.1 Da CE=-35

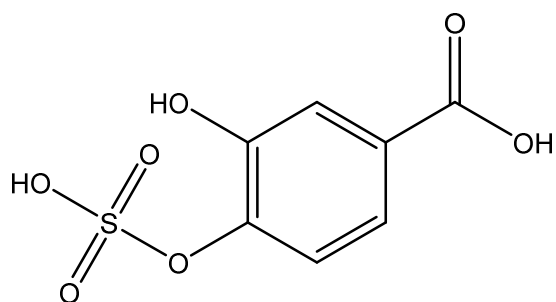


C21. Benzoic acid-4-sulfate or Benzoic acid-3-sulfate (RT=6.6 min)

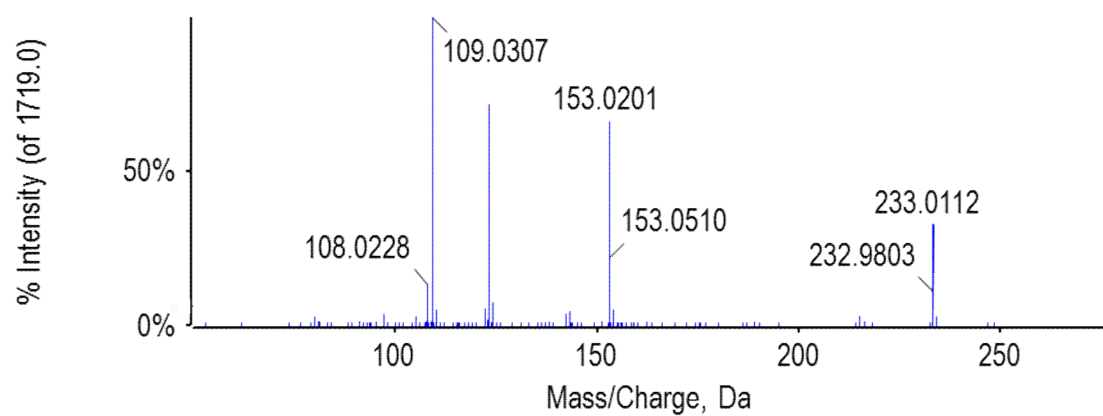
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 6.609 min

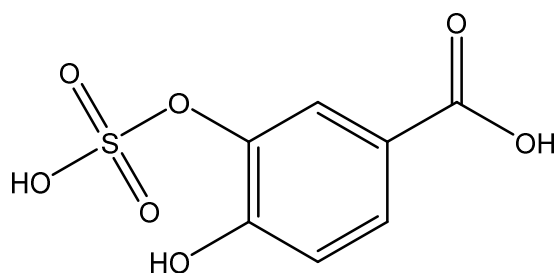
Precursor: 217.0 Da CE=-35



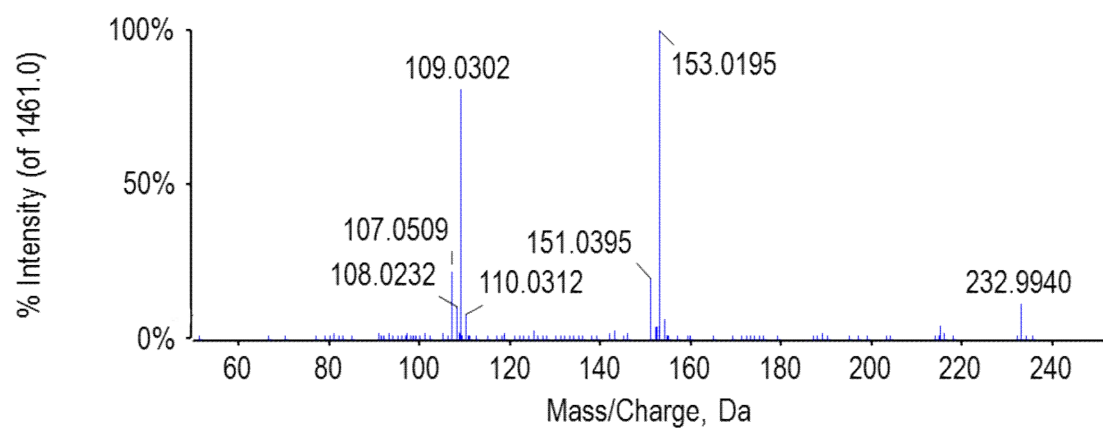
C22. 3-Hydroxybenzoic acid-4-sulfate (RT=6.7 min)

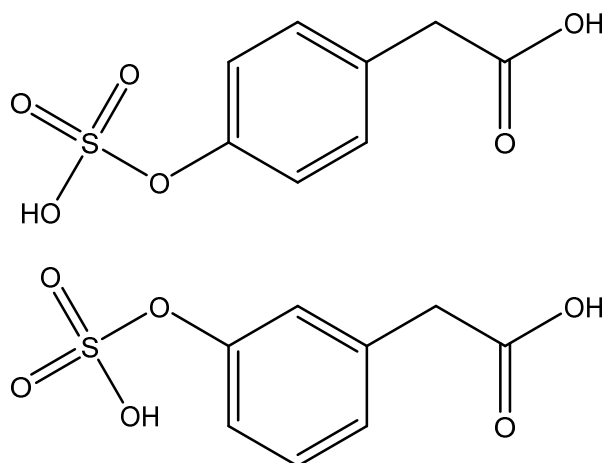
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 6.699 min
Precursor: 233.0 Da CE=-35



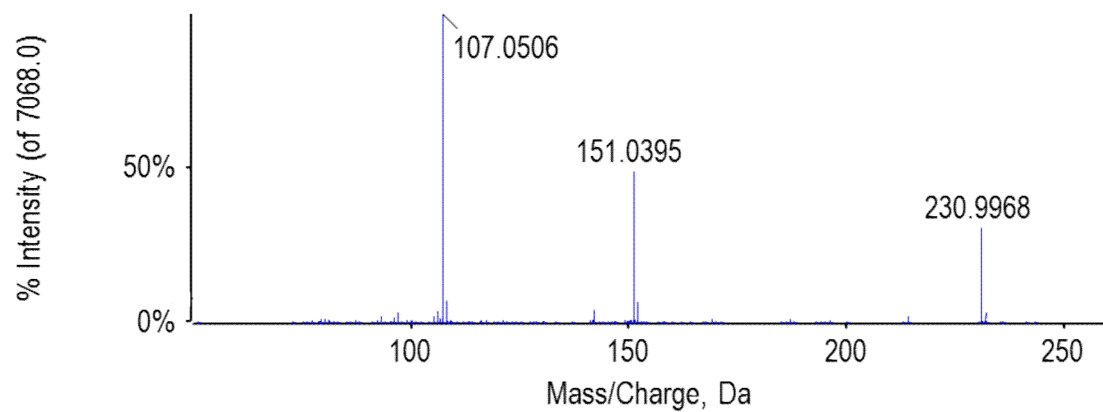
C23. 4-Hydroxybenzoic acid-3-sulfate (RT=7.2 min)

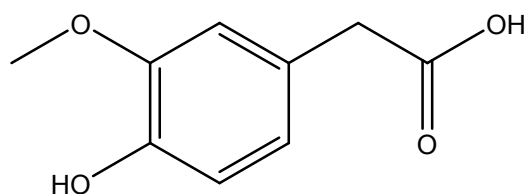
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 7.234 min
Precursor: 233.0 Da CE=-35



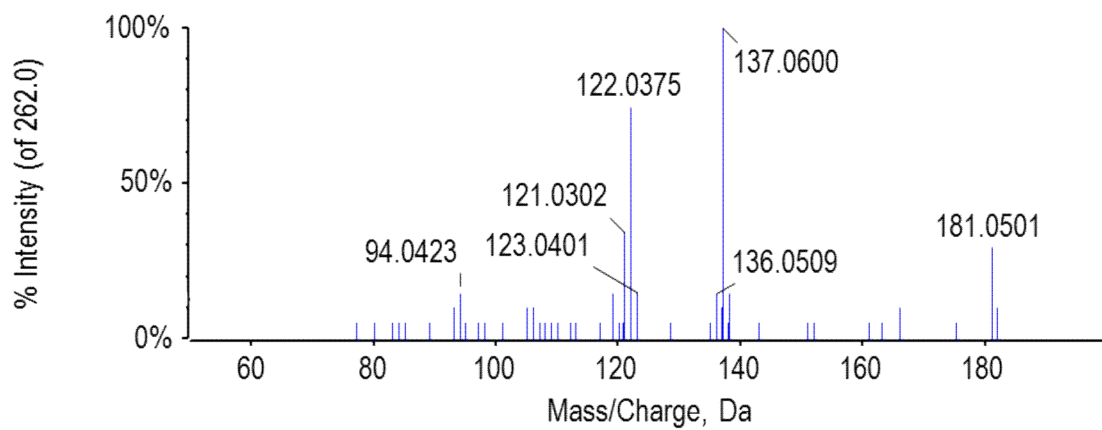
C24. Hydroxyphenylacetic acid-4'-sulfate or Hydroxyphenylacetic acid-3'-sulfate (RT=7.0 min)

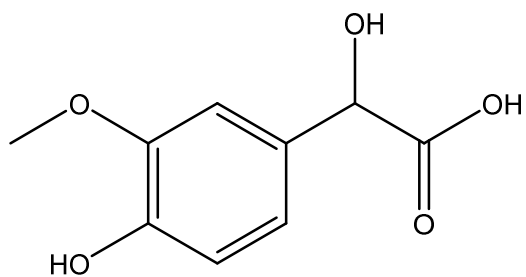
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 7.054 min
Precursor: 231.0 Da CE=-35



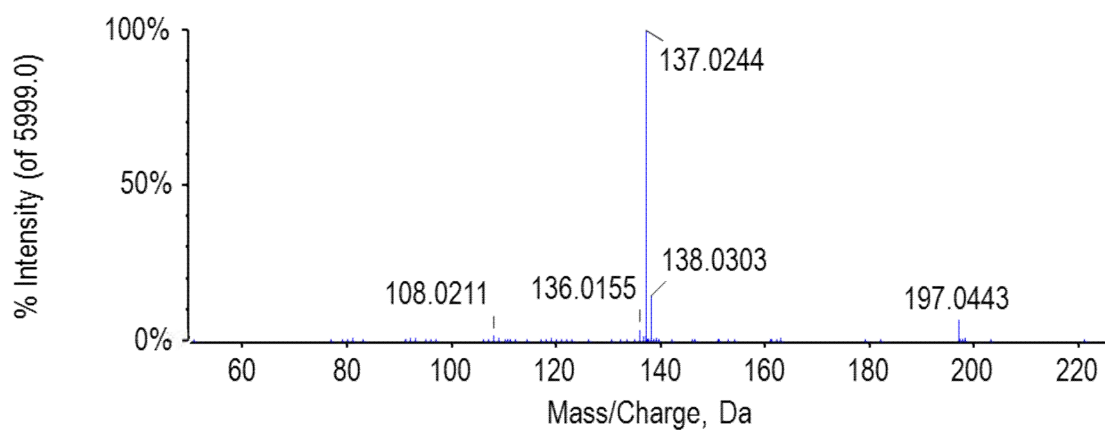
C25. 3'-Methoxy-4'-hydroxyphenylacetic acid (RT=9.5 min)Spectrum from Urine_S2_3, -TOF MS² (50 - 1500) from 9.398 min

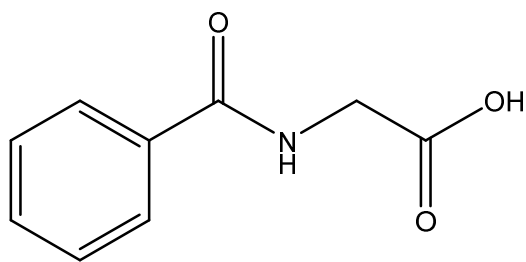
Precursor: 181.1 Da CE=-35



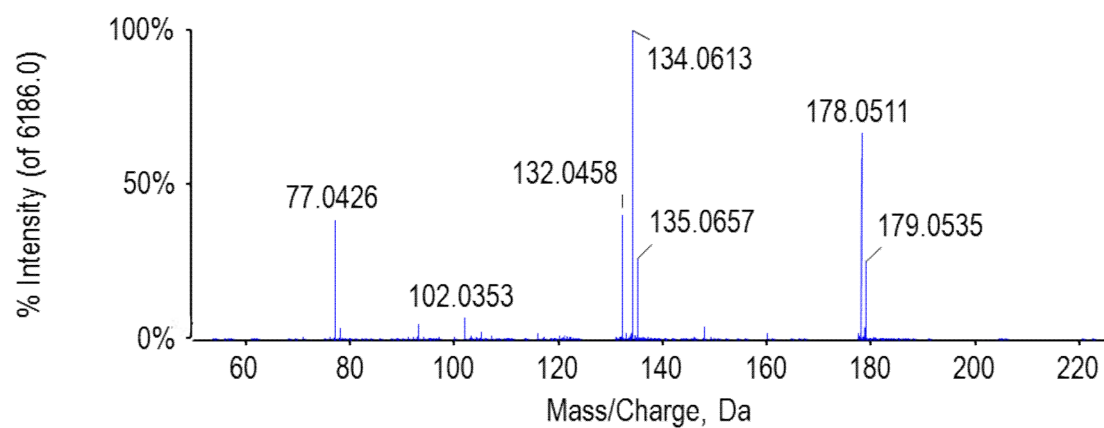
C26. 3'-Methoxy-4'-hydroxymandelic acid (RT=5.8 min)

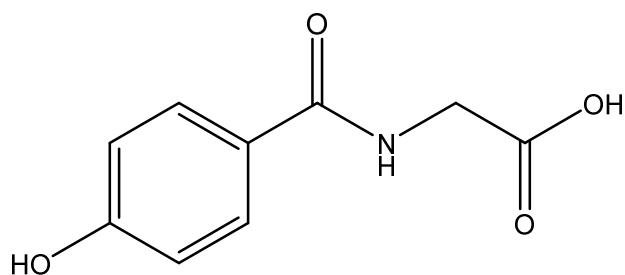
Spectrum from Urine_S2_3, -TOF MS² (50 - 1500) from 5.758 min
Precursor: 197.0 Da CE=-35



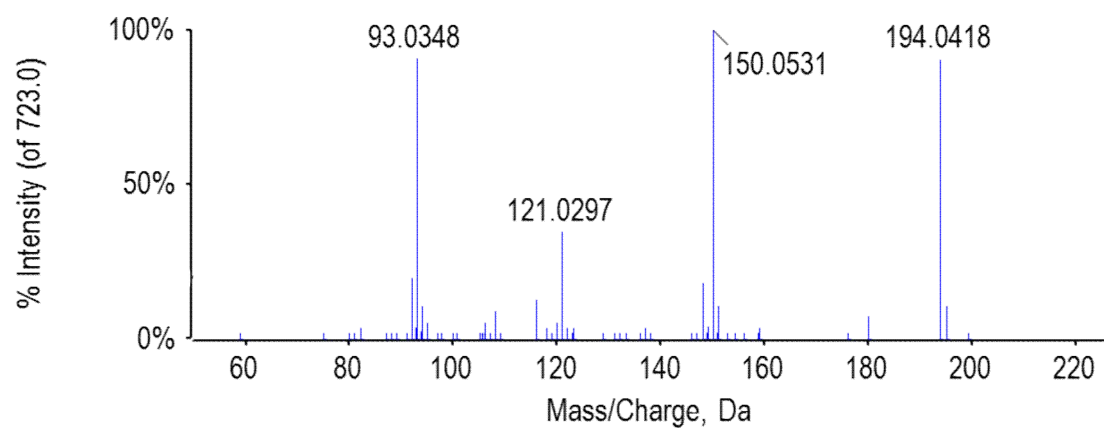
C27. Hippuric acid (RT=8.9 min)

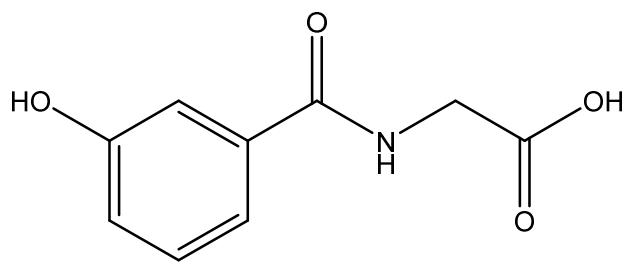
Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 8.869 min
Precursor: 178.1 Da CE=-35



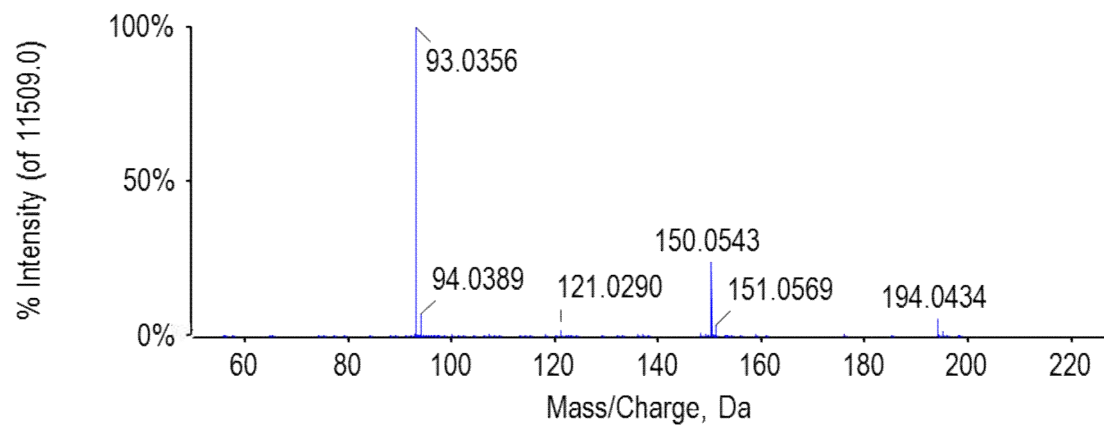
C28. 4'-Hydroxyhippuric acid (RT=7.3 min)Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 7.383 min

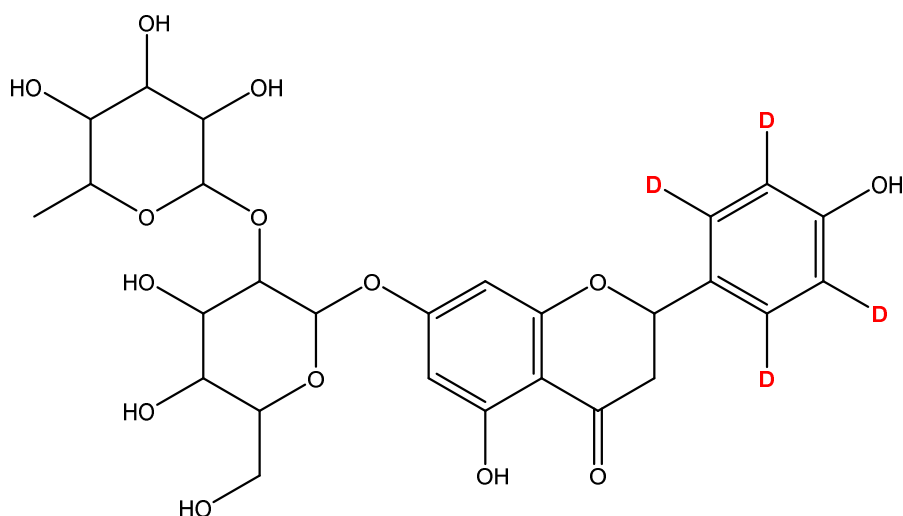
Precursor: 194.0 Da CE=-35



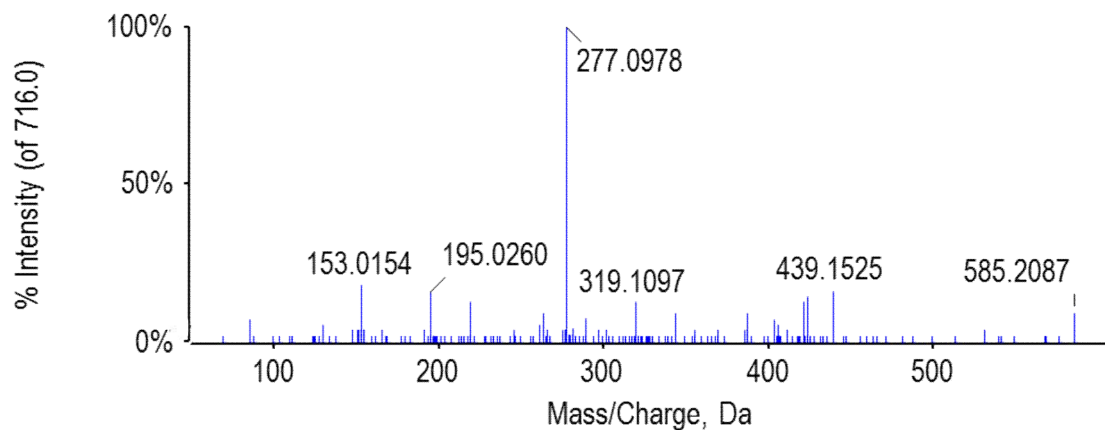
C29. 3'-Hydroxyhippuric acid (RT=10.3 min)

Spectrum from Urine_S1_2, -TOF MS² (50 - 1500) from 10.248 min
Precursor: 194.0 Da CE=-35



Part IV. Structures and product ion spectra of naringin-d4 (stable isotope labeled internal standard)**Naringin-d4 (RT=11.4 min)**

Spectrum from HJH_POS.wiff, +TOF MS² (50 - 1500) from 11.339 min
Precursor: 585.2 Da, CE=35



Spectrum from HJH_NEG.wiff, -TOF MS² (50 - 1500) from 11.345 min
Precursor: 583.2 Da CE=-35

