

**Proteomic and Direct Analysis in Real Time Mass Spectrometry Analysis of a Native
American Ceremonial Hat**

Timothy P. Cleland^{1*}, G. Asher Newsome^{1*}, R. Eric Hollinger²

*corresponding

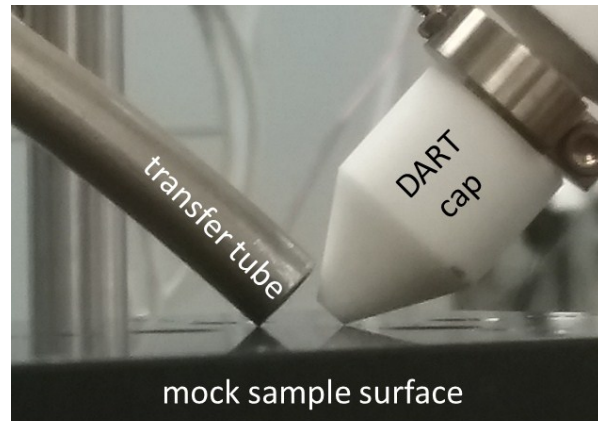
Electronic Supplementary Information

¹Smithsonian Institution, Museum Conservation Institute, Suitland, MD 20746

²Smithsonian Institution, National Museum of Natural History, Washington, DC 20560

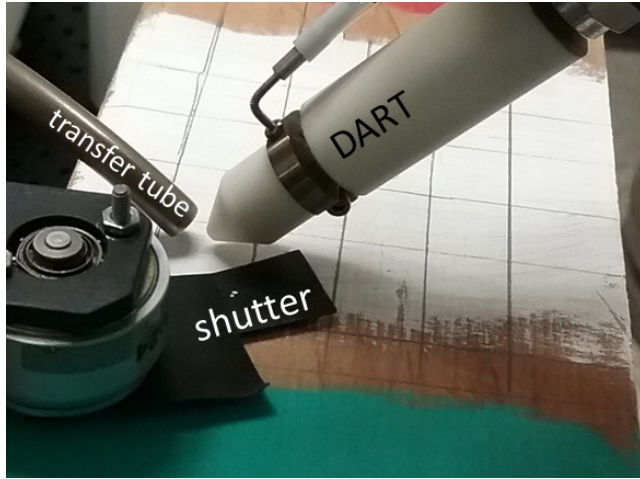


Supplementary Figure 1: Protein sampling locations from (A-B) the hat (E074339) and (C-D) the cylinder (E074441). TL numbers correspond to Tables 2 and 3.

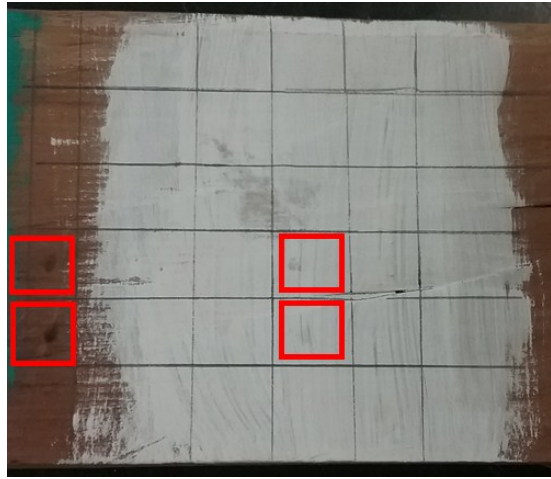


Supplemental Figure 2. Configuration for reflection mode DART with 30 cm transfer tube (shutter removed).

a)



b)

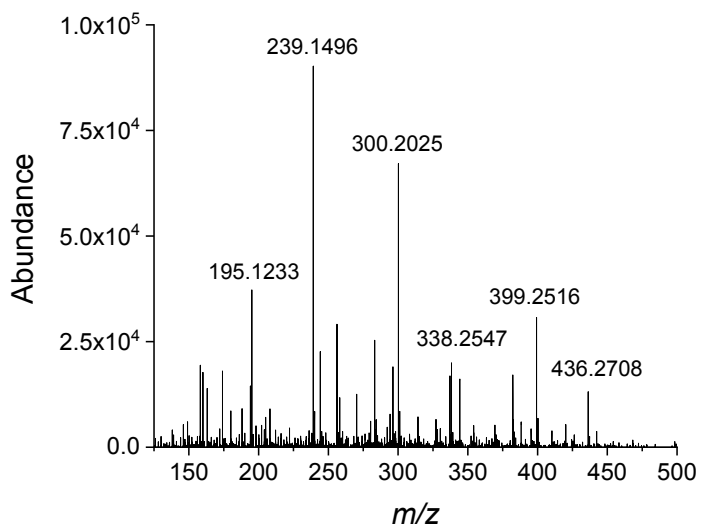


Supplemental Figure 3. Painted cedar wood test plank a) mounted for reflection mode DART analysis and b) following heated gas plume exposure. Areas with scorch marks resulting from 20 s exposures at 400 °C or higher helium temperature settings are highlighted in b) with red squares.

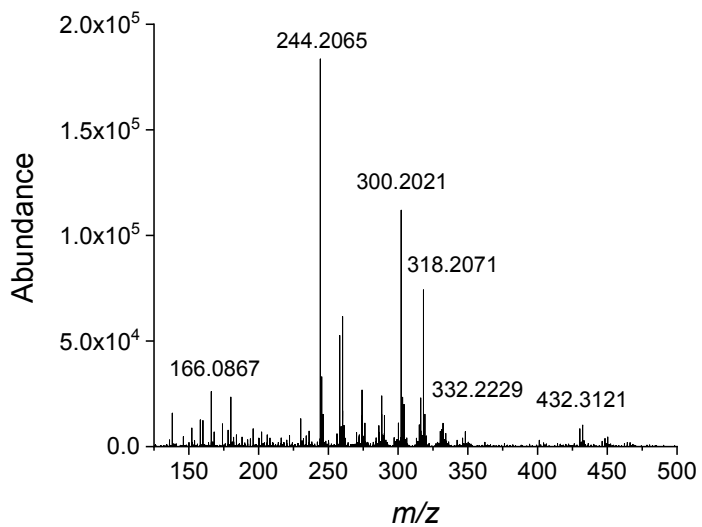


Supplementary Figure 4: DART sampling locations from (A-B) the hat (E074339) and (C-D) the cylinder (E074441). Listed names reflect Figure 3.

a)



b)



Supplemental Figure 5. Raw mass spectra observed from DART analysis of a) red-painted nose on hat (pictured in Figure 2a) and b) resin-coated, green-painted wood on edge of cylinder with 300 °C helium temperature setting.

Supplemental Table 1. Ions observed from DART analysis with 300 °C helium temperature setting of hat surfaces: 1) under rim, 2) interior rim, 3) stitch, 4) flat top, 5) surface green drop, 6) surface black fin, 7) red nose, 8) red front left, 9) and blue cheek.

ion mass	neutral chemical formula	Database ID	#1	#2	#3	#4	#5	#6	#7	#8	#9
138.0917	C ₈ H ₁₂ NO ⁺	1-(2-Methoxyethyl)pyridinium, fragment ion		√	√	√	√	√	√	√	√
149.0965	C ₁₀ H ₁₂ O	Anethole isomer		√		√	√	√		√	√
160.0762	C ₁₀ H ₉ NO	N-Acetylindole isomer	√	√	√	√	√	√	√	√	√
163.1233	C ₁₀ H ₁₄ N ₂	Nicotine		√	√	√	√	√	√	√	√
165.0914	C ₁₀ H ₁₂ O ₂	Eugenol isomer	√	√	√	√	√	√	√	√	√
166.0867	C ₉ H ₁₁ NO ₂	Benzocaine isomer		√	√	√	√	√	√	√	√
171.1022	C ₉ H ₁₄ O ₃	2-Furaldehyde diethyl acetal isomer			√					√	
174.0919	C ₁₁ H ₁₁ NO	N-Acetyl-2-methyl-indole isomer	√	√	√	√	√	√	√	√	√
175.0973	C ₈ H ₁₄ O ₄	Diethyl succinate isomer			√						
180.0813	C ₁₃ H ₉ N	Acridine isomer		√	√	√	√	√	√	√	√
180.1024	C ₁₀ H ₁₅ NO ₂	phenacetin isomer		√	√	√	√	√	√	√	√
188.1076	C ₁₂ H ₁₃ NO	N-Acetyl-2,3-dimethyl-indole isomer	√	√	√	√	√	√	√	√	√
189.1129	C ₉ H ₁₆ O ₄	Heptanedioic acid, dimethyl ester isomer			√						
195.1231	C ₈ H ₁₈ O ₅	Tetraethylene glycol			√	√	√	√	√	√	√
196.0974	C ₁₀ H ₁₃ NO ₃	Carbamic acid, 4-methoxyphenyl, ethyl ester isomer		√	√	√		√	√	√	√
202.1232	C ₁₃ H ₁₅ NO	(E)-3-Phenyl-1-(pyrrolidin-1-yl)prop-2-en-1-one isomer	√	√	√	√	√	√	√	√	√
206.1394	C ₉ H ₁₆ O ₄	Ammoniated C ₉ H ₁₆ O ₄			√						
208.1127	C ₁₅ H ₁₃ N	N-Benzylindole isomer	√	√	√	√	√	√	√	√	√
214.2534	C ₁₄ H ₃₁ N	1-Tetradecanamine isomer	√	√		√	√	√	√	√	√
218.1393	C ₁₀ H ₁₉ NO ₄	Glycine, N-methyl-N-ethoxycarbonyl-, isobutyl ester isomer			√			√		√	
228.2321	C ₁₄ H ₂₉ NO	Tetradecanamide isomer		√	√	√	√	√		√	√
230.1909	C ₁₆ H ₂₃ N	N-cyclohexyl-(2,4,6-trimethyl)benzaldehyde imine isomer		√		√	√	√	√	√	√

235.2064	C ₁₆ H ₂₆ O	Decyloxybenzene isomer			√	√					
237.1854	C ₁₅ H ₂₄ O ₂	Geranyl tiglate isomer			√	√	√	√		√	
239.1494	C ₁₀ H ₂₂ O ₆	Pentaethylene glycol		√	√	√	√	√	√	√	√
240.2328	C ₁₅ H ₂₉ NO	Propanamide, 3-cyclopentyl-N-heptyl-	√	√	√	√		√	√	√	
242.2847	C ₁₆ H ₃₅ N	1-Octanamine, n-octyl-		√		√	√	√	√	√	√
244.2064	C ₁₇ H ₂₅ N		√	√	√	√	√	√	√	√	√
254.2485	C ₁₆ H ₃₁ NO	But-2-enamide, N-decyl-N-methyl-3-methyl- isomer	√	√	√	√	√	√	√	√	√
256.2641	C ₁₆ H ₃₃ NO	Hexadecanamide isomer	√	√	√	√	√	√	√	√	√
258.1859	C ₁₇ H ₂₃ NO	Levorphanol isomer	√	√	√	√	√	√	√	√	√
260.1863	C ₁₃ H ₂₅ NO ₄	Glycine, N-methyl-N-ethoxycarbonyl-, heptyl ester isomer			√		√	√	√	√	
260.2016	C ₁₇ H ₂₅ NO	4'-Methyl-α-pyrrolidinohexanophenone isomer	√	√	√	√	√	√	√	√	√
263.0922	C ₁₄ H ₁₄ O ₅	8-(Hydroxymethyl)-6-methyl-2-oxo-2H-1-benzopyran-3-carboxylic acid, ethyl ester			√	√	√	√	√	√	√
263.2379	C ₁₈ H ₃₀ O	Farnesyl acetone isomer			√	√		√	√	√	
267.1750	C ₁₉ H ₂₂ O	Cyclohexanol,1-methyl-4,4-diphenyl-isomer			√	√	√	√		√	
269.0816	C ₁₆ H ₁₂ O ₄	4H-1-Benzopyran-4-one, 5-hydroxy-7-methoxy-2-phenyl-isomer		√	√	√	√	√		√	√
270.2071				√	√	√		√	√	√	√
270.3160	C ₁₈ H ₃₉ N	1-Octadecanamine isomer		√	√	√	√	√	√	√	√
274.1808	C ₁₇ H ₂₃ NO ₂	1,6-Octadien-3-ol, 3,7-dimethyl-, 2-aminobenzoate isomer	√	√	√	√	√	√	√	√	√
274.2020	C ₁₄ H ₂₇ NO ₄	Glycine, N-methyl-n-butoxycarbonyl-, isoheptyl ester isomer			√		√		√	√	
279.0941	C ₂₀ H ₁₀ N ₂		√		√	√		√	√	√	√
283.1700	C ₁₉ H ₂₂ O ₂	4-Butylbenzoic acid, 3,5-dimethylphenyl ester isomer		√	√	√		√	√	√	
283.1759	C ₁₂ H ₂₆ O ₇	Hexaethylene glycol	√	√	√	√	√		√	√	√
284.2954	C ₁₈ H ₃₇ NO	Octadecanamide isomer		√	√	√	√	√	√	√	√
285.1857	C ₁₉ H ₂₄ O ₂	4-Butylbenzoic acid, 3,5-		√	√	√	√	√		√	√

400.2702				√	√	√	√	√	√	√	√	√
401.3425	C ₂₇ H ₄₄ O ₂	7-Ketocholesterol isomer			√			√		√		
410.2546						√	√	√	√	√	√	√
410.2700	C ₂₆ H ₃₅ NO ₃	Glutaric acid, monoamide, N,N-di(4-methylphenyl)-, heptyl ester isomer	√	√				√				
412.2494	C ₂₅ H ₃₃ NO ₄	Etorphine isomer		√	√	√	√	√		√	√	
412.3432	C ₂₄ H ₄₅ NO ₄	Glycine, N-methyl-N-allyloxycarbonyl-, heptadecyl ester isomer		√	√	√	√	√	√	√	√	√
414.3013	C ₂₆ H ₃₉ NO ₃			√		√	√	√	√	√	√	√
414.3224	C ₂₃ H ₄₃ NO ₅			√	√	√	√	√	√	√	√	√
414.3588				√	√	√		√	√			
416.3168	C ₂₆ H ₄₁ NO ₃	Glutaric acid monoamide, N-(1,2,3,4-tetrahydronaphth-1-yl)-, undecyl ester isomer		√		√						√
420.2241	C ₂₂ H ₃₁ N ₂ O ₆				√	√		√	√	√	√	√
422.2912				√		√		√				
428.3381				√	√		√	√	√			
430.2964	C ₂₆ H ₃₉ NO ₄	Sebacic acid, 4-cyanophenyl nonyl ester isomer		√								
432.3121	C ₂₆ H ₄₁ NO ₄	Isonipecotic acid, N-(2-methoxybenzoyl)-, dodecyl ester		√		√						
436.2704	C ₂₄ H ₃₇ NO ₆	Sebacic acid, hexyl 2-(3-nitrophenyl)ethyl ester isomer				√	√	√	√	√	√	√
442.3174								√	√			
450.3226	C ₂₆ H ₄₃ NO ₅	2,6-Pyridinedicarboxylic acid, dodecyl 5-methoxy-3-methylpent-2-yl ester isomer		√								√
466.3176	C ₂₆ H ₄₃ NO ₆	Glycocholic acid		√		√			√			
500.3381	C ₃₀ H ₄₅ NO ₅											
506.2613	C ₂₄ H ₃₅ N ₅ O ₇	FDKP isomer			√	√	√	√	√	√	√	√

Supplemental Table 2. Ions observed from DART analysis with 300 °C helium temperature setting of cylinder and test plank surfaces: 10) top rim, 11) top rim with resin, 12) green drop, 13) crack green, 14) resin, 15) edge unpainted, 16) base rim, 17) raised nail head, and 18) test plank bare wood.

ion mass	neutral chemical formula	id	#10	#11	#12	#13	#14	#15	#16	#17	#18
138.0917	C ₈ H ₁₂ NO+	1-(2-Methoxyethyl)pyridinium, fragment ion	√	√	√		√	√	√		
149.0965	C ₁₀ H ₁₂ O	Anethole isomer		√	√			√	√		√
160.0762	C ₁₀ H ₉ NO	N-Acetylindole isomer	√	√	√		√	√	√		
163.1233	C ₁₀ H ₁₄ N ₂	Nicotine	√	√	√			√	√		
165.0914	C ₁₀ H ₁₂ O ₂	Eugenol isomer		√				√	√	√	√
166.0867	C ₉ H ₁₁ NO ₂	Benzocaine isomer	√	√	√		√	√	√		
171.1022	C ₉ H ₁₄ O ₃	2-Furaldehyde diethyl acetal isomer									
174.0919	C ₁₁ H ₁₁ NO	N-Acetyl-2-methyl-indole isomer	√	√	√	√	√	√	√		
175.0973	C ₈ H ₁₄ O ₄	Diethyl succinate isomer									
180.0813	C ₁₃ H ₉ N	Acridine isomer	√	√	√			√	√		
180.1024	C ₁₀ H ₁₅ NO ₂	phenacetin isomer	√	√	√		√	√	√		
188.1076	C ₁₂ H ₁₃ NO	N-Acetyl-2,3-dimethyl-indole isomer	√	√	√		√	√	√		
189.1129	C ₉ H ₁₆ O ₄	Heptanedioic acid, dimethyl ester isomer									
195.1231	C ₈ H ₁₈ O ₅	Tetraethylene glycol		√				√			
196.0974	C ₁₀ H ₁₃ NO ₃	Carbamic acid, 4-methoxyphenyl, ethyl ester isomer	√	√			√		√		
202.1232	C ₁₃ H ₁₅ NO	(E)-3-Phenyl-1-(pyrrolidin-1-yl)prop-2-en-1-one isomer	√	√	√		√	√	√		
206.1394	C ₉ H ₂₀ NO ₄										
208.1127	C ₁₅ H ₁₃ N	N-Benzylindole isomer	√	√	√		√	√	√		
214.2534	C ₁₄ H ₃₁ N	1-Tetradecanamine isomer	√	√	√		√		√		√
218.1393	C ₁₀ H ₁₉ NO ₄	Glycine, N-methyl-N-ethoxycarbonyl-, isobutyl ester isomer				√			√		

228.2321	C ₁₄ H ₂₉ NO	Tetradecanamide isomer	√	√	√			√	√		
230.1909	C ₁₆ H ₂₃ N	N-cyclohexyl-(2,4,6-trimethyl)benzaldehyde imine isomer	√	√	√	√	√	√	√		
235.2064	C ₁₆ H ₂₆ O	Decyloxybenzene isomer									
237.1854	C ₁₅ H ₂₄ O ₂	Geranyl tiglate isomer		√							√
239.1494	C ₁₀ H ₂₂ O ₆	Pentaethylene glycol	√	√					√		√
240.2328	C ₁₅ H ₂₉ NO	Propanamide, 3-cyclopentyl-N-heptyl-		√		√			√		
242.2847	C ₁₆ H ₃₅ N	1-Octanamine, n-octyl-	√	√	√						
244.2064	C ₁₇ H ₂₅ N		√	√	√	√	√	√	√		√
254.2485	C ₁₆ H ₃₁ NO	But-2-enamide, N-decyl-N-methyl-3-methyl- isomer	√	√	√	√		√	√		
256.2641	C ₁₆ H ₃₃ NO	Hexadecanamide isomer	√	√	√				√		
258.1859	C ₁₇ H ₂₃ NO	Levorphanol isomer	√	√	√	√	√	√	√		
260.1863	C ₁₃ H ₂₅ NO ₄	Glycine, N-methyl-N-ethoxycarbonyl-, heptyl ester isomer		√		√		√	√		
260.2016	C ₁₇ H ₂₅ NO	4'-Methyl- α -pyrrolidinohexanophenone isomer	√	√	√	√	√	√	√		
263.0922	C ₁₄ H ₁₄ O ₅	8-(Hydroxymethyl)-6-methyl-2-oxo-2H-1-benzopyran-3-carboxylic acid, ethyl ester									
263.2379	C ₁₈ H ₃₀ O	Farnesyl acetone isomer									
267.1750	C ₁₉ H ₂₂ O	Cyclohexanol,1-methyl-4,4-diphenyl-isomer	√	√	√			√	√		
269.0816	C ₁₆ H ₁₂ O ₄	4H-1-Benzopyran-4-one, 5-hydroxy-7-methoxy-2-phenyl-isomer	√	√	√			√	√		
270.2071				√		√		√	√		
270.3160	C ₁₈ H ₃₉ N	1-Octadecanamine isomer	√	√	√						
274.1808	C ₁₇ H ₂₃ NO ₂	1,6-Octadien-3-ol, 3,7-dimethyl-, 2-aminobenzoate isomer	√	√	√	√	√	√	√		
274.2020	C ₁₄ H ₂₇ NO ₄	Glycine, N-methyl-n-butoxycarbonyl-, isohexyl ester isomer		√		√		√	√		
279.0941	C ₂₀ H ₁₀ N ₂		√	√	√	√	√	√	√		
283.1700	C ₁₉ H ₂₂ O ₂	4-Butylbenzoic acid, 3,5-dimethylphenyl ester isomer	√		√				√		

283.1759	C ₁₂ H ₂₆ O ₇	Hexaethylene glycol										
284.2954	C ₁₈ H ₃₇ NO	Octadecanamide isomer	√									
285.1857	C ₁₉ H ₂₂ O ₂	4-Butylbenzoic acid, 3,5-dimethylphenyl ester isomer	√	√	√			√	√			
286.2020			√	√	√	√		√	√			
288.2176	C ₁₅ H ₂₉ NO ₄	Glycine, N-methyl-n-butoxycarbonyl-, heptyl ester isomer		√		√				√		
288.2330	C ₁₉ H ₂₉ NO	Procyclidine isomer	√	√			√	√				
288.2695	C ₂₀ H ₃₃ N		√	√	√			√	√			
290.2846	C ₂₀ H ₃₅ N	p-Tetradecylaniline		√	√			√	√			
292.2278	C ₁₈ H ₂₉ NO ₂	Nicotinic acid, dodecyl ester isomer	√	√	√	√	√	√	√			
294.2281	C ₁₄ H ₃₁ NO ₅	2-(2-{2-[2-(2-Diethylamino-ethoxy)-ethoxy]-ethoxy}-ethoxy)-ethanol	√	√	√	√		√	√			√
296.2594	C ₁₈ H ₃₃ NO ₂	Cyanoacetic acid, pentadecyl ester		√						√		
300.2025	C ₁₃ H ₂₅ N ₅ O ₃	L-Citrulline, N,N'-bis(dimethylaminomethylene)-, methyl ester	√	√	√			√	√			
301.2170	C ₂₀ H ₂₈ O ₂	Dehydroabietic acid isomer	√	√	√		√		√			√
302.2119	C ₁₉ H ₂₇ NO ₂	4-Cyanobenzoic acid, undecyl ester	√	√	√	√	√	√	√			
311.1649	C ₂₀ H ₂₂ O ₃	n-Butyl 4-oxo-4-(4-phenylphenyl)butanoate isomer	√	√	√			√	√			
314.2852	C ₂₂ H ₃₅ N			√	√	√		√	√			
315.1962	C ₂₀ H ₂₆ O ₃	m-Anisic acid, 2-(1-adamantyl)ethyl ester isomer	√	√	√		√	√	√			√
316.2126	C ₁₆ H ₂₉ NO ₅	l-Serine, N,O-bis(caproyl)-, methyl ester	√	√		√		√	√			
318.2072	C ₁₉ H ₂₇ NO ₃	1-Methyl-3-piperidyl cyclopentylphenylglycolate isomer	√	√	√		√	√	√			
327.2024	C ₁₄ H ₃₀ O ₈	Heptaethylene glycol				√						
329.2120	C ₂₁ H ₂₈ O ₃	7-Oxodehydroabietic acid, methyl ester isomer		√	√			√	√			
330.2283	C ₁₇ H ₃₁ NO ₅	1-Aminocyclopentanecarboxylic acid, N-(2-methoxyethoxycarbonyl)-, heptyl ester	√	√	√	√		√	√			

331.1912	C ₂₀ H ₂₆ O ₄	Dicyclohexyl phthalate isomer	√	√			√	√	√		
332.2229	C ₂₀ H ₂₉ NO ₃	1-Methyl-4-piperidyl cyclohexylphenylglycolate isomer	√	√	√		√	√	√		
337.1654	C ₁₈ H ₂₄ O ₆	Phthalic acid, butyl ester, ester with butyl glycolate isomer	√	√							
338.2547	C ₁₆ H ₃₅ NO ₆	2-[2-(2-{2-[2-(2-Diethylamino-ethox y)-ethoxy]-ethoxy}-ethoxy)-ethoxy]- ethanol	√	√		√		√	√		√
344.2289	C ₁₅ H ₂₉ N ₅ O ₄										
344.2438	C ₁₈ H ₃₃ NO ₅		√	√	√	√		√	√		
354.1918	C ₁₈ H ₂₇ NO ₆	Desoxyaxillarine isomer	√		√	√		√	√		
354.3009	C ₂₁ H ₃₉ NO ₃	Sarcosine, N-(cyclohexylcarbonyl)-, undecyl ester isomer	√	√	√			√	√		
356.2440	C ₁₉ H ₃₃ NO ₅		√	√	√	√		√	√		
356.3525	C ₂₂ H ₄₅ NO ₂	Carbonic acid, monoamide, N- octadecyl-, propyl ester isomer		√		√		√	√		
358.2596	C ₁₉ H ₃₅ NO ₅		√	√	√	√		√	√		
368.3168	C ₂₂ H ₄₁ NO ₃	Sarcosine, N-(3-methylbut-2-enoyl)-, tetradecyl ester isomer	√	√	√	√		√	√		
369.3850	C ₂₃ H ₄₈ N ₂ O	N-[3- (dimethylamino)propyl]octadecanamid e									
370.2597	C ₂₀ H ₃₅ NO ₅		√	√	√	√	√	√	√		
370.2961	C ₂₁ H ₃₉ NO ₄	Isonipecotic acid, N- isobutoxycarbonyl-, decyl ester isomer	√	√	√	√		√	√		√
370.3322	C ₂₂ H ₄₃ NO ₃	Oleic diethanolamide isomer	√	√	√	√		√	√		
372.2753	C ₁₉ H ₃₇ NO ₅		√	√	√	√		√	√		
378.2650	C ₂₂ H ₃₅ NO ₄	Sarcosine, N-(4-methoxybenzoyl)-, undecyl ester isomer	√	√	√			√	√		
382.2233			√	√	√	√		√	√		
382.2810	C ₁₉ H ₃₅ N ₅ O ₃			√		√		√			√
383.3321	C ₂₇ H ₄₂ O	Cholesta-4,6-dien-3-one		√		√		√	√	√	√
384.3117	C ₂₂ H ₄₁ NO ₄	Isonipecotic acid, N-methoxycarbonyl- , tetradecyl ester isomer	√	√	√	√		√	√		

