

A Method for Dextruxin Analysis by HPLC-PDA-ELSD-MS

Raquel P. Morais,^a Simone P. Lira,^b Mirna H. R. Selegim^c and Roberto G. S. Berlinck^{*,a}

^aInstituto de Química de São Carlos, Universidade de São Paulo, CP 780, 13560-970
 São Carlos-SP, Brazil

^bEscola Superior de Agricultura “Luiz de Queiroz”, Universidade de São Paulo, CP 9, 13418-900
 Piracicaba-SP, Brazil

^cDepartamento de Ecologia e Biologia Evolutiva, Universidade Federal de São Carlos, CP 676,
 13565-905 São Carlos-SP, Brazil

Table S1. Peak areas relative standard deviation (%) of repetibility (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C2-fr3-MF using UV; ELSD and MS HPLC detectors; peaks areas were measured relative to [Phe³, N-Me-Val⁵] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
1	-	-	-	-	-	-	3.09	1.57	2.72
2	3.92	5.09	1.51	-	-	-	3.79	1.43	5.25
unknown	2.73	4.50	1.85	-	-	-	1.17	3.74	3.90
3	3.62	3.13	0.43	-	-	-	3.20	2.27	1.19
4, 5, 6	2.48	1.17	2.40	-	-	-	3.44	1.06	4.18
unknown	-	-	-	-	-	-	0.97	2.42	5.31
7, 8, 9, 10	2.99	3.18	2.65	-	-	-	0.84	2.09	3.13
11	0.00	0.00	0.00	-	-	-	0.00	0.00	0.00
14, 15, 16	2.43	2.01	2.05	-	-	-	2.34	2.93	3.26
no destruxin	-	-	-	-	-	-	0.20	3.66	2.77

Table S2. Peak areas relative standard deviation (%) of repetibility (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C2-fr3-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
1	-	-	-	-	-	-	2.99	1.65	1.67
2	2.05	1.52	1.25	1.88	1.32	1.81	4.01	2.89	3.82
unknown	0.34	2.28	2.59	-	-	-	1.09	4.78	2.33
3	1.63	2.36	0.56	0.74	1.17	2.00	3.46	1.57	2.05
4, 5, 6	0.81	0.04	1.56	0.64	2.35	1.10	3.24	1.43	3.55
unknown	-	-	-	-	-	-	1.23	0.78	3.14
7, 8, 9, 10	1.76	0.55	1.81	2.52	1.27	2.89	0.76	1.40	1.23
11	3.01	1.79	0.84	-	-	-	0.27	2.95	2.24
14, 15, 16	1.20	2.25	1.63	2.34	2.91	0.64	2.36	1.98	1.36
no destruxin	-	-	-	-	-	-	0.17	3.98	2.60

*e-mail: rgsberlinck@iqsc.usp.br

Table S3. Retention times relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C2-fr3-MF using UV; ELSD and MS HPLC detectors. Retention times were measured relative to [Phe³, N-Me-Val⁵] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
1	-	-	-	-	-	-	1.24	0.51	0.12
2	0.24	0.22	0.06	-	-	-	1.52	0.49	0.04
unknown	0.22	0.17	0.23	-	-	-	1.46	0.42	0.18
3	0.16	0.19	0.03	-	-	-	1.34	0.30	0.05
4, 5, 6	0.09	0.74	0.06	-	-	-	1.28	0.14	0.03
unknown	-	-	-	-	-	-	1.23	0.20	0.05
7, 8, 9, 10	0.01	0.05	0.01	-	-	-	1.19	0.11	0.07
11	0.00	0.00	0.00	-	-	-	0	0	0
14, 15, 16	0.09	0.04	0.06	-	-	-	1.11	0.12	0.12
no destruxin	-	-	-	-	-	-	1.06	0.12	0.04

Table S4. Retention times relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C2-fr3-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
1	-	-	-	-	-	-	0.18	1.07	0.14
2	0.43	0.36	0.06	0.48	0.39	0.14	0.46	0.42	0.04
unknown	0.24	0.38	0.16	-	-	-	0.41	0.35	0.14
3	0.35	0.26	0.08	0.27	0.27	0.09	0.28	0.36	0.04
4, 5, 6	0.26	0.54	0.03	0.27	0.30	0.18	0.22	0.21	0.09
unknown	-	-	-	-	-	-	0.17	0.17	0.02
7, 8, 9, 10	0.19	0.14	0.08	0.11	0.10	0.16	0.13	0.15	0.09
11	0.20	0.13	0.07	-	-	-	1.06	0.16	0.07
14, 15, 16	0.12	0.10	0.12	0.11	0.11	0.08	0.16	0.08	0.16
no destruxin	-	-	-	-	-	-	0.04	0.18	0.05

Table S5. Peak areas relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C2-fr4-MF using UV; ELSD and MS HPLC detectors. Peaks areas were measured relative to [Phe³, *N*-Me-Val²] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
2	2.72	3.55	2.78	3.30	1.22	4.29	3.81	1.86	1.34
no destruxin	0.70	4.71	0.74	-	-	-	0.71	0.87	2.16
3	2.34	1.58	3.85	1.17	2.03	4.09	3.57	1.38	2.41
4, 5, 6	2.29	2.33	1.49	2.88	2.44	4.95	2.31	1.01	0.50
unknown	2.91	5.66	2.63	2.69	3.80	1.95	1.08	1.51	3.58
7, 8, 9, 10	0.06	1.68	1.86	2.59	0.90	4.29	0.60	4.30	1.65
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12, 13 and 14, 15, 16	0.20	3.58	3.40	1.20	1.82	3.11	1.02	1.57	2.00
17, 18, 19	-	-	-	-	-	-	1.12	3.37	1.66
20	-	-	-	-	-	-	1.13	2.70	1.75
unknown	1.11	3.31	2.36	2.44	0.80	2.57	0.46	0.10	1.42

Table S6. Peak areas relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C2-fr4-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
2	2.27	0.37	1.24	2.14	0.60	1.65	4.04	1.42	0.62
no destruxin	3.20	1.37	2.33	-	-	-	1.65	2.51	2.27
3	2.49	1.94	1.60	0.30	0.53	0.57	3.17	1.35	3.74
4, 5, 6	0.26	1.66	1.34	2.73	0.40	3.64	3.09	2.24	1.10
unknown	1.14	1.01	0.88	2.01	1.72	1.66	1.11	1.37	3.67
7, 8, 9, 10	2.50	3.64	4.66	1.26	2.08	0.82	1.58	0.99	0.12
11	2.52	1.56	2.81	1.35	1.53	3.48	0.98	1.42	1.58
12, 13 and 14, 15, 16	2.47	1.03	0.97	2.42	1.24	2.66	1.37	1.50	0.87
17, 18, 19	-	-	-	-	-	-	0.35	0.63	1.48
20	-	-	-	-	-	-	0.17	2.42	2.27
unknown	1.54	0.75	0.70	3.75	1.83	0.98	0.52	0.41	0.81

Table S7. Retention times relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C2-fr4-MF using UV; ELSD and MS HPLC detectors. Retention times were measured relative to [Phe³, N-Me-Val⁵] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
2	0.02	0.03	0.09	0.37	0.12	0.15	0.19	0.15	0.11
no destruxin	0.08	0.02	0.14	-	-	-	0.30	0.19	0.18
3	0.09	0.02	0.09	0.13	0.21	0.35	0.13	0.08	0.10
4, 5, 6	0.05	0.01	0.08	0.05	0.18	0.21	0.06	0.23	0.10
unknown	0.02	0.01	0.02	0.10	0.09	0.25	0.19	0.06	0.15
7, 8, 9, 10	0.05	0.03	0.07	0.09	0.12	0.15	1.21	0.12	0.07
11	0	0	0	0	0	0	0	0	0
12, 13 and 14, 15, 16	0.05	0.03	0.04	0.07	0.06	0.13	0.13	0.05	0.10
17, 18, 19	-	-	-	-	-	-	0.05	0.12	0.11
20	-	-	-	-	-	-	0.04	0.06	0.07
unknown	0.02	0.08	0.18	0.15	0.20	0.16	0.38	0.75	0.90

Table S8. Retention times relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C2-fr4-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
2	0.03	0.09	0.14	0.34	0.07	0.07	0.13	0.04	0.06
no destruxin	0.04	0.11	0.13	-	-	-	0.29	0.30	0.17
3	0.08	0.10	0.10	0.15	0.05	0.20	0.05	0.04	0.07
4, 5, 6	0.03	0.11	0.12	0.04	0.07	0.03	0.06	0.21	0.19
unknown	0.03	0.11	0.11	0.08	0.08	0.09	0.13	0.07	0.02
7, 8, 9, 10	0.05	0.10	0.11	0.11	0.06	0.05	1.17	0.06	0.11
11	0.04	0.12	0.13	0.03	0.17	0.19	0.09	0.12	0.16
12, 13 and 14, 15, 16	0.06	0.09	0.13	0.06	0.12	0.05	0.07	0.08	0.09
17, 18, 19	-	-	-	-	-	-	0.05	0.01	0.06
20	-	-	-	-	-	-	0.05	0.06	0.10
unknown	0.05	0.05	0.19	0.13	0.08	0.08	0.47	0.74	0.84

Table S9. Peak areas relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C3-fr3-MF using UV; ELSD and MS HPLC detectors. Peaks areas were measured relative to [Phe³, *N*-Me-Val²] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
no destruxin	1.78	1.58	3.50	-	-	-	0.44	0.51	1.19
1	1.77	2.79	4.29	-	-	-	1.76	0.58	0.89
2	0.66	3.42	4.67	3.34	3.30	1.88	1.12	0.66	3.12
unknown	2.55	5.65	2.98	-	-	-	3.21	0.60	4.45
3	1.03	2.73	2.61	3.97	1.48	3.18	2.91	0.92	2.19
4, 5, 6	0.23	1.08	1.77	4.97	1.88	2.41	1.43	0.29	2.77
unknown	3.93	3.65	5.32	-	-	-	4.26	2.18	2.01
7, 8, 9, 10	2.05	2.81	3.34	3.94	0.43	0.99	0.43	1.58	2.07
11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
unknown	1.78	1.58	3.50	3.38	2.54	4.64	1.31	1.82	1.01

Table S10. Peak areas relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C3-fr3-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
no destruxin	2.78	1.42	4.38	-	-	-	0.74	1.7	2.45
1	0.17	1.02	2.61	-	-	-	2.15	1.93	1.2
2	2.32	0.76	2.28	1.36	1.45	0.79	0.82	0.33	1.2
unknown	1.05	2.68	0.34	-	-	-	3.89	1.42	4.78
3	2.42	1.5	5.29	0.57	0.15	0.9	2.21	0.7	0.25
4, 5, 6	2.06	1.13	3.03	1.24	1.18	0.57	0.79	0.67	1.35
unknown	2.71	3.58	2.08	-	-	-	3.8	4.35	0.13
7, 8, 9, 10	1.12	4.87	1.46	1.14	3.34	1.86	0.88	1.38	1.71
11	1.84	0.47	3.34	3.66	1.67	2.69	0.69	0.39	1.93
unknown	2.78	1.42	4.38	3.52	2.22	2.96	1.23	0.71	2.81

Table S11. Retention times relative standard deviation (%) of repetibility (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C3-fr3-MF using UV; ELSD and MS HPLC detectors. Retention times were measured relative to [Phe³, N-Me-Val⁵] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
no destruxin	0.02	0.18	0.02	-	-	-	0.05	0.12	0.08
1	0.06	0.04	0.14	-	-	-	0.04	0.08	0.17
2	0.12	0.05	0.06	0.33	0.25	0.3	0.05	0.3	0.24
unknown	0.03	0.1	0.08	-	-	-	0.07	0.13	0.1
3	0.05	0.04	0.02	0.28	0.03	0	0.04	0.05	0.03
4, 5, 6	0.05	0.02	0.02	0.49	0.15	0.3	0.03	0.11	0.02
unknown	0.16	0.08	0.42	-	-	-	0.08	0.21	0.31
7, 8, 9, 10	0.07	0.03	0.03	0.33	0.28	0.15	0.12	0.15	0.15
11	0	0	0	0	0	0	0	0	0
unknown	-	-	-	0.3	0.25	0.16	0.02	0.12	0.1

Table S12. Retention times relative standard deviation (%) of repetibility (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C3-fr3-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
no destruxin	0.01	0.14	0.07	-	-	-	0.03	0.12	0.11
1	0.04	0.03	0.06	-	-	-	0.07	0.01	0.15
2	0.12	0.11	0.1	0.11	0.21	0.24	0.06	0.23	0.13
unknown	0.03	0.04	0.04	-	-	-	0.09	0.05	0.16
3	0.04	0.05	0.09	0.08	0.05	0.08	0.06	0.05	0.11
4, 5, 6	0.04	0.06	0.09	0.24	0.17	0.09	0.06	0.06	0.11
unknown	0.15	0.12	0.39	-	-	-	0.07	0.15	0.18
7, 8, 9, 10	0.06	0.07	0.11	0.2	0.32	0.18	0.13	0.08	0.07
11	0.02	0.06	0.08	0.29	0.04	0.08	0.03	0.08	0.13
unknown	-	-	-	0.07	0.28	0.12	0.03	0.04	0.11

Table S13. Peak areas relative standard deviation (%) of repetibility (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C3-fr4-MF using UV; ELSD and MS HPLC detectors. Peak areas were measured relative to [Phe³, N-Me-Val⁵] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
unknown	-	-	-	-	-	-	0.88	1.76	1.03
7, 8, 9, 10	2.01	2.05	5.32	3.54	2.46	3.48	0.99	1.35	4.47
11	0	0	0	0	0	0	0	0	0
12, 13	2.83	1.11	0.83	1.82	1.21	1.38	1.35	2.91	3.1
17, 18, 19	-	-	-	-	-	-	1.23	1.98	1.05
20	-	-	-	-	-	-	1.78	1.77	1.52
unknown	3.34	3.84	5.36	2.48	1.73	1.81	1.86	3.77	2.46

Table S14. Peak areas relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C3-fr4-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
unknown	-	-	-	-	-	-	1.2	3.41	3.33
7, 8, 9, 10	0.72	2.84	2.76	1.19	2.48	2.93	1.5	0.76	1.72
11	1.29	0.35	3.76	2.34	1.71	1.97	0.56	0.64	2.93
12, 13	1.91	0.51	3.23	3.58	1.75	0.65	1.83	2.11	2.78
17, 18, 19	-	-	-	-	-	-	1.69	3.27	2.37
20	-	-	-	-	-	-	1.36	2.64	1.53
unknown	2.36	1.51	2.45	0.3	0.69	0.28	1.84	2.08	0.56

Table S15. Retention times relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C3-fr4-MF using UV; ELSD and MS HPLC detectors. Retention times were measured relative to [Phe³, *N*-Me-Val⁵] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
unknown	-	-	-	-	-	-	0.29	0.08	0.28
7, 8, 9, 10	0.03	0.16	0.26	0.06	0.08	0.11	0.2	0.05	0.19
11	0	0	0	0	0	0	0	0	0
12, 13	0.14	0.29	0.27	0.07	0.09	0.05	0.27	0.06	0.25
17, 18, 19	-	-	-	-	-	-	0.2	0.11	0.34
20	-	-	-	-	-	-	0.39	0.06	0.24
unknown	0.23	0.05	0.22	0.14	0.19	0.13	0.32	0.24	0.51

Table S16. Retention times relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C3-fr4-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
unknown	-	-	-	-	-	-	0.08	0.09	0.1
7, 8, 9, 10	0.05	0.2	0.12	0.01	0.22	0.2	0.02	0.11	0.13
11	0.07	0.3	0.13	0.07	0.14	0.1	0.22	0.11	0.32
12, 13	0.2	0.22	0.15	0.13	0.05	0.05	0.13	0.08	0.09
17, 18, 19	-	-	-	-	-	-	0.08	0.07	0.03
20	-	-	-	-	-	-	0.19	0.12	0.1
unknown	0.18	0.27	0.14	0.2	0.16	0.19	0.12	0.13	0.54

Table S17. Peak areas relative standard deviation (%) of repetibility (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C4-fr4-MF using UV; ELSD and MS HPLC detectors. Peaks areas were measured relative to [Phe³, N-Me-Val⁵] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
4, 5, 6	1.89	1.22	3.52	-	-	-	0.56	4.58	1.11
unknown	2.22	2.04	3.85	-	-	-	2.59	3.89	2.41
unknown	1.36	3.92	2.03	0.66	3.47	1.38	2.53	4.65	4.32
7, 8, 9, 10	2.78	1.68	5.31	1.44	1.09	2.9	1.54	4.72	2.45
11	0	0	0	0	0	0	0	0	0
12, 13 and 14, 15, 16	5.68	2.45	5.18	0.38	0.55	0.85	2.29	4.61	3.98
20	1.89	1.22	3.52	0.66	3.47	1.38	2.31	2.44	4.25
unknown	2.22	2.04	3.85	1.44	1.09	2.9	1.57	3.24	0.77

Table S18. Peak areas relative standard deviation (%) of repetibility (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C4-fr4-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
4, 5, 6	0.22	1.35	1.13	-	-	-	1.71	5.57	0.61
unknown	0.68	2.8	2.11	-	-	-	3.58	4.75	2.55
unknown	0.77	1.91	1.31	0.56	1.65	2.05	0.63	2.34	4.7
7, 8, 9, 10	2.03	3.75	5.04	1.02	3.43	0.59	1.13	2.04	1.75
11	1.66	1.14	2.71	0.48	1.69	3.44	2.16	2.52	0.79
12, 13 and 14, 15, 16	4.34	1.08	2.75	0.67	1.67	3.52	0.57	0.43	4.71
20	0.22	1.35	1.13	0.56	1.65	2.05	3.44	0.79	4.95
unknown	0.68	2.8	2.11	1.02	3.43	0.59	0.74	0.14	0.17

Table S19. Retention times relative standard deviation (%) of repetibility (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C4-fr4-MF using UV; ELSD and MS HPLC detectors. Retention times were measured relative to [Phe³, N-Me-Val⁵] Dtx B (**11**) as internal standard

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
4, 5, 6	0.28	0.04	0.06	-	-	-	0.16	0.27	0.15
unknown	0.05	0.09	0.17	-	-	-	0.45	0.05	0.74
unknown	0.05	0.12	0.19	0.22	0.05	0.14	0.23	0.25	0.09
7, 8, 9, 10	0.07	0.09	0.13	0.03	0.06	0.09	0.14	0.32	0.07
11	0	0	0	0	0	0	0	0	0
12, 13 and 14, 15, 16	0.07	0.12	0.1	0.01	0.08	0.13	0.39	0.14	0.09
20	-	-	-	-	-	-	0.23	0.22	0.12
unknown	-	-	-	-	-	-	0.25	1.01	0.08

Table S20. Retention times relative standard deviation (%) of repeatability (RP). Intermediate precision (IP) and stability (S) measured for peaks observed in fraction C4-fr4-MF using UV; ELSD and MS HPLC detectors. No internal standard was used

Compound	UV			ELSD			MS		
	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S	RP (n = 3)	IP (n = 9)	S
4, 5, 6	0.41	0.09	0.05	-	-	-	0.07	0.15	0.19
unknown	0.1	0.09	0.13	-	-	-	0.61	0.11	0.76
unknown	0.11	0.03	0.08	0.15	0.05	0.23	0.05	0.09	0.11
7, 8, 9, 10	0.08	0.04	0.09	0.04	0.05	0.11	0.05	0.16	0.1
11	0.15	0.13	0.11	0.07	0.01	0.13	0.19	0.16	0.04
12, 13 and 14, 15, 16	0.13	0.06	0.05	0.06	0.07	0	0.2	0.18	0.1
20	-	-	-	-	-	-	0.06	0.06	0.16
unknown	-	-	-	-	-	-	0.15	0.85	0.11