Supplements

Materials and Methods

RP-HPLC/MS-APCI

HPLC equipment consisted of a 1090 Win system, PV5 ternary pump and automatic injector (HP 1090 series, Agilent, USA) and two Hichrom columns HIRPB-250AM 250 x 2.1 mm ID, 5 μm particle size, in series. This setup provided us with a high-efficiency column - approximately 26000 plates/250 mm. A quadrupole mass spectrometer system Navigator (Finnigan MAT, San Jose, CA, USA) was used for analysis. The instrument was fitted with an atmospheric pressure chemical ionization source (vaporizer temperature 390°C, capillary heater temperature 260°C, corona current 7 μA, sheath gas - high-purity nitrogen, pressure 0.45 MPa, and auxiliary gas (also nitrogen) flow rate 15 mL/min. Positively charged ions with *m/z* 200 - 1000 were scanned with a scan time of 0.5 s. The whole HPLC flow (0.35 mL/min) was introduced into the APCI source without any splitting. TAGs were separated using a gradient solvent program with acetonitrile (ACN) and 2-propanol (iPrOH) as follows: initial ACN/iPrOH (99:1, v/v); linear from 5 min to 150 min ACN/iPrOH 30:70, vol/vol); held until 30 min; the composition was returned to the initial conditions over 10 min. A peak threshold of 0.07 % intensity was applied to the mass spectra. Data acquisition and analyses were performed using PC with MassLab 2.0 for Windows XP applications/operating software.

TAGs analysis by chiral LC/MS-APCI

The LC system used for separation in the chiral mode was the same as that used in the reversed-phase mode. TAGs (~ 1 mg/mL in methanol) were chromatographed on two Astec cyclobond™ I 2000 DMP (3,5-dimethyl-phenyl-carbamate modified β-cyclodextrin) chiral LC columns (5 μm, 25 cm × 4.6 mm) connected in series, from Sigma. Mobile phase was a gradient from 90 % of A and 10% of B at 0 min to 50 % of A and 50 % of B during 180 min, and then isocratically for 30 min, where A is hexane and B is hexane-iPrOH (99:2, v/v) mixture [28]. The flow rate, column temperature, and injection volume were 0.5 mL/min, 25°C, and 10 μl, respectively. Other separation conditions were as used in the RP- LC, see above.

Table 1S. Relative quantities (%), retention time (RT, min), equivalent carbon number (ECN) and acyl carbon number (ACN) of molecular species of TAGs identified in protozoan *Khawkinea quartana*.

RT	TAG	ECN	ACN	DB	rel abund
19.4	E-E-21:6	29	61	16	12.6
20.2	19:5-E-D	29	61	16	22.8
20.7	17:4-E-D	29	59	15	24.0
21.4	17:4-E-E	29	57	14	24.0
21.6	D-E-D	30	64	17	43.3
21.9	E-E-D	30	62	16	43.3
22.3	19:4-E-D	31	61	15	33.1
22.7	A-19:5-D	31	61	15	19.7
22.8	Ln-E-E	32	58	13	57.2
23.0	E-E-A	32	60	14	37.3
23.5	19:4-E-E	31	59	14	33.1
23.8	A-E-19:5	31	59	14	19.7
24.1	21:4-E-D	33	63	15	18.0
24.4	A-21:5-D	33	63	15	17.6
24.5	17:3-E-E	31	57	13	21.6
24.7	A-E-D	32	62	15	37.3
24.8	A-E-21:6	33	63	15	10.9
24.9	Ln-E-19:5	31	57	13	30.0
25.2	21:4-E-E	33	61	14	18.0
25.4	A-E-E	32	60	14	37.3
25.6	19:5-E-A	32	60	14	19.7
25.8	19:3-E-E	33	59	13	42.7
26.1	A-A-19:5	33	59	13	17.0
26.2	17:2-E-E	33	57	12	19.2
27.1	M-21:5-D	33	55	11	12.1
27.2	M-E-21:6	33	55	11	7.6
27.4	17:3-Ln-E	33	55	11	28.4
28.4	Po-E-17:4	33	53	10	31.6
28.9	M-E-17:4	33	51	9	14.1
29.5	Po-E-E	34	56	11	57.2
30.0	Po-D-19:4	35	57	11	43.6
30.1	A-A-E	34	60	13	32.1
30.2	M-E-E	34	54	10	25.2
30.5	A-A-21:5	35	61	13	15.2
30.7	Po-E-D	34	58	12	57.2
31.0	19:2-E-E	35	59	12	13.2
31.1	Po-21:5-D	35	59	12	26.8
31.2	M-E-D	34	56	11	25.2
31.4	Po-E-21:6	35	59	12	16.4
31.6	A-21:5-Ln	35	59	12	23.1
31.8	O-E-21:6	35	59	12	12.1
32.0	O-19:5-D	35	59	12	21.9
32.7	19:3-Ln-E	35	57	11	56.4

32.9	A-E-Ln	34	58	12	49.2
33.2	Ln-21:5-Ln	35	57	11	35.2
33.6	19:5-E-O	35	57	11	21.9
34.2	E-E-L	34	58	12	42.1
34.3	Po-E-19:4	35	55	10	43.6
34.6	P-D-17:4	35	55	10	23.4
34.9	P-E-19:5	35	55	10	22.2
35.0	Ln-19:5-L	35	55	10	29.2
35.6	Ln-E-Ln	34	56	11	75.6
35.7	M-E-19:4	35	53	9	19.3
35.8	Po-17:3-E	35	53	9	28.4
36.5	O-E-D	36	60	12	41.5
37.4	P-E-D	36	58	11	42.1
38.1	A-A-Ln	36	58	11	42.3
38.3	O-E-E	36	58	11	41.5
39.0	P-E-E	36	56	10	42.1
40.2	A-E-L	36	58	11	36.3
40.3	A-Ln-Ln	36	56	10	65.0
40.4	O-21:5-D	37	61	12	19.6
40.9	P-21:5-D	37	59	11	19.8
41.0	P-E-21:6	37	59	11	12.2
41.2	21:4-E-L	37	59	11	17.5
41.4	A-21:5-L	37	59	11	17.1
41.8	A-E-Po	36	56	10	49.2
42.1	P-D-19:4	37	57	10	32.1
42.3	E-E-O	36	58	11	41.5
42.4	21:4-Ln-Ln	37	57	10	31.0
42.5	21:4-E-Po	37	57	10	23.6
42.5	Ln-E-L	36	56	10	55.6
42.7	L-21:6-L	37	57	10	33.0
42.8	A-21:5-Po	37	57	10	23.1
42.9	E-E-P	36	56	10	42.1
43.0	Ln-Ln-Ln	36	54	9	100.0
43.2	Ln-21:5-L	37	57	10	26.1
43.5	Ln-E-Po	36	54	9	75.6
43.6	gLn-Ln-Ln	36	54	9	21.4
43.7	Po-E-19:3	37	55	9	56.4
43.8	gLn-gLn-Ln	36	54	9	5.3
43.9	Po-19:3-E	37	55	9	56.4
44.0	Ln-21:5-Po	37	55	9	35.2
44.1	A-E-M	36	54	9	21.8
44.3	A-21:4-M	37	55	9	9.3
44.5	21:4-E-M	37	55	9	10.7
44.6	P-Ln-E	36	54	8	55.6
44.8	21:5-Ln-Po	37	55	9	35.2
44.9	Ln-E-M	36	52	8	33.2
45.1	L-19:5-L	37	55	9	21.6
45.2	A-19:5-P	37	55	9	19.2
45.4	A-A-L	38	58	10	31.2

45.9	Ln-21:5-M	37	53	8	15.8
46.1	Po-E-17:2	37	53	8	25.2
46.4	L-Ln-17:3	37	53	8	27.6
46.5	L-L-17:4	37	53	8	40.0
46.6	21:6-Po-Po	37	53	8	21.4
46.7	A-A-Po	38	56	9	42.3
47.0	Po-17:3-Ln	37	51	7	37.3
47.4	A-Ln-L	38	56	9	47.8
47.5	E-A-O	38	58	10	35.7
47.8	L-E-L	38	56	9	40.9
47.9	Ln-E-O	38	56	9	54.8
48.0	A-E-P	38	56	9	36.3
48.1	Po-17:4-Po	37	49	6	41.6
48.2	Po-A-A	38	56	9	42.3
48.3	Ln-A-Po	38	54	8	65.0
49.0	Po-E-L	38	54	8	55.6
49.1	D-Po-Po	38	54	8	75.6
49.2	Ln-Ln-L	38	54	8	73.5
49.3	E-21:4-O	39	59	10	17.3
49.5	21:5-A-O	39	59	10	16.9
49.8	A-A-M	38	54	8	18.8
50.0	Ln-E-P	38	54	8	55.6
50.1	21:4-Ln-L	39	57	9	22.9
50.2	Ln-Po-Ln	38	52	7	100.0
50.3	21:5-L-L	39	57	9	19.0
50.3	Po-Po-E	38	52	7	75.6
50.4	L-E-L	39	57	9	40.9
50.5	Ln-21:5-O	39	57	9	25.7
50.6	A-Ln-M	38	52	7	28.6
50.7	21:4-E-P	39	57	9	17.5
50.8	A-21:5-P	39	57	9	17.1
50.9	M-E-L	38	52	7	24.5
51.0	Ln-Ln-M	38	50	6	43.7
51.3	M-E-Po	38	50	6	33.2
51.5	P-Ln-21:5	39	55	8	26.1
51.6	M-E-M	38	48	5	14.8
51.7	Po-E-19:2	39	55	8	17.2
51.9	L-Ln-19:3	39	55	8	54.8
52.0	Ln-21:4-Po	39	55	8	31.0
52.3	Po-21:5-L	39	55	8	26.1
52.6	Ln-21:5-P	39	55	8	26.1
53.0	19:4-L-L	39	55	8	54.8
53.2	21:5-L-Po	39	55	8	26.1
53.4	A-L-L	40	56	8	35.2
53.6	Po-19:3-Ln	39	53	7	74.5
53.7	L-L-17:3	39	53	7	44.0
53.8	A-A-P	40	56	8	31.2
54.0	Po-Po-21:5	39	53	7	35.2
54.1	M-Po-E	38	50	6	33.2

54.2	21:4-Ln-M	39	53	7	14.0
54.3	Ln-L-L	40	54	7	54.0
54.4	M-21:5-L	39	53	7	11.7
54.5	Po-A-L	40	54	7	47.8
54.6	E-Ln-Po	40	54	9	75.6
54.7	E-L-Po	40	54	8	55.6
54.8	P-A-A	40	56	8	31.2
54.8	L-Ln-17:2	39	53	7	24.5
54.9	Ln-O-A	40	56	8	47.1
55.1	P-19:5-L	39	53	7	21.6
55.2	E-L-O	42	56	8	40.4
55.3	Ln-A-P	40	54	7	47.8
55.5	Po-19:4-Po	39	51	6	57.5
55.6	P-E-L	40	54	7	40.9
55.8	O-Ln-Ln	40	54	7	72.4
55.8	M-21:5-Po	39	51	6	15.8
55.9	Po-E-O	40	54	7	54.8
56.1	M-Po-21:5	39	51	6	15.8
56.2	Po-A-Po	40	52	6	65.0
56.4	21:4-L-L	41	57	8	17.0
56.5	M-21:5-M	39	49	5	7.2
56.6	Ln-O-21:4	41	57	8	22.6
56.7	Po-Po-17:3	39	49	5	37.3
56.8	21:5-L-O	41	57	8	19.0
57.0	gLn-L-L	40	54	7	11.9
57.1	P-19:2-E	41	55	7	12.8
57.2	L-Ln-19:2	41	55	7	16.7
57.4	Ln-Po-L	40	52	6	73.5
57.5	19:3-L-L	41	55	7	12.8
57.7	Ln-21:4-P	41	55	7	22.9
58.0	P-21:5-L	41	55	7	19.3
58.1	Ln-P-Ln	40	52	6	73.5
58.2	Po-21:5-O	41	55	7	25.7
58.3	E-O-O	42	56	7	39.8
58.5	A-M-L	40	52	6	21.2
58.6	P-A-L	42	54	6	35.2
58.7	P-E-O	42	54	6	40.4
58.8	Po-21:4-Po	41	53	6	31.0
58.9	Po-O-Ln	42	52	5	72.4
59.0	L-L-17:2	41	53	6	33.0
59.0	Po-E-P	40	52	6	55.6
59.1	21:4-M-L	41	53	6	10.4
59.2	Ln-Po-Po	40	50	5	100.0
59.3	Po-21:5-P	41	53	6	26.1
59.3	M-A-Po	40	50	5	28.6
59.4	M-E-P	40	50	5	24.5
59.5	Ln-M-L	40	50	5	32.3
59.6	Ln-M-Po	40	48	4	43.7
59.7	A-M-M	40	48	4	12.8

59.8	Po-Po-19:3	41	51	5	74.5
59.9	P-Po-17:2	41	47	3	24.5
60.0	L-Po-L	42	52	5	54.0
60.1	Ln-P-L	42	52	5	54.0
60.2	M-21:5-P	41	51	5	11.7
60.3	P-Po-17:3	41	49	4	27.6
60.4	Po-A-P	42	52	5	47.8
60.5	Ln-M-M	40	46	3	19.5
60.6	L-L-L	42	54	6	39.8
60.6	P-E-P	42	52	5	40.9
60.6	Po-17:2-Po	41	49	4	33.1
60.7	21:5-O-O	43	57	7	18.8
60.7	L-L-Po	42	52	5	54.0
60.8	M-Po-17:2	41	47	3	14.9
60.9	Po-Po-L	42	50	4	73.5
61.1	Ln-Po-P	42	50	4	73.5
61.2	L-Po-L	42	52	5	54.0
61.3	P-21:4-L	43	55	6	17.0
61.4	19:2-L-L	43	55	6	22.0
61.6	P-21:5-O	43	55	6	19.0
61.7	Po-21:4-P	43	53	5	22.9
62.0	P-21:5-P	43	53	5	19.3
62.2	M-L-L	42	50	4	23.9
62.3	P-Po-19:3	43	51	4	54.8
62.3	M-A-P	42	50	4	21.2
62.4	Po-Po-Po	42	48	3	100.0
62.6	Po-19:2-Po	43	51	4	22.5
62.8	P-L-17:2	43	51	4	18.2
62.8	Po-M-L	42	48	3	32.3
63.0	Po-17:2-O	43	51	4	24.2
63.1	M-21:4-P	43	51	4	10.4
63.4	M-Po-19:2	43	49	3	10.3
64.0	P-P-17:3	43	49	3	20.4
64.1	Ln-M-P	42	48	3	32.3
64.2	Po-M-Po	42	46	2	43.7
64.3	M-Po-Po	42	46	2	43.7
64.4	L-L-O	44	54	5	39.2
64.5	M-P-17:2	43	47	2	11.1
64.6	A-O-P	44	54	5	34.7
64.7	M-M-L	42	46	2	14.4
65.6	M-M-Po	42	44	1	19.5
65.7	M-M-M	42	42	0	8.8
65.8	O-Po-L	44	52	4	53.3
65.9	O-Po-Po	44	50	3	72.4
66.1	P-L-L	44	52	4	39.8
66.7	L-P-Po	44	50	3	54.0
66.9	Po-P-L	44	50	3	54.0
67.1	Ln-P-P	44	50	3	54.0
67.3	P-Po-Po	44	48	2	73.5

67.6	P-M-L	44	48	2	23.9
67.9	L-M-P	44	48	2	23.9
68.0	Po-M-P	44	46	1	32.3
68.3	P-L-19:2	45	53	4	12.5
68.5	P-O-Ln	44	52	4	53.3
68.6	P-M-M	44	44	0	14.4
68.7	Po-19:2-O	45	53	4	16.5
68.9	L-L-P	44	52	4	39.8
69.0	P-P-19:3	45	51	3	40.4
69.2	P-A-P	44	52	4	35.2
69.2	P-Po-19:2	45	51	3	16.7
69.4	19:2-M-M	45	49	2	4.8
69.6	O-Po-O	46	52	3	52.5
70.0	M-P-19:2	45	49	2	7.7
70.4	O-P-L	46	52	3	39.2
70.6	O-M-O	46	50	2	23.2
70.8	P-P-17:2	45	49	2	18.2
71.0	O-P-Po	46	50	2	53.3
71.6	P-P-L	46	50	2	39.8
71.7	L-O-O	46	54	4	38.7
71.9	P-Po-P	46	48	1	54.0
72.1	P-M-O	46	48	1	23.5
73.0	M-M-P	44	44	0	14.4
73.1	P-P-19:2	47	51	2	12.5
73.4	O-O-O	48	54	3	38.1
75.1	O-P-O	48	52	2	38.7
76.2	P-M-P	46	46	0	23.9
76.4	O-P-P	48	50	1	39.2
81.3	P-P-P	48	48	0	39.8

Table 2S. Relative quantities (%), retention time (RT, min) of molecular species of TAGs identified in *Mortierella alpina.*

RT	TAG	rel abund
26.1	A-A-19:5	27.3
35.0	Ln-19:5-L	46.5
45.1	L-L-19:5	34.8
45.2	A-19:5-P	31.0
46.4	L-Ln-17:3	18.5
46.5	L-L-17:4	45.0
47.0	Po-17:3-Ln	24.4
48.1	Po-17:4-Po	99.0
51.9	L-Ln-19:3	50.4
53.0	19:4-L-L	35.0
53.6	Po-19:3-Ln	62.4
53.7	L-L-17:3	65.3
54.8	L-Ln-17:2	20.6
55.1	P-19:5-L	34.8
55.5	Po-19:4-Po	44.0
56.7	Po-Po-17:3	23.1
57.2	L-Ln-19:2	55.5
57.5	19:3-L-L	8.8
59.0	L-L-17:2	37.0
59.8	Po-Po-19:3	46.6
59.9	P-Po-17:2	20.6
60.3	P-Po-17:3	18.5
60.6	Po-17:2-Po	41.6
60.8	M-Po-17:2	12.6
61.4	19:2-L-L	73.3
62.3	P-Po-19:3	28.4
62.6	Po-19:2-Po	41.4
62.8	P-L-17:2	15.1
63.0	Po-17:2-O	27.7
63.4	M-Po-19:2	34.0
64.0	P-P-17:3	13.2
64.5	M-P-17:2	9.2
68.3	P-L-19:2	40.7
68.7	Po-19:2-O	54.8
69.0	P-P-19:3	20.8
69.1	P-Po-19:2	51.8
69.4	19:2-M-M	16.3
70.0	M-P-19:2	25.9
70.8	P-P-17:2	15.1
73.1	P-P-19:2	40.7

Fig. 1S. Tandem mass spectrum of synthetic *sn*-LL19:3.

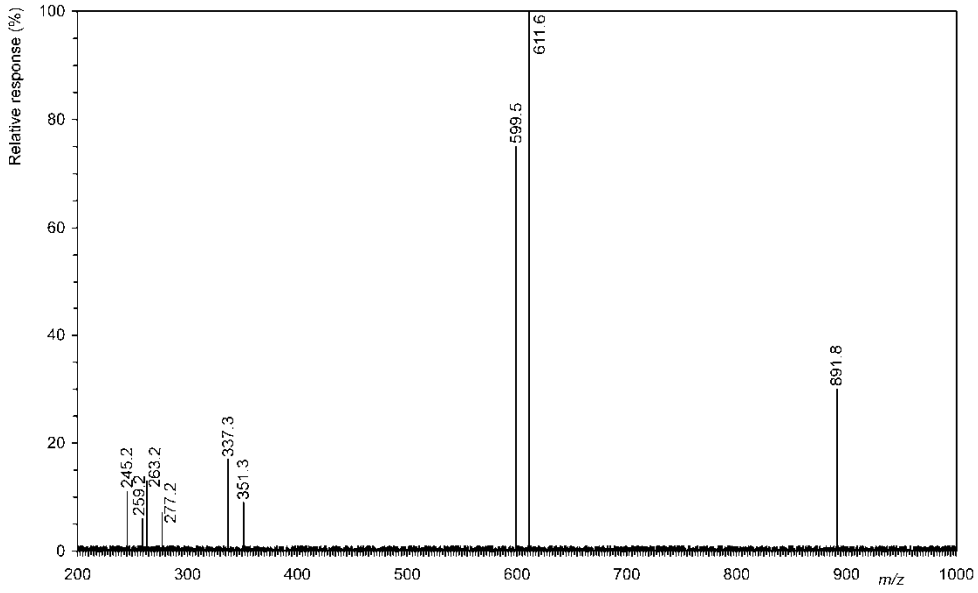

Fig. 2S. Tandem mass spectrum of synthetic s*n*-LL19:4.

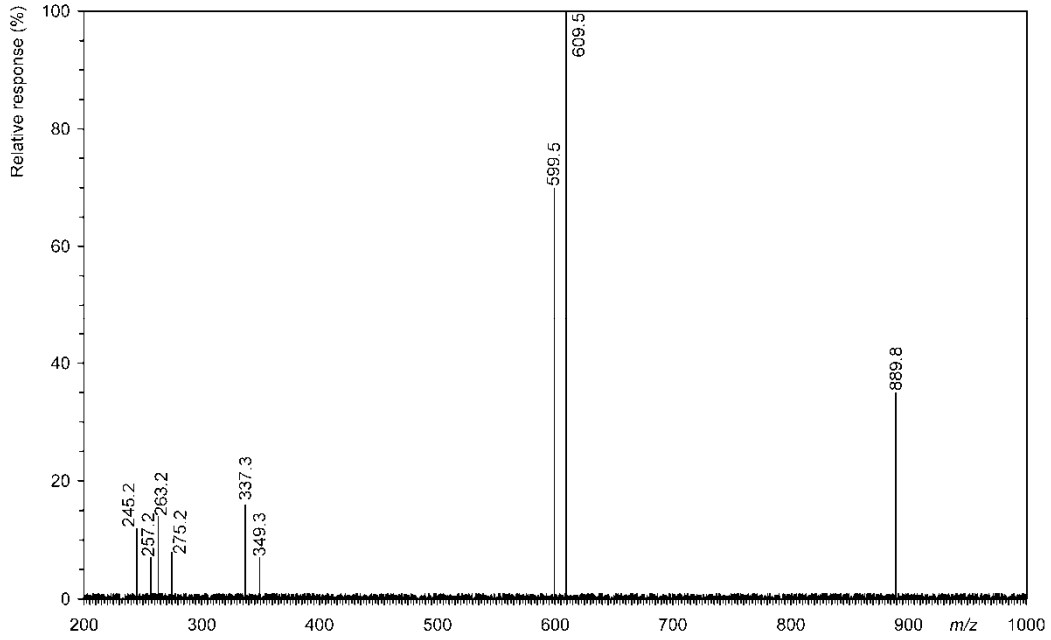

Fig..35S. Tandem mass spectrum of synthetic *sn*-LL21:4.

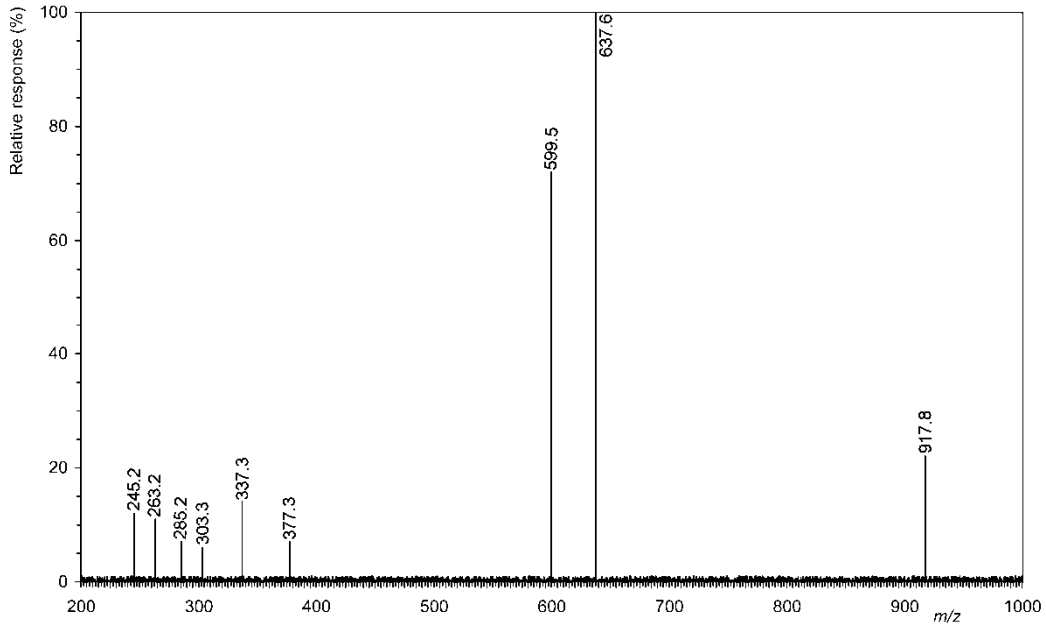

Fig. 4S. Tandem mass spectrum of synthetic s*n*-LL21:5.

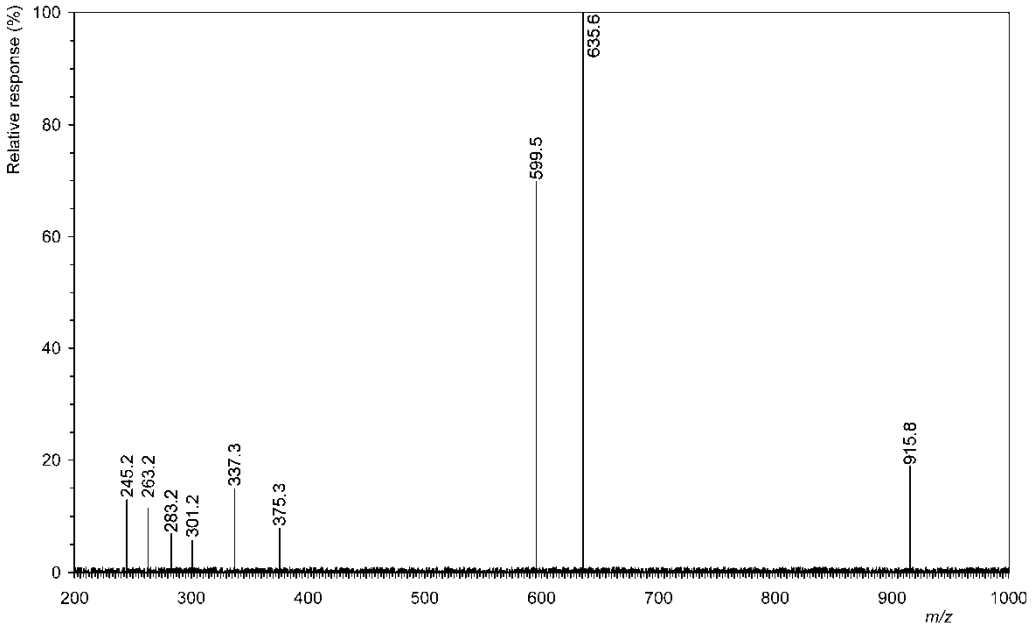

Fig. 5S. Mass spectrum of picolinyl ester of 19:5ω1 acid. For explanation of values see the text.

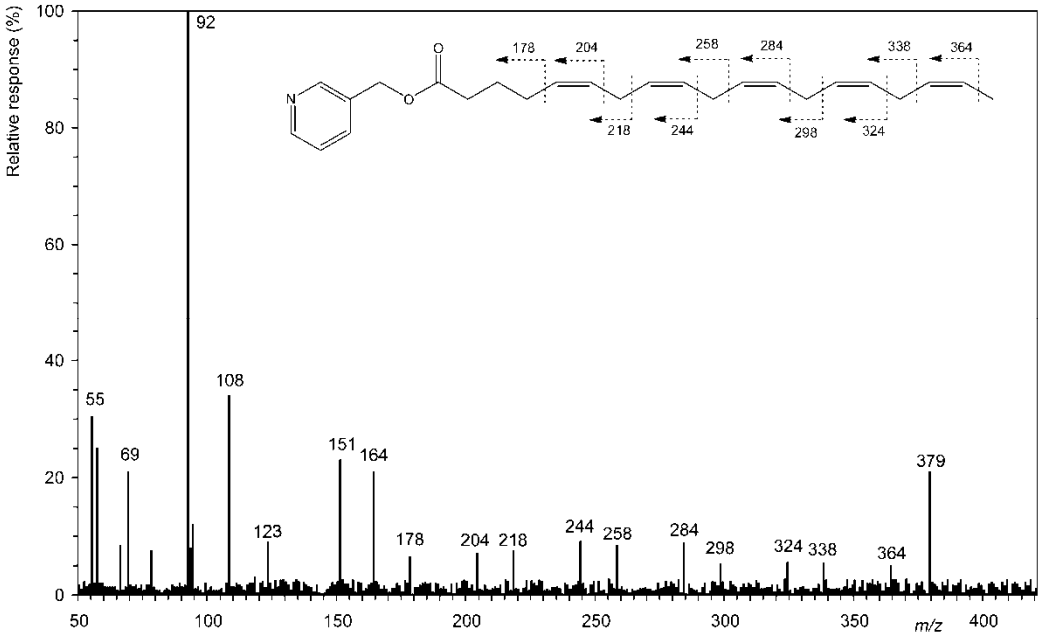

Fig. 6S. Mass spectrum of picolinyl ester of 21:5ω5 acid. For explanation of values see the text.