Supplements

4. Experimental

4.3. Isolation of lipids

The extraction procedure was based on the method of Bligh and Dyer (1959), except that 2-propanol was substituted for methanol, since 2-propanol does not serve as a substrate for phospholipases (Kates and Volcani, 1996). The alcohol-water mixture was cooled, one part chloroform was added and the lipids from the lyophilized cells of different cultivations of dinoflagellates were extracted for 30 min. Insoluble material was sedimented by centrifugation and the supernatant was separated into two phases. The aqueous phase was aspirated off and the chloroform phase was washed three times with two parts 1 M KCl each. The resulting chloroform phase was evaporated to dryness under reduced pressure.

Total lipid extracts were applied on Sep-Pak Vac Silica cartridge 35cc (Waters; with 10 grams of normal-phase silica), and TAGs were subsequently eluted from the cartridge with 40 mL of chloroform-methanol (9:1), which was injected for HPLC analysis. Further, polar lipids were eluted from the cartridge by a mixture of 50 ml of methanol acidified with 0.1% of formic acid. The eluate of polar lipids was evaporated and the oil samples were dissolved in an acetonitrile-2-propanol-hexane mixture (1:1:1, v/v/v).

4.4. FAMEs analysis

The lipids (both TAGs and polar lipids) (~5 mg) were saponified overnight in 10% potassium hydroxide-methanol at room temperature. A fatty acid fraction obtained from saponification was partitioned between alkali solution (pH 9) and diethyl ether to remove basic and neutral components. The aqueous phase, containing fatty acids, was acidified to pH 2 and extracted with hexane. The fatty acid fraction was methylated using CH_2N_2. GC-MS of fatty acid methyl ester (FAME) mixture was done on a Finnigan 1020 B (Thermo Fisher Scientific Inc., MA, USA) in EI mode. Splitless injection was at 100 °C, and a fused silica capillary column (Supelcowax 10; 60 m x 0.25 mm i.d., 0.25 mm film thickness; Supelco, Prague) was used. The temperature program was as follows: 100 °C for 1 min, subsequently increasing at 20 °C/min to 180 °C and at 2 °C/min to 280 °C, which was maintained for 1 min. The carrier gas was helium at a linear velocity of 60 cm/s. All spectra were scanned within the range of *m/z* 50–500. The structures of FAMEs were confirmed by comparison of retention times and fragmentation patterns with those of the standard FAMEs (Supelco, Prague) (Rezanka, 1993, Dembitsky and Rezanka, 2005).

4.5. HILIC/MS-ESI

The HPLC equipment consisted of a 1090 Win system, PV5 ternary pump and automatic injector (HP 1090 series, Hewlett Packard, USA), and Ascentis® Express OH5, ultra-high performance liquid chromatography (UHPLC) HILIC column (2.7 μm particle size, L × I.D. 15 cm × 2.1 mm) (Supelco, Prague, Czech Republic) with an injection volume of 10 μL. UHPLC was performed at a flow rate of 0.33 mL/min for the polar lipids from three cultivations, with a linear gradient from mobile phase containing methanol/acetonitrile/aqueous 1 mM ammonium acetate (50:30:20, v/v/v) to methanol/acetonitrile/aqueous 1 mM ammonium acetate (10:70:20, v/v/v) for 60 min. Column temperature was 35 °C and a re-equilibration period between runs was 30 min. The whole UHPLC flow was introduced into the ESI source without any splitting.

LTQ Orbitrap Velos (Thermo Fisher Scientific, Bremen, Germany), a high resolution hybrid mass spectrometer equipped with a heated electrospray interface (HESI) was used. ESI–MS analysis was performed in the Fourier transform positive ion mode. MS spectra were acquired with target mass resolution of R = 105,000 at *m/z* 800. The ion spray voltage was set at 3.5 kV and the scan range of the instruments was set at *m/z* 200–1500. Nitrogen was used as a nebulizer gas - set at 18 arbitrary units (sheath gas) and 7 arbitrary units (auxiliary gas). Helium was used as a collision gas for collision-induced dissociation (CID) experiments. The CID normalization energy of 35% was used for the fragmentation of parent ions. The MS/MS product ions were detected by the high resolution FT mode. Further source conditions in the positive mode: vaporizer temperature, 250°C; capillary temperature, 230°C; capillary voltage, 50 V; tube lens voltage, 170 V.

The same apparatus was used for negative ion mode. MS spectra were acquired with target mass resolution of R = 30,000 at *m/z* 400. The ion spray voltage was set at -2500V and the scan range of the instruments was set at m/z 200–2000. Nitrogen was used as a nebulizer gas – set at 18 arbitrary units (sheath gas) and 7 arbitrary units (aux gas). Helium was used as a collision gas for CID experiments. The CID normalization energy of 35% was used for the parent ions fragmentation. The MS/MS product ions were detected by the high resolution FT mode. The H-ESI temperature was set to 250°C.

4.6. Separation and identification of regioisomers of TAGs

LC equipment consisted of a 1090 Win system, PV5 ternary pump and automatic injector (HP 1090 series, Agilent, Santa Clara, CA, USA) and two columns Hichrom HIRPB (Hichrom Limited, UK) - 250A 250 x 2.1 mm ID, 5 μm particle size, in series. This setup was used as a high efficiency column with approximately 104 000 plates/m, flow rate of 1 mL/min and an injection volume of 10 μL, and column temperature of 25 °C. The TAGs were

separated using a solvent gradient program with acetonitrile (ACN) and 2-propanol (iPrOH) as follows: initial ACN/iPrOH (99:1, vol/vol); linear from 5 min to 110 min of ACN/iPrOH 30:70 (vol/vol); held for 10 min. The composition was returned to the initial conditions over 10 min. The performance was measured by triheptadecenoin (51:3) as an internal standard under the conditions given above.

LTQ Orbitrap Velos (Thermo Fisher Scientific, Bremen, Germany), a high resolution hybrid mass spectrometer equipped with HESI was used, see above.

Table 1S. Fatty acid composition (%) of different dinoflagellates.

Species	28:7n-6	28:8n-3	28:y	24:5n-6	24:6n-3	26:7n-3	References
Alexandrium tamarense		<0.2					Hammann et al., 2013
Amphidinium carterae	1.3	2.1					Leblond and Chapman, 2000
Amphidinium sp.	tr	tr		tr	0.8	tr	Mansour, 2005
Amphidinium sp.	tr	0.4		tr	1.0	tr	Mansour, 2005
Crypthecodinium cohnii		1.2					Van Pelt et al., 1999
Fragilidium sp.			2.0				Mansour et al., 1999a
Gymnodinium sanguineum			1.5				Mansour et al., 1999a
Gymnodinium sp.			2.2				Mansour et al., 1999a
Gymnodinium sp.	0.0	1.0					Leblond and Chapman, 2000
Karenia brevis	0.3	0.3					Mooney et al., 2007
Karenia brevis GL							Leblond et al., 2003
Karenia brevis PL	0.5	0.5					Leblond et al., 2003
Karenia brevis TAG		tr					Leblond et al., 2003
Karenia mikimotoi	0.0	0.2					Mooney et al., 2007
Karenia papilionacea (AB)	0.2	0.5					Mooney et al., 2007
Karenia papilionacea (PL)	0.2	0.5					Mooney et al., 2007
Karenia umbella	0.1	0.6					Mooney et al., 2007
Karlodinium sp.	0.0	0.9					Mooney et al., 2007
Karlodinium veneficum (DE01)	0.5	0.2					Mooney et al., 2007
Karlodinium veneficum (HU01)	0.5	0.2					Mooney et al., 2007
Karlodinium veneficum (SR01)	0.4	0.4					Mooney et al., 2007
Prorocentrum mexicanum	0.1	1.7					Mansour et al., 1999b
Prorocentrum micans	0.5	1.2					Leblond and Chapman, 2000
Prorocentrum micans	0.8	1.3					Mansour et al., 1999b
Scrippsiella sp.			1.7				Mansour et al., 1999a
Scrippsiella sp.		2.0					Mansour, 2005
Symbiodinium microadriaticum			0.9				Mansour et al., 1999a
Symbiodinium sp.+sea anemone[a]	+	+				+	Thomas et al., 2012
Takayama helix	0.5	0.6					Mooney et al., 2007

Takayama tasmanica	0.0	0.5	Mooney et al., 2007
Amphidinium carterae	0.2	0.8	**this paper**
Cystodinium sp.	0.3	0.5	**this paper**
Peridinium aciculiferum	0.4	1.3	**this paper**

+ present, - absent

[a] and 24:6 and 26:6;

GL-glycolipids, PL-phospholipids, TAG-triacylglycerols

28:y = Very-long-chain, highly unsaturated fatty acid(s) having seven or eight double bonds

tr, trace (less than 0.05%), Mansour et al., 2005b

tr, trace (less than 0.2%), Leblond et al., 2003

References not listed in the main text:

Hammann, S., Tillmann, U., Schroder, M., Vetter, W., 2013. Profiling the fatty acids from a strain of the microalgae *Alexandrium tamarense* by means of high-speed counter-current chromatography and gas chromatography coupled with mass spectrometry. J. Chromatogr. A, 1312, 93–103.

Mansour, M.P., Volkman, J.K., Jackson, A.E., Blackburn, S.I., 1999a. The fatty acid and sterol composition of five marine dinoflagellates. J. Phycol. 35, 710–720.

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Mooney, B.D., Nichols, P.D., de Salas, M.F., Hallegraeff, G.M., 2007. Lipid, fatty acid, and sterol composition of eight species of Kareniaceae (Dinophyta): Chemotaxonomy and putative lipid phycotoxins. J. Phycol. 43, 101–111.

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Van Pelt, C.K., Huang, M.C., Tschanz, C.L., Brenna, J.T., 1999. An octaene fatty acid, 4,7,10,13,16,19,22,25-octacosaoctaenoic acid (28:8n-3), found in marine oils. J. Lipid Res. 40, 1501–1505.

Table 2S. Description of tandem mass spectrum of *sn*-22:6/28:8/28:8 TAG.

m/z	Abundance[a]	Ion Description
293.2269	12	*sn*-1 acyl chain ($[RC=O]^+$ with loss of H_2O)
311.2375	23	*sn*-1 acyl chain ($[RC=O]^+$)
367.2637	9	*sn*-1 acyl chain ($[RC=O+74]^+$ with loss of H_2O)
373.2895	22	*sn*-2 acyl chain ($[RC=O]^+$ with loss of H_2O)
385.2743	24	*sn*-1 acyl chain ($[RC=O+74]^+$)
391.3001	45	*sn*-2 acyl chain ($[RC=O]^+$)
447.3263	17	*sn*-2 acyl chain ($[RC=O+74]^+$ with loss of H_2O)
465.3369	46	*sn*-2 acyl chain ($[RC=O+74]^+$)
775.5665	100	neutral loss of *sn*-2 RCOOH + NH_3 from $[M+NH_4]^+$
855.6285	78	neutral loss of *sn*-1 RCOOH + NH_3 from $[M+NH_4]^+$
1165.8582	24	precursor ion $[M+H]^+$ with loss of H_2O
1183.8688	12	precursor ion $[M+H]^+$
1200.8953	88	precursor ion $[M+NH_4]^+$

[a] The abundances for this table and all figures were determined in such a way that the greatest abundance was arbitrarily assigned a value of 100 (%) and the remaining abundances were referred to it as is normal in mass spectrometry analysis.

33 Table 3S. Description of tandem mass spectrum of *sn*-26:7/28:7/28:8 TAG.

m/z	Abundance	Ion Description
347.2738	8	*sn*-1 acyl chain ($[RC=O]^+$ with loss of H_2O)
365.2844	25	*sn*-1 acyl chain ($[RC=O]^+$)
373.2895	8	*sn*-3 acyl chain ($[RC=O]^+$ with loss of H_2O)
375.3051	9	*sn*-2 acyl chain ($[RC=O]^+$ with loss of H_2O)
391.3001	26	*sn*-3 acyl chain ($[RC=O]^+$)
393.3157	27	*sn*-2 acyl chain ($[RC=O]^+$)
421.3106	9	*sn*-1 acyl chain ($[RC=O+74]^+$ with loss of H_2O)
439.3212	42	*sn*-1 acyl chain ($[RC=O+74]^+$)
447.3263	8	*sn*-3 acyl chain ($[RC=O+74]^+$ with loss of H_2O)
449.3419	8	*sn*-2 acyl chain ($[RC=O+74]^+$ with loss of H_2O)
465.3369	45	*sn*-3 acyl chain ($[RC=O+74]^+$)
467.3525	42	*sn*-2 acyl chain ($[RC=O+74]^+$)
829.6135	54	Neutral loss of *sn*-2 RCOOH + NH_3 from $[M+NH_4]^+$
831.6291	90	Neutral loss of *sn*-3 RCOOH + NH_3 from $[M+NH_4]^+$
857.6442	100	Neutral loss of *sn*-1 RCOOH + NH_3 from $[M+NH_4]^+$
1221.9208	19	Precursor ion $[M+H]^+$ with loss of H_2O
1239.9314	11	Precursor ion $[M+H]^+$
1256.9585	85	Precursor ion $[M+NH_4]^+$

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Table 4S. Description of tandem mass spectrum of *sn*-28:7/28:8/28:8 TAG.

m/z	Abundance	Ion Description
373.2895	18	*sn*-2 acyl chain ($[RC=O]^+$ with loss of H_2O)
375.3051	9	*sn*-1 acyl chain ($[RC=O]^+$ with loss of H_2O)
391.3001	42	*sn*-2 acyl chain ($[RC=O]^+$)
393.3157	23	*sn*-1 acyl chain ($[RC=O]^+$)
447.3263	42	*sn*-2 acyl chain ($[RC=O+74]^+$ with loss of H_2O)
449.3419	23	*sn*-1 acyl chain ($[RC=O+74]^+$ with loss of H_2O)
465.3369	46	*sn*-2 acyl chain ($[RC=O+74]^+$)
467.3525	25	*sn*-1 acyl chain ($[RC=O+74]^+$)
855.6285	81	Neutral loss of *sn*-1 RCOOH + NH_3 from $[M+NH_4]^+$
857.6442	100	Neutral loss of *sn*-2 RCOOH + NH_3 from $[M+NH_4]^+$
1247.9365	23	Precursor ion $[M+H]^+$ with loss of H_2O
1265.9471	14	Precursor ion $[M+H]^+$
1282.9742	91	Precursor ion $[M+NH_4]^+$

Table 5S. The content of TAGs (in % of total triacylglycerols) from the three cultivated dinoflagellates (*Amphidinium carterae*, *Cystodinium* sp., and *Peridinium aciculiferum*).

TAG	*Amphidinium carterae*	*Cystodinium* sp.	*Peridinium aciculiferum*
18:5/18:5/18:5	1.50	1.63	1.60
18:5/18:5/22:6	2.38	2.19	2.69
18:5/18:5/20:5	3.65	4.73	4.45
18:5/20:5/22:6	6.16	6.58	7.93
18:5/18:5/20:4	0.22	0.13	0.16
22:6/22:6/22:6	1.26	1.35	1.33
20:5/22:6/22:6	2.34	2.75	2.87
20:5/20:5/22:6	2.78	2.88	2.36
20:5/20:5/20:5	0.82	0.83	0.84
20:5/20:5/18:4	1.04	1.09	1.08
18:5/18:5/18:1	0.46	0.41	0.43
18:5/18:5/16:1	0.31	0.23	0.26
20:5/20:5/20:4	0.23	0.14	0.17
18:2/18:5/22:6	0.36	0.29	0.32
16:1/18:5/22:6	0.29	0.21	0.24
22:6/28:8/28:8	0.25	0.16	0.19
22:6/24:6/28:8	0.22	0.13	0.16
18:2/22:6/22:6	0.27	0.19	0.21
22:6/24:6/26:7	0.21	0.12	0.15
18:2/20:5/22:6	0.24	0.15	0.18
16:1/20:5/22:6	0.26	0.18	0.20
18:2/18:4/22:6	0.21	0.12	0.15
26:7/28:8/28:8	0.19	0.09	0.12
24:6/28:8/28:8	0.19	0.09	0.12
16:0/18:5/22:6	9.31	13.16	11.43
22:6/28:7/28:8	0.23	0.14	0.17
20:5/20:5/16:1	0.24	0.15	0.18
16:1/18:4/22:6	0.25	0.16	0.19
18:2/18:3/18:5	0.32	0.25	0.27
18:2/22:6/24:6	0.23	0.14	0.17
18:1/22:6/22:6	0.64	0.62	0.63
18:2/22:5/22:6	0.25	0.16	0.19
16:0/22:6/22:6	7.40	7.52	9.11
18:2/20:4/22:6	0.23	0.14	0.17
16:0/20:5/22:6	8.04	10.74	8.35
20:5/20:5/18:1	0.34	0.27	0.29
16:1/20:4/22:6	0.24	0.15	0.18
18:1/18:4/22:6	0.30	0.22	0.25
16:0/20:5/20:5	8.78	10.73	8.53
16:1/18:3/22:6	0.36	0.29	0.32

18:2/18:3/20:5	0.29	0.21	0.24
16:0/18:4/22:6	0.69	0.68	0.69
18:3/18:3/18:3	0.22	0.13	0.16
18:2/18:2/18:5	0.29	0.21	0.24
28:7/28:8/28:8	0.18	0.08	0.11
26:7/28:7/28:8	0.19	0.09	0.12
24:6/28:7/28:8	0.19	0.09	0.12
18:5/16:1/16:1	0.25	0.16	0.19
18:2/22:6/24:5	0.17	0.07	0.10
18:1/22:5/22:6	0.22	0.13	0.16
18:1/20:4/22:6	0.25	0.16	0.19
16:0/20:4/22:6	0.28	0.20	0.23
18:2/18:2/22:6	0.30	0.22	0.25
22:6/18:3/16:0	0.44	0.39	0.41
18:4/18:4/16:0	0.97	1.01	1.00
18:2/18:2/20:5	0.27	0.19	0.21
16:1/18:2/22:6	0.23	0.14	0.17
18:2/18:3/18:3	0.21	0.12	0.15
18:5/18:1/18:2	0.36	0.29	0.32
18:4/18:2/18:2	0.23	0.14	0.17
18:1/18:4/18:3	0.27	0.19	0.21
20:5/16:1/16:1	0.22	0.13	0.16
16:0/18:2/18:5	0.29	0.21	0.24
18:5/18:1/16:1	0.22	0.13	0.16
16:0/16:1/18:5	0.32	0.25	0.27
18:1/22:6/24:5	0.23	0.14	0.17
18:0/22:5/22:6	0.28	0.20	0.23
18:2/18:2/24:6	0.19	0.09	0.12
18:1/18:2/22:6	0.21	0.12	0.15
18:2/18:2/22:5	0.18	0.08	0.11
16:1/18:2/22:5	0.20	0.11	0.14
20:4/18:2/18:2	0.19	0.09	0.12
20:4/20:4/16:0	0.23	0.14	0.17
22:6/18:1/16:1	0.23	0.14	0.17
18:2/18:2/18:3	0.18	0.08	0.11
22:6/16:1/16:0	0.40	0.34	0.36
18:5/18:1/18:1	0.25	0.16	0.19
20:5/18:1/18:2	0.23	0.14	0.17
16:0/18:2/20:5	0.28	0.20	0.23
16:0/18:2/18:4	0.22	0.13	0.16
18:1/18:3/18:3	0.23	0.14	0.17
20:5/18:1/16:1	0.26	0.18	0.20
16:1/18:2/18:3	0.21	0.12	0.15
18:1/18:2/24:6	0.20	0.11	0.14

16:0/18:2/24:6	0.24	0.15	0.18
18:3/18:3/16:0	0.18	0.08	0.11
18:1/18:2/22:5	0.20	0.11	0.14
20:5/18:1/18:1	0.23	0.14	0.17
18:1/18:2/18:3	0.19	0.09	0.12
16:0/18:1/22:6	0.83	0.84	0.85
16:0/18:2/22:5	0.26	0.18	0.20
20:5/16:1/16:0	0.35	0.28	0.30
16:1/16:1/18:3	0.22	0.13	0.16
14:0/18:2/18:3	0.23	0.14	0.17
14:0/16:1/18:3	0.24	0.15	0.18
18:4/18:1/18:1	0.29	0.21	0.24
16:0/18:1/18:4	0.53	0.49	0.51
18:2/18:2/18:2	0.20	0.11	0.14
16:0/18:2/18:3	0.35	0.28	0.30
16:0/16:1/18:3	0.26	0.18	0.20
16:1/16:1/18:2	0.21	0.12	0.15
16:0/18:2/20:4	0.24	0.15	0.18
16:1/18:2/18:2	0.21	0.12	0.15
16:0/16:0/20:5	6.01	6.90	6.69
18:1/18:3/16:1	0.23	0.14	0.17
18:3/18:1/14:0	0.26	0.18	0.20
14:0/18:2/18:2	0.19	0.09	0.12
18:1/18:1/24:6	0.20	0.11	0.14
18:2/16:1/14:0	0.23	0.14	0.17
18:1/20:1/22:6	0.19	0.09	0.12
18:0/18:1/22:6	0.27	0.19	0.21
18:1/18:1/18:3	0.24	0.15	0.18
18:0/18:2/22:5	0.20	0.11	0.14
16:0/18:1/22:5	0.31	0.23	0.26
14:0/16:0/18:3	0.26	0.18	0.20
18:0/18:2/18:3	0.22	0.13	0.16
16:1/16:1/14:0	0.24	0.15	0.18
18:3/18:1/16:0	0.32	0.25	0.27
18:1/18:2/18:2	0.16	0.06	0.09
18:3/18:0/16:1	0.22	0.13	0.16
16:0/18:1/20:4	0.26	0.18	0.20
18:0/18:1/18:4	0.28	0.20	0.23
16:1/18:1/18:2	0.17	0.07	0.10
16:1/16:1/18:1	0.23	0.14	0.17
16:0/18:2/18:2	0.32	0.25	0.27
16:0/16:1/18:2	0.35	0.28	0.30
16:0/16:0/18:3	0.60	0.57	0.59
16:1/16:1/16:0	0.21	0.12	0.15

18:1/16:1/14:0	0.25	0.16	0.19
14:0/16:0/18:2	0.27	0.19	0.21
14:0/16:1/18:1	0.26	0.18	0.20
16:0/18:1/24:5	0.24	0.15	0.18
16:1/16:0/14:0	0.24	0.15	0.18
16:0/18:0/22:5	0.21	0.12	0.15
16:0/18:1/22:4	0.20	0.11	0.14
18:0/18:1/20:4	0.20	0.11	0.14
18:0/18:2/18:2	0.21	0.12	0.15
18:1/18:1/18:2	0.23	0.14	0.17
16:1/18:1/18:1	0.24	0.15	0.18
18:1/18:2/16:0	0.20	0.11	0.14
18:1/18:1/16:1	0.24	0.15	0.18
18:1/18:1/14:0	0.28	0.20	0.23
18:1/16:1/16:0	0.26	0.18	0.20
16:0/16:0/18:2	0.28	0.14	0.21
16:0/16:0/16:1	0.55	0.51	0.53
18:1/16:0/14:0	0.27	0.19	0.21
14:0/16:0/16:0	0.65	0.63	0.64
18:1/18:1/18:1	0.26	0.18	0.20
18:0/18:1/18:2	0.22	0.13	0.16
16:0/18:1/18:1	0.27	0.19	0.21
16:0/18:0/18:2	0.27	0.19	0.21
18:1/16:0/16:0	0.30	0.22	0.25
16:0/16:0/16:0	0.41	0.35	0.37
18:1/18:1/18:0	0.25	0.16	0.19
16:0/18:0/18:1	0.16	0.06	0.09

Table 6S. Description of tandem mass spectrum of 28:7/28:8-DAG.

m/z	Abundance	Ion Description
373.2891	8	Sn-1 acyl chain ($[RC{=}O]^+$ with loss of H_2O)
375.3048	12	Sn-2 acyl chain ($[RC{=}O]^+$ with loss of H_2O)
391.2997	24	Sn-1 acyl chain ($[RC{=}O]^+$)
393.3154	33	Sn-2 acyl chain ($[RC{=}O]^+$)
447.3259	11	Sn-1 acyl chain ($[RC{=}O +74]^+$ with loss of H_2O)
449.3416	19	Sn-2 acyl chain ($[RC{=}O +74]^+$ with loss of H_2O)
465.3369	47	Neutral loss of sn-2 RCOOH + NH_3 from $[M+NH_4]^+$
467.3525	25	Neutral loss of sn-1 RCOOH + NH_3 from $[M+NH_4]^+$
857.6448	100	Precursor ion $[M+H]^+$ with loss of H_2O
875.6554	6	Precursor ion $[M+H]^+$
892.6819	2	Precursor ion $[M+NH_4]^+$

Table 7S. Description of tandem mass spectrum of *sn*-28:8/16:0-PC.

m/z	Abundance	Ion Description
152.9958	89	Glycerol-3-phosphate ion with loss of H_2O
168.0431	36	Phosphocholine with loss of methyl
224.0690	17	Phosphocholine with loss of methyl and H_2O
255.2329	14	*sn*-2 $RCOO^-$ ion
363.3060	9	Loss of CO_2 from *sn*-1 $RCOO^-$ ion
407.2953	8	*sn*-1 $RCOO^-$ ion
462.2989	6	Neutral loss of *sn*-1 RCOOH group, loss of methyl and acetate from precursor ion
480.3094	7	Loss of *sn*-1 acyl chain as ketene (RCH=C=O), methyl and acetate from precursor ion
614.3617	23	Neutral loss of *sn*-2 RCOOH group, loss of methyl and acetate from precursor ion
632.3719	45	Loss of *sn*-2 acyl chain as ketene (RCH=C=O), methyl and acetate from precursor ion
799.5286	8	Loss of choline and acetate from precursor ion
870.6021	100	Loss of methyl and acetate from precursor ion, i.e. $[M-15]^-$
944.6391	12	Precursor ion $[M+CH_3COO]^-$

Table 8S. Description of tandem mass spectrum of *sn*-28:8/16:0-PA.

m/z	Abundance	Ion Description
152.9960	24	Glycerol-3-phosphate ion with loss of H_2O
171.0067	11	Glycerol-3-phosphate ion
255.2328	100	*sn*-2 $RCOO^-$ ion
363.3060	12	Loss of CO_2 from *sn*-1 $RCOO^-$ ion
391.2253	19	Neutral loss of *sn*-1 RCOOH group from $[M-H]^-$
407.2957	19	*sn*-1 $RCOO^-$ ion
409.2368	24	Loss of *sn*-1 acyl chain as ketene (RCH=C=O) from $[M-H]^-$
543.2879	38	Neutral loss of *sn*-2 RCOOH group from $[M-H]^-$
561.2990	42	Loss of *sn*-2 acyl chain as ketene (RCH=C=O) from $[M-H]^-$
799.5281	33	Precursor ion $[M-H]^-$

Table 9S. Description of tandem mass spectrum of *sn*-28:8-LPC

m/z	Abundance	Ion Description
152.9958	65	Glycerol-3-phosphate ion with loss of H_2O
168.0431	17	Phosphocholine with loss of methyl
224.0693	4	Neutral loss of *sn*-1 RCOOH group. loss of methyl and acetate from precursor ion
242.0799	6	Loss of *sn*-1 acyl chain as ketene (RCH=C=O). methyl and acetate from precursor ion
363.3057	12	Loss of CO_2 from *sn*-1 $RCOO^-$ ion
407.2956	45	*sn*-1 $RCOO^-$ ion
561.2987	3	Loss of choline and acetate from precursor ion
632.3722	100	Loss of methyl and acetate from precursor ion, i.e. $[M-CH_3]^-$
706.4089	8	Precursor ion $[M+CH_3COO]^-$

Table 10S. Description of tandem mass spectrum of *sn*-28:8-LPA

m/z	Abundance	Ion Description
152.9958	100	Glycerol-3-phosphate ion with loss of H_2O
171.0064	16	Glycerol-3-phosphate ion
363.3052	26	Loss of CO_2 from *sn*-1 $RCOO^-$ ion
407.2950	81	*sn*-1 $RCOO^-$ ion
561.2987	27	Precursor ion $[M-H]^-$