Supporting Information for

Comprehensive Dual Liquid Chromatography with Quadruple Mass Spectrometry (LC1MS2×LC1MS2 = LC2MS4) for Analysis of *Parinari Curatellifolia* and Other Seed Oil Triacylglycerols

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Contents of Supporting Information:

- More detailed RFN DAG composition of *Parinari curatellifolia* seed oil extract (Table S-19)
- RFN DAG composition of SBO by APCI-MS (Table S-20)

8. Detailed compositions of TAGs for CPO, PSO, and SBO.
   - Detailed RFN triacylglycerol (TAG) composition of CPO by APCI-MS (Table S-21)
   - Detailed RFN TAG composition of PSO by APCI-MS (Table S-22)
   - Detailed RFN TAG composition of SBO by APCI-MS (Table S-23)
9. ^{2}D UHPLC contour plot for CPO.
   - ^{2}D UHPLC Plots for CPO by APPI-MS on TSQ Quantum Access Max mass spectrometer (Fig. S-4)
   - ^{2}D UHPLC Plots for CPO by ESI-MS on LCQ Deca XP mass spectrometer (Fig. S-5)
10. ^{2}D UPHLC contour plot for SBO.
   - ^{2}D UHPLC Plots for SBO by APPI-MS on TSQ Quantum Access Max mass spectrometer (Fig. S-6)
   - ^{2}D UHPLC Plots for SBO by ESI-MS on LCQ Deca XP mass spectrometer (Fig. S-7)

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1. Experimental Section

Chemicals

a) Boron Trifluoride (BF_3) – 14 % in methanol obtained from Sigma-Aldrich (St. Louis, MO).
b) Chloroform – Sigma-Aldrich 99.9 % A.C.S. HPLC grade.
c) Dichloromethane (DCM) – Fisher Scientific (Pittsburgh, PA) Optima grade.
d) Ethanol (EtOH) – Sigma-Aldrich 100 % (200 proof) HPLC/Spectrophotometric grade.
e) Isooctane (2,2,4-trimethyl pentane) – Mallinckrodt (Paris, KY).
f) Methanol (MeOH) – Fisher Scientific Optima LC/MS grade.
g) Potassium chloride (KCl) – certified A.C.S. grade obtained from Fisher Scientific.
h) Sodium chloride (NaCl) – A.C.S. reagent grade obtained from Sigma (St. Louis, MO).
i) Sodium Hydroxide (NaOH) – A.C.S. reagent grade obtained from Aldrich (Milwaukee, WI).
j) Water – Obtained from in-house Millipore (Bedford, MA) Milli-Q Water Purification System.

Qualitative Standards

a) Multi-component FAME Standard - GLC Reference Standard 68B from Nu-Check Prep (Elysian, MN) contains 18 FAME derivatives of fatty acids ranging from C14 to C24 and was prepared as a solution at 100 mg in 50 mL isooctane.
b) Multi-component FAME Standard – GLC Reference Standard 14B from Nu-Check Prep contains the FAME derivatives of the five odd carbon number unsaturated fatty acids from C13:0 to C21:0. It was prepared as a solution at 100 mg in 50 mL isooctane.
c) Methyl Tricosanoate (FAME derivative of C23:0 fatty acid) – Obtained from Nu-Check Prep and prepared as a solution at 15 mg in 25 mL isooctane.
d) Methyl Pentacosanoate (FAME derivative of C25:0 fatty acid) – Obtained from Santa Cruz Biotechnology, Inc. (Dallas, TX) and prepared as a solution at 15 mg in 25 mL isooctane.
e) Methyl hexacosanoate (FAME derivative of C26:0 fatty acid) – Obtained from Matreya LLC (Pleasant Gap, PA) and prepared as a solution at 15 mg in 25 mL isooctane.

Folch Extraction of *Parinari curatellifolia* Seeds

Parinari curatellifolia seeds were obtained from Top Tropicals (Ft. Myers, FL). Seeds were placed in a -80 °C freezer for two hours. The hard, thick shells were then cracked with a hammer, and the inner, white endosperms were obtained. The average seed mass, including the shell, was 5.2 g, and the average recovered portion was 0.41 g, or about 8 % of the total. The endosperms were ground in an electric grinder. The resulting oily meal was collected, and 0.2 g portions were weighed for extraction. The extraction of Folch *et al.*[1] was performed using two successive 4 mL portions of 2:1 chloroform: methanol. For the initial portion stirring was for 20 min. Samples were then centrifuged at 1000 rpm for 2 min and the supernatant was recovered. This procedure was then repeated, but for the second portion stirring was for 5 min. The recovered extracts were

combined and washed with 2 mL of aqueous 0.1 % KCl. A final centrifugation at 1000 rpm for 2 min was performed, and the lower, chloroform layers were collected. Solvent evaporation to constant mass was performed at room temperature under a stream of nitrogen gas. The final, oily residues obtained were on average 45 % by mass of the ground portions weighed for extraction. A solution of 67.6 mg PSO in 50 mL de-aerated (da-) dichloromethane (DCM) / methanol (MeOH) (1:1), = 1.352 mg/mL, was initially prepared and kept at -2 °C. Later, this solution was brought to room temperature and 25.0 mL was transferred to a 25.0 mL flask, 1.0 mL was removed, and 1.0 mL of 25.0 μg/mL d_6-α-tocopherol internal standard (IS) was added to give 1.298 mg/mL *P. curatellifolia* with 1.0 μg/mL IS.

The CPO was obtained by hexane Soxhlet extraction as previously described.[2] 1.3768 mg was added to an amber volumetric flask, ~30 mL of da-DCM/MeOH (1:1) was added with swirling, 4.0 mL of 25.0 μg/mL d_6-α-tocopherol IS was added, and the solution was made to 100 mL with da-DCM/MeOH (1:1) to give 1.3768 mg/mL oil with 1.0 μg/mL IS.

An 8 fluid ounce bottle of organic wild soybean (Glycine soja) oil (SBO) with an expiration date of 11/2019 was purchased from an online marketplace and was used as received. A solution of 1.3162 mg/mL SBO with 1.0 μg/mL d_6-α-tocopherol IS was prepared the same way as the CPO.

2. FAME Preparation of Oil Samples and GC Analysis

For all oil samples FAME derivatives were prepared as described in **AOCS Official Method Ce 1b-89** with the following modifications:

a) The parts of the method related to the absolute determination of eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) were omitted.
b) The entire procedure was performed at room temperature (22 °C). Saponification with 0.5 M methanolic NaOH was overnight (16 – 20 hrs), and BF_3 treatment was for 45 - 60 min.
c) For each sample, two extractions using 1 mL isooctane for each were performed; however, the evaporation of the combined extracts to 1 mL was omitted.

GC Apparatus

a) GC column – Supelco (Bellefonte, PA) Omegawax 250, 30 m x 0.25 mm x 0.25 μm film thickness.
b) Gas Chromatograph – Agilent Technologies (Santa Clara, CA) 6890N GC with G2613A injector, split/splitless inlet, flame ionization detector (FID), and using OpenLab CDS ChemStation Edition for GC Systems (Rev. C.01.05 [35]) software.
c) GC-MS – Agilent Technologies 5975C Inert XL EI/CI MSD with 7890A GC System and G4513A injector, split/splitless inlet, and using MassHunter GC/MS Acquisition (B.07.00 SP1.1549) software.

GC-FID Method

The GC-FID method was as described in **AOCS Official Method Ce 1b-89** with the following specifications and modifications:

a) Carrier gas – Helium with operation in constant flow mode at 1 mL/min.
b) FID – Temperature set at 270 °C with hydrogen flow at 45 mL/min, air flow at 450 mL/min, and make-up gas (Nitrogen) flow at 45 mL/min.
c) Inlet – Temperature set at 250 °C; 1 μL injection; operation in split mode at 50:1 split.
d) Oven – Initial temperature of 170 °C, temperature gradient of 1 °C/min to 250 °C.
e) Run Time – 80 min.

GC-MSD Method

The GC part of the GC-MSD method was similar to that described above for the GC-FID method. Total ion current chromatograms were acquired in scanning mode from *m/z* 50 to m/z 450 at 1.9 scans/second and a step size of 0.1 *m/z*. Samples were run using electron ionization (EI) mode and again using positive ion chemical ionization (CI) mode with methane reagent gas.

3. HPLC and MS Instruments and Conditions

A) Agilent 1200 HPLC *(Agilent Technologies, Santa Clara, CA)*

Solvent module with membrane degasser (G1379B), quaternary pump (G1311A), autosampler (G1329A) with 1290 thermostat (G1330B) at 15 °C, thermostatted column compartment (G1316A), diode array detector (DAD) SL (G1315C), two-channel 24-bit analog-to-digital converter #1 (ADC) (35900E).

Two Inertsil ODS-2 columns in series, 25 cm × 4.6 mm, 5 µm particles (GL Sciences, Torrance, CA, USA) joined by a circularly bent 7-cm piece of 0.007 in. i.d. stainless steel tubing.

Columns were maintained at 10 °C throughout. 20 µL of standards and samples injected.

I. ^{1}D Gradient elution as follows:

1) Fat-soluble vitamin (FSV) standards:

Table S-1. ^{1}D HPLC gradient for fat-soluble vitamins.

Time (min)	%A (MeOH)	%B (ACN)	%C (EtOH)	%D (DCM)
0.0	95.0	0.0	5.0	0.0
25.0	95.0	0.0	5.0	0.0
30.0	60.0	0.0	15.0	25.0
40.0	65.0	0.0	10.0	25.0
50.0	65.0	0.0	10.0	25.0
51.0	95.0	0.0	5.0	0.0
54.0	95.0	0.0	5.0	0.0

2) Seed oil extracts:

Table S-2. ^{1}D HPLC gradient for seed oil extracts.

Time (min)	%A (MeOH)	%B (ACN)	%C (EtOH)	%D (DCM)
0.0	95.0	0.0	5.0	0.0
25.0	95.0	0.0	5.0	0.0
30.0	60.0	0.0	15.0	25.0
40.0	65.0	0.0	10.0	25.0
50.0	65.0	0.0	10.0	25.0
70.0	65.0	0.0	10.0	25.0
90.0	50.0	0.0	25.0	25.0
100.0	35.0	0.0	40.0	25.0
110.0	30.0	0.0	45.0	25.0
118.0	30.0	0.0	45.0	25.0
120.0	95.0	0.0	5.0	0.0
130.0	95.0	0.0	5.0	0.0

II. ^{1}D Detector settings:

Table S-3. ^{1}D HPLC detector settings.

^{1}D Diode Array Detector (DAD)				
Wavelength (λ_{nm})	**Bandwidth ($\Delta\lambda_{nm}$)**	**Reference λ_{nm}**	**Reference $\Delta\lambda_{nm}$**	**Analyte(s)**
210	5	360	100	Generic
248	9	360	100	Phylloquinone (Vit. K_1)
265	9	360	100	Vitamin D_2 & D_3
297	11	450	100	Tocopherols (Vit. E)
326	11	450	100	Retinol (Vit. A), Retinyl Acetate, Retinyl Palmitate

^{1}D Fluorescence Detector (FLD)		
Excitation Wavelength (λ_{nm})	**Emission Wavelength (λ_{nm})**	**Analyte(s)**
Zero order [Xe lamp: 200-1200 nm]	310	α-Tocopheryl Acetate
Zero order (all λ)	330	Tocopherols (Vit. E)
Zero order (all λ)	420	Fluorescent 18:4-containing TAG reported in *Parinari glaberrimum*
Zero order (all λ)	470	Retinol (Vit. A), Retinyl Acetate, Retinyl Palmitate

^{1}D Corona Charged Aerosol Detector (CAD)	
Parameter	**Setting**
Range	20 pA
Filter	3
Power function	1.00
Gas (Nitrogen)	35 psi
Output offset	0%

^{1}D Evaporative Light Scattering Detector (ELSD) – Not Reported due to temporary signal failure	
Parameter	**Setting**
Evaporator	80 ^{o}C
Nebulizer	90 ^{o}C
Gas (Nitrogen)	1.20
Photomultiplier	8.4
Data Rate	40 Hz
Smoothing	5

B) Agilent 1290 UHPLC *(Agilent Technologies, Santa Clara, CA)*

Solvent module with membrane degasser, Infinity binary pump (G4220A), Infinity autosampler (G4226A - disconnected) with FC/ALS Thermostat (G1330B), thermostatted column compartment (G1316C), Infinity diode array detector (DAD) (G4212A), 8-port, 2-position, 1200 bar column-switching valve (G1170A).
Lab-made Ag-Ion column from ES Industries strong cation exchange column (Epic-SCX, #122191-ESCX), 10.0 cm × 2.1 mm, 3 µm, 120 Å, particles (ES Industries, West Berlin, NJ, USA).
Column was maintained at 10 °C throughout. Gradient stop time 1.86 min. Modulation time 1.91 min.

I. ^{2}D Shifted gradient elution as follows:

1) Fat-soluble vitamin (FSV) standards:

Table S-4. ^{2}D UHPLC shifted gradient for fat-soluble vitamins. See Figure S-1.

	^{2}D Time (min)				
^{1}D Time (min)	**0.00**	**0.55**	**1.5**	**1.70**	**1.80**
0.0	100.0	100.0	90.0	90.0	100.0
40.0	100.0	100.0	90.0	90.0	100.0
50.0	100.0	100.0	10.0	10.0	100.0
60.0	100.0	100.0	35.0	35.0	100.0
70.0	100.0	100.0	60.0	60.0	100.0
120.0	100.0	100.0	90.0	90.0	100.0
130.0	100.0	100.0	90.0	90.0	100.0

Time programmed exactly as 130 min run for seed oils to ensure identical gradient, and OpenLab ChemStation automatically truncated runs at 54 min.

2) Cherry (*Prunus cerasus*) and *Parinari curatellifolia* seed oil extracts:

Table S-5. ^{2}D UHPLC shifted gradient for cherry and parinari seed oil extracts. See Figure S-2.

	^{2}D Time (min)				
^{1}D Time (min)	**0.00**	**0.55**	**1.5**	**1.70**	**1.80**
0.0	100.0	100.0	90.0	90.0	100.0
40.0	100.0	100.0	90.0	90.0	100.0
50.0	100.0	100.0	10.0	10.0	100.0
60.0	100.0	100.0	35.0	35.0	100.0
70.0	100.0	100.0	60.0	60.0	100.0
120.0	100.0	100.0	90.0	90.0	100.0
130.0	100.0	100.0	90.0	90.0	100.0

3) Commercial wild soybean (*Glycine soja*) oil:

Table S-6. ^{2}D UHPLC shifted gradient for cherry and parinari seed oil extracts. See Figure S-3.

	^{2}D Time (min)				
^{1}D Time (min)	**0.00**	**0.55**	**1.5**	**1.70**	**1.80**
0.0	100.0	100.0	95.0	95.0	100.0
40.0	100.0	100.0	95.0	95.0	100.0
50.0	100.0	100.0	25.0	10.0	100.0
60.0	100.0	100.0	40.0	35.0	100.0
70.0	100.0	100.0	90.0	90.0	100.0
120.0	100.0	100.0	95.0	95.0	100.0
130.0	100.0	100.0	95.0	95.0	100.0

II. ^{2}D Detector settings:

Table S-7. ^{2}D HPLC detector settings (Identical to ^{1}D DAD settings).

^{2}D Diode Array Detector (DAD)				
Wavelength (λ_{nm})	Bandwidth ($\Delta\lambda_{nm}$)	Reference λ_{nm}	Reference $\Delta\lambda_{nm}$	Analyte
210	5	360	100	Generic
248	9	360	100	Phylloquinone (Vit. K_1)
265	9	360	100	Vitamin D_2 & D_3
297	11	450	100	Tocopherols (Vit. E)
326	11	450	100	Retinol (Vit. A), Retinyl Acetate, Retinyl Palmitate

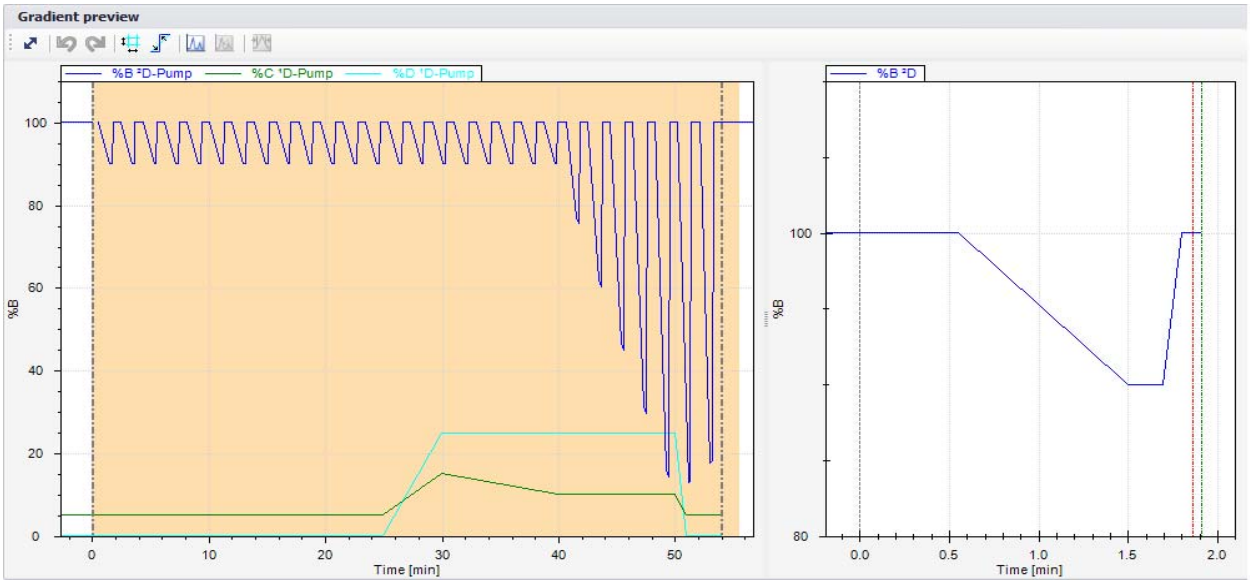

Figure S-1. ^{2}D UHPLC shifted gradient for fat-soluble vitamins. See Table S-4.

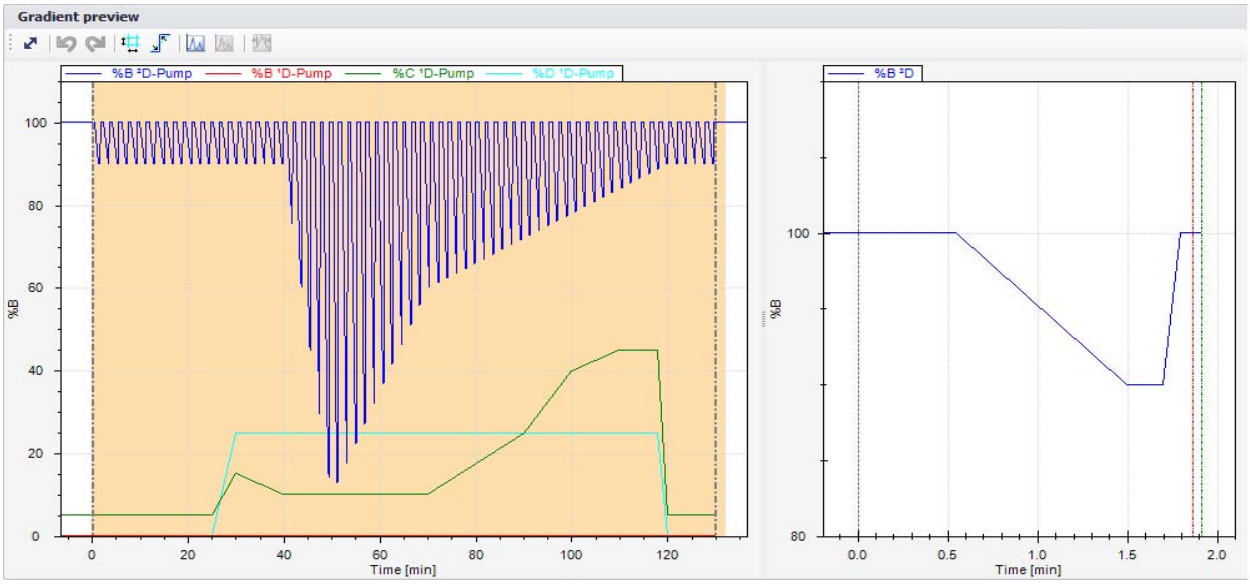

Figure S-2. ^{2}D UHPLC shifted gradient for cherry and parinari seed oil extracts. See Table S-5.

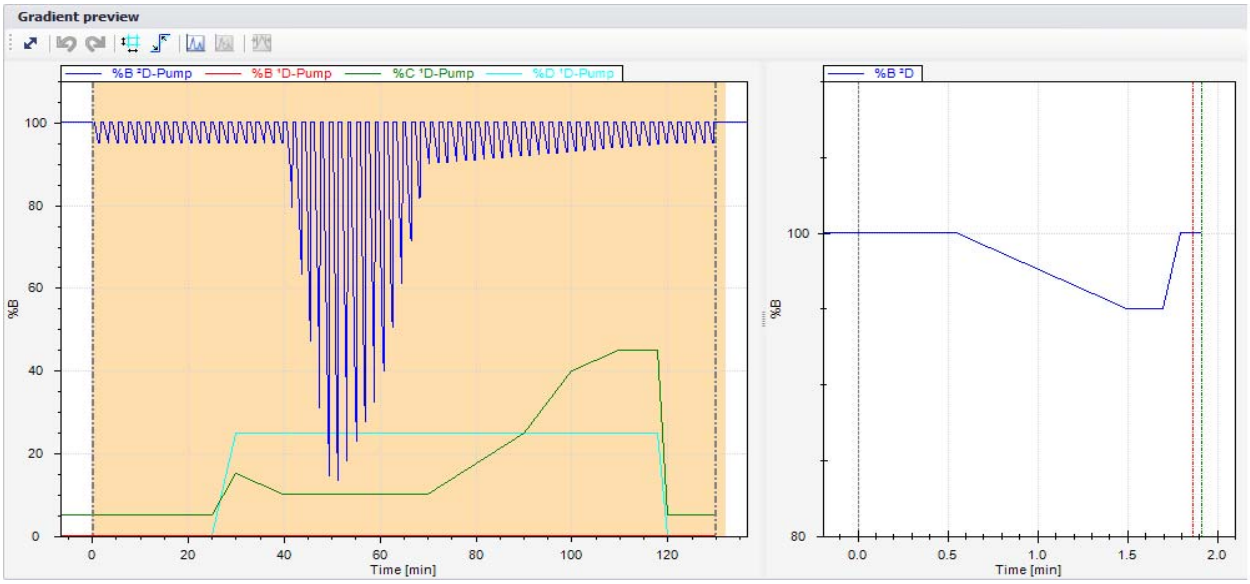

Figure S-3. ^{2}D UHPLC shifted gradient for commercial wild soybean (*Glycine soja*) samples. See Table S-6.

4. Mass Spectrometer Operating Conditions

A) ^{1}D HPLC detection.

Table S-8. QExactive high resolution accurate mass Orbitrap™ mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) for qualitative ^{1}D HPLC analysis.

All runs use ammonium formate (NH_4OCOH) in methanol (1:4) at 20 μL/min supplied by Applied Biosystems AB140C dual piston syringe pump.

Fat-Soluble Vitamin Analysis			
Full-Scan ESI-MS		**Data-Dependent Acquisition (DDA) MS/MS**	
Parameter	**Setting**	**Parameter**	**Setting**
Source parameters	See below	In-source CID	0.0 eV
Run time	54 min	Precursor resolution	140,000
In-source CID	45.0 eV	Product resolution	70,000
Resolution	140,000	Precursor scan range	*m/z* 300-750
Scan range	*m/z* 200-2000	Loop	Top 2 precursors
AGC target	3e6	Isolation window	1.0 *m/z*
Max. inj. time	200 ms	Norm. collision energy	50
Mode	Centroid	Max. inj. time	Pre:100 ms/Prod:50 ms
Polarity	+ and -		

Cherry and Parinari Extract 130 min Analysis			
Up to 44 min same as FSV above. Soybean Oil the same, but first segment = 50 min.			
Full-Scan ESI-MS		**TAG DDA MS/MS**	
Parameter	**Setting**	**Parameter**	**Setting**
Sheath gas (Nitrogen)	25	In-source CID	0.0 eV
Auxiliary gas (Nitrogen)	0	Resolution	Pre:140,000/Prod:70,000
Sweep gas	0	Precursor scan range	*m/z* 700-1100
Spray voltage	4000 V	Loop	Top 2 precursors
Capillary temp.	250 °C	Isolation window	1.0 *m/z*
Run time	130 min	Norm. collision energy	15
In-source CID	45.0 eV	**DAG DDA MS/MS**	
Resolution	140,000	In-source CID	**80.0 eV**
Scan range	*m/z* 200-2000	Resolution	Pre:140,000/Prod:70,000
AGC target	3e6	Precursor scan range	*m/z* 350-750
Max. inj. time	200 ms	Loop	Top 3 precursors
Mode	Centroid	Isolation window	1.0 *m/z*
Polarity	+ and -	Norm. collision energy	35

Table S-9. TSQ Vantage EMR tandem sector quadrupole mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). Multi-segment qualitative and SIM and SRM quantitative analysis parameters for ^{1}D HPLC.

Fat-Soluble Vitamin Analysis

APCI Source Parameters

Parameter	Setting
Vaporizer heater	400 °C
Sheath gas (Nitrogen)	50
Auxiliary gas (Nitrogen)	5
Sweep gas	0
Capillary temp.	250 °C
Declustering voltage	0 V

1.0 mTorr Argon collision induced dissociation (CID) gas turned on throughout all scans.
All scans except precursor scans used Q3. All used 0.7 FWHM peak widths unless otherwise stated.
All scans were in (+) ion mode with centroided masses.

Segment 1 (0-2 min)	
Scan event 1. Q3 Full-scan MS	
Scan range	*m/z* 200-2000
Scan time	1.8 s
Scan events 2. & 3. DDA MS/MS	
Signal threshold	1e4
Scan time	1.0 s
Collision energy	19 V
Repeat	Top 2 precursors

Segment 2 (2-18 min)		
Scan event 1. Full-scan MS same as Segment 1		
Scan event 2. 1 DDA MS/MS same as Segment 1		
Scan event 3. Q3 Selected Ion Monitoring (**SIM**)		
0.5 s scan time	0.5 scan width	
m/z	**Analyte**	
269.227	All retinols	
287.238	Retinol (Vit. A)	
301.217	Retinoic Acid	
329.248	Retinyl Acetate	
Scan event 4. Selected Rxn. Monitoring (**SRM**)		
Scan time 0.5 s	Scan width 0.5	CID 19 V
Precursor (*m/z*)	**Product (*m/z*)**	**Analyte**
269.227	93.070	Retinol
301.217	159.123	Retinoic Acid
329.248	269.227	Ret. Acetate

Segment 3 (18-36 min)		
Scan event 1. Full-scan MS same as Segment 1		
Scan event 2. DDA MS/MS same as Segment 1		
Scan event 3. Q3 Selected Ion Monitoring (**SIM**)		
0.5 s scan time	0.5 scan width	
m/z	**Analyte**	
385.347	Cholecalciferol (Vit. D_3)	
397.347	Ergocalciferol (Vit. D_2)	

Segment 3 - Scan Event 3 – SIM Continued	
m/z	**Analyte**
403.358	δ-Tocopherol
416.365	γ,β-Tocopherol $[M]^{+}\cdot$
417.373	γ,β-Tocopherol $[M+H]^{+}$
431.389	α-Tocopherol
437.427	d_6-α-Tocopherol

Scan event 4. Selected Reaction Monitoring (**SRM**)		
Scan time 0.5 s	Scan width 0.5	CID 19 V
Precursor (*m/z*)	**Product (*m/z*)**	**Analyte**
385.347	367.337	Vitamin D_3
397.347	379.337	Vitamin D_2
403.358	137.122	δ-Tocopherol
416.365	151.133	γ,β-Tocopherol
417.373	151.133	γ,β-Tocopherol
431.389	165.149	α-Tocopherol
437.427	171.167	d_6-α-Tocopherol

Segment 4 (36-44 min)	
Scan event 1. Full-scan MS same as Segment 1	
Scan event 2. 1 DDA MS/MS same as Segment 1	
Scan event 3. Q3 Selected Ion Monitoring (**SIM**)	
0.5 s scan time	0.5 scan width
m/z	**Analyte**
451.358	Phylloquinone (Vit. K_1)
473.400	α-Tocopheryl Acetate

Scan event 4. Selected Reaction Monitoring (**SRM**)		
Scan time 0.5 s	Scan width 0.5	CID 19 V
Precursor (*m/z*)	**Product (*m/z*)**	**Analyte**
451.358	187.240	Vitamin K_1
473.400	207.250	α-Toco. Acetate

Segment 5 (44-54 min)
Identical to Segment 4 for these analyses.
SIM and SRM for β-Carotene removed.

Table S-10. TSQ Vantage EMR tandem sector quadrupole mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). Multi-segment qualitative and SIM and SRM quantitative analysis parameters for ^{1}D HPLC analysis.

Cherry and Parinari Seed Oil Extract Analysis			
APCI Source Parameters – Same as for FSV given in Table 9			
1.0 mTorr Argon CID gas turned on throughout all scans. All scans except precursor scans used Q3 with 0.7 FWHM peak widths unless otherwise stated. All scans were in (+) ion centroid mode.			
Segment 1 (0-2 min)		**Segment 5 (44-130 min)**	
Scan event 1. Same Full-Scan MS as for FSV.		**Scan event 1.** Same Full-Scan MS as for FSV.	
Scan event 2. Same 1 DDA MS/MS as for FSV.		**Scan event 2.** Narrow range full-scan MS of TAGs	
Scan event 3. Same DDA MS/MS as for FSV.		Scan range	*m/z* 800-1100
Segment 2 (2-18 min)		Scan time	0.40 s
Scan event 1. Same Full-Scan MS as for FSV.		**Scan event 3.** DDA MS/MS of TAGs	
Scan event 2. Same 1 DDA MS/MS as for FSV.		Signal threshold	1e4
Scan event 3. Same 4 x **SIM** as for FSV.		Scan time	1.0 s
Scan event 4. Same 3 x **SRM** as for FSV.		Collision energy	30 V
Segment 3 (18-36 min)		Repeat	Top precursor only
Scan event 1. Same Full-Scan MS as for FSV.		**Scan event 4.** Narrow range MS of $[DAG]^{+}$	
Scan event 2. Same 1 DDA MS/MS as for FSV.		Scan range	*m/z* 400-750
Scan event 3. Same 7 x **SIM** as for FSV.		Scan time	0.45 s
Scan event 4. Same 7 x **SRM** as for FSV.		**Scan event 5.** DDA MS/MS of $[DAG]^{+}$	
Segment 4 (36-44 min)		Signal threshold	1e4
Scan event 1. Same Full-Scan MS as for FSV.		Scan time	0.75 s
Scan event 2. Same 1 DDA MS/MS as for FSV.		Collision energy	40 V
Scan event 3. Same 2 x **SIM** as for FSV.		Repeat	Top precursor only
Scan event 4. Same 2 x **SRM** as for FSV.		**Segment 5. 54-130 min for Soybean Oil only.**	

B) ^{2}D UHPLC detection.

Table S-11. TSQ Quantum Access Max tandem sector quadrupole mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). Full-scan MS for ^{2}D UHPLC qualitative analysis.

Fat-Soluble Vitamin and Seed Oil Extract Analysis	
APPI Source Parameters	
Parameter	**Setting**
Vaporizer heater	400 °C
Sheath gas (Nitrogen)	60
Auxiliary gas (Nitrogen)	5
Sweep gas	0
Capillary temp.	270 °C
Skimmer offset	10 V

1.0 mTorr Argon CID gas turned on throughout all scans. All scans except precursor scans used Q3. All used 0.7 FWHM peak widths unless otherwise stated. All scans were in (+) ion centroid mode.
All runs use acetone dopant at 20 μL/min by Applied Biosystems AB140B dual piston syringe pump.

Scan event 1. Q3 Full-scan MS		**Scan events 2. Data-dependent MS/MS**	
Scan range	*m/z* 150-2000	Signal threshold	1e4
Scan time	1.0 s	Scan time	0.9 s
Runt time 53.50 min for FSVs. Run time 129.50 min for seed oil extracts.		Collision energy	50 V
		Repeat	Top precursor only

Table S-12. LCQ Deca XP hyperbolic ion trap mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). Full-scan MS for ^{2}D UHPLC qualitative analysis.

Fat-Soluble Vitamin and Seed Oil Extract Analysis			
APPI Source Parameters			
Parameter		**Setting**	
Sheath gas (Nitrogen)		35	
Auxiliary gas (Nitrogen)		5	
Capillary temp.		265 °C	
Spray Voltage		5000 V	
All scans were in (+) ion mode with centroided masses. All runs use ammonium formate (NH_4OCOH) in methanol (1:4) at 20 μL/min supplied by Applied Biosystems AB140C dual piston syringe pump.			
Scan event 1. Full-scan MS		**Scan events 2&3. Data-dependent MS/MS**	
Scan range	*m/z* 200-1050	Signal threshold	1e4
Scan time	1.0 s	Precursor range	*m/z* 200-1050
Runt time 54.0 min for FSVs. Run time 130.0 min for seed oil extracts.		Norm. Coll. Energy	45.0%
		Activation Q	0.350
		Activation time	900 ms
		Isolation width	2.0 *m/z*
		Repeat	Top 2 precursor

5. External standard results for tocopherols by APCI-MS, internal standard and external standard results by UV detection.

Table S-13. Internal and external standard results by UV detection and external standard results by SIM and SRM APCI-MS from ^{1}D HPLC, in ppm (= μg/g oil).

	Internal Standard Method									
		α-Toco	SD	r^2	γ-Toco	SD	r^2	δ-Toco	SD	r^2
Cherry	UV	217	22	0.9765	636	14	0.9662	151	10	0.9893
Parinari	UV	5427[a]	104		616	31				
Soybean	UV				193	19		205	12	
	External Standard Method									
		α-Toco	SD	r^2	γ-Toco	SD	r^2	δ-Toco	SD	r^2
Cherry	UV	217	22	0.9765	717	17	0.9738	118	13	0.9947
	SIM	278	18	0.9898	583	13	0.9766	98.0	5.1	0.9762
	SRM	244	21	0.9328	717	40	0.9459	126	10	0.9324
Parinari	UV	5427[a]	104		688	39				
	SIM	643.3	1.6		705	27				
	SRM	631	95		849	127				
Soybean	UV				168	24		186	15	
	SIM	30.8	1.8		150.8	4.3		213	11	
	SRM	42.0	1.2		174.2	6.9		187	17	

[a]This value highlights the danger of interfering species in UV detection.

Table S-14. Limits of detection (LOD) and limits of quantification (LOQ) calculated from calibration lines. Observed LOD and LOQ (*e.g.* from sequential dilution) are likely lower.

	Internal Standard Method			
		α-Toco (ppm)	**γ-Toco (ppm)**	**δ-Toco (ppm)**
LOD[a]	**UV**	200	15	44
b+3*$\sigma_{0.125}$	**SIM**	7.5	79	99
	SRM	6.5	42	23
LOQ[b]	**UV**	668	51	146
b+10*$\sigma_{0.125}$	**SIM**	25	264	330
	SRM	22	139	76
	External Standard Method			
		α-Toco (ppm)	**γ-Toco (ppm)**	**δ-Toco (ppm)**
LOD[a]	**UV**	200	36	71
b+3*$\sigma_{0.125}$	**SIM**	25	59	81
	SRM	20	39	13
LOQ[b]	**UV**	668	120	235
b+10*$\sigma_{0.125}$	**SIM**	82	196	271
	SRM	68	131	42

[a]Limit of Detection (LOD) area (E.S.) or ratio (I.S.) = (intercept (b) + 3 x standard deviation of lowest standard [0.125 μg/mL]) put into calibration equation and converted to ppm (=μg/g oil).

[b]Limit of Quantification (LOQ) area (E.S.) or ratio (I.S.) = (intercept (b) + 10 x standard deviation of lowest standard [0.125 μg/mL]) put into calibration equation and converted to ppm (=μg/g oil).

The results for UV detection of α-tocopherol in Table S-14 demonstrate the shortcomings of UV detection in real samples. Any other sterols or other molecules that absorb at all at the wavelength of 297 nm in the time range around 33.8 min will contribute to the peak area attributed to α-tocopherol. For instance, the second peak of di-eleosteroyl diacylglycerol, ElEl = *m/z* 595.5 $[DAG]^+$ and *m/z* 613.5 $[M+H]^+$, eluted overlapped with α-tocopherol (both at 33.78 min by APCI-MS) and was present in a much larger amount than α-tocopherol. Therefore, even a small absorbance of 18:3 at 297 nm would skew the results for α-tocopherol, as observed. By both SIM and SRM APCI-MS this overlap presented no problem.

It is important to note that both internal standard and external standard UV and APCI-MS approaches showed higher levels of tocopherols than were observed in the results from the commercial labs previously presented. Thus, all of these approaches, when coupled to an extract-and-shoot sample preparation approach, identified larger amounts of tocopherols than were found using the commonly used heated saponification, extraction and collection, followed by derivatization approach widely used.[3] Even when cherry kernels were analyzed without saponification and derivatization, the amount of tocopherols varied greatly with extraction conditions,[4] with the extraction of Folch *et al.*[1] commonly considered the 'gold standard'.[5]

Of course, as we previously reported with vitamin D, UV data should not be trusted without MS data to prove that the peaks are pure. And if not pure, as in the case of α-tocopherol, UV data should not be used for quantification.

On the other hand, as with vitamin D,[6] if MS data can be used to prove that the peaks are pure, UV data may be more sensitive and show lower standard deviations than APCI-MS, since APCI inherently has more chemical noise associated with the ionization process. This is demonstrated by the lower LOD and LOQ for γ-tocopherol in Table S-14, since these values are based on the standard deviation in the lowest standard (0.125 μg/mL).

6. Detailed compositions of FAMEs for PSO, CPO, and SBO.

Table S-15. Detailed response factor normalized and GC-FID fatty acid compositions of *Parinari curatellifolia* seed oil, including compositions of isomers of 18:3 (CN:db) and oxo-eleostearic acid.

	Parinari Seed Oil (PSO)					
	APPI-MS	**SD**	**GC-FID**			
M (14:0)	0.000%	0.000%	0.033%			
Po (16:1)	0.020%	0.001%	0.018%			
P (16:0)	9.136%	0.042%	9.287%		**GC-FID**	**SD**
El (all 18:3)	48.768%	0.096%	48.840%	α-El	90.00%	0.07%
L (18:2)	14.379%	0.137%	13.992%	β-El	7.63%	0.06%
O (18:1)	17.709%	0.060%	17.518%	Ln	0.09%	0.00%
S (18:0)	7.267%	0.113%	7.589%	18:3x1	1.70%	0.04%
A (20:0)	0.402%	0.006%	0.395%	18:3x2	0.38%	0.01%
G (20:1)	0.688%	0.014%	0.695%	18:3x3	0.14%	0.01%
21:0	0.003%	0.000%	0.000%	18:3x4	0.06%	0.01%
B (22:0)	0.031%	0.000%	0.032%		100.00%	
23:0	0.005%	0.000%	0.014%		**GC-FID**	**SD**
Lg (24:0)	0.022%	0.001%	0.033%	oxo-El-1	3.60%	0.49%
25:0	0.004%	0.000%	0.012%	oxo-El-2	81.01%	0.76%
Ce (26:0)	0.003%	0.000%	0.000%	oxo-El-3	2.07%	0.34%
oxo-El	1.563%	0.017%	1.543%	oxo-El-4	13.32%	0.30%
Sum	100.000%		100.000%		100.00%	

Table S-16. Detailed response factor normalized and GC-FID fatty acid compositions of cherry pit oil (not including isomers).

Cherry Pit Oil (CPO)			
FA	**APCI-MS**	**SD**	**GC-FID**
M	0.006%	0.000%	0.069%
Po	0.629%	0.030%	0.626%
P	8.841%	0.120%	8.324%
El	5.766%	0.115%	5.760%
L	32.650%	0.243%	33.320%
O	47.825%	0.203%	47.598%
S	2.437%	0.011%	2.507%
A	0.943%	0.008%	0.916%
G	0.423%	0.002%	0.405%
21	0.015%	0.001%	0.015%
B	0.208%	0.001%	0.202%
23	0.025%	0.001%	0.031%
Lg	0.193%	0.006%	0.187%
25	0.017%	0.001%	0.022%
Ce	0.022%	0.001%	0.018%
Sum	100.000%		100.000%

Table S-17. Detailed response factor normalized and GC-FID fatty acid compositions of soybean oil (not including isomers, discussed below).

Soybean Oil (SBO)			
FA	**APCI-MS**	**SD**	**GC-FID**
M	0.002%	0.000%	0.094%
Po	0.098%	0.009%	0.102%
P	12.109%	0.064%	11.953%
Ln	7.406%	0.103%	7.519%
L	52.699%	0.474%	51.515%
O	22.369%	0.189%	23.619%
S	4.286%	0.113%	4.175%
A	0.336%	0.008%	0.323%
G	0.197%	0.005%	0.184%
21	0.023%	0.000%	0.021%
B	0.341%	0.012%	0.329%
23	0.016%	0.000%	0.032%
Lg	0.106%	0.005%	0.102%
25	0.005%	0.000%	0.008%
Ce	0.007%	0.001%	0.021%
Sum	100.000%		100.000%

GC-FID FA compositions were determined from the weight percentage of fatty acid methyl esters (FAME) and converted from weight percent FAME to mole percent FA.

As expected, the composition in Table S-16 is in excellent agreement to the FA composition given for CPO previously.[2] Similarly, the FA composition for wild SBO (*Glycine soja*) is in excellent agreement with the composition of SBO from a dietary supplement recently reported using the 'dilute-and-shoot' approach with quadruple parallel mass spectrometry.[7]

7. Detailed compositions of diacylglycerols for CPO, PSO, and SBO.

Table S-18. Diacylglyerol (DAG) composition of CPO by response factor normalized APCI-MS.

Cherry Pit Oil (CPO)			
DAG	**% Comp.**	**SD**	**2/1**
ElEl	0.03%	0.01%	0.62
LEl	1.11%	0.07%	0.66
LL	18.14%	0.56%	0.47
OEl	0.54%	0.02%	0.54
PoO	0.19%	0.04%	0.64
PoP	0.57%	0.10%	0.54
OL	28.72%	1.62%	0.35
PL	12.06%	1.06%	0.23
OO	22.40%	1.14%	0.28
OP	11.38%	0.13%	0.28
SL	2.98%	0.09%	0.29
OS	1.89%	1.64%	0.26
Sum	100.00%		
DAG/TAG	1.08%	±0.03%	

Table S-19. More detailed diacylglycerol (DAG) composition of *Parinari curatellifolia* seed oil extract by response factor normalized APCI-MS.

Parinari Seed Oil (PSO)			
DAG	**% Comp.**	**SD**	**2/1**
oxEloxEl	0.02%	0.00%	
oxEoEo	0.75%	0.07%	0.21
oxEoL	0.10%	0.01%	0.28
oxEoO	0.17%	0.01%	**0.23**
oxEoP	0.10%	0.01%	0.30
ElEl	17.91%	0.62%	2.57
LEl	11.25%	0.10%	2.72
LL	11.49%	0.10%	4.19
OEl	12.60%	0.30%	1.57
PoO	0.75%	0.03%	1.61
PoP	0.06%	0.01%	1.37
OL	14.53%	0.45%	3.43
PL	6.73%	0.10%	1.53
OO	6.87%	0.17%	1.50
OP	6.91%	0.11%	0.72
SL	4.72%	0.17%	1.59
OS	5.03%	0.14%	0.52
Sum	100.00%		
DAG/TAG	1.52%	±0.05%	

Table S-20. Diacylglycerol (DAG) composition of SBO by response factor normalized APCI-MS.

Soybean Oil (SBO)			
DAG	**% Comp.**	**SD**	**2/1**
LnLn	0.49%	0.07%	0.34
LLn	7.29%	0.19%	0.54
LL	43.73%	1.39%	0.56
OLn	1.02%	0.18%	0.40
PoO	0.00%	0.00%	
PoP	0.03%	0.01%	0.71
OL	15.84%	1.20%	0.39
PL	15.78%	0.37%	0.20
OO	4.90%	0.22%	0.26
OP	3.93%	0.07%	0.29
SL	5.33%	0.10%	0.27
OS	1.67%	0.08%	0.26
Sum	100.00%		
DAG/TAG	1.39%	±0.04%	

8. Detailed compositions of TAGs for CPO, PSO, and SBO.

Table S-21. Detailed triacylglycerol (TAG) composition of CPO by response factor normalized APCI-MS. Structures shown here are not regiospecific.

Cherry Pit Oil (CPO)							
TAG	**RT**	**% Comp.**	**SD**	**TAG**	**RT**	**% Comp.**	**SD**
ElElEl	55.10	0.017%	0.001%	**LOA**	94.47	0.880%	0.021%
ElElL	56.80	0.634%	0.012%	**LLB**	94.98	0.153%	0.002%
LLEl	58.46	5.377%	0.066%	**POS**	95.97	0.380%	0.003%
LLL	60.33	3.964%	0.025%	**PLA**	96.46	0.218%	0.009%
ElElO	62.14	0.211%	0.008%	**SSL**	96.54	0.112%	0.003%
ElElP	63.32	0.040%	0.003%	**OL-21**	98.76	0.019%	0.001%
OLEl	64.22	4.258%	0.275%	**LL-23**	99.18	0.024%	0.000%
PLEl	65.50	2.044%	0.084%	**PPS**	99.76	0.001%	0.000%
LLO	66.35	13.434%	0.372%	**LElLg**	100.66	0.010%	0.000%
PoPL	67.27	0.902%	0.110%	**SOG**	101.77	0.018%	0.005%
LLP	67.76	3.506%	0.044%	**OOA**	102.36	0.755%	0.015%
ElElG	68.73	0.002%	0.000%	**OLB**	102.64	0.178%	0.003%
MOL	69.53	0.019%	0.001%	**LLLg**	102.95	0.140%	0.003%
EoEoS	71.12	0.028%	0.002%	**POA**	104.27	0.202%	0.001%
OOEl	71.12	2.090%	0.017%	**SSO**	104.37	0.130%	0.002%
POEl	72.73	0.614%	0.009%	**PBL**	104.42	0.058%	0.001%
OOL	73.73	16.632%	0.332%	**SLA**	104.68	0.060%	0.002%
LLG	73.86	0.318%	0.016%	**OO-21**	105.87	0.012%	0.002%
POPo	74.81	0.992%	0.117%	**OL-23**	106.04	0.028%	0.001%
POL	75.42	7.442%	0.144%	**LL-25**	106.25	0.016%	0.001%
LLS	76.40	0.774%	0.018%	**OOB**	108.92	0.148%	0.005%
PPL	77.30	0.597%	0.012%	**OLLg**	109.10	0.167%	0.003%
LElA	79.60	0.027%	0.001%	**LLCe**	109.28	0.017%	0.000%
ElElA	80.13	0.002%	0.000%	**PLLg**	110.63	0.052%	0.004%
SOEl	82.46	0.989%	0.033%	**POB**	110.65	0.046%	0.002%
OOO	82.51	17.235%	0.247%	**SLB**	110.83	0.020%	0.001%
OLG	82.59	0.477%	0.004%	**SOA**	110.89	0.057%	0.004%
OOP	84.44	6.991%	0.153%	**OO-23**	111.81	0.023%	0.001%
PLG	84.54	0.193%	0.015%	**OL-25**	111.95	0.018%	0.000%
SLO	85.28	1.695%	0.011%	**OOLg**	114.76	0.152%	0.009%
LLA	86.08	0.622%	0.009%	**OLCe**	114.83	0.020%	0.002%
POP	86.51	0.606%	0.001%	**PLCe**	116.40	0.005%	0.000%
SLP	87.36	0.309%	0.003%	**POLg**	116.42	0.042%	0.002%
PPP	89.98	0.001%	0.000%	**SLLg**	116.79	0.009%	0.001%
LL-21	90.60	0.016%	0.001%	**SOB**	116.82	0.011%	0.002%
OOG	91.14	0.270%	0.002%	**OO-25**	117.64	0.016%	0.002%
ElOA	91.70	0.027%	0.003%	**OOCe**	120.56	0.018%	0.001%
LElB	92.27	0.012%	0.000%	**POCe**	122.44	0.006%	0.002%
OOS	93.82	2.332%	0.005%	**SOLg**	122.79	0.011%	0.001%
EoSS	93.98	0.066%	0.020%	**OOMo**	126.67	0.001%	0.000%
				Sum		99.999%	

Table S-22. Detailed triacylglycerol (TAG) composition of PSO by response factor normalized APCI-MS. TAG structures given are not regiospecific.

Parinari Seed Oil (PSO)							
TAG	**RT**	**% Comp.**	**SD**	**TAG**	**RT**	**% Comp.**	**SD**
oxEloxEloxEl	32.02	0.000%	0.000%	**ElEl-21**	84.80	0.008%	0.000%
oxEloxElEl	40.28	0.030%	0.001%	**SLO**	85.04	1.392%	0.062%
oxEloxElL	41.35	0.005%	0.000%	**LLA**	85.83	0.026%	0.001%
oxEloxElO	43.58	0.011%	0.000%	**POP**	86.29	0.528%	0.018%
oxEloxElP	43.91	0.011%	0.001%	**SLP**	87.09	0.930%	0.026%
oxElElEl	46.02	1.269%	0.019%	**ElElB**	89.30	0.032%	0.001%
oxElElL	47.08	0.384%	0.009%	**PPP**	89.64	0.022%	0.000%
oxEloxElS	47.38	0.013%	0.000%	**OOG**	90.98	0.071%	0.001%
oxElLL	48.20	0.034%	0.002%	**ElOA**	91.46	0.122%	0.010%
oxElElO	50.54	0.865%	0.006%	**LElB**	92.04	0.010%	0.000%
oxElElP	51.23	0.676%	0.022%	**ElEl-23**	93.65	0.011%	0.000%
oxElLO	51.87	0.085%	0.001%	**OOS**	93.68	0.845%	0.026%
oxElLP	52.56	0.043%	0.001%	**ElSS**	93.83	0.934%	0.023%
oxElOO	56.21	0.143%	0.004%	**LLB**	94.84	0.003%	0.000%
oxElElS	56.26	0.850%	0.018%	**POS**	95.79	0.747%	0.009%
oxElOP	56.83	0.058%	0.000%	**PLA**	96.36	0.136%	0.001%
oxElPP	57.75	0.008%	0.000%	**SSL**	96.38	0.400%	0.012%
oxElLS	57.85	0.047%	0.003%	**ElElLg**	97.90	0.028%	0.001%
oxElOS	63.36	0.060%	0.004%	**OL-21**	98.41	0.001%	0.000%
oxElSP	64.23	0.038%	0.001%	**LL-23**	98.96	0.001%	0.000%
oxElSS	72.40	0.019%	0.002%	**PPS**	99.31	0.051%	0.001%
ElElEl	55.11	12.036%	0.191%	**LElLg**	100.40	0.009%	0.000%
ElElL	56.70	8.252%	0.143%	**SOG**	101.83	0.043%	0.007%
LLEl	58.47	3.348%	0.092%	**ElEl-25**	101.83	0.008%	0.000%
LLL	60.31	0.405%	0.013%	**OOA**	102.10	0.030%	0.002%
ElElO	62.05	11.267%	0.153%	**OLB**	102.46	0.015%	0.001%
ElElP	63.23	8.090%	0.141%	**LLLg**	102.80	0.003%	0.000%
OLEl	64.10	7.790%	0.254%	**POA**	104.09	0.091%	0.002%
PLEl	65.44	4.556%	0.134%	**SSO**	104.19	0.339%	0.009%
LLO	66.33	1.018%	0.020%	**PBL**	104.37	0.012%	0.000%
PoPL	66.95	0.008%	0.001%	**SLA**	104.45	0.034%	0.001%
LLP	67.64	0.863%	0.024%	**ElElCe**	105.19	0.006%	0.000%
ElElG	68.65	1.274%	0.038%	**OL-23**	105.83	0.002%	0.000%
ElElS	70.83	8.941%	0.531%	**OOB**	108.76	0.004%	0.000%
OOEl	70.94	4.202%	0.118%	**OLLg**	108.88	0.008%	0.001%
POEl	72.50	3.003%	0.084%	**PLLg**	110.44	0.006%	0.000%
LLG	73.27	0.185%	0.042%	**SLB**	110.51	0.006%	0.001%
OOL	73.53	1.782%	0.048%	**SOA**	110.62	0.028%	0.001%
PPEl	74.35	0.429%	0.014%	**POB**	110.66	0.008%	0.000%
POPo	74.40	0.041%	0.002%	**OO-23**	111.52	0.002%	0.000%
POL	75.30	2.094%	0.033%	**OL-25**	111.75	0.002%	0.000%
LLS	76.15	0.484%	0.012%	**OOLg**	114.56	0.005%	0.000%
PPL	77.15	0.701%	0.012%	**OLCe**	114.71	0.002%	0.000%
LElA	79.48	0.277%	0.001%	**POLg**	116.16	0.003%	0.001%
ElElA	79.89	0.474%	0.010%	**PLCe**	116.35	0.001%	0.000%
SOEl	82.19	2.995%	0.100%	**SOB**	116.54	0.003%	0.000%
OOO	82.21	0.961%	0.018%	**SLLg**	116.57	0.003%	0.000%
OLG	82.29	0.342%	0.051%	**OO-25**	117.51	0.001%	0.000%
OOP	84.24	1.413%	0.030%	**POCe**	122.29	0.002%	0.001%
ElSP	84.32	0.974%	0.059%	**SOLg**	122.81	0.004%	0.002%
PLG	84.37	0.168%	0.045%	**Sum**		100.000%	

Table S-23. Detailed triacylglycerol (TAG) composition of SBO by response factor normalized APCI-MS. TAG structures are not regiospecific.

Soybean Oil							
TAG	**RT**	**% Comp.**	**SD**	**TAG**	**RT**	**% Comp.**	**SD**
LnLnLn	49.69	0.068%	0.002%	**LLB**	95.03	0.319%	0.004%
LnLnL	52.73	0.919%	0.012%	**POS**	95.97	0.560%	0.009%
LLLn	56.28	6.383%	0.026%	**PLA**	96.53	0.239%	0.007%
LnLnO	57.15	0.537%	0.118%	**SSL**	96.63	0.463%	0.017%
LnLnP	58.18	0.207%	0.007%	**LLnLg**	96.94	0.028%	0.001%
LLL	60.32	16.528%	0.303%	**OL-21**	98.69	0.022%	0.000%
OLLn	61.32	4.870%	0.130%	**LL-23**	99.14	0.027%	0.001%
PLLn	62.55	3.175%	0.097%	**PPS**	99.59	0.009%	0.000%
LLO	66.38	14.021%	0.518%	**OOA**	102.25	0.071%	0.004%
PoPL	66.99	0.009%	0.002%	**OLB**	102.68	0.183%	0.010%
OOLn	67.70	2.337%	0.017%	**LLLg**	102.91	0.093%	0.005%
LLP	67.75	12.466%	0.073%	**SSO**	104.28	0.165%	0.011%
PoOL	68.88	0.247%	0.022%	**POA**	104.32	0.092%	0.006%
POLn	68.95	1.274%	0.098%	**PBL**	104.38	0.181%	0.008%
PPLn	70.72	0.140%	0.008%	**SLA**	104.55	0.104%	0.005%
OOL	73.79	5.986%	0.094%	**OO-21**	105.81	0.008%	0.001%
LLG	73.89	0.262%	0.010%	**OL-23**	106.05	0.015%	0.000%
POPo	74.86	0.039%	0.006%	**LL-25**	106.37	0.008%	0.000%
POL	75.45	7.306%	0.040%	**OOB**	108.90	0.096%	0.005%
LLS	76.37	4.198%	0.048%	**OLLg**	109.08	0.057%	0.002%
PPL	77.28	2.301%	0.041%	**LLCe**	109.18	0.007%	0.001%
SOLn	77.91	0.409%	0.015%	**POB**	110.57	0.055%	0.003%
LLnA	78.93	0.057%	0.005%	**PLLg**	110.69	0.072%	0.003%
OOO	82.51	2.809%	0.131%	**SOA**	110.81	0.031%	0.002%
OLG	82.59	0.151%	0.004%	**SLB**	110.90	0.080%	0.004%
PLG	84.47	0.131%	0.020%	**OO-23**	111.80	0.006%	0.001%
OOP	84.47	2.620%	0.100%	**OL-25**	111.99	0.005%	0.000%
SLO	85.33	3.370%	0.198%	**OOLg**	114.74	0.031%	0.001%
LLA	86.07	0.247%	0.013%	**OLCe**	114.79	0.005%	0.001%
POP	86.45	0.641%	0.041%	**POLg**	116.40	0.015%	0.003%
SLP	87.37	1.736%	0.054%	**PLCe**	116.41	0.004%	0.000%
LLnB	88.32	0.091%	0.005%	**SLLg**	116.78	0.018%	0.001%
MOS	89.92	0.006%	0.001%	**SOB**	116.86	0.026%	0.002%
PPP	89.92	0.008%	0.000%	**OO-25**	117.68	0.002%	0.000%
LL-21	90.61	0.038%	0.001%	**OOCe**	120.50	0.002%	0.000%
OOG	91.23	0.054%	0.003%	**POCe**	122.58	0.001%	0.000%
OOS	93.80	1.068%	0.041%	**SLCe**	122.66	0.001%	0.000%
LOA	94.54	0.177%	0.007%	**SOLg**	122.86	0.007%	0.000%
				Sum		100.000%	

9. ^{2}D UHPLC Plots for cherry pit oil.

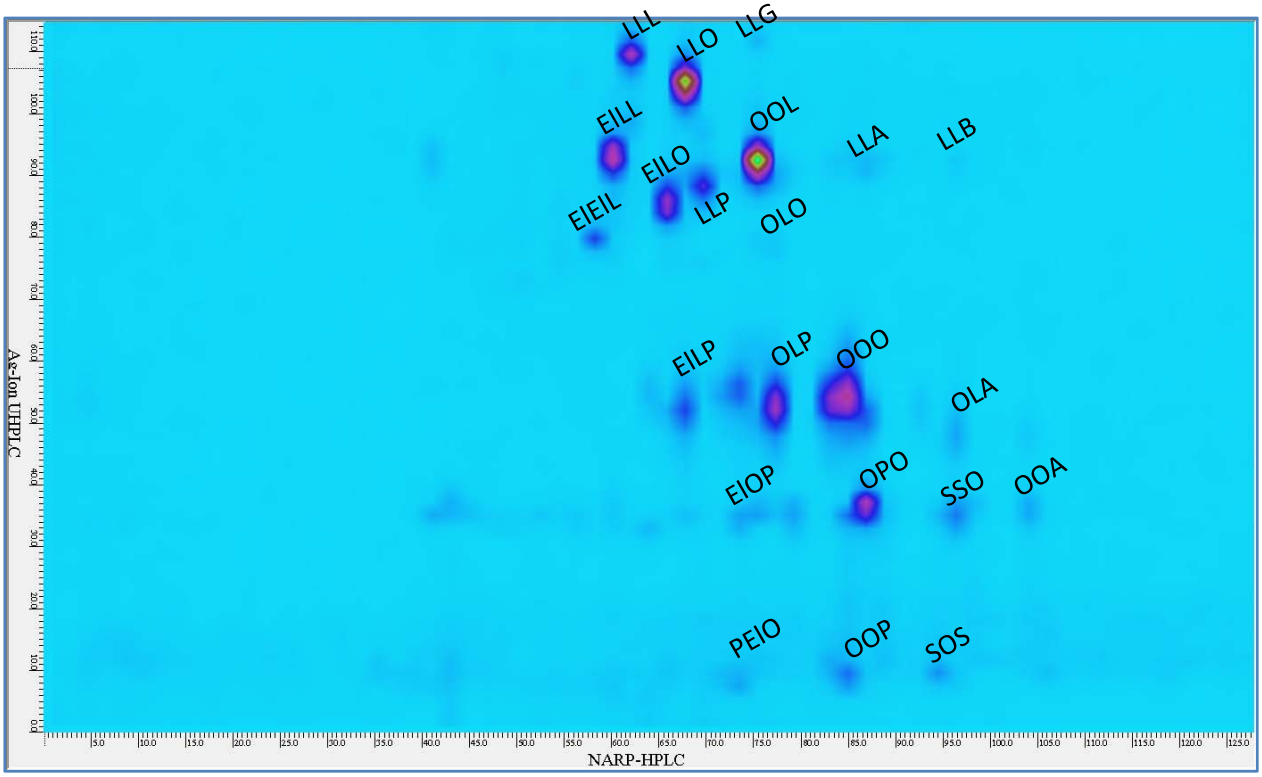

Figure S-4. ^{2}D UHPLC contour plot of cherry pit oil by APPI-MS on TSQ Quantum Access Max.

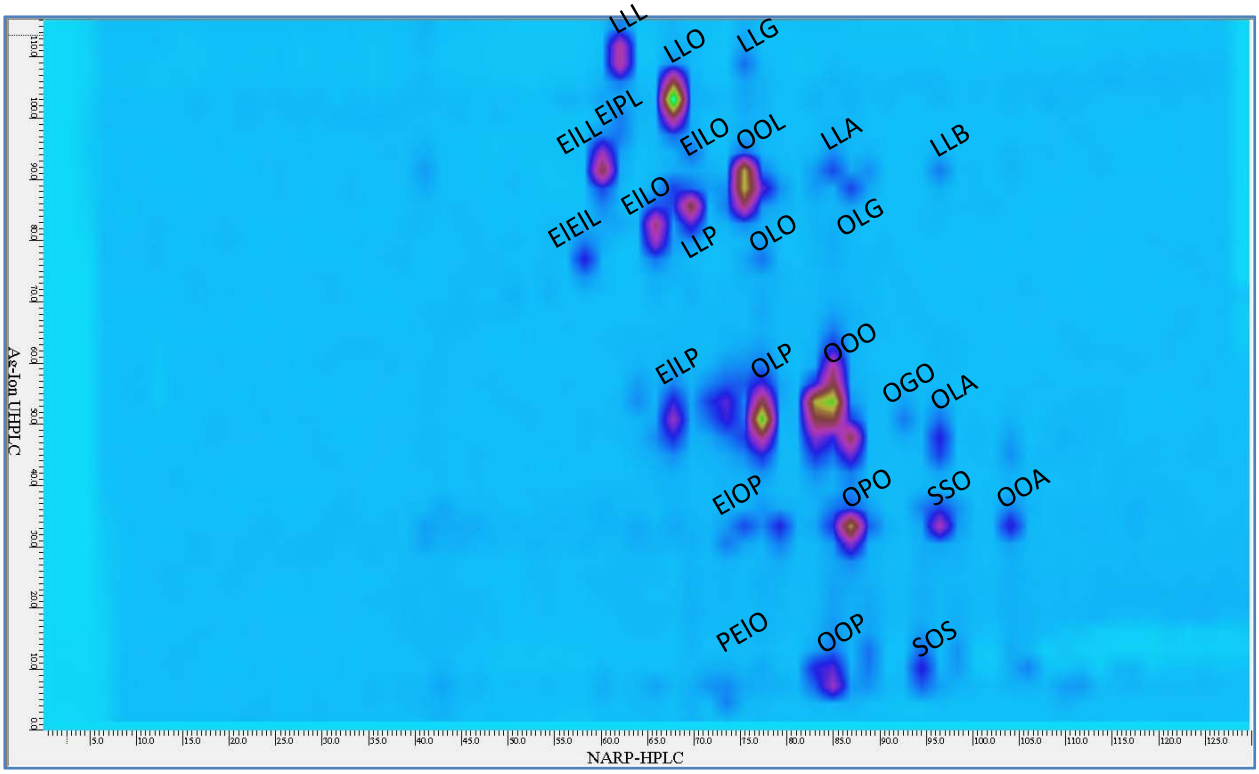

Figure S-5. ^{2}D UHPLC contour plot of cherry pit oil by ESI-MS on LCQ Deca XP.

10. ^{2}D UHPLC Plots for soybean oil.

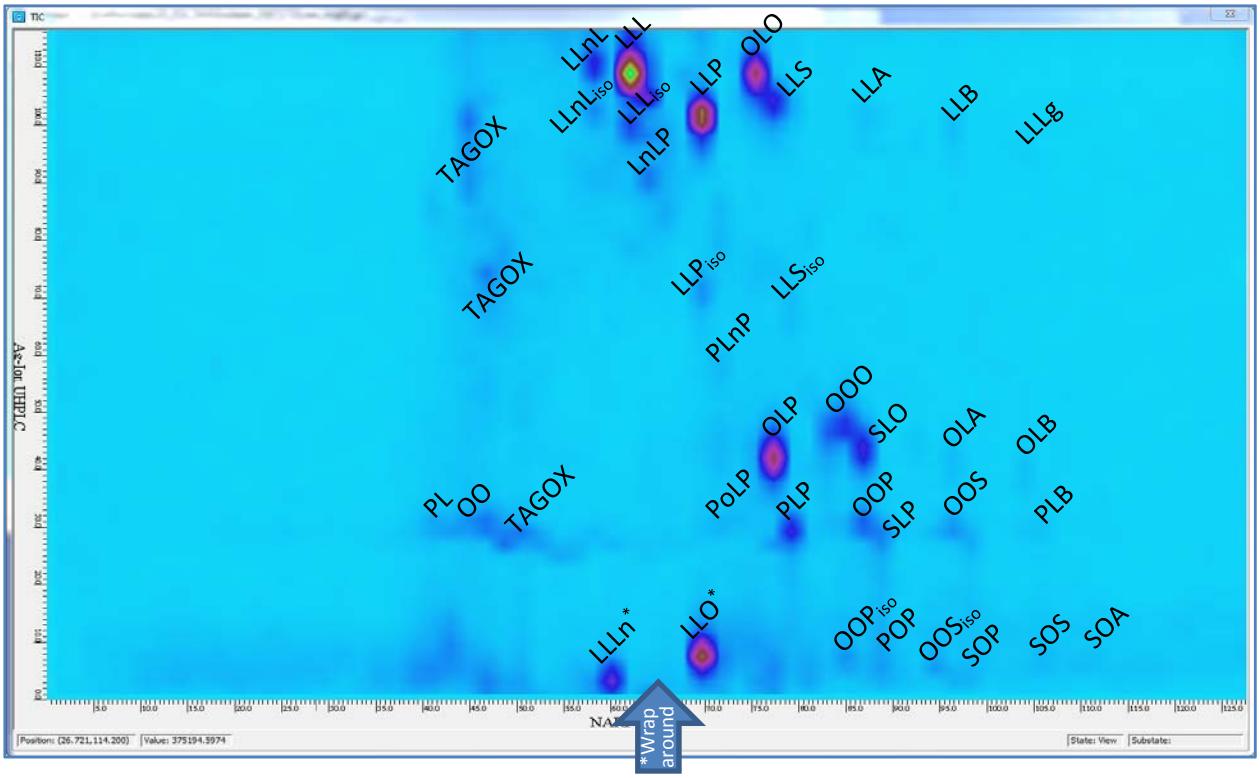

Figure S-6. ^{2}D UHPLC contour plot of soybean oil by APPI-MS on TSQ Quantum Access Max.

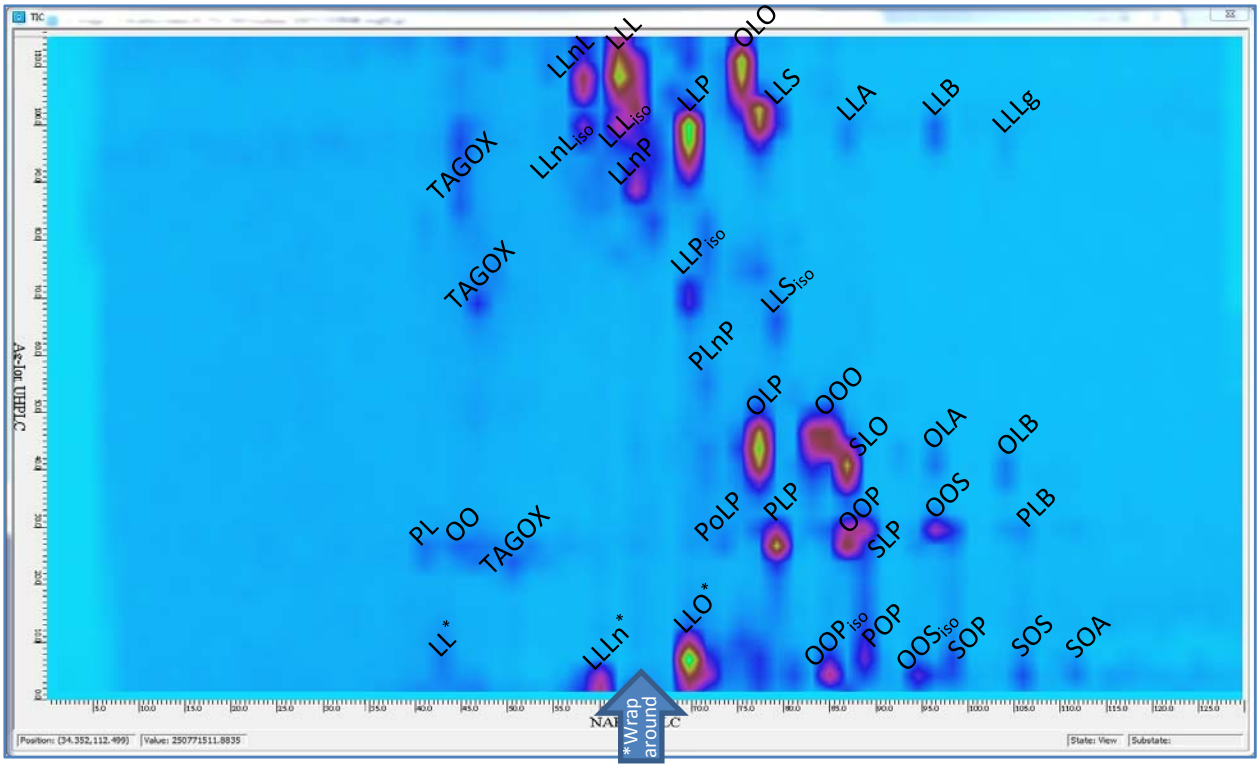

Figure S-7. ^{2}D UHPLC contour plot of soybean oil by ESI-MS on LCQ Deca XP.

Figures S-6 and S-7 show that TAGs with few degrees of unsaturation could be forced to be retained on the column longer by using a sharper reverse gradient, shown in Figure S-3. Notice the elution time of OLO in Figures S-6 and S-7 compared to OOL in Figures S-4 and S-5. However, LLLn and LLO experienced "wraparound" by eluting in the next modulation period, due to the lower ACN composition. Therefore, we have increased the ACN percentage to be intermediate between the gradient used for eleostearic acid-containing oils and this gradient. But we show these data to demonstrate the control that fine-tuning the ACN composition allows and because the quantification of the FSV and TAGs from the ^{1}D was unaffected.

The TAG identities are given by the masses of the $[M+NH_4]^+$ ions in ESI-MS spectra, and by $[M+H]^+$ and $[DAG]^+$ fragments in APPI-MS spectra. As we reported previously, the $[DAG]^+$ fragment ratios in ESI-MS and APPI-MS mass spectra are not as consistent for regioisomer identification as APCI-MS mass spectra.[8] Therefore, regioisomers identities for SBO were taken from our earlier report of SBO isomers[7] and were inferred from elution characteristics in the ^{2}D UHPLC chromatograms, not solely from $[DAG]^+$ ratios. APPI-MS has the distinct advantage that it is a non-contact ionization mode, unlike APCI-MS that accumulates a 'glob' of residue on the corona needle after extended exposure to solvents containing acetonitrile. But the $[DAG]^+$ fragment ratios are not as directly correlated with the regioisomeric positions of FAs in TAGs as in APCI-MS spectra. Thus, there is a trade-off in the use of APPI-MS versus APCI-MS.

The soybean oil analyzed for these experiments was a Halal SBO ordered from an online supplier, and showed higher levels of 18:3 isomers by GC-FID and GC-MS than most SBOs we have analyzed in the past, as well as some early-eluting TAG oxidation products (TAGOX). Normal linolenic acid represented 63.9% of all 18:3 species by GC-FID, another isomer was 15.8%, a third was 15.0%, and a fourth was 5.4%. Linoleic acid also showed isomers, with normal linoleic acid being 96.0% by GC-FID, one isomer being 2.1% and another being 1.9%. Two isomers of 18:1 were present, with oleic acid being 94.2% and the second isomer being 5.8%. Thus, Figures S-6 and S-7 show some of the minor TAG peaks labelled with "iso" to indicate additional isomer peaks. The combination of oxidation products and isomers may indicate that the oil was not stored properly prior to sale, or may indicate sample production or processing issues. Based on the current status of literature precedent, the ESI-MS and APPI-MS mass spectra were not sufficiently definitive to allow localization of the double bond positions. Of course, with adequate standards, the 2D-LC retention times could be used to identify the isomers, since, in many cases, they were separated on the new Ag-Ion UHPLC column. Since individual double bond isomers have not been specifically identified, the results for SBO FAs, DAGs, and TAGs in Tables S-17, S-20, and S-23, respectively, represent the sum of all isomers for each FA.

Supporting Information References

(1) Folch, J.; Lees, M.; Sloane-Stanley, G. H. *J. Biol. Chem.* **1957**, *226*, 497-509.
(2) Korlesky, N. M.; Stolp, L. J.; Kodali, D. R.; Goldschmidt, R.; Byrdwell, W. C. *J. Am. Oil Chem. Soc.* **2016**, 1-11.
(3) Slover, H. T.; Thompson, R. H.; Merola, G. V. *J. Am. Oil Chem. Soc.* **1983**, *60*, 1524-1528.
(4) Matthäus, B.; Özcan, M. M. *J. Food Lipids* **2009**, *16*, 187-199.
(5) Sheng, J.; Vannela, R.; Rittmann, B. E. *Bioresour. Technol.* **2011**, *102*, 1697-1703.
(6) Byrdwell, W. C. *J. Agric. Food Chem.* **2009**, *57*, 2135-2146.
(7) Byrdwell, W. C. *Anal. Bioanal. Chem.* **2015**, *407*, 5143-5160.
(8) Byrdwell, W. C. *J. Am. Oil Chem. Soc.* **2015**, *92*, 1533-1547.