NMR Data

The esters were dissolved in 400 µl deuterated chloroform. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 500 and 126 MHz, respectively, with Avance-HD 500 spectrometers operating at 27 °C. ^{1}H-detected experiments including two-dimensional COSY, HSQC, and HMBC were measured with an inverse 1H/13C probe head, and direct 13C measurements were performed with a QNP 13C/31P/29Si/19F/1H cryoprobe. All experiments were done in full automation using standard parameter sets of the TOPSPIN 3.2 software package (Bruker, Billerica, MA, USA). ^{13}C-NMR spectra were recorded in proton-decoupled mode. Data processing was done with MestreNova software.

Cholestanyl heptanoate (**IS_1**)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.69 (1H, tt, J = 11.2 Hz, 4.9 Hz, St-3), 2.25 (2H, t, J = 7.5 Hz, FA-2), 1.95 (1H, dt, J = 12.5 Hz, 3.3 Hz, St-17), 1.86 - 1.76 (2H, m), 1.72 (1H, dt, J = 13.3 Hz, 3.6 Hz, St-9), 1.64 (1H, dq, J = 13.0 Hz, 3.4 Hz, St-20), 1.62 - 1.43 (8H, m), 1.39 - 0.93 (26H, m), 0.89 (3H, d, J = 6.5 Hz, St-21), 0.88 (3H, d, J = 4.8 Hz, FA-7), 0.86 (3H, d, J = 2.3 Hz, St-26/27), 0.85 (3H, d, J = 2.4 Hz, St-26/27), 0.81 (3H, s, St-19), 0.64 (3H, s, St-18)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 173.62 (FA-1), 73.58 (St-3), 56.55, 56.39, 54.35, 44.79, 42.72, 40.11, 39.65, 36.90, 36.30, 35.95, 35.60, 34.93, 34.21, 32.13, 31.61, 28.94, 28.76, 28.39, 28.16, 27.66, 25.20, 24.35, 23.98, 22.97, 22.71, 22.63, 21.34, 18.81 (St-21), 14.19 (FA-7), 12.37 (St-18/19), 12.21 (St-18/19)

Cholestanyl oleate (**IS_2**)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 5.42-5.28 (2H, m, FA-9, FA-10), 4.69 (1H, tt, J = 11.2 Hz, 4.8 Hz, St-3), 2.25 (2H, t, J = 7.6 Hz, FA-2), 2.06-1.92 (5H, m), 1.85-1.76 (2H, m), 1.72 (1H, dt, J = 13.3 Hz, 3.7 Hz, St-17), 1.68-1.43 (9H, m), 1.41-0.94 (40H, m), 0.91-0.84 (12H, m, FA-18, St-21, St-26, St-27), 0.81 (3H, s, St-19), 0.64 (3H, s, St-18)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 173.61 (FA-1), 130.12 (FA-9/10), 129.91 (FA-9/10), 73.60 (St-3), 56.55, 56.38, 54.35, 44.79, 42.72, 40.11, 39.65, 36.90, 36.30, 35.95, 35.60, 34.91, 34.21, 32.13, 32.06, 29.92, 29.83, 29.68, 29.48, 29.31, 29.25, 29.24, 28.76, 28.39, 28.16, 27.66, 27.37, 27.31, 25.23, 24.35, 23.98, 22.98, 22.85, 22.72, 21.34, 18.81 (St-21), 14.29 (FA-18), 12.38 (St-18/19), 12.21 (St-18/19)

Cholestanyl 9-hydroxynonanoate (**IS_3**)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.73-4.64 (1H, m, St-3), 3.63 (2H, t, J = 6.6 Hz, FA-9), 2.24 (2H, t, J = 7.5 Hz, FA-2), 1.95 (1H, dt, J = 12.6 Hz, 3.4 Hz, St-17), 1.85-1.75 (2H, m), 1.71 (1H, dt, J = 13.4 Hz, 3.7 Hz, St-9), 1.64 (2H, dq, J = 13.5 Hz, 3.6 Hz, St-20), 1.61-1.42 (9H, m), 1.39-0.92 (30H, m), 0.89 (3H, d, J = 6.6 Hz, St-21), 0.86 (3H, d, J = 2.4 Hz, St-26/27), 0.85 (3H, d, J = 2.4 Hz, St-26/27), 0.81 (3H, s, St-19), 0.64 (3H, s, St-18)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 173.59 (FA-1), 73.62 (St-3), 63.14 (FA-9), 56.53, 56.37, 54.33, 52.72, 44.77, 42.71, 40.10, 39.64, 36.88, 36.29, 35.93, 35.59, 34.87, 34.20, 32.88, 32.12, 29.33, 29.14, 28.74, 28.38, 28.15, 27.65, 25.78, 25.17, 24.34, 23.96, 22.96, 22.70, 21.33, 18.80 (St-21), 12.37 (St-18/19), 12.20 (St-18/19)

Cholestanyl *cis*-9,10-epoxystearate (**IS_4**)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.75-4.64 (1H, m, St-3), 2.95-2.90 (2H, m, FA-9/10), 2.26 (2H, t, J = 7.5 Hz, FA-2), 1.95 (1H, dt , J = 12.6 Hz, 3.4 Hz, St-17), 1.85-1.76 (2H, m), 1.71 (1H, dt, J = 13.3 Hz, 3.7 Hz, St-9), 1.67-0.93 (53H, m), 0.89 (3H, d, J = 6.5 Hz, St-21), 0.88 (3H, d, J = 6.7 Hz, FA-18), 0.86 (3H, d, J = 2.2 Hz, St-26/27), 0.85 (3H, d, J = 2.3 Hz, St-26/27), 0.81 (3H, s, St-19), 0.64 (3H, s, St-18)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 173.78 (FA-1), 73.74 (St-3), 57.65 (FA-9/10), 57.60 (FA-9/10), 56.51, 56.36, 54.31, 44.75, 42.69, 40.08, 39.63, 36.86, 36.28, 35.93, 35.57, 34.87, 34.17, 32.10, 31.99, 29.68, 29.67, 29.47, 29.36, 29.31, 29.13, 28.73, 28.37, 28.14, 27.89, 27.85, 27.63, 26.71, 26.66, 25.16, 24.33, 23.96, 22.96, 22.81, 22.70, 21.31, 18.78 (St-21), 14.26 (FA-18), 12.35 (St-18/19), 12.18 (St-18/19)

Cholestanyl 6-oxoheptanoate (**IS_5**)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.72-4.64 (1H, m, St-3), 2.46-2.41 (2H, m, FA-5), 2.29-2.24 (2H, m, FA-2), 2.13 (3H, s, FA-7), 1.95 (1H, dt, J = 12.6 Hz, 3.3 Hz, St-17), 1.84-1.75 (2H, m), 1.72 (1H, dt, J = 13.4 Hz, 3.7 Hz, St-9), 1.64 (1H, dq, J = 12.5 Hz, 3.2 Hz, St-20), 1.61 (1H, s), 1.60 (4H, t, J = 3.7 Hz, FA-3/4), 1.57-1.43 (5H, m), 1.38-0.93 (20H, m), 0.89 (3H, d, J = 6.6 Hz, St-21), 0.86 (3H, d, J = 2.4 Hz, St-26/27), 0.85 (3H, d, J = 2.4 Hz, St-26/27), 0.81 (3H, s, St-19), 0.64 (3H, s, St-18)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 208.75 (FA-6), 173.09 (FA-1), 73.79 (St-3), 56.53, 56.37, 54.33, 44.77, 43.43 (FA-5), 42.71, 40.10, 39.64, 36.87, 36.29, 35.93, 35.58, 34.57, 34.18, 32.11, 30.04 (FA-7), 28.74, 28.38, 28.14, 27.63, 24.63, 24.33, 23.96, 23.30, 22.96, 22.70, 21.32, 18.80 (St-21), 12.36 (St-18/19), 12.20 (St-18/19)

Sitostanyl 9,10-dihydroxystearate **7b**

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.69 (1H, tt, J = 10.9 Hz, 4.9 Hz, St-3), 3.42-3.36 (2H, m, FA-9/10), 2.25 (2H, t, J = 7.5 Hz, FA-2), 2.09-0.96 (58H, m), 0.91-0.79 (18H, m, FA-18, St-19, St-21, St-24^2, St-26, St-27), 0.64 (3H, s, St-18)

^{13}C-NMR (125 MHz, $CDCl_3$): δ =173.62 (FA-1), 74.66, 74.61, 73.64 (St-3), 56.52, 56.26, 54.32 (St-18), 45.92, 44.76, 42.70, 40.08, 36.87, 36.30, 35.58, 34.85, 34.19, 34.01, 33.75, 33.69, 32.11, 32.02, 29.83, 29.71, 29.56, 29.43, 29.29, 29.22, 29.13, 28.74, 28.40, 27.64, 26.14, 25.82, 25.69, 25.14, 24.34, 23.16, 22.82, 21.32, 19.96, 19.15, 18.85 (St-21), 14.27 (FA-18), 12.36 (St-18/19/24^2), 12.19 (St-18/19/24^2), 12.11 (St-18/19/24^2)

Sitostanyl *cis*-9,10-epoxystearate **10b**

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 4.69 (1H, tt, J = 10.9 Hz, 4.9 Hz, St-3), 2.92-2.86 (2H, m, FA-9/10), 2.25 (2H, t, J = 7.5 Hz, FA-2), 1.95 (1H, dt, J = 12.6Hz, 3.4 Hz, St-17), 1.86-1.75 (2H, m), 1.72 (1H, dt, J = 13.4 Hz, 3.7 Hz, St-9), 1.68-1.53 (7H, m), 1.52-1.45 (7H, m), 1.44-1.38 (2H, m), 1.38-1.29 (14H, m), 1.29-1.23 (12H, m), 1.22-0.92 (12H, m), 0.91-0.79 (18H, m, FA-18, St-19, St-21, FA-18, St-24^2, St-26, St-27), 0.64 (3H, s, St-18)

^{13}C-NMR (125 MHz, $CDCl_3$): δ =173.54 (FA-1), 73.61 (St-3), 57.39 (FA-9/10), 57.35 (FA-9/10), 56.53, 56.26, 54.32, 45.92, 44.77, 42.70, 40.08, 36.88, 36.30, 35.59, 34.86, 34.20, 34.02, 32.12, 32.00, 29.70, 29.68, 29.49, 29.49, 29.33, 29.22, 29.14, 28.74, 28.40, 27.97, 27.93, 27.65, 26.75, 26.70, 26.14, 25.17, 24.35, 23.16, 22.82, 21.32, 19.96, 19.15, 18.86 (St-21), 14.27 (FA-18), 12.37 (St-18/19/24^2), 12.19 (St-18/19/24^2), 12.11 (St-18/19/24^2)

Sitostanyl 10-oxo-dec-8(*E*)-enoate **16**

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.50 (1H, d, J = 7.93 Hz, FA-10), 6.84 (1H, dt, J = 15.6 Hz, 6.8 Hz, FA-8), 6.11 (1H, ddt, J= 15.6 Hz, 7.9 Hz, 1.5 Hz, FA-9), 4.69 (1H, tt, J = 11.4 Hz, 4.9 Hz, St-3), 2.37-2.28 (2H, m, FA-7), 2.25 (2H, t, J = 7.5 Hz, FA-2), 1.95 (1H, dt, J = 12.6 Hz, 3.4 Hz, St-17), 1.85-1.75 (2H, m), 1.72 (1H, dt, J = 13.3 Hz, 3.6 Hz, St-9), 1.69-1.41 (14H, m, FA-3, FS-6), 1.39-0.92 (22H, m), 0.91-0.78 (15H, m, (St-19, St-21, St-24^2, St-26, St-27), 0.64 (3H, s, St-18)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 194.28 (FA-10), 173.39 (FA-1), 158.93 (FA-8), 133.15 (FA-9), 73.70 (St-3), 56.53, 56.27, 54.32, 45.93, 44.77, 42.71, 40.09, 36.87, 36.30, 35.59, 34.75, 34.20, 34.02, 32.12, 29.24, 28.91, 28.75, 28.40, 27.76, 27.65, 26.16, 25.00, 24.34, 23.17, 21.32, 19.96, 19.16, 18.86 (St-21), 12.37 (St-18/19/24^2), 12.20 (St-18/19/24^2), 12.11 (St-18/19/24^2)

Sitostanyl 11-oxo-undec-9(*E*)-enoate **18**

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 9.49 (1H, d, J = 7.9 Hz, FA-11), 6.84 (1H, dt, J = 15.6 Hz, 6.8 Hz, FA-9), 6.11 (1H, dtt, J = 15.6 Hz, 7.9 Hz, 1.5 Hz, FA-10), 4.69 (1H, tt, J = 11.3 Hz, 5.1 Hz, St-3), 2.32 (2H, dq, J = 7.2 Hz, 1.3 Hz, FA-8), 2.25 (2H, d, J = 7.5 Hz, FA-2), 1.95 (1H, dt, J = 12.6 Hz, 3.4 Hz, St-17), 1.86-1.75 (2H, m), 1.71 (1H, dt, J = 13.3 Hz, 3.6 Hz, St-9), 1-68-1.42 (11H, m), 1.38-0.91 (27H, m), 0.90-0.77 (15H, m, St-19, St-21, St-24^2, St-26, St-27), 0.64 (3H, s, St-18)

^{13}C-NMR (125 MHz, $CDCl_3$): δ = 194.28 (FA-11), 173.47 (FA-1), 159.05 (FA-9), 133.11 (FA-10), 73.64 (St-3), 56.53, 56.27, 54.32, 45.93, 44.77, 42.70, 40.08, 36.87, 36.29, 35.59, 34.80, 34.20, 34.02, 32.83, 32.11, 29.23, 29.10, 29.06, 26.06, 28.75, 28.40, 27.88, 27.65, 26.16, 25.10, 24.34, 23.17, 21.32, 19.96, 19.16, 18.86 (St-21), 12.36 (St-18/19/24^2), 12.19 (St-18/19/24^2), 12.11 (St-18/19/24^2)

HPLC-ELSD analysis

The purity (79 %) of cholestanyl *cis*-9,10-epoxystearate (**IS_4**) was determined using an evaporative light scattering detector (ELSD) under the following conditions: The HPLC consisted of a Jasco AS 2055 Plus auto sampler, 2 Jasco PU-2087 pumps, equipped with an analytical TP Cell 1.0 mm, a Jasco DAD MD-2010 (all devices from Jasco, Groß-Umstadt, Germany) and a SEDEX 90 LT-ELSD (Sedere, Alfortville Cedex, France). Ten µL of 0.1 mg/mL solutions in ethyl acetate were injected on a Nucleosil RP-8 column, 4.6 x 250 mm, 5 µm particle size was used with a flow rate of 0.8 mL/min. The mobile phase was composed of 90% methanol and 10% H_2O, and the percentage of methanol was raised to 100% within 25 min. Instrument control and data acquisition were performed using ChromPass 1.9 (Jasco, Groß-Umstadt, Germany).

Table S1. Retention times of sitostanyl oleate and ACOPs of sitostanyl oleate relative to the respective internal standards.

		RRT[a]
(A) nonpolar oxidation products		
IS_1	cholestanyl heptanoate	
1	sitostanyl heptanoate	1.165
2	sitostanyl octanoate	1.275
intact esters		
IS_2	cholestanyl oleate	
3	sitostanyl oleate	1.145
(B) hydroxy fatty acid esters		
IS_3	cholestanyl 9-hydroxynonanoate	
4	sitostanyl 7-hydroxyheptanoate	1.000
5	sitostanyl 8-hydroxyoctanoate	1.082
6	sitostanyl 9-hydroxynonanoate	1.177
7 a	sitostanyl dihydroxystearate	1.159
7 b	sitostanyl 9,10-dihydroxystearate	1.261
8 a	sitostanyl 8/11 hydroxyoctadec-9(*E*)-enoate	2.675
8 b,c,d	sitostanyl hydroxyoctadecenoate	2.790; 2.967; 3.124
(C) epoxy fatty acid esters		
IS_4	cholestanyl *cis*-9,10-epoxystearate	
9 a	sitostanyl epoxyoctadecenoate	1.096
9 b	sitostanyl 9/10/11/12 epoxyoctadecenoate	1.133
10 a	sitostanyl *trans*-9,10-epoxystearate	1.200
10 b	sitostanyl *cis*-9,10-epoxy-stearate	1.214
(D) oxo fatty acid esters		
IS_5	cholestanyl 6-oxoheptanoate	
11	sitostanyl 4-oxoheptanoate	1.067
12[b]	sitostanyl 6-oxohexanoate / 5-oxohexanoate	1.106; 1.145
13[b]	sitostanyl 7-oxoheptanoate / 6-oxoheptanoate	1.223; 1.266
14[b]	sitostanyl 8-oxooctanoate	1.368; 1.421
15[b]	sitostanyl 9-oxononanoate	1.539; 1.606
16	sitostanyl 10-oxodec-8(*E*)-enoate	1.620
17[b]	sitostanyl 10-oxodecanoate / 9-oxodecanoate	1.740; 1.823
18	sitostanyl 11-oxoundec-9(*E*)-enoate	1.832
19 a,b,c,d	sitostanyl 8/9/10/11-oxooctadecenoate	3.959; 4.082; 4.175; 4.374
20	sitostanyl 8/9/10/11-oxostearate	4.453

[a] retention time on Kinetex C8, 1.7 µm relative to the internal standard (IS_1-IS_5)

[b] retention times of both peaks formed upon analysis of the oxime derivatives of aldehyde ACOPs

Table S2. Characteristics of curves established to assess the linearity of the instrument response determined by linear regression analysis of the peak areas versus the concentrations of the analytes.

	Slope	**Intercept**	**r^2**
cholestanyl heptanoate	40922	-822.97	0.9995
cholestanyl 9-hydroxynonanoate	3098.3	1322.5	0.9956
cholestanyl *cis*-9,10-epoxystearate	4508.4	-5440.8	0.9996
cholestanyl 6-oxoheptanoate	52626	-143.8	0.9977

Table S3. Coefficients of variation (CV) obtained for the quantification of ACOPs formed in three independently heated sitostanyl oleate samples.

			CV [%]
(A) nonpolar oxidation products			
1	sitostanyl	heptanoate	8.51
2	sitostanyl	octanoate	10.64
intact esters			
3	sitostanyl	oleate	4.61
(B) hydroxy fatty acid esters			
4	sitostanyl	7-hydroxyheptanoate	10.54
5	sitostanyl	8-hydroxyoctanoate	4.70
6	sitostanyl	9-hydroxynonanoate	16.50
7 a,b	sitostanyl	dihydroxystearate	11.03
8 a,b,c,d	sitostanyl	hydroxyoctadecenoate	4.94
(C) epoxy fatty acid esters			
9 a,b	sitostanyl	epoxyoctadecenoate	10.72
10 a,b	sitostanyl	9,10-epoxystearate	10.56
(D) oxo fatty acid esters			
11	sitostanyl	4-oxoheptanoate	12.82
12	sitostanyl	6-oxohexanoate / 5-oxohexanoate	6.32
13	sitostanyl	7-oxoheptanoate / 6-oxoheptanoate	3.21
14	sitostanyl	8-oxooctanoate	3.02
15	sitostanyl	9-oxononanoate	3.78
16	sitostanyl	10-oxodec-8-enoate	5.18
17	sitostanyl	10-oxodecanoate / 9-oxodecanoate	3.94
18	sitostanyl	11-oxoundec-9-enoate	5.36
19 a,b,c,d	sitostanyl	8/9/10/11-oxooctadecenoate	8.13
20	sitostanyl	8/9/10/11-oxostearate	12.79

Semi-quantitative assessment of the ACOPs: Exemplary calculation for sitostanyl 11-oxoundec-9-enoate (18).

The calculation underlying the semi-quantitative assessment of sitostanyl 11-oxoundec-9-enoate is provided as example.

The calculations for the oxo fatty acid esters were based on the following parameters:

- Weight of each sitostanyl oleate sample subjected to heat-treatment: 18 ± 0.1 mg
- Purity of sitostanyl oleate: 80%
- Heat treated sitostanyl oleate (18 ± 0.1 mg) was dissolved in a final volume of 10 mL
- For analysis of oxo fatty acid esters, an aliquot of 1460 µL was subjected to oximation and UHPLC-MS/MS analysis
- Added amount of internal standard cholestanyl 6-oxoheptanoate: 3.2 mg (purity 96%)

For the selected example, in one of the three heated sitostanyl oleate samples, the area of the internal standard (IS) was determined to be 283602 and the area of sitostanyl 11-oxoundec-9-enoate was determined to be 283766.

Thus, the following amount of sitostanyl 11-oxoundec-9-enoate in the 1460 µL-aliquot was calculated:

$$Amount\ (per\ 1460\ \mu L\ aliquot) = \frac{Area\ analyte}{Area\ IS} * Amount\ IS(1460\ \mu L\ aliquot) = \frac{283766}{283602} * (3.2\ \mu g * 0.96) = 3.07\ \mu g$$

The resulting concentration of sitostanyl 11-oxoundec-9-enoate per mg of ester was calculated accordingly:

$$Concentration\ = \frac{Amount\ (per\ 1460\ \mu L\ aliquot)}{(weight\ sitostanyl\ oleate * purity\ sitostanyl\ oleate) * 1.46\ mL/10mL)} =$$

$$\frac{3.07\ \mu g}{(18.0\ mg * 0.8) * 1.46\ mL/10mL} = \frac{1.46\ \mu g}{mg}$$

The quantities of all other analytes have been calculated accordingly, taking the respective aliquots that were subjected to analyses as well as the added amounts and purities of internal standards into account.