

Analytical and Bioanalytical Chemistry

Electronic Supplementary Material

**Countercurrent chromatographic fractionation followed by
gas chromatography/mass spectrometry identification of alkylresorcinols
in rye**

Tim Hammerschick, Tim Wagner, Walter Vetter

Table S1 GC/MS-SIM measurement conditions with corresponding analytes

Time window	Time period	Recorded ions	Analytes**
a	7-24 min	<i>m/z</i> 73, 313, 328, 335, 337, 339, 341, 350, 352, 454, 356	silylated free fatty acids FA16:0, FA18:0, FA18:1, FA18:2, FA18:3
b*	24-28 min	<i>m/z</i> 74, 87, 323, 339, 354	ISTD 22:0-ME
c*	28-29.1 min	<i>m/z</i> 442.3, 444.3, 446.3, 448.3, 450.3	silylated AR14:x, AR13:x oxo, mAR13:x
d*	29.1-30 min	<i>m/z</i> 456.3, 458.3 460.3, 462.3, 464.3	silylated AR15:x, AR14:x oxo, mAR14:x
e*	30-31.7 min	<i>m/z</i> 470.4, 472.4, 474.4, 476.4, 478.4	silylated AR16:x, AR15:x oxo, mAR15:x
f*	31.7-33 min	<i>m/z</i> 484.4, 486.4, 488.4, 490.4, 492.4	silylated AR17:x, AR16:x oxo, mAR16:x
g*	33-34.4 min	<i>m/z</i> 498.4, 500.4, 502.4, 504.4, 506.4	silylated AR18:x, AR17:x oxo, mAR17:x
h*	34.4-35.6 min	<i>m/z</i> 512.4, 514.4, 516.4, 518.4, 520.4	silylated AR19:x, AR18:x oxo, mAR18:x
i*	35.6-36.8 min	<i>m/z</i> 526.4, 528.4, 530.4, 532.4, 534.4	silylated AR20:x, AR19:x oxo, mAR19:x
j*	36.8-37.9 min	<i>m/z</i> 540.4, 542.4, 544.4, 546.4, 548.4	silylated AR21:x, AR20:x oxo, mAR20:x
k*	37.9-39.1 min	<i>m/z</i> 554.4, 556.4, 558.4, 560.4, 562.4	silylated AR22:x, AR21:x oxo, mAR21:x
l*	39.1-40.1 min	<i>m/z</i> 568.4, 570.4, 572.4, 574.4, 576.4	silylated AR23:x, AR22:x oxo, mAR22:x
m*	40.1-41.5 min	<i>m/z</i> 582.5, 584.5, 586.5, 588.5, 590.5	silylated AR24:x, AR23:x oxo, mAR23:x
n*	41.5-43 min	<i>m/z</i> 596.5, 598.5, 600.5, 602.5, 604.5	silylated AR25:x, AR24:x oxo, mAR24:x
o*	43-44.8 min	<i>m/z</i> 610.5, 612.5, 614.5, 616.5, 618.5	silylated AR26:x, AR25:x oxo, mAR25:x
p*	44.8-54.5 min	<i>m/z</i> 624.5, 626.5, 628.5, 630.5, 632.5	silylated AR27:x, AR26:x oxo, mAR26:x

**m/z* 267.1, 268.1, 281.1 and 282.1 were recorded from the second time window (b) onwards during the remaining run

** x = 0 – 4

Table S2 Important key fragment ions in GC/MS for determining the position of the double bonds of silylated monounsaturated ARs in DMDS adduct 1. Bold letters indicate which fragment ion pairs were detected

AR	M ⁺	<i>n-3</i>		<i>n-4</i>		<i>n-5</i>		<i>n-6</i>		<i>n-7</i>		<i>n-8</i>		<i>n-9</i>		<i>n-10</i>	
		A ^a	R ^b	A ^a	R ^b	A ^a	R ^b	A ^a	R ^b	A ^a	R ^b	A ^a	R ^b	A ^a	R ^b	A ^a	R ^b
AR15:1	602	89	513	103	499	117	485	131	471	145	457	159	443	173	429	187	415
AR16:1	616	89	527	103	513	117	499	131	485	145	471	159	457	173	443	187	429
AR17:1	630	89	541	103	527	117	513	131	499	145	485	159	471	173	457	187	443
AR18:1	644	89	555	103	541	117	527	131	513	145	499	159	485	173	471	187	457
AR19:1	658	89	569	103	555	117	541	131	527	145	513	159	499	173	485	187	471
AR20:1	672	89	583	103	569	117	555	131	541	145	527	159	513	173	499	187	485
AR21:1	686	89	597	103	583	117	569	131	555	145	541	159	527	173	513	187	499
AR22:1	700	89	611	103	597	117	583	131	569	145	555	159	541	173	527	187	513
AR23:1	714	89	625	103	611	117	597	131	583	145	569	159	555	173	541	187	527
AR24:1	728	89	639	103	625	117	611	131	597	145	583	159	569	173	555	187	541
AR25:1	742	89	653	103	639	117	625	131	611	145	597	159	583	173	569	187	555
AR26:1	756	89	667	103	653	117	639	131	625	145	611	159	597	173	583	187	569
AR27:1	770	89	681	103	667	117	653	131	639	145	625	159	611	173	597	187	583

^a *m/z* values (61 + *n* • 14) for fragment ions including the terminal part of the alkyl chain ([H(CH₂)_{*n*}CH=SCH₃]⁺)

^b *m/z* values (359 + *n* • 14) for fragment ions including the silylated resorcinol moiety ([CH₃S=CH(CH₂)_{*n*}C₆H₂SCH₃(OSi(CH₃)₃)₂]⁺)

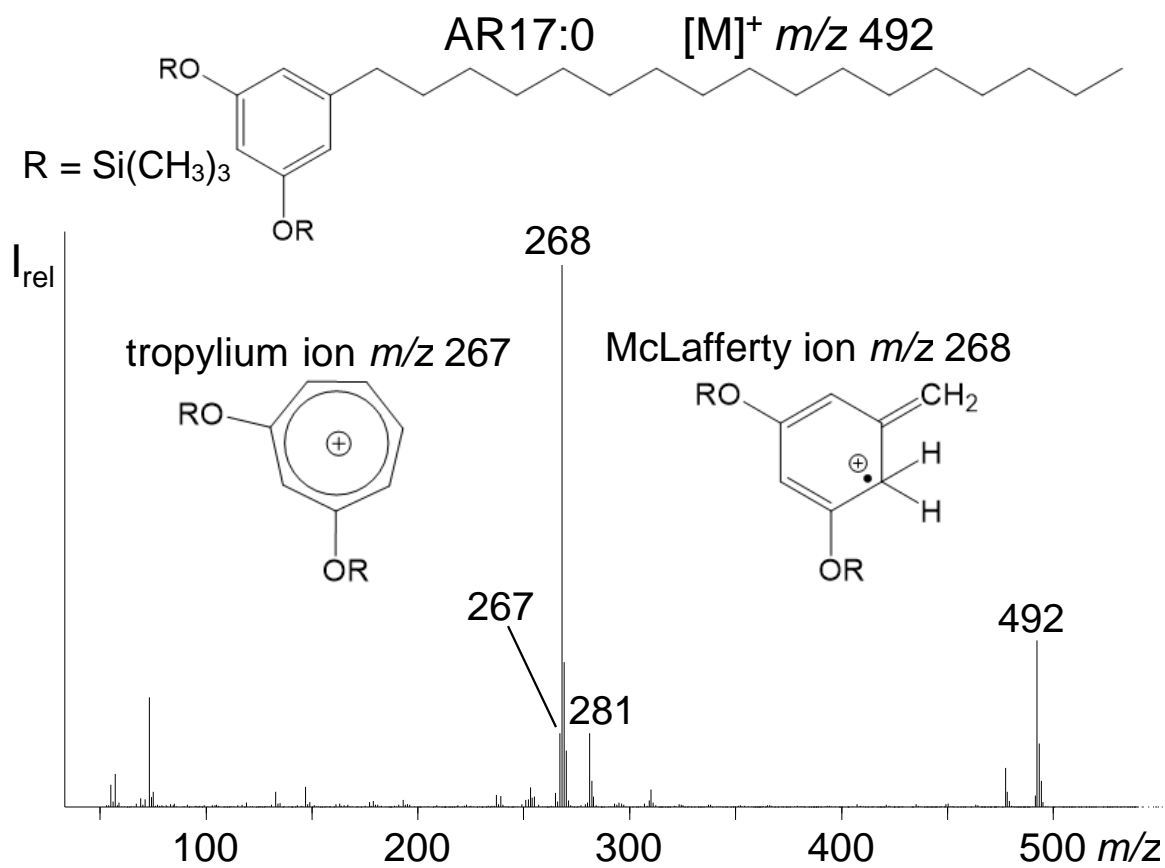


Fig. S1 Characteristic GC/MS fragment ions of silylated alkylresorcinols using the example of AR17:0

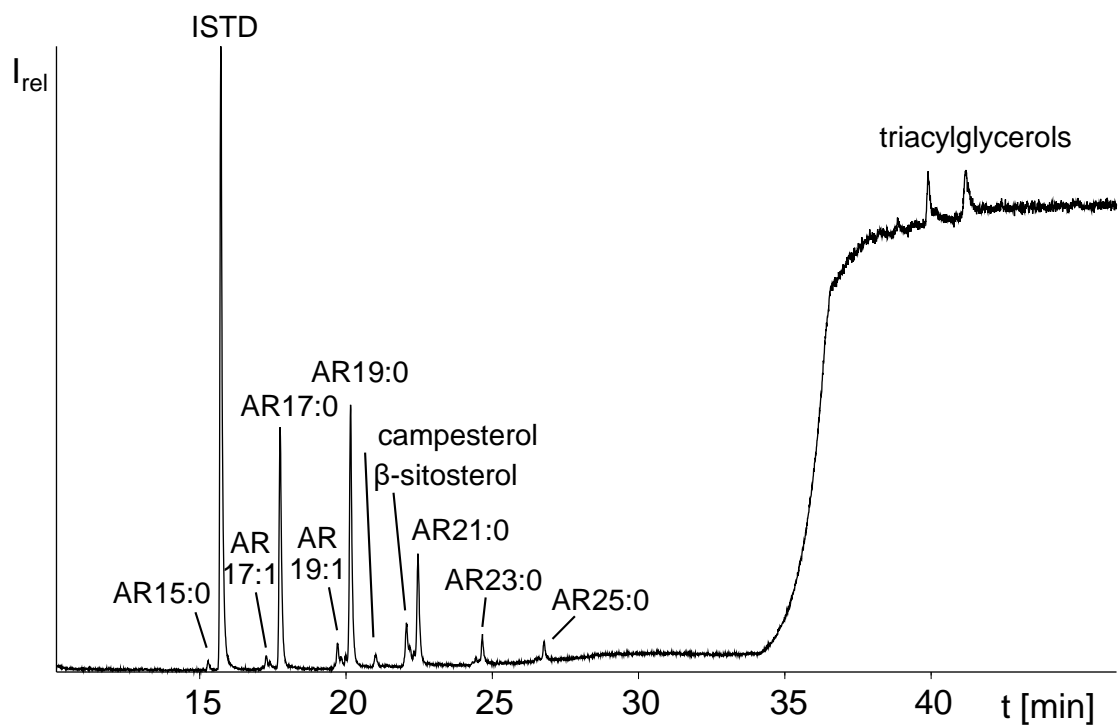


Fig. S2 GC/MS chromatogram (full scan mode) of silylated rye grain extract measured on GC/MS system 1 (ZB-1HT, 100 °C (1 min) – 10 °C/min – 250 °C (5 min) – 5 °C/min – 300 °C – 30 °C/min – 350 °C (10 min))

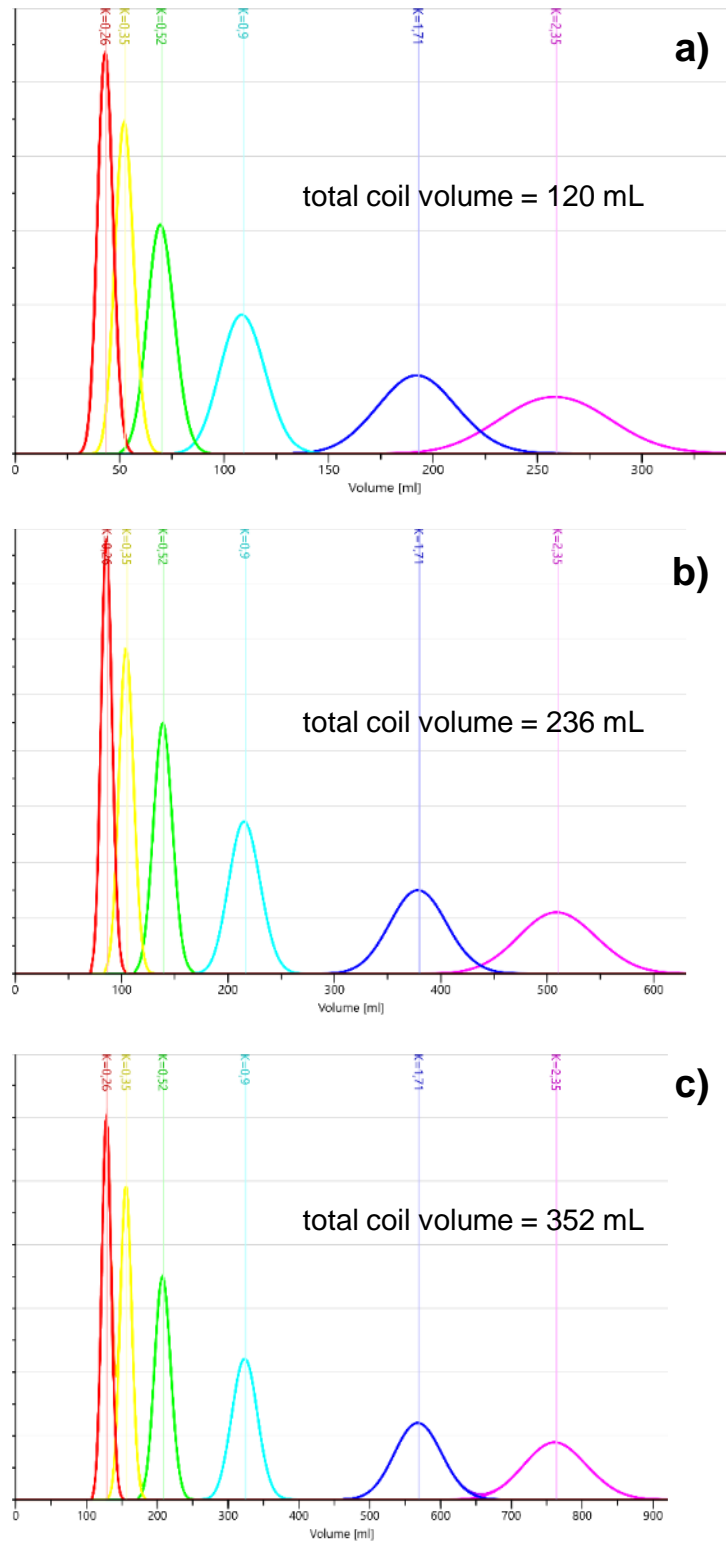


Fig. S3 Predicted elution volumes of AR15:0 (K=0.26), AR17:0 (K=0.35), AR19:0 (K=0.52), AR21:0 (K=0.9), AR23:0 (K=1.71) and AR25:0 (K=2.35) with a total coil volume of (a) 120 mL, (b) 236 mL and (c) 352 mL. The calculation with “PromISE 2“ was performed with $S_f=86\%$, 2 mL/min flow, 870 RPM, efficiency 0.03, 10 mL injection volume in head-to-tail mode

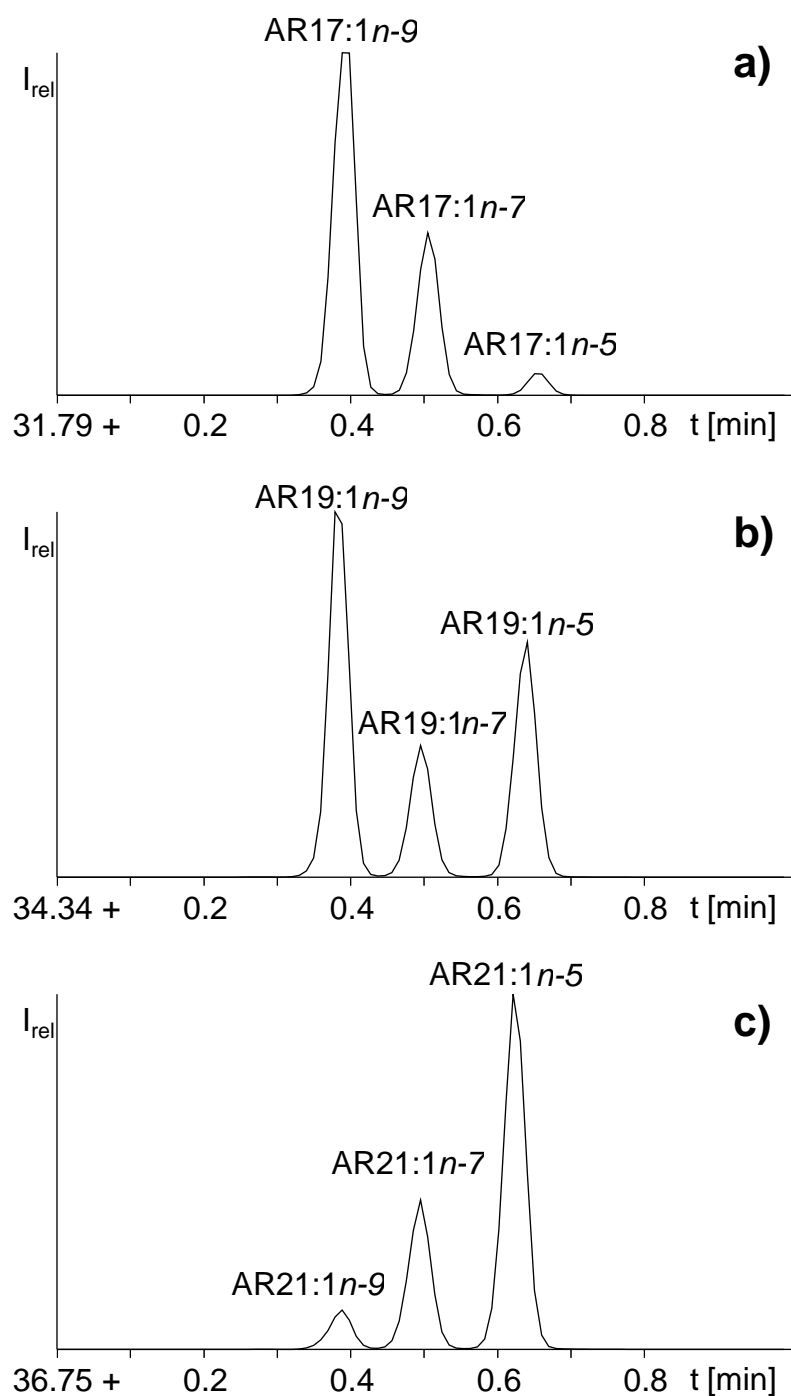


Fig. S4 GC/MS chromatograms (excerpts) containing the monounsaturated alkenylresorcinols of the silylated CCC fractions (a) 9, (b) 14 and (c) 22 (system 2, Optima 5HT, 55 °C (1 min) – 10 °C/min – 200 °C – 5 °C/min – 320 °C (15 min))

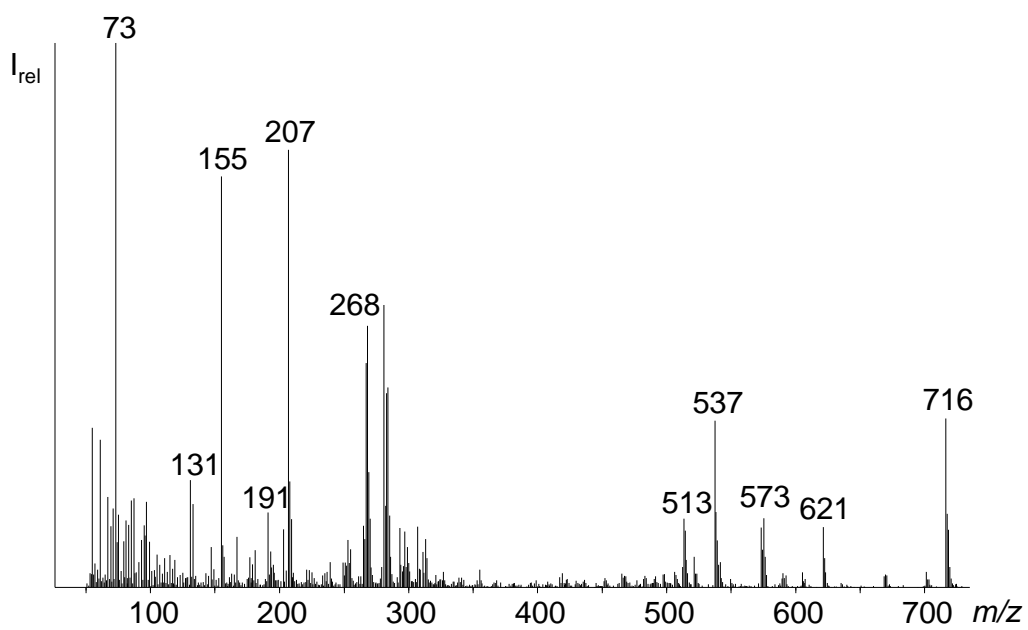


Fig. S5 GC/MS spectrum of the silylated DMDS adduct 1 of AR21:2 ($C_{36}H_{68}S_4Si_2O_2$)

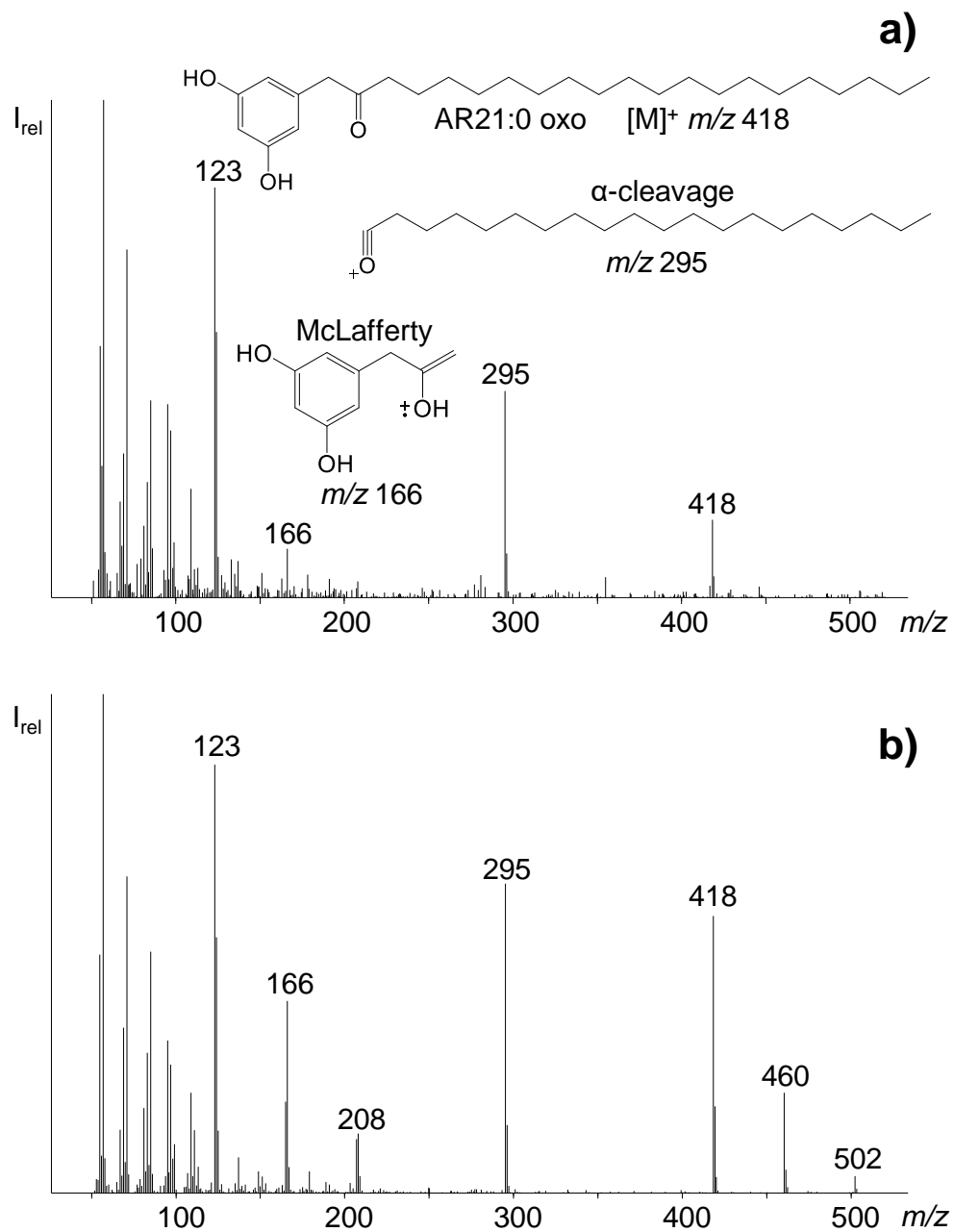


Fig. S6 GC/MS spectra of **(a)** AR21:0 oxo underivatized with the structures of the fragment ions produced by McLafferty re-arrangement and α -cleavage and **(b)** AR21:0 oxo acetylated