Supporting Information

Identification and quantitation of reaction products from quinic acid, quinic acid lactone and chlorogenic acid with Strecker aldehydes in roasted coffee.

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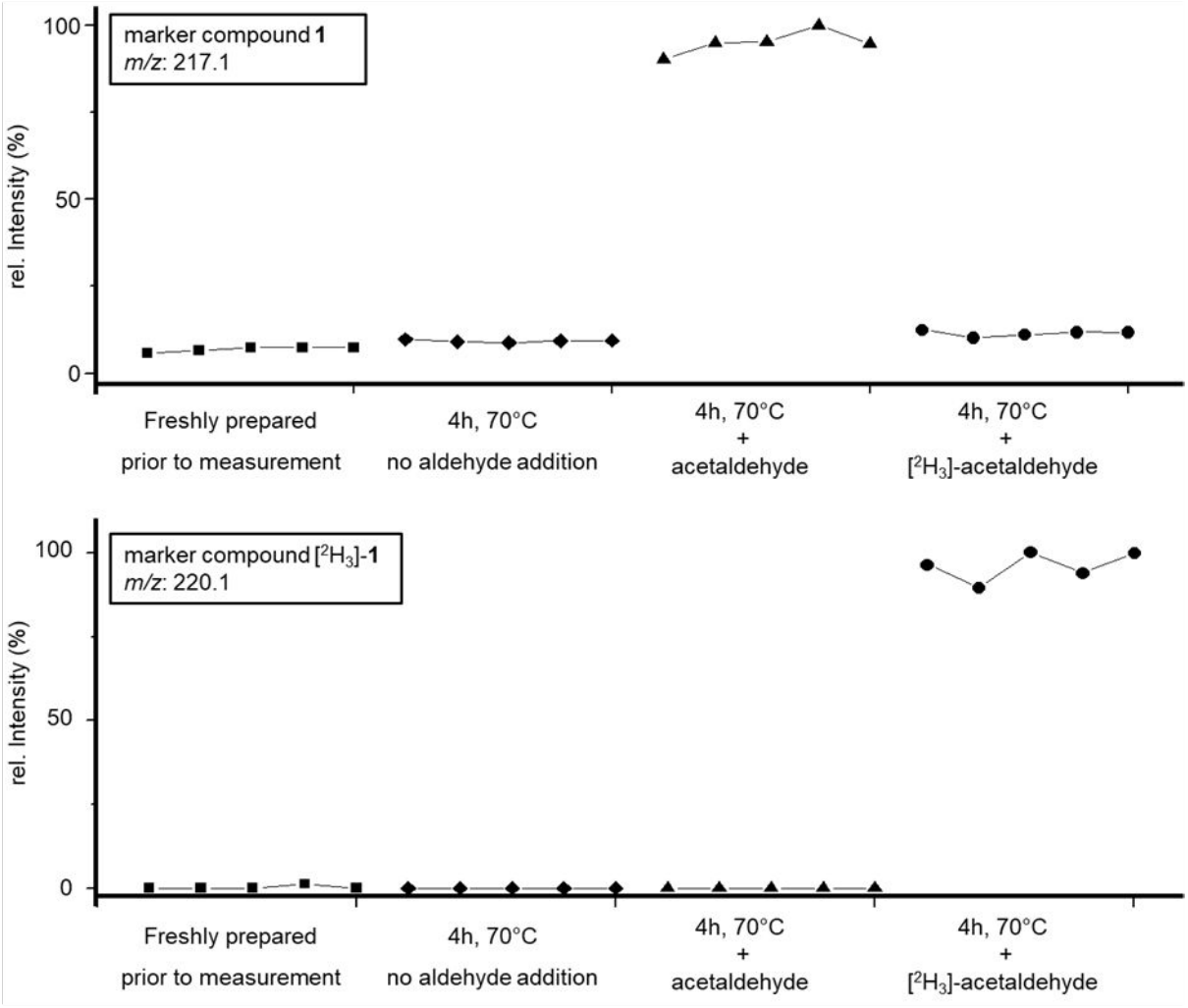

Figure S1. Trendplots depicting 5 injection per coffee sample spiked with: acetaldehyde and stored for 4 h at 70°C (▲), [$^2H_3$]-acetaldehyde and stored for 4 h at 70°C(●), stored for 4 h at 70°C without aldehyde addition (◆) and freshly prepared prior to measurement (■).

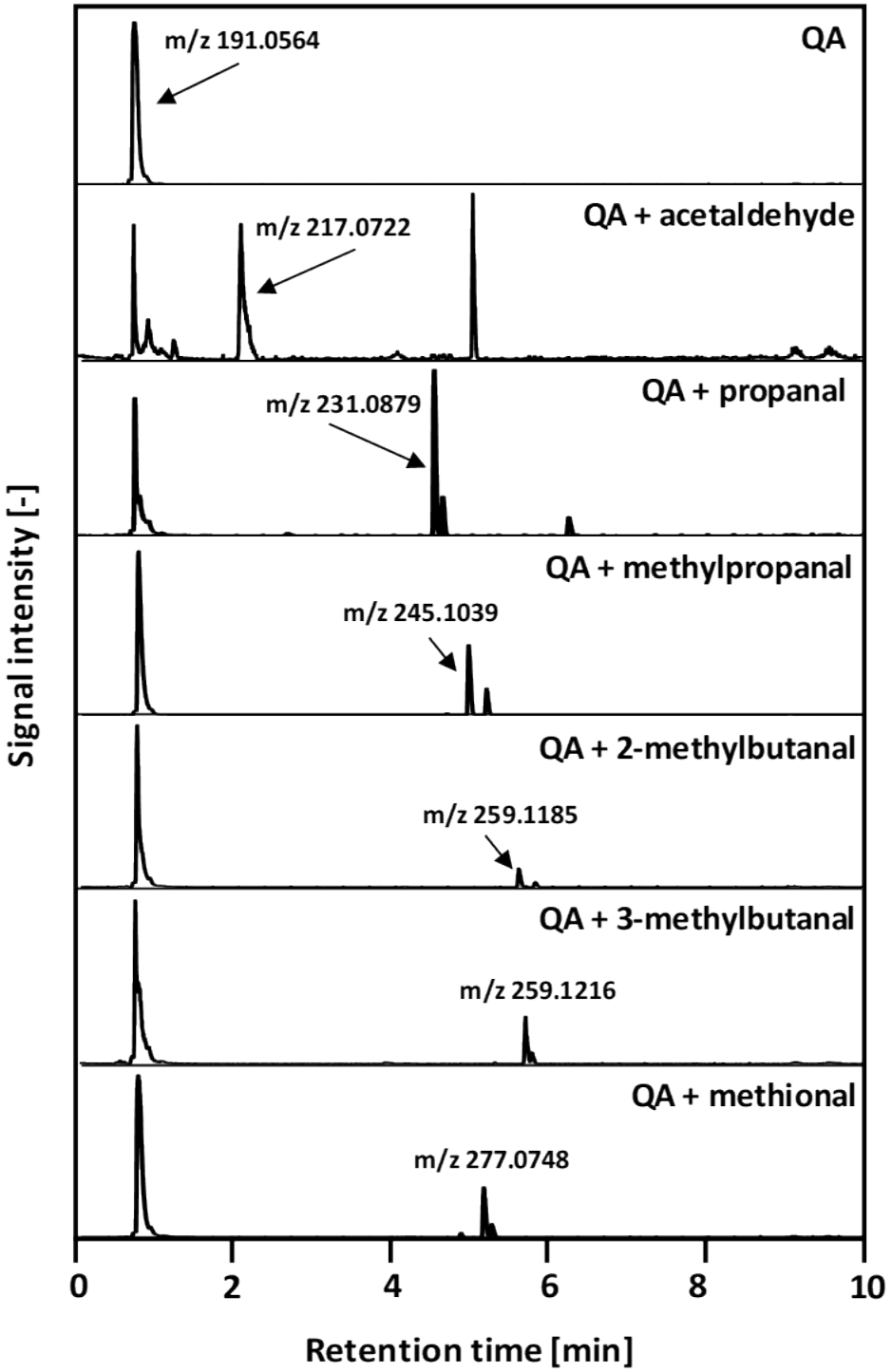

Figure S2. UPLC-TOF-MS (ESI$^-$) chromatograms in full scan (50-1200 Da) and resolution mode of binary reaction mixtures (pH 5.5, 44h, 70°C) consisting of quinic acid (QA) and one of the following aldehydes: acetaldehyde, propanal, methylpropanal, 2-methylbutanal, 3-methylbutanal and methional.

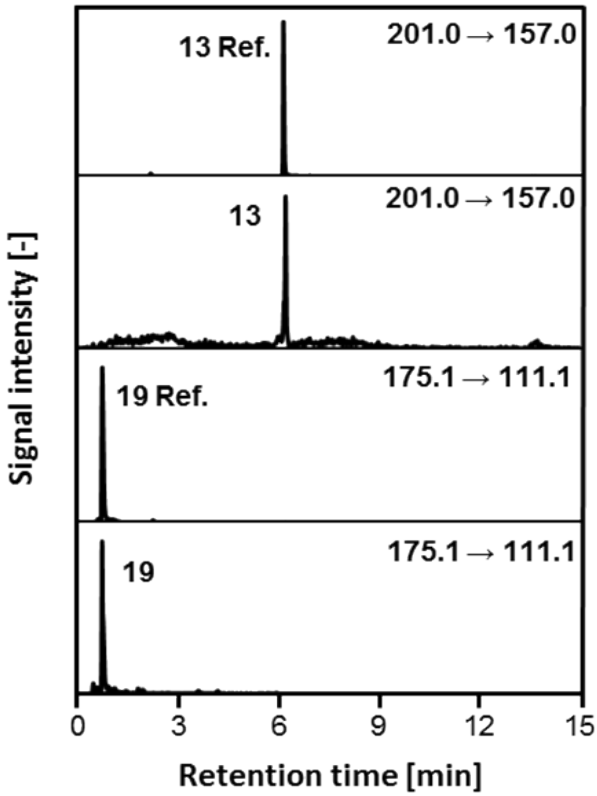

Figure S3. UHPLC-MS/MS (ESI$^+$) chromatograms in the MRM mode of identified conjugate (**13**) and precursor substance (**19**) in a brew prepared from a very dark roast coffee (5.4 g/100 mL), and reference substances Ref-(**13**) and Ref-(**19**) used for quantitation via external matrix calibration.

50 **Table S1.** Optimized specific mass spectrometric parameters for the quantitation of

51 Strecker aldehyde adducts by means of UHPLC-MS/MS_{MRM}.

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Compound	Q1 *m/z*	Q3 *m/z*	DP[a] (V)	CE[b] (V)	CXP[c] (V)
1	216.9	172.8	-100	-18	-27
[$^2H_4$]-1	221.0	173.0	-110	-22	-25
2	231.0	172.9	-95	-22	-23
3	244.8	173.0	-55	-24	-19
4 + 5	258.9	172.9	-25	-24	-19
6	276.9	173.0	-5	-24	-19
7	378.9	217.2	-15	-18	-23
[$^2H_4$]-7	382.9	221.0	-65	-20	-3
8	393.0	231.0	-15	-16	-23
9	406.9	244.9	-55	-22	-27
10 + 11	420.9	258.8	-10	-24	-31
12	438.9	277.2	-45	-34	-5
13	201.0	157.0	91	13	18
14	215.0	138.9	91	17	16
15	229.1	211.0	91	13	24
16 + 17	243.1	139.0	116	17	16

18	261.1	111.0	126	25	16
19	175.1	111.1	51	15	6

[a]DP = declustering potential. [b]CE = collision energy. [c]CXP = cell exit potential.

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54 Intraday precision, as well as interday precision was determined to be ≤5 % and
55 deemed sufficient for the present study.

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57 The following equations were used for quantification QA/- and CQA/adducts via SIDA:

58 y = 7.0554x + 0.0107 (**1**/[$^2H_4$]-**1**, r^2 = 0.9987),

59 y = 1.741x + 0.0215 (**2**/[$^2H_4$]-**1**, r^2 = 0.9998),

60 y = 2.1414x + 0.0215 (**3**/[$^2H_4$]-**1**, r^2 = 0.9998),

61 y = 0.6831x – 0.0022 (**6**/[$^2H_4$]-**1**, r^2 = 0.9963),

62 y = 0.1003x + 0.0082 (**7**/[$^2H_4$]-**7**, r^2 = 0.9965),

63 y = 0.5525x + 0.0011 (**8**/[$^2H_4$]-**7**, r^2 = 0.9999),

64 y = 0.1857x – 0.0004 (**9**/[$^2H_4$]-**7**, r^2 = 0.9999),

65 y = 1.4839x – 0.0092 (**10, 11**/[$^2H_4$]-**7**, r^2 = 0.9990),

66 y = 1.4839x – 0.0092 (**12**/[$^2H_4$]-**7**, r^2 = 0.9990).

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68 QAL and QAL/acetaldehyde were quantified with the following linear regression via
69 external matrix calibration:

70 y = 5E+06x – 180802 (r^2 = 0.9974, **13**).

71 y = 5E+06x – 24393 (r^2 = 0.9963, **19**).

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74 **Table S2.** Determination of recovery rates, LOQ and LOD for Strecker aldehyde
75 adducts using the high molecular weight fraction >10 kDa isolated from a medium roast
76 coffee beverage as analyte free coffee matrix.
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compound	recovery rate (%) at spiking level			mean value (%, ± SD)	LOQ[a] (µg/L)	LOD[b] (µg/L)
	low	medium	high			
1	100.0	104.9	94.5	99.8 (± 4.2)	5.7	1.7
2	77.5	76.3	123.5	99.9 (± 23.6)	3.6	1.1
3	76.7	90.7	119.1	97.9 (± 21.2)	15.4	4.6
4 + 5	74.4	100.0	112.1	93.3 (± 18.8)	13.1	3.9
6	104.7	118.5	102.1	110.3 (± 8.2)	12.1	3.6
7	69.0	71.6	89.9	76.8 (± 1.3)	18.7	5.6
8	84.5	73.3	94.8	84.2 (± 8.8)	4.3	1.3
9	74.8	84.8	90.1	84.5 (± 4.6)	6.8	2.1
10 + 11	103.0	106.5	83.1	97.5 (± 10.3)	15.1	4.5
12	84.5	90.4	103.8	92.9 (± 8.1)	7.4	2.2

[a]Limit of Quantitation (LOQ) and Limit of Detection (LOD). [b]LOD is approximated with LOQ x 0.3.

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Preparative HPLC conditions for isolation of compounds 1-12.

QA/acetaldehyde **(1)***:* starting with 5 % B, the concentration of B was kept isocratic for 5 min, then increased to 100 % B within 10 min, and maintained at 100 % B for 1 min.

QA/methylpropanal **(2)** *and QA/propanal* **(3)***:* starting with 10 % B, the content of B was increased to 35 % B within 10 min, then raised to 100 % B in 5 min, and finally maintained at 100 % B for 1 min.

QA/2-, 3-methylbutanal **(4,5)** *and QA/methional* **(6)**: starting with 10 % B, the content of B was raised to 35 % B within 8 min, then to 100 % B in 5 min, and finally maintained at 100 % B for 4 min.

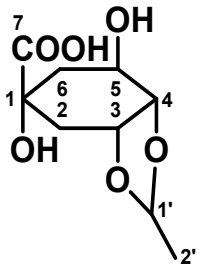
CQA/acetaldehyde **(7)** *and CQA/propanal* **(8)**: starting with 15 % B, the content of B was increased to 48 % within 11 min, then to 60 % in 1 min, and finally to 100 % B within 2 min, then kept at 100 % B for 1 min.

CQA/methylpropanal **(9)**: starting with 15 % B, the content of B was increased to 50 % within 16 min, then raised to 100 % B in 3 min, and maintained at 100 % B for 1 min.

CQA/2-, 3-methylbutanal **(10,11)** *and CQA/methional* **(12)***:* starting with 15 % B, the content of B was raised to 48 % within 11 min, then to 60 % B in 1 min and, finally, to 100 % B in 2 min and kept at 100 % B for 1 additional min.

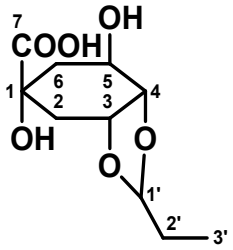
Compound characterization of 1-12 by means of UHPLC-TOF-MS and 1-D and 2-D NMR experiments.

(3aR,5R,7R,7aS)-5,7-dihydroxy-2-methylhexahydrobenzo[d][1,3]dioxole-5-carboxylic acid (**1**).



UHPLC-TOF-MS (ESI$^-$): *m/z* 217.0722 [M - H]$^-$ (measured), m/z 217.0718 (calculated for [$C_9H_{13}O_6$]$^-$). ^{1}H-NMR (400 MHz, D_2O, COSY): δ(ppm): 1.45 [d, 3H, *J*=4.9 Hz, H-C(2`)], 1.86-2.14 [m, 4H, H-C(6), H-C(2)], 3.92 [m, 1H, H-C(5)], 4.00 [m, 1H, H-C(4)], 4.38 [m, 1H, H-C(3)], 5.18 [q, 1H, *J*=4.9 Hz, H-C(1`)]. ^{13}C-NMR (100 MHz, D_2O, HMBC): δ(ppm): 22.9 [C(2`)], 37.1 [C(2)], 41.5 [C(6)], 71.7 [C(5)], 78.0 [C(1)], 79.0 [C(3)], 81.7 [C(4)], 104.4 [C(1`)], 184.7 [C(7)].

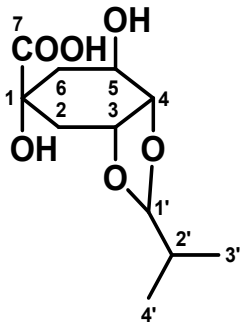
(3aR,5R,7R,7aS)-5,7-dihydroxy-2-isopropylhexahydrobenzo[d][1,3]dioxole-5-carboxylic acid (**2**).



UHPLC-TOF-MS (ESI$^-$): *m/z* 231.0879 [M - H]$^-$ (measured), m/z 231.0874 (calculated for [$C_{10}H_{15}O_6$]$^-$). ^{1}H-NMR (400 MHz, MeOD-*d3*, COSY): δ(ppm): 0.91 [t, 3H, *J*=7.5 Hz, H-C(3`)], 1.69 [m, 2H, H-C(2`)], 1.87-2.16 [m, 4H, H-C(6), H-C(6)], 3.88 [m, 1H, H-

C(4)], 3.94 [m, 1H, H-C(3)], 4.32 [m, 1H, H-C(5)], 4.95 [m, 1H , H-C(1`)]. $^{13}$C-NMR (100 MHz, MeOD-*d4*, HMBC): δ(ppm): 7.0 [C(3`)], 26.4 [C(2`)], 34.3 [C(2)], 39.3 [C(6)], 64.7 [C(5)], 75.1 [C(1)], 75.5 [C(3)], 79.1 [C(4)], 105.5 [C(1`)], 182.0 [C(7)].

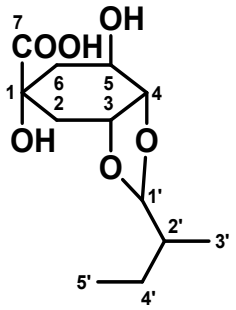
(3aR,5R,7R,7aS)-5,7-dihydroxy-2-isopropylhexahydrobenzo[d][1,3]dioxole-5-carboxylic acid (**3**).



UHPLC-TOF-MS (ESI$^-$): *m/z* 245.1039 [M - H]$^-$ (measured), m/z 245.1031 (calculated for [$C_{11}H_{17}O_6$]$^-$). ^{1}H-NMR (400 MHz, D_2O, COSY): δ(ppm): 0.98 [dd, 6H, *J*=6.9, 2.6 Hz, H-C(3`), H-C(4`)], 1.91 [m, 1H, H-C(2`)], 1.95-2.29 [m, 4H, H-C(6), H-C(2)], 3.99 [m, 1H, H-C(4)], 4.01 [m, 1H, H-C(3)], 4.38 [dt, 1H, *J*=5.4, 2.8 Hz, H-C(5)], 4.83 [d, 1H, *J*=4.4 Hz, H-C(1`)]. ^{13}C-NMR (100 MHz, D_2O, HMBC): δ(ppm): 18.6 [C(3`)/C(4`)], 18.9 [C(3`)/C(4`)], 33.9 [C(2`)], 36.4 [C(2)] 40.9 [C(6)], 70.6 [C(5)], 78.3 [C(1)], 78.5 [C(3)], 81.4 [C(4)], 111.7 [C(1`)], 181.6 [C(7)].

143 *(3aR,5R,7R,7aS)-2-(sec-butyl)-5,7-dihydroxyhexahydrobenzo[d][1,3]dioxole-5-*

144 *carboxylic acid* (**4**).



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146 UHPLC-TOF-MS (ESI$^-$): *m/z* 259.1185 [M - H]$^-$ (measured), m/z 259.1187 (calculated

147 for [$C_{12}H_{19}O_6$]$^-$). ^{1}H-NMR (400 MHz, MeOD-*d3*, COSY): δ(ppm): 0.90 [m, 3H, H-C(5`)],

148 0.98 [m, 3H, H-C(3`)] 1.24 [m, 1H, H-C(4`)], 1.64 [m, 2H, H-C(2`)], 1.88-2.16 [m, 4H,

149 H-C(6), H-C(2)], 3.86 [m, 1H, H-C(4)], 4.01 [ddd, *J* = 11.5, 7.2, 4.3 Hz, 1H, H-C(3)],

150 4.28 [m, 1H, H-C(5)], 4.79 [m, 1H , H-C(1`)]. ^{13}C-NMR (100 MHz, MeOD-*d3*, HMBC):

151 δ(ppm): 11.1 [C(5`)], 14.2 [C(3`)] 23.7 [C(4`)], 34.6 [C(2)], 38.7 [C(2`)], 39.6 [C(6)], 63.7

152 [C(5)], 73.9 [C(1)], 75.1 [C(3)], 79.1 [C(4)], 107.6 [C(1`)], 175.7 [C(7)].

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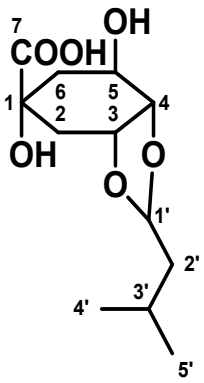
154 *(3aR,5R,7R,7aS)-5,7-dihydroxy-2-isobutylhexahydrobenzo[d][1,3]dioxole-5-*

155 *carboxylic acid* (**5**).



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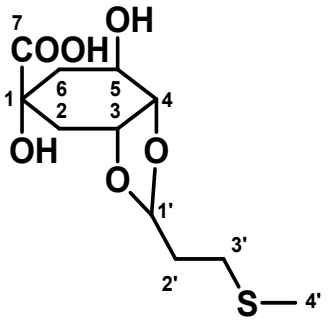
157 UHPLC-TOF-MS (ESI$^-$): *m/z* 259.1216 [M - H]$^-$ (measured), m/z 259.1187 (calculated

158 for [$C_{12}H_{19}O_6$]$^-$). ^{1}H-NMR (400 MHz, MeOD-*d4*, COSY): δ(ppm): 0.97 [m, 6H, H-C(4`),

H-C(5`)], 1.25 [m, 1H, H-C(2`)], 1.66 [m, 2H, H-C(3`)], 1.76-2.33 [m, 4H, H-C(6), H-C(2)], 3.96 [m, 1H, H-C(4)], 4.32 [m, 1H, H-C(3)], 4.74 [m, 1H, H-C(5)], 4.74 [m, 1H, H-C(1`)]. ^{13}C-NMR (100 MHz, MeOD-*d3*, HMBC): δ(ppm): 11.1 [C(4`), C(5`)], 23.7 [C(2`)], 34.6 [C(2)], 38.7 [C(3`)], 39.6 [C(6)], 63.7 [C(5)], 73.9 [C(1)], 75.1 [C(3)], 79.1 [C(4)], 107.6 [C(1`)], 175.7 [C(7)].

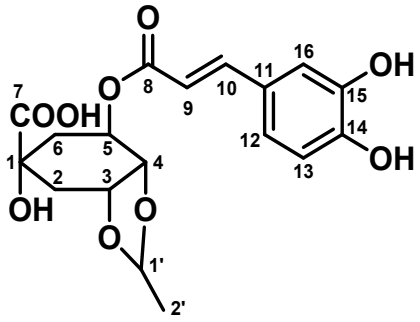
(3aR,5R,7R,7aS)-5,7-dihydroxy-2-(2-methylthio)ethyl)hexahydrobenzo[d][1,3]dioxole-5- carboxylic acid (**6**).



UHPLC-TOF-MS (ESI$^-$): *m/z* 277.0748 [M - H]$^-$ (measured), m/z 277.0751 (calculated for [$C_{11}H_{17}O_6S$]$^-$). ^{1}H-NMR (400 MHz, MeOD-*d3*, COSY): δ(ppm): 1.79 [m, 2H, H-C(6)], 1.93 [m, 2H, H-C(2`)], 1.95-2.28 [m, 5H, H-C(2), H-C(4`)], 2.53 [m, 2H, H-C(3`)], 3.79 [m, 1H, H-C(4)], 4.22 [m, 1H, H-C(3)], 4.35 [m, 1H, H-C(5)], 4.89 [m, 1H, H-C(1`)]. ^{13}C-NMR (100 MHz, MeOD-*d4*, HMBC): δ(ppm): 15.2 [C(4`)], 28.1 [C(3`)], 33.6 [C(2`)], 37.1 [C(2)], 37.7 [C(6)], 71.3 [C(5)], 72.4 [C(1)], 73.6 [C(3)], 78.3 [C(4)], 103.2 [C(1`)], 180.5 [C(7)].

179 *(3aR,5S,7R,7aR)-7-(3,4-dihydroxycinnamic acid)-5-hydroxy-2-*

180 *methylhexahydrobenzo[d][1,3]dioxole-5-carboxylic acid* (**7**).



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182 UV/vis (0.1% aqueous formic acid/acetonitrile, 1/1, v/v): λ_{max}= 220 nm, 324 nm,

183 UHPLC-TOF-MS (ESI$^-$): *m/z* 379.1035 [M - H]$^-$ (measured), m/z 389.1035 (calculated

184 for [$C_{18}H_{19}O_9$]$^-$). ^{1}H-NMR (400 MHz, DMSO-*d6*, COSY): δ(ppm): 1.32 [d, 3H, *J*=4.8 Hz,

185 H-C(2`)], 1.81-2.22 [m, 4H, H-C(2), H-C(6)], 4.06 [m, 1H, H-C(4)], 4.24 [m, 1H, H-

186 C(3)], 5.06 [q, 1H, *J*=4.8 Hz, H-C(1`)], 5.21 [m, 1H, H-C(5)], 6.25 [d, 1H, *J*=15.7 Hz, H-

187 C(9)], 6.76 [d, 1H, *J*=7.9 Hz, H-C(13)], 7.00 [dd, 1H, *J*=8.1, 1.8 Hz, H-C(12)], 7.05 [d,

188 1H, *J*=1.9 Hz, H-C(16)], 7.47 [d, 1H, *J*= 15.9 Hz, H-C(10)]. ^{13}C-NMR (100 MHz, DMSO-

189 *d6*, HMBC): δ(ppm): 20.7 [C(2`)], 35.5 [C(2)], 36.9 [C(6)], 72.1 [C(5)], 72.9 [C(1)], 75.1

190 [C(3)], 76.7 [C(4)], 101.3 [C(1`)], 115.0 [C(9)], 116.2 [C(16)], 117.1 [C(13)], 121.9

191 [C(12)], 125.6 [C(11)], 145.9 [C(10)], 147.5 [C(14)/C(15)], 150.5 [C(14)/C(15)], 163.9

192 [C(8)], 177.8 [C(7)].

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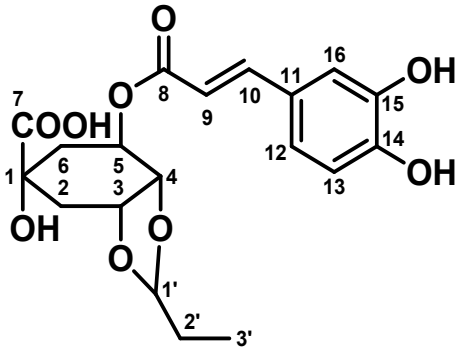
199 *(3aR,5S,7R,7aR)-7-(3,4-dihydroxycinnamic acid)-5-hydroxy-2-*

200 *isopropylhexahydrobenzo[d][1,3]dioxole-5-carboxylic acid* (**8**).



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202 UV/vis (0.1% aqueous formic acid/acetonitrile 1/1, v/v): λ_{max}= 220 nm, 324 nm,

203 UHPLC-TOF-MS (ESI$^-$): *m/z* 393.1176 [M - H]$^-$ (measured), m/z 393.1191 (calculated

204 for [$C_{19}H_{21}O_9$]$^-$). ^{1}H-NMR (400 MHz, MeOD-*d3, COSY*): δ(ppm): 0.90 [t, 3H, *J*=7.7 Hz,

205 H-C(3`)], 1.61 [m, 2H, C-H(2`)], 1.79-2.20 [m, 4H, H-C(2), H-C(6)], 4.09 [m, 1H, H-

206 C(4)], 4.26 [m, 1H, H-C(3)], 4.87 [t, 1H, *J*=4.7 Hz, H-C(1`)], 5.21 [m, 1H, H-C(5)], 6.24

207 [d, 1H, *J*=15.9 Hz, H-C(9)], 6.78 [d, 1H, *J*=8.1 Hz, H-C(13)], 7.00 [dd, 1H, *J*=8.2, 2.1

208 Hz, H-C(12)], 7.06 [d, 1H, *J*=2.1 Hz, H-C(16)], 7.48 [d, 1H, *J*=15.9 Hz, H-C(10)].

209 ^{13}C-NMR (100 MHz, MeOD-*d4, HMBC*)**:** δ(ppm): 10.4 [C(3`)], 27.2 [C(2`)], 35.4 [C(2)],

210 36.5 [C(6)], 69.3 [C(5)], 70.7 [C(1)], 71.5 [C(3)], 73.2 [C(4)], 104.8 [C(1`)], 114.4 [C(9)],

211 115.0 [C(16)], 115.2 [C(13)], 116.2 [C(12)], 126.4 [C(11)], , 145.6 [C(10)], 146.0

212 [C(14)/C(15)], 148.7 [C(14)/C(15)], 167.2 [C(8)], 176.6 [C(7)].

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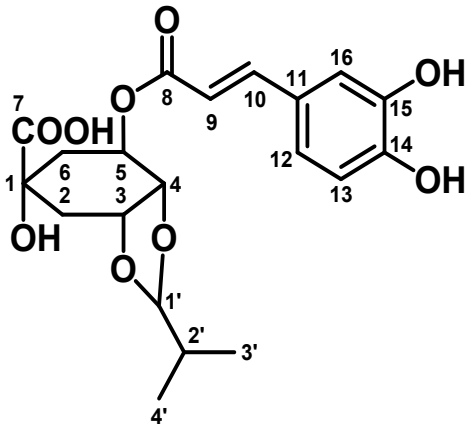
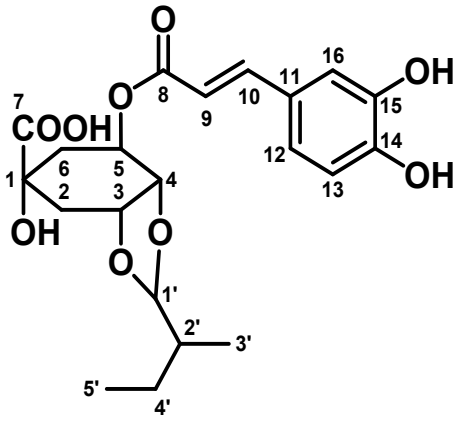
(3aR,5S,7R,7aR)-7-(3,4-dihydroxycinnamic acid)-2-ethyl-5-hydroxyhexahydrobenzo[d][1,3]dioxole-5-carboxylic acid (**9**).



UV/vis (0.1% aqueous formic acid/acetonitrile 1/1, v/v): λ_{max}= 220 nm, 324 nm, UHPLC-TOF-MS (ESI$^-$): *m/z* 407.1347 [M - H]$^-$ (measured), m/z 407.1348 (calculated for [$C_{20}H_{23}O_9$]$^-$). ^{1}H-NMR (400 MHz, MeOD-*d3*, COSY): δ(ppm): 0.98 [dd, 6H, *J*=6.8 Hz, H-C(3`), H-C(4`)], 1.86 [m, 1H, H-C(2`)], 1.96-2.39 [m, 4H, H-C(2), H-C(6) ], 4.15 [m, 1H, H-C(4)], 4.36 [dt, 1H, *J*=5.4; 3.4 Hz, H-C(3)], 4.73 [d, 1H, *J*=4.7 Hz, H-C(1`)], 5.37 [dt, 1H, *J*=4.5, 7.3, 11.6 Hz, H-C(5)], 6.26 [d, 1H, *J*=15.9 Hz, H-C(9)], 6.78 [d, 1H, *J*=8.2 Hz, H-C(13)], 6.95 [dd, 1H, *J*=8.2, 1.9 Hz, H-C(12)], 7.05 [d, 1H, *J*=1.9 Hz, H-C(16)], 7.56 [d, 1H, *J*=15.8 Hz, H-C(10)]. ^{13}C-NMR (100 MHz, MeOD-*d3*, HMBC): δ(ppm): 17.2 [C(3`)/C(4`)], 17.3 [C(3`)/C(4`)], 33.2 [C(2`)], 35.8 [C(2)], 37.5 [C(6)], 72.9 [C(5)], 74.6 [C(1)], 76.7 [C(3)], 77.7 [C(4)], 109.7 [C(1`)], 115.1 [C(9)], 115.2 [C(16)], 116.5 [C(13)], 123.0 [C(12)], 127.8 [C(11)], 146.8 [C(10)], 147.1 [C(14/15)], 148.6 [C(14/15)], 168.4 [C(8)], 178.4 [C(7)].

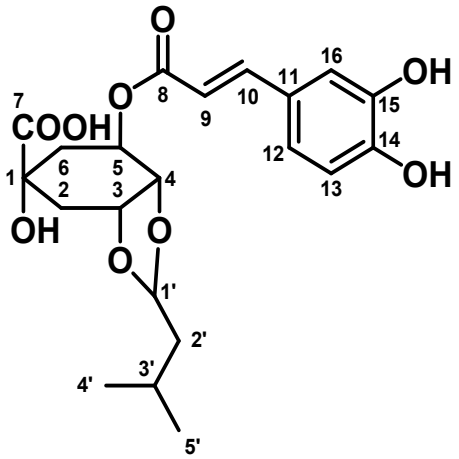
(3aR,5S,7R,7aR)-2-(sec-butyl)-7-(3,4-dihydroxycinnamic acid)-5-hydroxyhexahydrobenzo[d][1,3]dioxole-5-carboxylic acid (**10**).



UV/vis (0.1% aqueous formic acid/acetonitrile 1/1, v/v): λ_{max}= 220 nm, 324 nm, UHPLC-TOF-MS (ESI$^-$): *m/z* 421.1501 [M - H]$^-$ (measured), m/z 421.1504 (calculated for [$C_{21}H_{25}O_9$]$^-$). ^{1}H-NMR (400 MHz, MeOD-*d3,* COSY): δ(ppm): 0.89 [m, 3H, H-C(5`)], 0.96 [m, 3H, H-C(3`)], 1.14 [m, 2H, H-C(4`)], 1.56 [m, 1H, H-C(2`)], 1.85-2.29 [m, 4H, H-C(2), H-C(6)], 4.09 [m, 1H, H-C(4)], 4.26 [m, 1H, H-C(3)], 4.73 [d, 1H, *J*=4.0 Hz, H-C(1`)], 5.24 [m, 1H, H-C(5)], 6.24 [d, 1H, *J*=15.9 Hz, H-C(9)], 6.78 [d, 1H, *J*=8.1 Hz, H-C(13)], 7.00 [dd, 1H, *J*=8.1, 2.1 Hz, H-C(12)], 7.06 [d, 1H, *J*=2.1 Hz, H-C(16)], 7.48 [d, 1H, *J*=15.9 Hz, H-C(10)]. $^{13}$C-NMR (100 MHz, MeOD-*d4*, HMBC): δ(ppm): 11.8 [C(5`)], 14.1 [C(3`)], 24.1 [C(4`)], 35.3 [C(2)], 35.9 [C(2`)] 36.5 [C(6)], 68.6 [C(5)], 71.5 [C(1)], 71.7 [C(3)], 73.2 [C(4)], 107.0 [C(1`)], 114.4 [C(9)], 115.0 [C(16)], 115.2 [C(13)], 116.2 [C(12)], 126.4 [C(11)], 145.7 [C(10)], 147.6 [C(15/16)], 148.0 [C(15/16)], 167.2 [C(8)], 176.6 [C(7)].

255 *(3aR,5S,7R,7aR)-7-(3,4-dihydroxycinnamic acid)-5-hydroxy-2-*

256 *isobutylhexahydrobenzo[d][1,3]dioxole-5-carboxylic acid* (**11**).



257

258 UV/vis (0.1% aqueous formic acid/acetonitrile 1/1, v/v): λ_{max}= 220 nm, 324 nm,

259 UHPLC-TOF-MS (ESI$^-$): *m/z* 421.1503 [M - H]$^-$ (measured), m/z 421.1504 (calculated

260 for [$C_{21}H_{25}O_9$]$^-$). ^{1}H-NMR (400 MHz, MeOD-*d3*, COSY): δ(ppm): 0.90 [m, 6H, H-C(4`),

261 H-C(5`)], 1.50 [t, 2H, *J*=5.5 Hz, H-C(2`)], 1.78 [m, 1H, H-C(3`)], 1.83-2.27 [m, 4H, H-

262 C(2), H-C(6)], 4.06 [m, 1H, H-C(4)], 4.24 [m, 1H, H-C(3)], 4.94 [t, 1H, *J*=4.0 Hz, H-

263 C(1`)], 5.20 [m, 1H, H-C(5)], 6.24 [d, 1H, *J*=15.9 Hz, H-C(9)], 6.78 [d, 1H, *J*=8.1 Hz, H-

264 C(13)], 7.00 [dd, 1H, *J*=8.1, 2.1 Hz, H-C(12)], 7.06 [d, 1H, *J*=2.1 Hz, H-C(16)], 7.48 [d,

265 1H, *J*=15.9 Hz, H-C(10)]. ^{13}C-NMR (100 MHz, MeOD-*d3*, HMBC): δ(ppm): 23.3

266 [C(4`),C(5`)], 24.4 [C(2`)], 32.8 [C(3`)], 35.7 [C(2)], 37.5 [C(6)], 68.1 [C(5)], 71.3 [C(1)],

267 73.2 [C(3)], 76.8 [C(4)], 103.4 [C(1`)], 114.4 [C(9)], 115.0 [C(16)], 115.2 [C(13)], 116.2

268 [C(12)], 126.4 [C(11)], 145.7 [C(10)], 146.6 [C(14/15)], 147.0 [C(14/15)], 167.2 [C(8)],

269 176.6 [C(7)].

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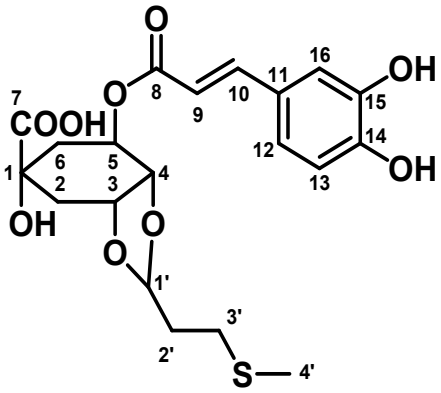
(3aR,5S,7R,7aR)-7-(3,4-dihydroxycinnamic acid)-5-hydroxy-2-(2-(methylthio)ethyl)hexahydrobenzo[d][1,3]dioxole-5-carboxylic acid (**12**).



UV/vis (0.1% aqueous formic acid/acetonitrile 1/1, v/v): λ_{max}= 220 nm, 324 nm, UHPLC-TOF-MS (ESI$^-$): *m/z* 439.1066 [M - H]$^-$ (measured), m/z 439.1068 (calculated for [$C_{20}H_{23}O_9S$]$^-$). ^{1}H-NMR (400 MHz, MeOD-*d3*, COSY): δ(ppm): 1.96-2.06 [m, 3H, H-C(6α), H-C(2α), H-C-(2β)], 2.11 [s, 3H, H-C(4`)], 2.30 [m, 2H, H-C(2`)], 2.39 [m, 1H, H-C(6β)], 2.66 [d, 2H, *J*=7.7 Hz, H-C(3`)], 4.18 [m, 1H, H-C(4)], 4.39 [m, 1H, H-C(3)], 5.11 [t, 1H, *J*=4.0 Hz, H-C(1`)], 5.39 [m, 1H, H-C(5)], 6.28 [d, 1H, *J*=15.9 Hz, H-C(9)], 6.80 [d, 1H, *J*=8.1 Hz, H-C(13)], 7.00 [dd, 1H, *J*=8.1, 2.1 Hz, H-C(12)], 7.07 [d, 1H, *J*=2.1 Hz, H-C(16)], 7.58 [d, 1H, *J*=15.9 Hz, H-C(10)]. ^{13}C-NMR (100 MHz, MeOD-*d3*, HMBC): δ(ppm): 14.0 [C(4`)], 27.6 [C(3`)], 33.9 [C(2)], 34.3 [C(2`)], 36.7 [C(6)], 70.9 [C(5)], 73.2 [C(1)], 75.5 [C(3)], 76.7 [C(4)], 103.3 [C(1`)], 113.8 [C(9)], 114.4 [C(16)], 115.2 [C(13)], 115.2 [C(12)], 121.4 [C(11)], 145.0 [C(10)], 145.6 [C(14)/ C(15)], 145.9 [C(14)(C(15)], 167.2 [C(8)], 176.6 [C(7)].

293 **Chemical characterization of quinic acid γ-lactone.**

294 *(1S,3R,4R,5R)-1,3,4-trihydroxy-6-oxabicyclo[3.2.1]octan-7-one (Quinic acid-γ-*
295 *lactone)* (**19**).

296 UHPLC-TOF-MS (ESI$^+$): *m/z* 175.0639 [M + H]$^+$ (measured), m/z 175.0601 (calculated
297 for [$C_7H_{11}O_5$]$^+$). ^{1}H-NMR (400 MHz, D_2O, COSY): δ(ppm): 1.81-2.44 [m, 4H, H-C(2), H-
298 C(6)], 3.78 [ddd, 1H, *J* = 11.4, 6.7, 4.5 Hz, H-C(3)], 4.06 [t, 1H, *J* = 4.7 Hz, H-C(4)],
299 4.82 [t, 1H, *J* = 5.4 Hz, H-C(5)]

300

301 **Preparative HPLC conditions for isolation of compounds 13-18.**
302 *QAL/propanal* **(14)**: starting with isocratic elution at 10 % B for 5 min, the content of B
303 was increased to 35 % within 2 min, then raised to 55 % in 2 min and, finally, to 100 %
304 B within 2 min, and kept at 100 % B for 5 min.

305 *QAL/methylpropanal* **(15)** *and QAL/2-methylbutanal* **(16)**: starting with isocratic elution
306 at 10 % B for 5 min, the content of B was increased to 35 % within 2 min, then raised
307 to 50 % in 7 min and, finally, to 100 % B within 10 min, and kept at 100 % B for 2 min.

308 *QAL/3-methylbutanal* **(17)**: starting with isocratic elution for 4 min at 15% B, the content
309 of B was increased to 50% B in 4 min, then raised to 78% within 10 min and, finally, to
310 100% B in 1 min and kept isocratic at 100% B for 2 additional min.

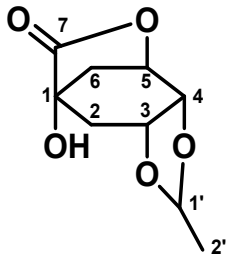
311 *QAL/methional* **(18)***:* starting with isocratic elution for 5 min at 15% B, the content of B
312 was increased to 35% B within 2 min, raised to 50% B in 7 min, in 16 min to 100% B,
313 and kept at 100 % B for 3 min.

314 All collected fractions were concentrated under reduced pressure and adjusted to pH 7
315 with NaOH (0.1 mol/L) before freeze-drying for 48 h. Major reaction products were
316 analyzed by means of UHPLC-TOF-MS and 1D-, 2D-NMR experiments, and their
317 molecular structures were determined as adducts of quinic acid lactone and the

corresponding aldehyde, linked covalently by acetalization via the cis-diol part of the quinic acid lactone.

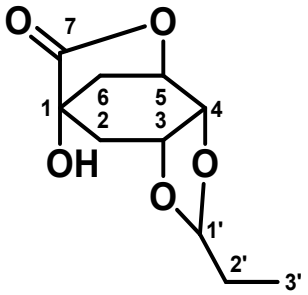
Compound characterization of 13-18 by means of UHPLC-TOF-MS and 1-D and 2-D NMR experiments.

(3aR,4R,7S,8aR)-7-hydroxy-2-methyltetrahydro-4,7-methano[1,3]dioxolo[4,5-c]oxepin-6(4H)-one (**13**).



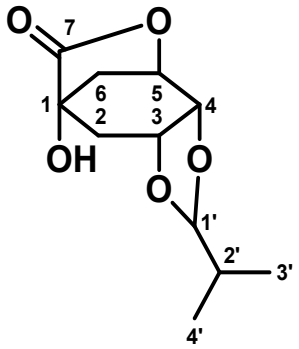
UHPLC-TOF-MS (ESI$^-$): m/z 199.1839 [M-H]$^-$ (measured), m/z 199.1900 (calculated for [$C_9H_{11}O_5$]$^-$). ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm): 1.43 [d, 3H, *J*=4.8 Hz, 3H, H-C(2`)], 2.25-2.68 [m, 4H, H-C(2), H-C(6)], 4.19 [dt, *J*=1.9, 6.7 Hz, 1H, H-C(3)], 4.34 [m, 1H, H-C(4)], 4.71 [m, 1H, H-C(5)], 4.98 [q, 1H, *J*=4.8 Hz, H-C(1`)]. ^{13}C-NMR (100 MHz, $CDCl_3$): δ(ppm): 19.4 [C(2`)], 34.0 [C(6)], 37.6 [C(2)], 71.3 [C(1)], 72.6 [C(3)], 72.7 [C(4)], 75.7 [C(5)], 101.4 [C(1`)], 178.8 [C(7)].

(3aR,4R,7S,8aR)-2-ethyl-7-hydroxytetrahydro-4,7-methano[1,3]dioxolo[4,5-c]oxepin-6(4H)-one (**14**).



UHPLC-TOF-MS (ESI$^+$): *m/z* 237.0748 [M+Na]$^+$ (measured), *m/z* 237.0739 (calculated für [$C_{10}H_{13}O_5Na$]$^+$). ^{1}H-NMR (500 MHz, MeOD-d_3): δ(ppm): 0.99 [t, 3H *J*=7.6 Hz, H-C(3`)], 1.54 [m, 2H; H-C(2`)], 2.11-2.57 [m, 4H, H-C(2), H-C(6)], 4.19 [m, 1H, H-C(3)], 4.40 [m, 1H, H-C(4)], 4.59 [m, 1H, H-C(5)], 5.30 [t, 1H, *J*=4.7 Hz, H-C(1`)]. $^{13}$C-NMR (125 MHz, MeOD-$d_3$): δ(ppm): 8.7 [C(3`)], 28.0 [C(2`)], 35.8 [C(6)], 39.0 [C(2)], 72.6 [C(1)], 74.2 [C(4)], 74.3 [C(3)], 76.9 [C(5)], 106.6 [C(1`)], 180.5 [C(7)].

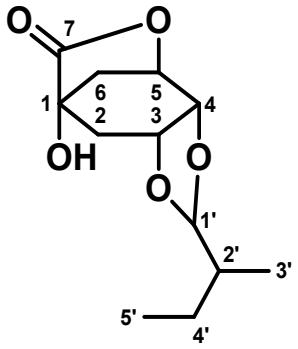
(3aR,4R,7S,8aR)-7-hydroxy-2-isopropyltetrahydro-4,7-methano[1,3]dioxolo[4,5-c]oxepin-6(4H)-one (**15**).



UHPLC-TOF-MS (ESI$^+$): m/z 229.0915 [M+H]$^+$ (measured), m/z 229.0998 (calculated for [$C_{11}H_{17}O_5$]$^+$). ^{1}H-NMR (500 MHz, MeOD-d_3): δ(ppm): 1.01 [d, 3H, *J*=2.8 Hz, H-C(3`)/H-C(4`)], 1.02 [d, 3H, *J*=2.8 Hz, H-C(3`)/H-C(4`)], 1.87 [m, 1H, H-C(2`)], 1.89-2.31 [m, 4H, H-C(2), H-C(6)], 3.89 [m, 1H, H-C(3)], 3.94 [m, 1H, H-C(4)], 4.35 [m,

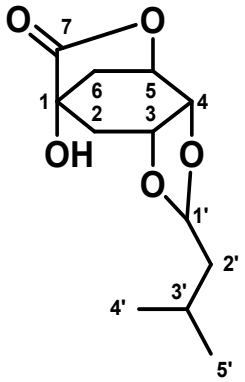
1H, H-C(5)], 4.67 [d, 1H, *J*=5.0 Hz, H-C(1)]. ^{13}C-NMR (125 MHz, MeOD-d_3): δ(ppm): 17.9 [C(3`)/ C(4`)], 18.0 [C(3`)/ C(4`)], 33.7 [C(2`)], 37.4 [C(6)], 39.8 [C(2)], 69.5 [C(1)], 75.1 [C(4)], 76.4 [C(3)], 80.4 [C(5)], 109.6 [C(1`)], 183.5 [C(7)].

(3aR,4R,7S,8aR)-2-(sec-butyl)-7-hydroxytetrahydro-4,7-methano[1,3]dioxolo[4,5-c]oxepin-6(4H)-one (**16**).



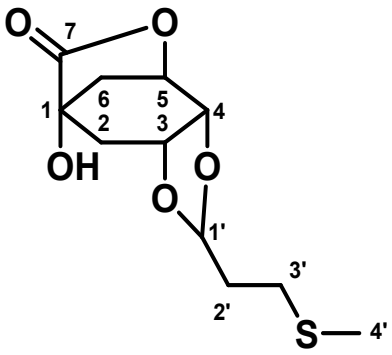
UHPLC-TOF-MS (ESI$^+$): 265.1046 [M+Na]$^+$ (measured), 265.1052 (calculated for [$C_{12}H_{17}O_5Na$]$^+$). ^{1}H-NMR (500 MHz, MeOD-d_3): δ(ppm): 0.97 [t, 3H, *J*=7.4 Hz, H-C(5`)], 1.01 [d, 2H, *J*=6.7 Hz, H-C(3`)], 1.24 [m, 1H, H-C(2`)], 1.67 [m, 2H, H-C(4`)], 1.86-2.30 [m, 4H, H-C(2), H-C(6)], 3.89 [m, 1H, H-C(3)], 3.95 [m, 1H, H-C(4)], 4.28 [m, 1H, H-C(5)], 4.75 [d, 1H, *J*=4.6 Hz, H-C(1`)]. $^{13}$C-NMR (125 MHz, MeOD-$d_3$, HMBC): δ(ppm): 24.0 [C(5`)], 24.2 [C(3`)], 35.5 [C(4`)], 35.8 [C(6)], 37.8 [C(2`)], 39.0 [C(2)], 64.7 [C(1)], 66.8 [C(4)], 74.1 [C(3)], 79.1 [C(5)], 107.3 [C(1`)], 182.3 [C(7)].

(3aR,4R,7S,8aR)-7-hydroxy-2-isobutyltetrahydro-4,7-methano[1,3]dioxolo[4,5-c]oxepin-6(4H)-one (**17**).



UHPLC-TOF-MS (ESI$^+$): m/z 265.1051 [M+Na]$^+$ (measured), m/z 265.1052 (calculated for [$C_{12}H_{17}O_5Na$]$^+$). ^{1}H-NMR (400 MHz, MeOD-d_3): δ(ppm): 0.99 [d, 6H, *J*=0.9 Hz, H-C(4`), H-C(5`)], 1.63 [m, 2H, H-C(2`)], 1.86 [m, 1H, H-C(3`)], 2.11-2.56 [m, 4H, H-C(2), H-C(6), 4.18 [dt, 1H, *J*=1.9, 6.7 Hz, H-C(3)], 4.39 [m, 1H, H-C(4)], 4.65 [m, 1H, H-C(5)], 4.93 [t, 1H, *J*=5.1 Hz, H-C(1`)]. $^{13}$C-NMR (100 MHz, MeOD-$d_3$): δ(ppm): 23.7 [C(4`), C(5`)], 26.2 [C(3`)], 35.8 [C(6)], 39.0 [C(2)], 44.2 [C(2`)], 72.6 [C(1)], 74.2 [C(4)], 74.3 [C(3)], 76.9 [C(5)], 105.2 [C(1`)], 180.6 [C(7)].

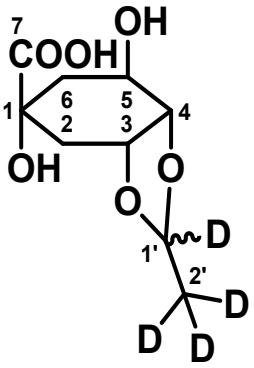
(3aR,4R,7S,8aR)-7-hydroxy-2-(2-(methylthio)ethyl)tetrahydro-4,7-methano[1,3]dioxolo[4,5-c]oxepin-6(4H)-one (**18**).



UHPLC-TOF-MS (ESI$^+$): m/z 283.0617 [M+Na]$^+$ (measured), m/z 283.0616 (calculated for [$C_{11}H_{15}O_6SNa$]$^+$). ^{1}H-NMR (500 MHz, MeOD-*d$_3$*): δ(ppm): 2.03 [s, 3H, H-C(4`)], 2.10 [m, 1H, H-C(2β)], 2.13 [m, 2H, H-C(2`)], 2.26-2.56 [m, 3H, H-C(2α), H-C(6α), H-C(6β)], 2.65 [m, 2H, H-C(3`)], 4.22 [m, 1H, H-C(3)], 4.42 [m, 1H, H-C(4)], 4.72 [m, 1H, H-C(5)], 4.99 [t, 1H, *J*=4.6 Hz, H-C(1`)]. ^{13}C-NMR (125 MHz, MeOD-*d$_3$*): δ(ppm): 15.9 [C(4`)], 29.7 [C(3`)], 34.9 [C(2`)], 35.8 [C(6)], 38.9 [C(2)], 72.6 [C(1)], 74.3 [C(3)], 74.4 [C(4)], 76.8 [C(5)], 104.6 [C(1`)], 180.5 [C(7)].

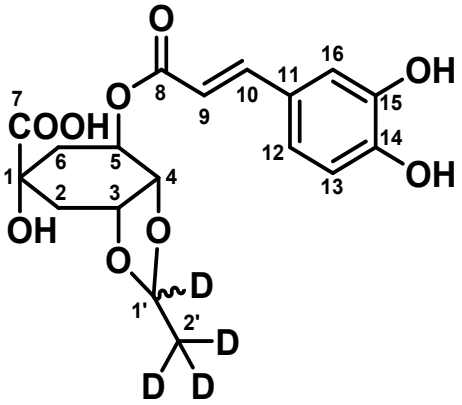
Compound characterization of stable isotopically labeled standards for SIDA by means of UHPLC-TOF-MS and 1-D and 2-D NMR experiments.

[$^2H_4$]-(3aS,5S,7S,7aR)-5,7-dihydroxy-2-(methyl-d3)hexahydrobenzo[d][1,3]dioxole-5-carboxylic acid ([$^2H_4$]-**1**).



UPLC-TOF-MS (ESI$^-$): *m/z* 221.0963 [M - H]$^-$ (measured), m/z 221.0969 (calculated for [$C_9{}^1H_9{}^2H_4O_6$]$^-$). ^{1}H-NMR (400 MHz, D_2O, COSY): δ(ppm): 1.86-2.14 [m, 4H, H-C(6), H-C(2)], 3.92 [m, 1H, H-C(4)], 3.98 [m, 1H, H-C(3)], 4.37 [m, 1H, H-C(5)].

[$^2H_4$]-(3aS,5R,7S,7aS)-7-(3,4-dihydroxycinnamic acid)-5-hydroxy-2-(methyl-d3)hexahydrobenzo[d][1,3]dioxole-5-carboxylic acid ([$^2H_4$]-**7**).



UV/vis (0.1% aqueous formic acid/acetonitrile): λ_{max}= 324 nm, UPLC-TOF-MS (ESI$^-$): *m/z* 383.1276 [M - H]$^-$ (measured), m/z 383.1286 (calculated for [$C_{18}{}^1H_{15}{}^2H_4O_9$]$^-$). ^{1}H-NMR (400 MHz, DMSO-*d6*, COSY): δ(ppm): 1.81-2.09 [m, 4H, H-C(6), H-C(2)], 4.07 [m, 1H, H-C(4)], 4.26 [m, 1H, H-C(3)], 5.21 [m, 1H, H-C(5)], 6.25 [d, 1H, *J*=15.9 Hz, H-C(9)], 6.78 [d, 1H, *J*=8.1 Hz, H-C(13)], 7.02 [dd, 1H, *J*=8.2, 1.9 Hz H-C(12)], 7.07 [d, 1H, *J*=1.9 Hz, H-C(16)], 7.48 [d, 1H, *J*= 15.9 Hz, H-C(10)].