Supporting Information

Sensomics Analysis of Key Bitter Compounds in the Hard Resin of Hops (*Humulus lupulus L.*) and their Contribution to the Bitter Profile of Pilsner-type Beer

Michael Dresel, Andreas Dunkel, and Thomas Hofmann*

Chair of Food Chemistry and Molecular and Sensory Science, Technische Universität München, Lise-Meitner-Str. 34, D-84354 Freising, Germany

Chromatographic Separation of MPLC-Fractions of ε-Resin. MPLC fractions were separated using an HPLC system (Varian, Middelburg, Niederlande) consisting of two ProStar 210 pumps, a 7725i type Rheodyne injection valve (Rheodyne, Bensheim, Germany), and a ProStar 330 diode array detector monitoring the effluent between 220 and 400 nm. Chromatography was performed on a 250 x 21.2 mm, 5 µm, Luna Phenyl-Hexyl column (Phenomenex, Aschaffenburg, Germany) operated with a flow rate of 15 mL/min and using water (0.1 % formic acid) as solvent A and acetonitrile (0.1 % formic acid) as solvent B. Data acquisition was performed by means of Star Chromatography Workstation Software, Version 6.2.

MPLC fraction e2 (yield: 3.35%). Aliquots of fraction e2 (100 mg) dissolved in acetonitrile (1.6 mL; 12.5%, v/v) were separated using the following gradient: 15% solvent

B for 4.0 min, increasing solvent B to 22% within 20 min, and, then, increasing solvent B to 28% within 1.0 min. Solvent B was kept for 16 min at 28% and, finally, increased to 100% within an additional minute, followed by isocratic elution for 1.5 min. After 45 min, solvent B decreased again to 15% within 1.5 min and was kept for 5.0 min prior to the next injection. A total of 14 fractions, namely fractions e2-1 to e2-14, were collected, separated from solvent in vacuum, and was, then, subjected to a taste dilution analysis (**Figure 3**).

MPLC fraction e3 (yield: 2.99%). Aliquots of subfraction e3 (90 mg) dissolved in acetonitrile (1.6 mL; 20%, v/v) were separated using following gradient: 30% solvent B for 19.5 min, increasing solvent B to 40% within 1.5 min and, then, to 50% within 6.0 min. Solvent B was kept for 4.0 min at 50% and, finally, increased to 100% within an additional minute, followed by isocratic elution for 1.5 min. After 33.5 min, solvent B decreased again to 30% within 1.5 min and was kept for 5.0 min prior to the next injection. A total of 13 fractions, namely fractions e3-1 to e3-13, were collected, separated from solvent in vacuum, and was, then, subjected to a taste dilution Analysis (**Figure 3**).

MPLC fraction e4 (yield: 3.20%). Aliquots of subfraction e4 (50 mg) dissolved in acetonitrile (1.8 mL; 33%, v/v) were separated using the following gradient: 32.5% solvent B for 2.0 min and then increasing solvent B to 47% within 14 min. Solvent B was kept at 47% for 3.0 min and, finally, increased to 100% within an additional minute, followed by isocratic elution for 3.0 min. After 23 min, solvent B decreased again to 32.5% within 2.0 min and was kept for 5.0 min prior to the next injection. A total of 5 fractions, namely fractions e4-1 to e4-5, were collected, separated from solvent in vacuum, and subjected to a taste dilution analysis (**Figure 3**).

MPLC fraction e5 (yield: 3.64). Aliquots of subfraction e5 (50 mg) dissolved in acetonitrile (1.5 mL, 33%, v/v) were separated using the following gradient: 36% solvent B for 25 min, increasing solvent B to 70% within 5.0 min and, then, to 100% within an additional minute, followed by isocratic elution for 7.5 min. After 38.5 min, solvent B

decreased again to 30% within 2.5 min and was kept for 4.0 min prior to the next injection. A total of 5 fractions, namely fractions e5-1 to e5-5, were collected, separated from solvent in vacuum, and subjected to a taste dilution analysis (**Figure 3**).

MPLC fraction e6 (yield: 3.16%). Aliquots of subfraction e6 (50 mg) dissolved in acetonitrile (1.7 mL, 30%, v/v) were separated using the following gradient: 38% solvent B for 25 min and, then, increasing solvent B to 55% within 0.5 min. Solvent B was kept at 55% for 5 min and, finally, increased to 100% within an additional 1.5 min, followed by isocratic elution for 7.0 min. After 39 min, solvent B decreased again to 38% within 2.0 min and was kept for 4.0 min prior to the next injection. A total of 11 fractions, namely fractions e6-1 to e6-11, were collected, separated from solvent in vacuum, and subjected to a taste dilution analysis (**Figure 3**).

MPLC fraction e7 (yield: 2.59%). Aliquots of subfraction e7 (25 mg) dissolved in acetonitrile (1.8 mL, 40%, v/v) were separated using a gradient as follows: 40% solvent B for 3.0 min and, then, increasing solvent B to 43% within 1.0 min. Solvent B was kept for 11 min at 43% and, then, increasing solvent B to 65% within 13 min. and, finally, increased to 100% within an additional 4.0 min, followed by isocratic elution for 3.0 min. After 35 min, solvent B decreased again to 40% within 3.0 min and was kept for 2.0 min prior to the next injection. A total of 16 fractions, namely fractions e7-1 to e7-16, were collected, separated from solvent in vacuum, and subjected to a taste dilution analysis (**Figure 3**).

MPLC fraction e8 (yield: 2.69%). Aliquots of subfraction e8 (25 mg) dissolved in acetonitrile (1.7 mL, 45%, v/v) were separated using the following gradient: 47% solvent B for 14 min and, then, increasing solvent B to 55% within 0.5 min. Solvent B was kept for 5.0 min at 55% and, finally, increased to 100% within an additional 10 min, followed by isocratic elution for 3.5 min. After 33 min, solvent B decreased again to 47% within 1.0 min and was kept for 3.0 min prior to the next injection. A total of 8 fractions, namely fractions

e8-1 to e8-8, were collected, separated from solvent in vacuum, and subjected to a taste dilution analysis (**Figure 3**).

MPLC fraction e9 (yield: 18.38%). Aliquots of subfraction e9 (20 mg) dissolved in acetonitrile (1.7 mL, 35%, v/v) were separated using the following gradient: Starting with 48%, solvent B is increasing to 50% within 7.0 min, and was kept for 28.5 min at 50% and, finally, increased to 100% within an additional 1.5 min, followed by isocratic elution for 7.0 min. After 44 min, solvent B decreased again to 48% within 2.0 min and was kept for 4.0 min prior to the next injection. A total of 9 fractions, namely fractions e9-1 to e9-9, were collected, separated from solvent in vacuum, and subjected to a taste dilution analysis (**Figure 3**).

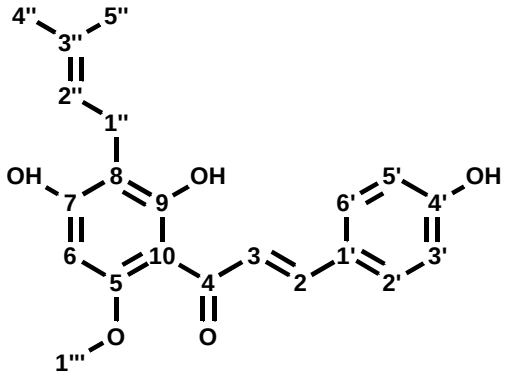
MPLC fraction e10 (yield: 31.33%). Aliquots of subfraction e10 (50 mg) dissolved in acetonitrile (1.7 mL, 40%, v/v) were separated using the following gradient: 57% solvent B for 32 min and, then, increasing solvent B to 73% within 1.0 min. Solvent B was kept for 8.5 min at 73% and, finally, increased to 100% within an additional 0.5 min, followed by isocratic elution for 3.0 min. After 45 min, solvent B decreased again to 57% within 1.5 min and was kept for 3.5 min prior to the next injection. A total of 13 fractions, namely fractions e10-13 to e10-13, were collected, separated from solvent in vacuum, and subjected to a taste dilution analysis (**Figure 3**).

MPLC fraction e11 (yield: 22,86%). Aliquots of subfraction e11 (200 mg) dissolved in acetonitrile (1.5 mL, 60%, v/v) were separated using the following gradient: 65% solvent B for 1.0 min and, then, increasing solvent B to 68% within 7.0 min. Solvent B increased to 70% within 1 min and was kept for 1 min at 70% before solvent B increased to 90% within 28 min and, finally, increased to 100% within an additional 3.0 min, followed by isocratic elution for 4.0 min. After 45 min, solvent B decreased again to 65% within 2.0 min and was kept for 3.0 min prior to the next injection. A total of 15 fractions, namely fractions e11-1 to

e11-15, were collected, separated from solvent in vacuum, and subjected to a taste dilution analysis (**Figure 3**).

Spectroscopic data of all isolated and synthesized compounds.

Xanthohumol (**5**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 368 nm

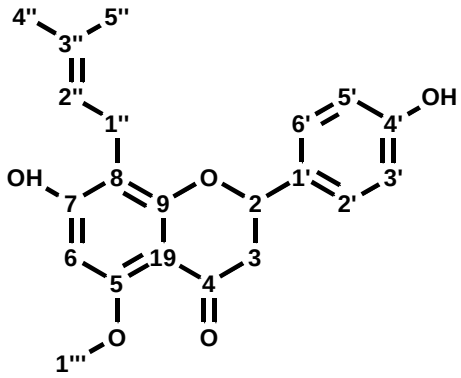
LC-TOF-MS (ESI-):
measured: m/z 353,1394; calculated for $[C_{21}H_{22}O_5\text{-}H^+]^-$: m/z 353,1394

LC-MS/MS (ESI^-):
m/z (%) 353 (100, $[M - H]^-$), 219 (17), 119 (75)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,65 [s, 3H, H−C(4″)]; 1,75 [s, 3H, H−C(5″)]; 3,23 [d, 2H, J = 7,1 Hz, H−C(1″)]; 3,89 [s, 3H, H−C(1‴)]; 5,20 [m, 1H, J = 7,1 Hz, H−C(2″)]; 6,01 [s, 1H, H-C(6)]; 6,82 [m, 2H, J = 8,6 Hz, H-C(3′ / 5′)]; 7,49 [m, 2H, J = 8,6 Hz, H-C(2′ / 6′)]; 7,67 [d, 1H, J = 15,5 Hz, H-C(2)]; 7,79 [d, 1H, J = 15.5 Hz, H-C(3)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,9 [C(4″)]; 22,3 [C(1″)]; 26.0 [C(5″)]; 56,2 [C(1‴)]; 91,4 [C(6)]; 106,5 [C(10)]; 109,4 [C(8)]; 116,9 [C(3′ / 5′)]; 124,3 [C(2″)]; 125,9 [C(3)]; 128,3 [C(1′)]; 131,2 [C(2′ / 6′)]; 131,4 [C(3″)]; 143,3 [C(2)]; 161,1 [C(4′)]; 162,4 [C(5)]; 163,7 [C(7)]; 166,2 [C(9)]; 194,1 [C(4)]

Isoxanthohumol (**6**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 287 nm

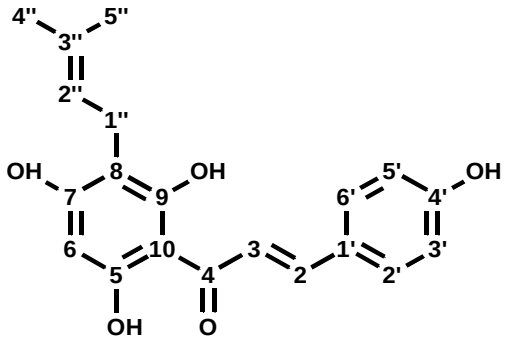
LC-TOF-MS (ESI-):
measured: m/z 353,1404; calculated for $[C_{21}H_{22}O_5\text{-}H^+]^-$: m/z 353,1394

LC-MS/MS (ESI^-):
m/z (%) 353 (80, $[M - H]^-$), 219 (50), 119 (100)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,56 [s, 3H, H−C(4″)]; 1,61 [s, 3H, H−C(5″)]; 2,66 [dd, 1H, J = 2,9 & 16,6 Hz, H−C(3eq)]; 2,97 [dd, 1H, J = 12,7 & 16,6 Hz, H−C(3ax)]; 3,20 [d, 2H, J = 6,9 Hz, H−C(1″)]; 3,79 [s, 3H, H−C(1‴)]; 5,13 [t, 1H, J = 6,9 Hz, H−C(2″)]; 5,27 [dd, 1H, J = 2,9 & 12,7 Hz, H-C(2)]; 6,11 [s, 1H, H-C(6)]; 6,81 [m, 2H, J = 8,7 Hz, H-C(3′ / 5′)]; 7,30 [m, 2H, J = 8,7 Hz, H-C(2′ / 6′)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,9 [C(4″)]; 22,7 [C(1″)]; 26.0 [C(5″)]; 46,2 [C(3)]; 56,0 [C(1‴)]; 80,0 [C(2)]; 93,4 [C(6)]; 106,0 [C(10)]; 110,1 [C(8)]; 116,3 [C(3′ / 5′)]; 123,9 [C(2″)]; 128,9 [C(2′ / 6′)]; 131,7 [C(1′)]; 131,8 [C(3″)]; 159,0 [C(4′)]; 161,9 [C(5)]; 164,0 [C(7)]; 164,4 [C(9)]; 193,1 [C(4)]

106 Desmethylxanthohumol (**7**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 362 nm

LC-TOF-MS (ESI-):
measured: m/z 339,1255; calculated for $[C_{20}H_{20}O_5\text{-}H^+]^-$: m/z 339,1232

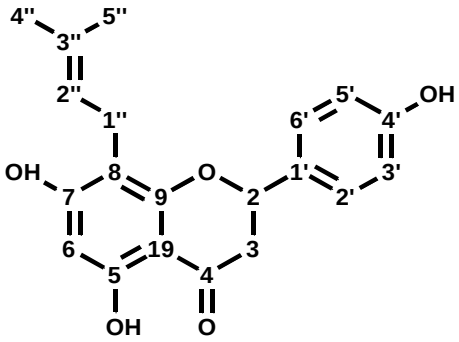
LC-MS/MS (ESI^-):
m/z (%) 339 (100, $[M - H]^-$), 219 (15), 119 (80)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,65 [s, 3H, H-C(4″)]; 1,75 [s, 3H, H-C(5″)]; 3,20 [m, 2H, H-C(1″)]; 5,18 [m, 1H, H-C(2″)]; 5,93 [s, 1H, H-C(6)]; 6,81 [m, 2H, H-C(3′ / 5′)]; 7,48 [m, 2H, H-C(2′ / 6′)]; 7,68 [d, 1H, J = 15,5 Hz, H-C(2)]; 8,07 [m, 1H, J = 15,5 Hz, H-C(3)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,9 [C(5″)]; 22,3 [C(1″)]; 26,0 [C(4″)]; 95,3 [C(6)]; 105,9 [C(10)]; 108,4 [C(8)]; 116,8 [C(3′ / 5′)]; 124,6 [C(2″)]; 126,0 [C(3)]; 128,6 [C(1′)]; 131,1 [C(3″)]; 131,2 [C(2′ / 6′)]; 143,2 [C(2)]; 160,9 [C(4′)]; 161,2 [C(9)]; 162,6 [C(5)]; 165,6 [C(7)]; 194,3 [C(4)]

107

108 8-Prenylnaringenin (**8**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 291 nm

LC-TOF-MS (ESI-):
measured: m/z 339,1215; calculated for $[C_{20}H_{20}O_5\text{-}H^+]^-$: m/z 339,1238

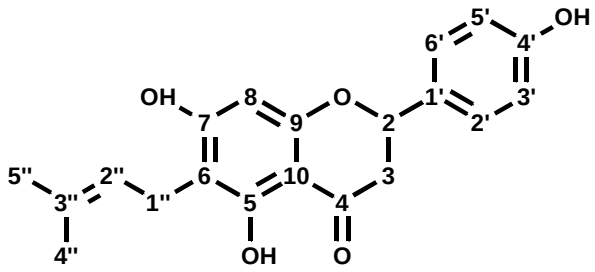
LC-MS/MS (ESI^-):
m/z (%) 353 (82, $[M - H]^-$), 219 (45), 119 (100)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,57 [s, 3H, H−C(4″)]; 1,61 [s, 3H, H−C(5″)]; 2,71 [dd, 1H, J = 3,0 & 17,0 Hz, H−C(3eq)];)]; 3,07 [dd, 1H, J = 12,8 Hz & 17,0 Hz, H−C(3ax)];]; 3,17 [d, 2H, J = 7,0 Hz, H−C(1″)]; 5,13 [t, 1H, J = 7,0 Hz, H−C(2″)]; 5,32 [dd, 1H, J = 3,0 Hz & 12,8 Hz, H-C(2)]; 5,92 [s, 1H, H-C(6)]; 6,82 [m, 2H, J = 8,5 Hz, H-C(3′ / 5′)]; 7,31 [m, 2H, J = 8,5 Hz, H-C(2′ / 6′)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,9 [C(4″)]; 22,5 [C(1″)]; 26.0 [C(5″)]; 44,0 [C(3)]; 80,3 [C(2)]; 96,4 [C(6)]; 103,4 [C(10)]; 109,0 [C(8)]; 116,3 [C(3′ / 5′)]; 124,0 [C(2″)]; 129,0 [C(2′ / 6′)]; 131,4 [C(1′)]; 131,6 [C(3″)]; 158,9 [C(4′)]; 161,6 [C(9)]; 163,2 [C(5)]; 166,1 [C(7)]; 198,2 [C(4)]

109

110 6-Prenylnaringenin (**9**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 291 nm

LC-TOF-MS (ESI-):
measured: m/z 339,1215; calculated for $[C_{20}H_{20}O_5\text{-}H^+]^-$: m/z 339,1238

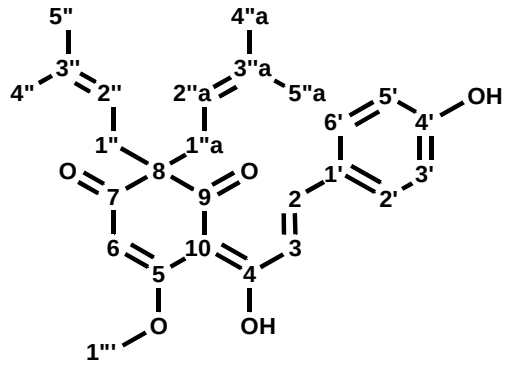
LC-MS/MS (ESI^-):
m/z (%) 353 (78, $[M - H]^-$), 219 (47), 119 (100)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,65 [s, 3H, H−C(4″)]; 1,75 [s, 3H, H−C(5″)]; 2,68 [dd, 1H, J = 3,1 Hz & 16,9 Hz, H−C(3eq)];)]; 3,09 [dd, 1H, J = 13,1 & 16,9 Hz, H−C(3ax)];]; 3,20 [d, 2H, J = 6,9 Hz, H−C(1″)]; 5,18 [t, 1H, J = 6,9 Hz, H−C(2″)]; 5,30 [dd, 1H, J = 3,1 Hz & 13,1 Hz, H-C(2)]; 5,93 [s, 1H, H-C(6)]; 6,81 [m, 2H, J = 8,5 Hz, H-C(3′ / 5′)]; 7,31 [m, 2H, J = 8,5 Hz, H-C(2′ / 6′)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,8 [C(4″)]; 21,9 [C(1″)]; 26.0 [C(5″)]; 44,2 [C(3)]; 80,4 [C(2)]; 95,4 [C(6)]; 103,2 [C(10)]; 109,7 [C(8)]; 116,3 [C(3′ / 5′)]; 123,9 [C(2″)]; 129,0 [C(2′ / 6′)]; 131,3 [C(1′)]; 131,6 [C(3″)]; 159,0 [C(4′)]; 162,4 [C(9)]; 162,6 [C(5)]; 166,1 [C(7)]; 197,9 [C(4)]

111

112 4′-Hydroxytunicatachalcone (**10**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 406 nm

LC-TOF-MS (ESI-):
measured: m/z 421,2014; calculated for $[C_{26}H_{30}O_5\text{-}H^+]^-$: m/z 421,2015

LC-MS/MS (ESI$^-$):
m/z (%) 421 (12, $[M - H]^-$), 245 (1), 217 (2), 119 (100), 93 (3)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,56 [s, 12H, H−C(4″ / 4″a / 5″ / 5″a)]; 2,58 [m, 3H, H−C(1″ / 1″a)]; 3,99 [s, 3H, H−C(1‴)]; 4,84 [m, 2H, H−C(2″ / 2″a)]; 5,56 [s, 1H, H−C(6)]; 6,85 [m, 2H, J = 8,9 Hz, H-C(3′ / 5′)]; 7,54 [m, 2H, J = 8,9 Hz, H-C(2′ / 6′)]; 7,61 [d, 1H, J = 15,7 Hz, H-C(3)]; 7,88 [d, 1H, J = 15,7 Hz, H-C(2)]

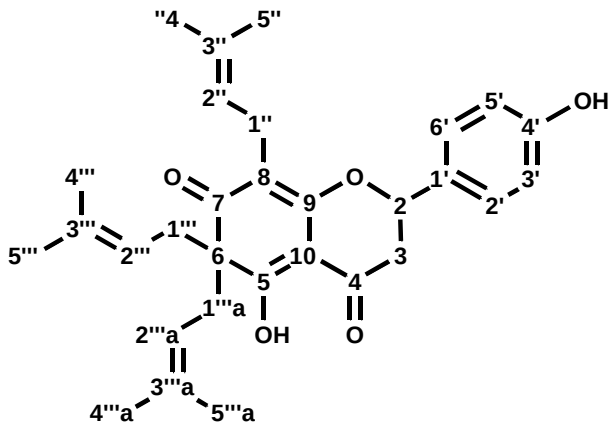
^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,9 [C(5″ / 5″a)]; 25,8 [C(4″ / 4″a)]; 39,5 [C(1″ / 1″a)]; 57,1 [C(1‴)]; 62,6 [C(8)]; 98,9 [C(6)]; 106,1 [C(10)]; 116,6 [C(3′ / 5′)]; 118,8 [C(2″ / 2″a)]; 119,1 [C(3)]; 128,1 [C(1′)]; 131,8 [C(2′ / 6′)]; 136,2 [C(3″ / 3″a)]; 145,9 [C(2)]; 161,9 [C(4′)]; 174,3 [C(5)]; 180,3 [C(4)]; 199,8 [C(7)]; 205,9 [C(9)]

^{1}H NMR (500 MHz, DMSO; COSY): δ [ppm]: 1,50 [s, 6H, H−C(4″ / 4″a)]; 1,52 [s, 6H, H−C(5″ / 5″a)]; 2,52 [m, 3H, J = 7,5 Hz, H−C(1″ / 1″a)]; 3,94 [s, 3H, H−C(1‴)]; 4,78 [t, 2H, J = 7,5 Hz, H−C(2″ / 2″a)]; 5,52 [s, 1H, H−C(6)]; 6,86 [m, 2H, J = 8,6 Hz, H-C(3′ / 5′)]; 7,59 [d, 1H, J = 15,5 Hz, H-C(3)]; 7,63 [m, 2H, J = 8,6 Hz, H-C(2′ / 6′)]; 7,84 [d, 1H, J = 15,5 Hz, H-C(2)]

^{13}C NMR (125 MHz, DMSO; HSQC, HMBC): δ (ppm): 18,6 [C(5″ / 5″a)]; 26,6 [C(4″ / 4″a)]; 38,6 [C(1″ / 1″a)]; 57,6 [C(1‴)]; 61,8 [C(8)]; 99,2 [C(6)]; 105,9 [C(10)]; 117,1 [C(3′ / 5′)]; 119,1 [C(2″ / 2″a)]; 119,3 [C(3)]; 126,8 [C(1′)]; 132,1 [C(2′ / 6′)]; 135,2 [C(3″ / 3″a)]; 145,4 [C(2)]; 161,6 [C(4′)]; 171,5 [C(5)]; 179,7 [C(4)]; 196,4 [C(7)]; 205,7 [C(9)]

113

Isoxantholupon (**11**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 308 nm

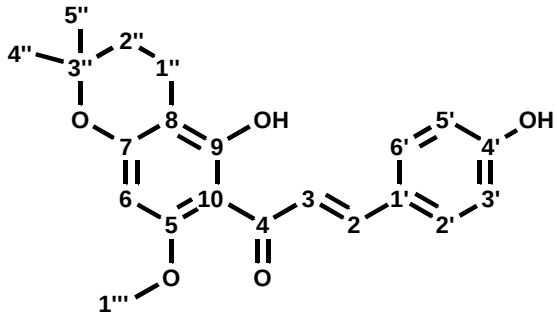
LC-TOF-MS (ESI-):
measured: m/z 475,2492; calculated for $[C_{30}H_{35}O_5\text{-}H^+]^-$: m/z 475,2484

LC-MS/MS (ESI^-):
m/z (%) 475.2 (100, $[M - H]^-$), 363 (29), 286 (26), 257 (15), 243 (95), 119 (55)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,51 / 1,53 / 1,555 / 1,59 [s, 4x 3H, H−C(4‴ / 4‴a / 5‴ / 5‴a)]; 1,545 [s, 3H, H−C(4″)]; 1,61 [s, 3H, H−C(5″)]; 2,60 / 2,62 [d, 2x 2H, J = 6,75 Hz & 7,35 Hz, H−C(1‴ / 1‴a)]; 2,96 [dd, 1H, J = 7,0 Hz & 18,2 Hz, H−C(3eq)]; 3,00 [d, 2H, J = 7,0 Hz, H-C(1″)]; 3,16 [dd, 1H, J = 9,8 Hz & 18,2 Hz, H−C(3ax)]; 4,71 / 4,82 [t, 2x 2H, J = 6,75 Hz & 7,35 Hz, H−C(2‴ / 2‴a)]; 4,89 [t, 2H, J = 7,0 Hz, H−C(2″)]; 5,3 [dd, 1H, J = 4,0 Hz, J = 9,8 Hz, H−C(2)]; 6,82 [m, 2H, J = 8,9 Hz, H-C(3′ / 5′)]; 7,28 [m, 2H, J = 8,9 Hz, H-C(2′ / 6′)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,93 / 17,96 / 17,99 [C(4″ / 4‴ / 4‴a)]; 22,2 [C(1″)]; 25,96 / 26,02 / 26,04 [C(5″ / 5‴ / 5‴a)]; 38,5 [C(3)]; 39,1 / 39,7 [C(1‴ / 1‴a) 61,9 [C(6)]; 78,3 [C(2)]; 105,3 [C(10)]; 114,8 [C(8)]; 116,5 [C(3′ / 5′)]; 118,97 / 118.99 [C(2‴ / 2‴a)]; 123,5 [C(2″)]; 129,1 [C(2′ / 6′)]; 130,3 [C(1′)]; 131,9 [C(3″)]; 136,12 / 136.24 [C(3‴ / 3‴a)]; 159,2 [C(4′)]; 165,7 [C(9)]; 185,7 [C(4)]; 198,6 [C(7)]

1″,2″-Dihydroxanthohumol C (**12**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 368 nm

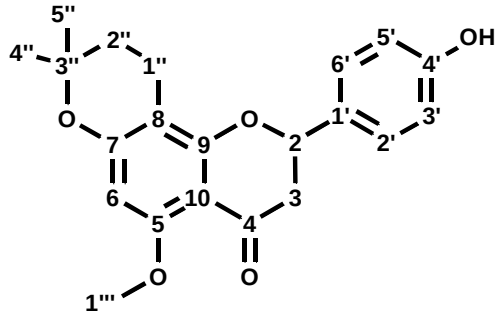
LC-TOF-MS (ESI-):
measured: m/z 353,1395; calculated for $[C_{21}H_{22}O_5\text{-}H^+]^-$: m/z 353,1394

LC-MS/MS (ESI^-):
m/z (%) 353 (100, $[M - H]^-$), 297 (1), 119 (49)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,33 [s, 6H, H−C(4″ / 5″)]; 1,80 [t, 2H, J = 6,7 Hz, H−C(2″)]; 2,58 [t, 2H, J = 6,7 Hz, H−C(1″)]; 3,88 [s, 3H, H−C(1‴)]; 5,93 [s, 1H, H-C(6)]; 6,83 [m, 2H, J = 8,7 Hz, H-C(3′ / 5′)]; 7,50 [m, 2H, J = 8,7 Hz, H-C(2′ / 6′)]; 7,68 [d, 1H, J = 15,9 Hz, H-C(3)]; 7,81 [d, 1H, J = 15,9 Hz, H-C(2)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,1 [C(1″)]; 26,9 [C(4″ / 5″)]; 33,0 [C(2″)]; 56,2 [C(1‴)]; 77,1 [C(3″)]; 93,0 [C(6)]; 102,9 [C(8)]; 106,4 [C(10)]; 116,9 [C(3′ / 5′)]; 125,6 [C(3)]; 128,4 [C(1′)]; 131,3 [C(2′ / 6′)]; 143,7 [C(2)]; 161,1 [C(4′)]; 162,22 [C(5)]; 162,26 [C(9)]; 166,1 [C(7)]; 194,1 [C(4)]

118 1″,2″-Dihydroisoxanthohumol C (**13**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 286 nm

LC-TOF-MS (ESI-):
measured: m/z 369,1335; calculated for $[C_{21}H_{22}O_5\text{-}H^+]^-$: m/z 369,1338

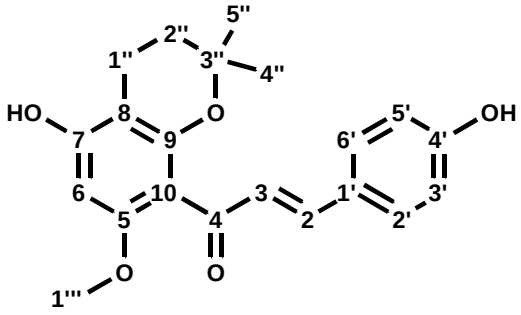
LC-MS/MS (ESI$^-$):
m/z (%) 369 (30, $[M - H]^-$), 119 (100)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,32 / 1,33 [s, 2x 3H, H-C(4″ / 5″)]; 1,78 [m, 2H, H-C(2″)]; 2,58 [dt, 1H, J = 1,1 Hz & 6,8 Hz, H-C(1″)]; 2,68 [dd, 1H, J = 3,2 Hz & 16,6 Hz, H-C(3eq)]; 3,00 [dd, 1H, J = 13,0 Hz & 16,6 Hz, H-C(3ax)]; 3,78[s, 3H, H-C(1‴)]; 5,35 [dd, 1H, J = 3,2 Hz & 13,0 Hz, H-C(2)]; 6,04 [s, 1H, H-C(6)]; 6,82 [m, 2H, J = 8,5 Hz, H-C(3′ / 5′)]; 7,32 [m, 2H, J = 8,5 Hz, H-C(2′ / 6′)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,5 [C(1″)]; 26,4 / 27,2 [C(4″ / 5″)]; 329 [C(2″)]; 46,0 [C(3″)]; 56,1 [C(1‴)]; 77,2 [C(3″)]; 80,1 [C(2)]; 94,9 [C(6)]; 103,2 [C(10)]; 105,9 [C(8)]; 116,3 [C(3′ / 5′)]; 128,8 [C(2′ /6′)]; 158,9 [C(4′)]; 161,7 [C(5)]; 162,7 [C(9)]; 163,6 [C(7)]; 192,7 [C(4)]

119

120 1″,2″-Dihydroxanthohumol K (**14**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 325 nm

LC-TOF-MS (ESI-):
measured: m/z 353,1392; calculated for $[C_{21}H_{22}O_5\text{-}H^+]^-$: m/z 353,1394

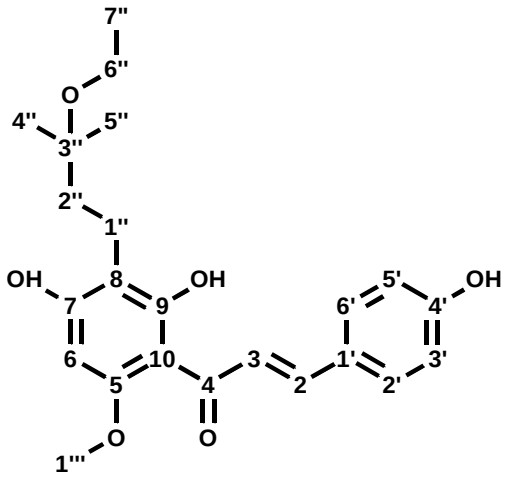
LC-MS/MS (ESI$^-$):
m/z (%) 353 (100, $[M - H]^-$), 233 (9), 119 (47)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,22 [s, 6H, H−C(4″ / 5″)]; 1,76 [t, 2H, J = 6,9 Hz, H−C(2″)]; 2,62 [t, 2H, J = 6,9 Hz, H−C(1″)]; 3,69 [s, 3H, H−C(1‴)]; 6,11 [s, 1H, H-C(6)]; 6,77 [d, 1H, J = 16,0 Hz, H-C(3)]; 6,80 [m, 2H, J = 8,7 Hz, H-C(3′ / 5′)]; 7,23 [d, 1H, J = 16,0 Hz, H-C(2)]; 7,41 [m, 2H, J = 8,7 Hz, H-C(2′ / 6′)];

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 16,9 [C(1″)]; 26,1 [C(4″ / 5″)]; 32,3 [C(2″)]; 55,3 [C(1‴)]; 75,0 [C(3″)]; 91,1 [C(6)]; 101,9 [C(8)]; 110,1 [C(10)]; 116,2 [C(3′ / 5′)]; 126,4 [C(3)]; 126,8 [C(1′)]; 130,6 [C(2′ / 6′)]; 146,3 [C(2)]; 153,6 [C(7)]; 157,3 [C(5)]; 158,1 [C(9)]; 160,6 [C(4′)]; 197,6 [C(4)]

121

Xanthohumol P (**15**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 367 nm

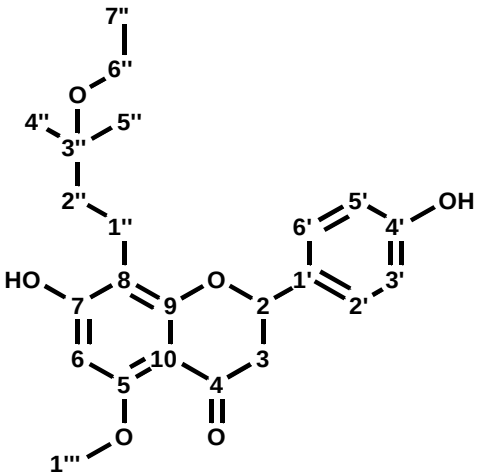
LC-TOF-MS (ESI-):
measured: m/z 399,1802; calculated for $[C_{23}H_{28}O_6\text{-}H^+]^-$: m/z 399,1808

LC-MS/MS (ESI^-):
m/z (%) 399 (57, $[M - H]^-$), 119 (100), 353 (64), 232 (20), 174 (13)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,18 [t, 3H, H−C(7″)]; 1,23 [s, 6H, H−C(4″ / 5″)]; 1,65 [m, 2H, J = 7,1 & 8,5, H−C(2″)]; 2,58 [m, 2H, J = 7,1 & 8,5), H−C(1″)]; 3,53 [dd, 2H, H−C(6″)]; 3,90 [s, 3H, H−C(1‴)]; 6,03 [s, 1H, H−C(6)]; 6,87 [m, 2H, J = 8,7 Hz, H-C(3′ / 5′)]; 7,50 [m, 2H, J = 8,7 Hz, H-C(2′ / 6′)]; 7,67 [d, 1H, J = 15,5 Hz, H-C(3)]; 7,80 [d, 1H, J = 15,5 Hz, H-C(2)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 16.3 [C(7″)]; 17.8 [C(1″)]; 26.3 [C(4″ / 5″)]; 39.0 [C(2″)]; 56.2 [C(1‴)]; 57.5 [C(6″)]; 76.4 [C(3″)]; 91.7 [C(6)]; 106.5 [C(10)]; 110.0 [C(8)]; 116.9 [C(3′ / 5′)]; 125.9 [C(3)]; 128.5 [C(1′)]; 131.3 [C(2′ / 6′)]; 143.4 [C(2)]; 161.1 [C(4′)]; 162.4 [C(5)]; 163.8[C(9)]; 166.2 [C(7)]; 194.1 [C(4)]

Isoxanthohumol P (**16**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 287 nm

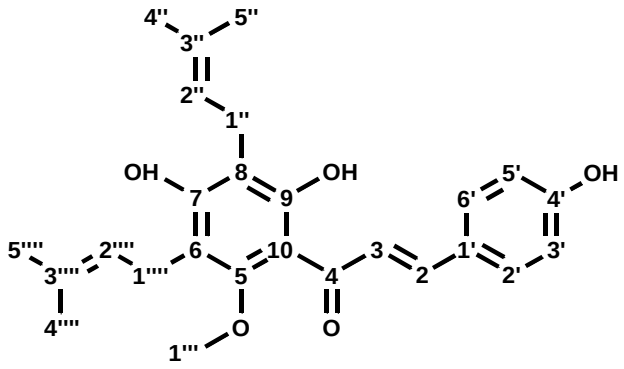
LC-TOF-MS (ESI-):
measured: m/z 399,1804; calculated for $[C_{23}H_{28}O_6\text{-}H^+]^-$: m/z 399,1808

LC-MS/MS (ESI^-):
m/z (%) 399 (10), 265 (21), 119 (100)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,12 [s, 6H, H−C(4″ / 5″)]; 1,12 [t, 3H, H−C(7″)]; 1,60 [m, 2H, H−C(2″)]; 2,54 [m, 2H, H−C(1″)]; 2,67 [dd, 1H, J = 3,2 & 16,9, H−C(3eq)]; 3,02 [dd, 1H, J = 12,8 & 16,9, H−C(3ax)]; 3,34 [dd, 2H, H−C(6″)]; 3,79 [s, 3H, H−C(1‴)]; 5,32 [dd, 1H, J = 3,2 & 12,8, H−C(2)]; 6,12 [s, 1H, H−C(6)]; 6,81 [m, 2H, J = 8,8 Hz, H-C(3′ / 5′)]; 7,33 [m, 2H, J = 8,8 Hz, H-C(2′ / 6′)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 15.8 [C(7″)]; 17.5 [C(1″)]; 25.3, 27.1 [C(4″ / 5″)]; 38.0 [C(2″)]; 45.9 [C(3)]; 55.3 [C(6″)]; 56.4 [C(1‴)]; 75.6 [C(3″)]; 79.8 [C(2)]; 93.8 [C(6)]; 105.3 [C(10)]; 109.9 [C(8)]; 115.8 [C(3′ / 5′)]; 128.4 [C(2′ / 6′)]; 130.6 [C(1′)]; 158.2 [C(4′)]; 161.2 [C(5)]; 163.3 [C(9)]; 163.2 [C(7)]; 192.4 [C(4)]

126 5′-Prenylxanthohumol (**17**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 368 nm

LC-TOF-MS (ESI-):
measured: m/z 421,2005; calculated for $[C_{26}H_{30}O_5\text{-}H^+]^-$: m/z 421,2015

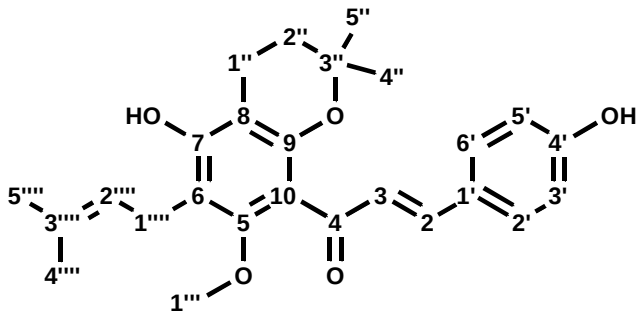
LC-MS/MS (ESI$^-$):
m/z (%) 421 (100, $[M - H]^-$), 301 (4), 286 (2), 243 (7), 119 (48)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,67 [s, 3H, H−C(5‴′)]; 1,70 [s, 3H, H−C(5″)]; 1,78 [s, 3H, H−C(4‴′)]; 1,80 [s, 3H, H−C(4″)]; 3,33 [d, 2H, J = 7,0 Hz, H−C(1″)]; 3,36 [d, 2H, J = 7,1 Hz, H−C(1‴′)]; 3,62 [s, 3H, H−C(1‴′)]; 5,16 [m, 1H, J = 7,0 Hz, H−C(2″)]; 5,18 [m, 1H, J = 7,1 Hz, H−C(2‴′)]; 6,84 [m, 2H, J = 8,5 Hz, H-C(3′ / 5′)]; 7,53 [m, 2H, J = 8,5 Hz, H-C(2′ / 6′)]; 7,78 [d, 1H, J = 15,6 Hz, H−C(2)]; 7,83 [d, 1H, J = 15,6 Hz, H−C(3)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,98 / 18,03 [C(4″ / 4‴′)]; 22,7 / 23,5 [C(1″ / 1‴′)]; 25,91 / 25,96 [C(5″ / 5‴′)]; 63,6 [C(1‴′)]; 109,8 [C(10)]; 113,1 [C(8)]; 115,8 [C(6)]; 117,0 [C(3′ / 5′)]; 123.43 [C(2‴′)]; 123,48 [C(2″)]; 124,5 [C(3)]; 128,2 [C(1′)]; 131,5 [C(2′ / 6′)]; 132,4 [C(3″)]; 132,6 [C(3‴′)]; 144,7 [C(2)]; 160,3 [C(5)]; 161,3 [C(4′)]; 161,6 [C(9)]; 162,9 [C(7)]; 194,6 [C(4)]

127

128 1″,2″-Dihydroxanthohumol F (**18**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 326 nm

LC-TOF-MS (ESI-):
measured: m/z 421,2008; calculated for $[C_{26}H_{30}O_5\text{-}H^+]^-$: m/z 421,2015

LC-MS/MS (ESI^-):
m/z (%)421 (100, $[M - H]^-$), 119 (98), 365 (10)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,22 [s, 6H, H−C(4″ / 5″)]; 1,68 [s, 3H, H−C(4‴)]; 1,76 [s, 3H, H−C(5‴)]; 1,79 [t, 2H, J = 6,8 Hz, H−C(2″)]; 2,65 [t, 2H, J = 6,8 Hz, H−C(1″)]; ~3,30 (unter Methanolsignal) [2H, H−C(1‴)]; 3,61 [s, 3H, H−C(1‴)]; 5,20 [m, 1H, H−C(2‴)]; 6,80 [m, 2H, H-C(3′ / 5′)]; 6,82 [d, 1H, J = 15,9 Hz, H-C(2)] 7,25 [d, 1H, J = 15,9 Hz, H-C(3)]; 7,43 [m, 2H, H-C(2′ / 6′)]

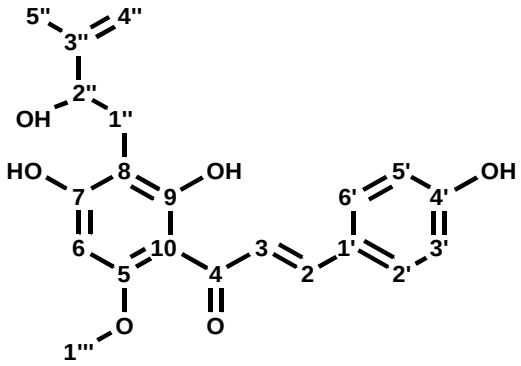
^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 18,0 [C(5‴)]; 18,2 [C(1″)]; 23,5 [C(1‴)]; 25,9 [C(4‴)]; 26,8 [C(4″ / 5″)]; 33,1 [C(2″)]; 63,1 [C(1‴)]; 75,4[C(3″)]; 106,6 [C(8)]; 115,1 [C(6)]; 116,4 [C(10)]; 117,0 [C(3′ / 5′)]; 124,8 [C(2‴)]; 127,0 [C(1′)]; 127,5 [C(3)]; 131,5 [C(2′ / 6′)]; 131,9 [C(3‴)]; 147,6 [C(2)]; 151,7 [C(9)]; 156,3 [C(5)]; 156,4 [C(7)]; 161,5 [C(4′)]; 198,3 [C(4)]

^{1}H NMR (500 MHz, DMSO; COSY): δ [ppm]: 1,15 [s, 6H, H−C(4″ / 5″)]; 1,63 [s, 3H, H−C(4‴)]; 1,70 [s, 3H, H−C(5‴)]; 1,72 [t, 2H, J = 6,8 Hz, H−C(2″)]; 2,57 [t, 2H, J = 6,8 Hz, H−C(1″)]; 3,20 [d, 2H, H−C(1‴)]; 3,53 [s, 3H, H−C(1‴)]; 5,14 [m, 1H, H−C(2‴)]; 6,76 [d, 1H, J = 15,9 Hz, H-C(2)]; 6,78 [m, 2H, H-C(3′ / 5′)]; 7,10 [d, 1H, J = 15,9 Hz, H-C(3)]; 7,47 [m, 2H, H-C(2′ / 6′)]

^{13}C NMR (125 MHz, DMSO; HSQC, HMBC): δ (ppm): 16,8 [C(1″)]; 17,9 [C(5‴)]; 22,5 [C(1‴)]; 25,6 [C(4‴)]; 26,4 [C(4″, 5″)]; 31,6 [C(2″)]; 62,3 [C(1‴)]; 74,0 [C(3″)]; 105,2 [C(8)]; 113,5 [C(6)]; 115,5 [C(10)]; 116,1 [C(3′, 5′)]; 124,0 [C(2‴)]; 125,6 [C(1′)]; 126,2 [C(3)]; 129,9 [C(2′, 6′)]; 130,4 [C(3‴)]; 143,9 [C(2)]; 149,9 [C(9)]; 154,5 [C(5)]; 154,7 [C(7)]; 159,9 [C(4′)]; 193,9 [C(4)]

129

Xanthohumol D (**19**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 367 nm

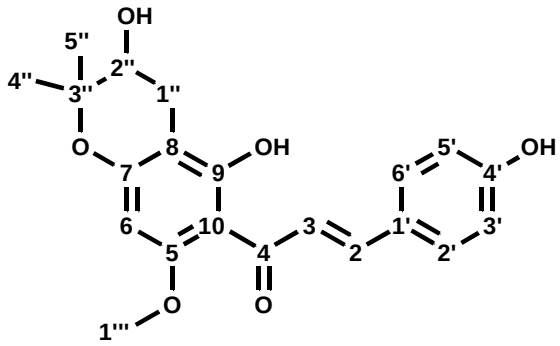
LC-TOF-MS (ESI-):
measured: m/z 369,1326; calculated for $[C_{21}H_{22}O_6\text{-}H^+]^-$: m/z 369,1338

LC-MS/MS (ESI^-):
m/z (%) 353 (100, $[M - H]^-$), 219 (17), 119 (75)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,81 [s, 3H, H-C(5″)]; 2,79 [dd, 1H, J = 5,6 & 13,8 Hz, H-C(1″)]; 2,96 [dd, 1H, J = 7,3 & 13,8 Hz, H-C(2″)]; 3,91 [s, 3H, H-C(1‴)]; 4,34 [t, 1H, J = 6,5 Hz, H-C(2″)]; 4,71 [s, 1H, H-C(4″)]; 4,81 [s, 1H, H-C(4″)]; 6,04 [s, 1H, H-C(6)]; 6,83 [m, 2H, H-C(3′ / 5′)]; 7,50 [m, 2H, H-C(2′ / 6′)]; 7,68 [d, 1H, J = 15,6 Hz, H-C(2)]; 7,79 [d, 1H, J = 15,6 Hz, H-C(3)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 17,9 [C(5″)]; 29,8 [C(1″)]; 56,2 [C(1‴)]; 76,7 [C(2″)]; 92,1 [C(6)]; 106,7 [C(8 / 10)]; 110,9 [C(4″)]; 116,5 [C(3′ / 5′)]; 125,8 [C(3)]; 128,4 [C(1′)]; 131,3 [C(2′ / 6′)]; 143,6 [C(2)]; 148,8 [C(3″)]; 161,1 [C(4′)]; 162,9 [C(5)]; 164,8 [C(7)]; 166,6 [C(9)]; 194,2 [C(4)]

Xanthohumol B (**20**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 368 nm

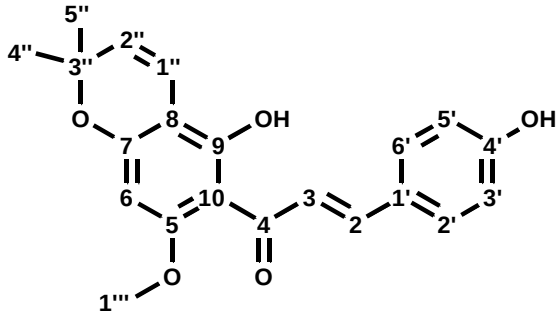
LC-TOF-MS (ESI-):
measured: m/z 369,1327; calculated for $[C_{21}H_{22}O_6\text{-}H^+]^-$: m/z 369,1338

LC-MS/MS (ESI^-):
m/z (%) 369 (100, $[M - H]^-$), 119 (60), 93 (1)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,30 [s, 3H, H-C(4″)]; 1,35 [s, 3H, H-C(5″)]; 2,52 [dd, 1H, J = 6,9 Hz & 16,7 Hz, H-C(1″)]; 2,85 [dd, 1H, J = 5,3 Hz & 16,7 Hz, H-C(1″)]; 3,77 [dd, 2H, J = 5,3 Hz & 6,9 Hz, H-C(2″)]; 3,90 [s, 3H, H-C(1‴)]; 5,99 [s, 1H, H-C(6)]; 6,83 [m, 2H, H-C(3′,5′)]; 7,50 [m, 2H, H-C(2′,6′)]; 7,70 [d, 1H, J = 15,4 Hz, H-C(2)]; 7,81 [d, 1H, J = 15,4 Hz, H-C(3)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 21,39 [C(4″)]; 25,72 [C(5″)]; 26,18 [C(1″)]; 56,31 [C(1‴)]; 69,92 [C(2″)]; 79,70 [C(3″)]; 92,86 [C(6)]; 101,69 [C(8)]; 106,72 [C(10)]; 116,91 [C(3′,5′)]; 125,50 [C(3)]; 128,37 [C(1′)]; 131,36 [C(2′,6′)]; 143,88 [C(2)]; 161,19 [C(4′)]; 161,29 [C(7)]; 162,48 [C(5)]; 166,30 [C(9)]; 194,15 [C(4)]

Xanthohumol C (**21**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 370 nm

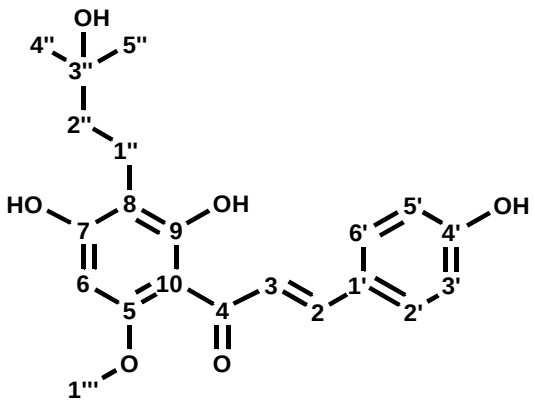
LC-TOF-MS (ESI-):
measured: m/z 351,1222; calculated for $[C_{21}H_{20}O_5\text{-}H^+]^-$: m/z 351,1232

LC-MS/MS (ESI^-):
m/z (%) 351 (100, $[M - H]^-$), 231 (5), 119 (66)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,43 [s, 6H, H−C(4″ / 5″)]; 3,94 [s, 3H, H−C(1‴)]; 5,52 [d, 1H, J = 9,8 Hz, H−C(2″)]; 6,03 [s, 1H, H-C(6)]; 6,62 [d, 1H, J = 9,8 Hz, H−C(1″)]; 6,83 [m, 2H, J = 8,6 Hz, H-C(3′ / 5′)]; 7,51 [m, 2H, J = 8,6 Hz, H-C(2′ / 6′)]; 7,71 [d, 1H, J = 15,5 Hz, H-C(3)]; 7,78 [d, 1H, J = 15,5 Hz, H-C(2)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 28,6 [C(4″ / 5″)];56,6[C(1‴)]; 79,2 [C(3″)]; 92,8 [C(6)]; 103,9 [C(8)]; 107,0 [C(10)]; 116,9 [C(1″)]; 116,9 [C(3′ / 5′)]; 125,3 [C(3)]; 126,7 [C(2″)]; 128,3 [C(1′)]; 131,4 [C(2′ / 6′)]; 144,2 [C(2)]; 161,2 [C(4′)]; 161,6 [C(7)]; 163,06 [C(9)]; 164,2 [C(5)]; 194,3 [C(4)]

Xanthohumol H (**22**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 368 nm

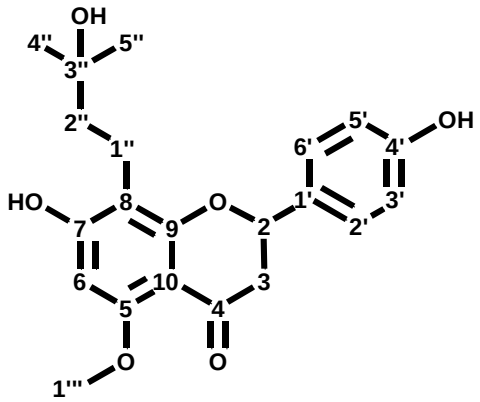
LC-TOF-MS (ESI-):
measured: m/z 371,1488; calculated for $[C_{21}H_{24}O_6\text{-}H^+]^-$: m/z 371,1495

LC-MS/MS (ESI^-):
m/z (%) 371 (100, $[M - H]^-$), 251 (23), 119 (33)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,23 [s, 6H, H−C(4″ / 5″)]; 1,65 [m, 2H, H−C(2″)]; 2,57 [m, 2H, H−C(1″)]; 3,28 [s, 3H, H−C(6″)]; 3,91 [s, 3H, H−C(1‴)]; 6,04 [s, 1H, H−C(6)]; 6,83 [m, 2H, J = 8,5 Hz, H-C(3′ / 5′)]; 7,50 [m, 2H, J = 8,5 Hz, H-C(2′ / 6′)]; 7,67 [d, 1H, J = 15,6 Hz, H-C(3)]; 7,80 [d, 1H, J = 15,6 Hz, H-C(2)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 18,6 [C(1″)]; 26,4 [C(4″ / 5″)]; 39,4 [C(2″)]; 50,6 [C(6″)]; 57,1 [C(1‴)]; 77,5 [C(3″)]; 92,5 [C(6)]; 110,8 [C(8)]; 117,8 [C(3′ / 5′)]; 126,7 [C(3)]; 129,3 [C(1′)]; 132,1 [C(2′ / 6′)]; 144,3 [C(2)]; 161,9 [C(4′)]; 163,3 [C(5)]; 164,7 [C(9)]; 167,1 [C(7)]; 195,0 [C(4)]

Isoxanthohumol H (**23**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 286 nm

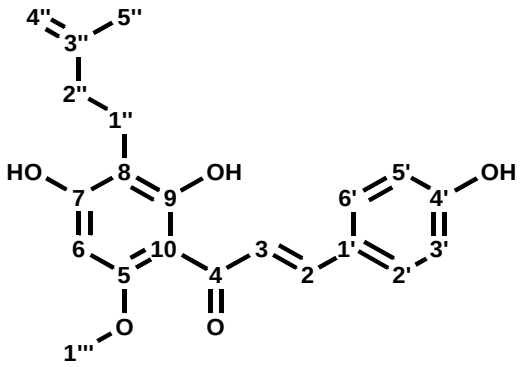
LC-TOF-MS (ESI-):
measured: m/z 371,1495; calculated for $[C_{21}H_{24}O_6\text{-}H^+]^-$: m/z 371,1495

LC-MS/MS (ESI^-):
m/z (%) 371 (10), 251 (22), 163 (5), 119 (90)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,16 [s, 6H, H−C(4″ / 5″)]; 1,61 [m, 2H, H−C(2″)]; 2,61 [m, 2H, H−C(1″)]; 2,69 [dd, 1H, J = 3,2 & 16,8, H−C(3eq)]; 2,97 [dd, 1H, J = 13,0 & 16,8 H−C(3ax)]; 3,80 [s, 3H, H−C(1‴)]; 5,31 [dd, 1H, J = 3,2 & 13,0, H−C(2)]; 6,12 [s, 1H, H−C(6)]; 6,81 [m, 2H, J = 8,0 Hz, H-C(3′ / 5′)]; 7,34 [m, 2H, J = 8,0 Hz, H-C(2′ / 6′)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 19,0 [C(1″)]; 28,8 [C(4″ / 5″)]; 43,8 [C(2″)]; 46,3 [C(3)]; 56,0 [C(1‴)]; 71,7 [C(3″)]; 79,9 [C(2)]; 93,5 [C(6)]; 105,9 [C(10)]; 110,7 [C(8)]; 116,3 [C(3′ / 5′)]; 128,7 [C(2′ / 6′)]; 131,6 [C(1′)]; 158,8 [C(4′)]; 161,8 [C(5)]; 163,9 [C(9)]; 164,4 [C(7)]; 193,0 [C(4)]

Xanthohumol N (**24**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 368 nm

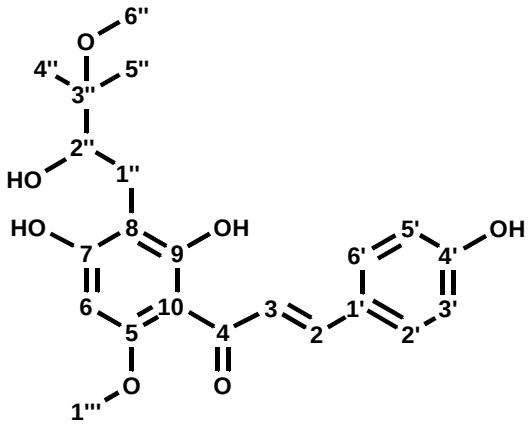
LC-TOF-MS (ESI-):
measured: m/z 353,1394; calculated for $[C_{21}H_{22}O_6\text{-}H^+]^-$: m/z 353,1394

LC-MS/MS (ESI^-):
m/z (%) 353 (100, $[M - H]^-$), 219 (23), 163 (40), 119 (85)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,79 [s, 3H, H−C(5″)]; 2,18 [m, 2H, J = 8,1, H−C(2″)]; 2,69 [m, 2H, J = 8,1, H−C(1″)]; 3,28 [s, 3H, H−C(6″)]; 3,90 [s, 3H, H−C(1‴)]; 4,66 [s, 2H H-C(4″)]; 6,03 [s, 1H, H−C(6)]; 6,83 [m, 2H, J = 8,7 Hz, H-C(3′ / 5′)]; 7,50 [m, 2H, J = 8,7 Hz, H-C(2′ / 6′)]; 7,67 [d, 1H, J = 15,5 Hz, H-C(3)]; 7,80 [d, 1H, J = 15,5 Hz, H-C(2)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 22,1 [C(1″)]; 22,6 [C(5″)]; 37,9 [C(2″)]; 56,2 [C(1‴)]; 91,6 [C(6)]; 106,5 [C(10)]; 109,7 [C(8)]; 110,1 [C(4″)]; 116,9 [C(3′ / 5′)]; 125,9 [C(3)]; 128,5 [C(1′)]; 131,2 [C(2′ / 6′)]; 143,3 [C(2)]; 161,0 [C(4′)]; 162,5 [C(5)]; 163,9 [C(7)]; 166,2 [C(9)]; 194,1 [C(4)]

142 2″-Hydroxyxanthohumol M (**25**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 364 nm

LC-TOF-MS (ESI-):
measured: m/z 401,1588; calculated for $[C_{22}H_{26}O_7\text{-}H^+]^-$: m/z 401,1600

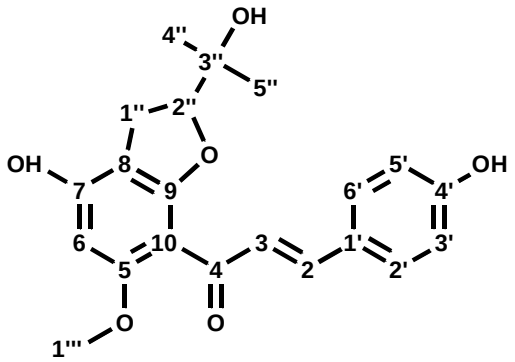
LC-MS/MS (ESI^-):
m/z (%) 401 (100, $[M - H]^-$), 280 (49), 164 (22), 119 (100),

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,23 [s, 6H, H-C(4″ / 5″)]; 2,59 [m, 1H, J = 9,8 & 14,2 Hz, H-C(1″a)]; 3,01 [dd, 1H, J = 2,3 & 14,2 Hz, H-C(1″b)]; 3,28 [s, 3H, H-C(6″)]; 3,72 [dd, 1H, J = 2,3 & 9,8 Hz, H-C(2″)]; 3,92 [s, 3H, H-C(1‴)]; 6,08 [s, 1H, H-C(6)]; 6,83 [m, 2H, H-C(3′ / 5′)]; 7,50 [m, 2H, H-C(2′ / 6′)]; 7,69 [d, 1H, J = 15,5 Hz, H-C(2)]; 7,80 [d, 1H, J = 15,5 Hz, H-C(3)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 21,0 [C(4″)]; 21,2 [C(5″)]; 25,7 [C(1″)]; 49,5 [C(6″)]; 56,3 [C(1‴)]; 78,0 [C(2″)]; 78,8 [C(3″)]; 92,4 [C(6)]; 106,6 [C(10)]; 107,7 [C(8)]; 116,9 [C(3′ / 5′)]; 125,7 [C(3)]; 128,4 [C(1′)]; 131,3 [C(2′ / 6′)]; 143,7 [C(2)]; 161,1 [C(4′)]; 162,9 [C(5)]; 164,9 [C(7)]; 166,3 [C(9)]; 194,2 [C(4)]

143

144 Xanthohumol I (**26**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 326 nm

LC-TOF-MS (ESI-):
measured: m/z 369,1333; calculated for $[C_{21}H_{22}O_6\text{-}H^+]^-$: m/z 369,1338

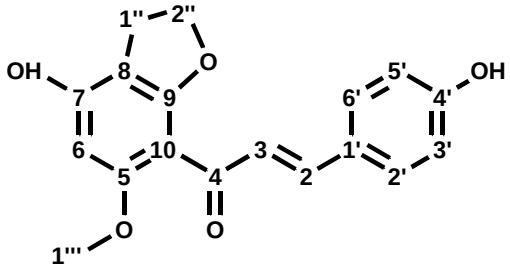
LC-MS/MS (ESI^-):
m/z (%) 369 (100, $[M - H]^-$), 175 (5), 119 (25)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,19 [s, 3H, H−C(4″)]; 1,27 [s, 3H, H−C(5″)]; 3,02 [dd, 1H, J = 8,7 Hz, H−C(1″a)]; 3,03 [dd, 1H, J = 9,0 Hz, H−C(1″b)]; 3,77 [s, 3H, H−C(1‴)]; 4,66 [dd, 1H, J = 8,7 Hz & 9,0 Hz, H−C(2″)]; 6,02 [s, 1H, H-C(6)]; 6,81 [m, 2H, J = 8,6 Hz, H-C(3′ / 5′)]; 7,13 [d, 1H, J = 15,7 Hz, H-C(3)]; 7,49 [m, 2H, J = 8,6 Hz, H-C(2′ / 6′)]; 7,49 [d, 1H, J = 15,7 Hz, H-C(2)];

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 25,2 [C(4″)]; 25,6 [C(5″)]; 27,8 [C(1″)]; 56,5 [C(1‴)]; 72,4 [C(3″)]; 92,4 [C(2″)]; 93,0 [C(6)]; 107,0 [C(8)]; 107,1 [C(10)]; 116,9 [C(3′ / 5′)]; 126,3 [C(3)]; 127,9 [C(1′)]; 131,4 [C(2′ / 6′)]; 144,7 [C(2)]; 158,2 [C(9)]; 161,3 [C(5)]; 161,4 [C(4′)]; 162,8 [C(7)]; 193,4 [C(4)]

145

146 Xanthohumol O (**27**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 327 nm

LC-TOF-MS (ESI-):
measured: m/z 309,0756; calculated for $[C_{21}H_{22}O_6\text{-}H^+]^-$: m/z 309,0763

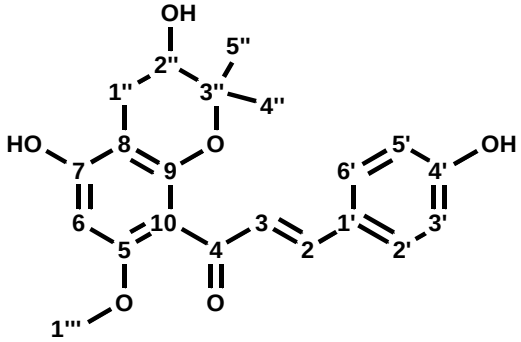
LC-MS/MS (ESI^-):
m/z (%) 309 (100, $[M - H]^-$), 293 (6), 265 (3), 132 (7), 97 (25), 80 (13)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 3,89 [s, 3H, H−C(1‴)]; 6,46 [s, 1H, H-C(6)]; 6,82 [m, 2H, J = 8,6 Hz, H-C(3′ / 5′)]; 6,86 [d, 1H, J = 2,2 Hz, H−C(1″)]; 7,27 [d, 1H, J = 15,7 Hz, H-C(2)]; 7,50 [m, 2H, J = 8,6 Hz, H-C(2′ / 6′)]; 7,55 [d, 1H, J = 15,7 Hz, H-C(3)]; 7,59 [dd, 1H, J = 2,2 Hz, H−C(2″)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 95,2 [C(6)]; 104,6,2 [C(1″)]; 107,8 [C(10)]; 112,5 [C(8)]; 116,9 [C(3′ / 5′)]; 126,1 [C(2)]; 128,0 [C(1′)]; 131,5 [C(2′ / 6′)]; 144,5 [C(2″)]; 144,92 [C(3)]; 156,7 [C(7)]; 159,6 [C(5)]; 161,3 [C(4′)]; 191,9 [C(4)]

147

148 Xanthohumol L (**28**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 325 nm

LC-TOF-MS (ESI-):
measured: m/z 369,1342; calculated for $[C_{21}H_{22}O_6\text{-}H^+]^-$: m/z 353,1338

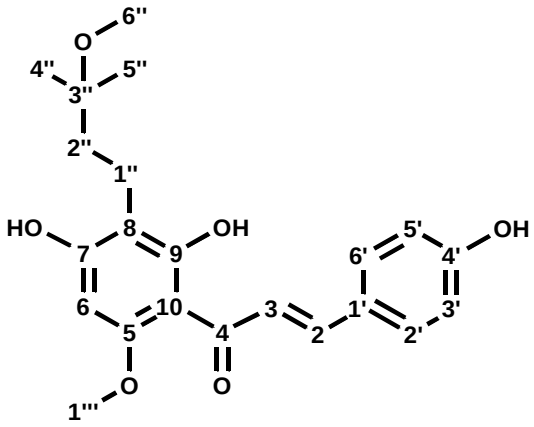
LC-MS/MS (ESI^-):
m/z (%) 369 (100, $[M - H]^-$), 297 (3), 119 (33)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,17 [s, 3H, H−C(4″)]; 1,24 [s, 3H, H−C(5″)]; 2,52 [dd, 1H, J = 7,7 & 17,1 Hz, H−C(1″a)]; 2,88 [dd, 1H, J = 5,7 & 17,1 Hz, H−C(1″b)]; 3,69 [s, 3H, H−C(1‴)]; 3,71 [dd, 1H, J = 5,7 & 7,7 Hz, H−C(2″)]; 6,14 [s, 1H, H-C(6)]; 6,79 [d, 1H, J = 16,1 Hz, H-C(3)]; 6,80 [m, 2H, J = 8,7 Hz, H-C(3′ / 5′)]; 7,27 [d, 1H, J = 16,1 Hz, H-C(2)]; 7,43 [m, 2H, J = 8,7 Hz, H-C(2′ / 6′)];

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 20,8 [C(4″)]; 25,8 [C(5″)]; 26,8 [C(1″)]; 56,1 [C(1‴)]; 70,2[C(2″)]; 78,6 [C(3″)]; 92,3 [C(6)]; 101,8 [C(8)]; 110,8 [C(10)]; 117,0 [C(3′ / 5′)]; 127,1 [C(3)]; 127,6 [C(1′)]; 131,4 [C(2′ / 6′)]; 147,1 [C(2)]; 153,5 [C(9)]; 158,4 [C(5)]; 159,1 [C(7)]; 161,4 [C(4′)]; 198,0 [C(4)]

149

Xanthohumol M (**29**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 368 nm

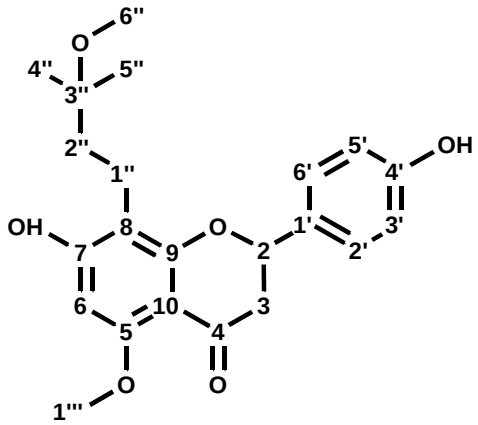
LC-TOF-MS (ESI-):
measured: m/z 385,1664; calculated for $[C_{22}H_{26}O_6\text{-}H^+]^-$: m/z 385,1657

LC-MS/MS (ESI^-):
m/z (%) 385 (100, $[M - H]^-$), 265 (2), 163 (1), 119 (87)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,23 [s, 6H, H−C(4″ / 5″)]; 1,65 [m, 2H, H−C(2″)]; 2,57 [m, 2H, H−C(1″)]; 3,28 [s, 3H, H−C(6″)]; 3,91 [s, 3H, H−C(1‴)]; 6,04 [s, 1H, H−C(6)]; 6,83 [m, 2H, J = 8,5 Hz, H-C(3′ / 5′)]; 7,50 [m, 2H, J = 8,5 Hz, H-C(2′ / 6′)]; 7,67 [d, 1H, J = 15,6 Hz, H-C(3)]; 7,80 [d, 1H, J = 15,6 Hz, H-C(2)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 18,6 [C(1″)]; 26,4 [C(4″ / 5″)]; 39,4 [C(2″)]; 50,6 [C(6″)]; 57,1 [C(1‴)]; 77,5 [C(3″)]; 92,5 [C(6)]; 110,8 [C(8)]; 117,8 [C(3′ / 5′)]; 126,7 [C(3)]; 129,3 [C(1′)]; 132,1 [C(2′ / 6′)]; 144,3 [C(2)]; 161,9 [C(4′)]; 163,3 [C(5)]; 164,7 [C(9)]; 167,1 [C(7)]; 195,0 [C(4)]

Isoxanthohumol M (**30**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 289 nm

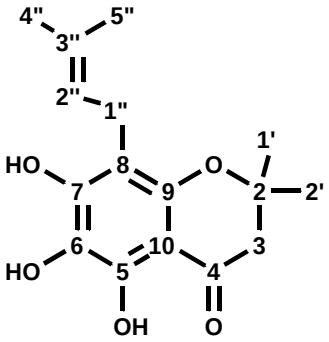
LC-TOF-MS (ESI-):
measured: m/z 385.1664; calculated for $[C_{22}H_{26}O_6\text{-}H^+]^-$: m/z 385.1657

LC-MS/MS (ESI^-):
m/z (%) 385 (8, [M - H]-), 265 (19), 197(4), 165 (6), 163 (5), 119 (100)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,13 [s, 6H, H−C(4″ / 5″)]; 1,60 [m, 2H, H−C(2″)]; 2,53 [m, 2H, H−C(1″)]; 2,66 [dd, 1H, J = 3,0 & 16,9, H−C(3eq)]; 3,00 [dd, 1H, J = 12,9 & 16,9, H−C(3ax)]; 3,06 [s, 3H, H−C(6″)]; 3,80 [s, 3H, H−C(1‴)]; 5,30 [dd, 1H, J = 3,0 & 12,9, H−C(2)]; 6,13 [s, 1H, H−C(6)]; 6,81 [m, 2H, J = 8,7 Hz, H-C(3′ / 5′)]; 7,33 [m, 2H, J = 8,7 Hz, H-C(2′ / 6′)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 18,1 [C(1″)]; 25,6, 27.2 [C(4″ / 5″)]; 38,7 [C(2″)]; 46,2 [C(3)]; 49,3 [C(6″)]; 56,0 [C(1‴)]; 76,4 [C(3″)]; 80,1 [C(2)]; 93,5 [C(6)]; 105,9 [C(10)]; 110,5 [C(8)]; 116,2 [C(3′ / 5′)]; 129,0 [C(2′ / 6′)]; 131,4 [C(1′)]; 158,9 [C(4′)]; 161,9 [C(5)]; 163,9 [C(9)]; 164,4 [C(7)]; 192,9 [C(4)]

2″,3″-Dehydrocyclohumulohydrochinon (**31**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 292 nm

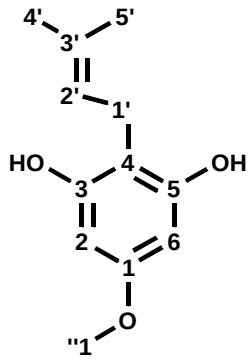
LC-TOF-MS (ESI-):
measured: m/z 291,1222; calculated for $[C_{16}H_{20}O_5\text{-}H^+]^-$: m/z 291,1238

LC-MS/MS (ESI$^-$):
m/z (%) 291 (80, $[M - H]^-$), 207 (25), 235 (23), 136 (21), 135 (19)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1,41 [s, 6H, H−C(1′ / 2′)]; 1,64 [s, 3H, H−C(4″)]; 1,76 [s, 3H, H−C(5″)]; 2,67 [s, 2H, H−C(3)]; 3,20 [d, 2H, J = 7,3 Hz, H−C(1″)]; 5,15 [t, 1H, J = 7,3 Hz, H−C(2″)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 16,6 [C(5″)]; 21,2 [C(1″)]; 24.5 [C(4″)]; 25,5 [C(1′ / 2′)]; 49,5 [C(3)]; 78,0 [C(2)]; 101,0 [C(10)]; 107,8 [C(8)]; 122,8 [C(2″)]; 129,9 [C(3″)]; 147,6 [C(5)]; 151,7 [C(9)]; 154,1 [C(7)]; 197,3 [C(4)]

1-Methoxy-4-prenylphloroglucinol (**32**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 292 nm

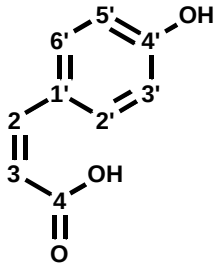
LC-TOF-MS (ESI-):
measured: m/z 207.1035; calculated for $[C_{12}H_{15}O_3\text{-}H^+]^-$: m/z 207.1027

LC-MS/MS (ESI$^-$):
m/z (%) 207 (100, $[M - H]^-$), 137 (25), 121 (14), 109 (10), 149 (9)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 1.65 [s, 3H, H−C(4′)]; 1.75 [s, 3H, H−C(5′)]; 3.2 [d, 2H, J = 7.3 Hz, H−C(1′)]; 3.83 [s, 3H, H−C(1″)]; 5.21 [m, 1H, J = 7.3 Hz, H−C(2′)]; 5.42 [s, 1H, H−C(2)]; 6.04 [s, 1H, H−C(6)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 17.8 [C(5′)]; 22.0 [C(1′)]; 25.9 [C(4′)]; 56.2 [C(1″)]; 93.4 [C(6)]; 99.8 [C(2)]; 105.9 [C(4)]; 123.2 [C(2″)]; 132.4 [C(3′)]; 159.6 [C(1)]; 167.9 [C(5)]; 173.3 [C(3)]

158 *cis-p*-coumaric acid (**33a**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 301 nm

LC-TOF-MS (ESI-):
measured: m/z 163,0400; calculated for $[C_9H_8O_3\text{-}H^+]^-$: m/z 163,0395

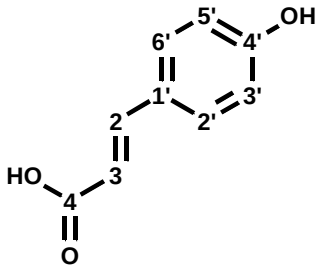
LC-MS/MS (ESI^-):
m/z (%) 163 (100, $[M - H]^-$), 119 (50), 93 (6)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 5,77 [d, 1H, J = 12,8 Hz, H-C(3)]; 6,73 [m, 2H, J = 8,5 Hz, H-C(3′ / 5′)]; 6,77 [d, 1H, J = 12,8 Hz, H-C(2)]; 7,59 [m, 2H, J = 8.5 Hz, H-C(2′ / 6′)];

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 115,8 [C(3′ / 5′)]; 118,2 [C(3)]; 128,0 [C(1′)]; 133,2 [C(2′ / 6′)]; 142,7 [C(2)]; 159,6 [C(4′)]; 171,1 [C(4)]

159

160 *trans-p*-coumaric acid (**33b**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 301 nm

LC-TOF-MS (ESI-):
measured: m/z 163,0400; calculated for $[C_9H_8O_3\text{-}H^+]^-$: m/z 163,0395

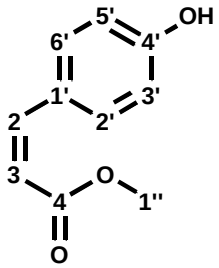
LC-MS/MS (ESI^-):
m/z (%) 163 (100, $[M - H]^-$), 119 (50), 93 (6)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 6,29 [d, 1H, J = 15,9 Hz, H-C(3)]; 6,82 [m, 2H, J = 8,5 Hz, H-C(3′ / 5′)]; 7,45 [m, 2H, J = 8.5 Hz, H-C(2′ / 6′)]; 7,60 [d, 1H, J = 15,9 Hz, H-C(2)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 115,7 [C(3)]; 116,9 [C(3′ / 5′)]; 127,2 [C(1′)]; 131,0 [C(2′ / 6′)]; 146,7 [C(2)]; 161,1 [C(4′)]; 171,1 [C(4)]

161

162 *cis-p*-coumaric acid methyl ester (**34a**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 294 nm

LC-TOF-MS (ESI-):
measured: m/z 177,0557; calculated for $[C_{10}H_{10}O_3\text{-}H^+]^-$: m/z 177,0552

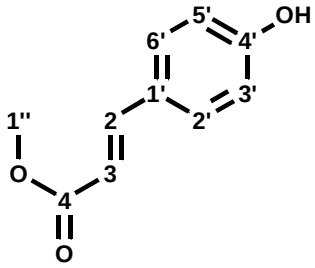
LC-MS/MS (ESI^-):
m/z (%) 177 (100, $[M - H]^-$), 118 (9), 117 (40)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 3,72 [s, 3H, H-C(1″)]; 5,79 [d, 1H, J = 12,9 Hz, H-C(3)]; 6,77 [m, 2H, J = 8,8 Hz, H-C(3′ / 5′)]; 6,88 [d, 1H, J = 12,9 Hz, H-C(2)]; 7,64 [m, 2H, J = 8.8 Hz, H-C(2′ / 6′)];

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 51,6 [C(1″)]; 115,9 [C(3′ / 5′)]; 116,4 [C(3)]; 127,5 [C(1′)]; 133,6 [C(2′ / 6′)]; 145,0 [C(2)]; 160,0 [C(4′)]; 168,9 [C(4)]

163

trans-p-coumaric acid methyl ester (**34b**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 294 nm

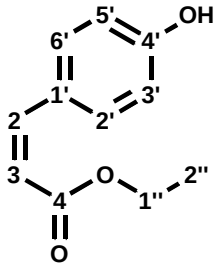
LC-TOF-MS (ESI-):
measured: m/z 177,0557; calculated for $[C_{10}H_{10}O_3\text{-}H^+]^-$: m/z 177,0552

LC-MS/MS (ESI^-):
m/z (%) 177 (100, $[M - H]^-$), 118 (9), 117 (40)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 3,78 [s, 3H, H-C(1″)]; 6,35 [d, 1H, J = 15,7 Hz, H-C(3)]; 6,83 [m, 2H, J = 8,5 Hz, H-C(3′ / 5′)]; 7,47 [m, 2H, J = 8.5 Hz, H-C(2′ / 6′)]; 7,64 [d, 1H, J = 15,7 Hz, H-C(2)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 52,1 [C(1″)]; 114,9 [C(3)]; 116,8 [C(3′ / 5′)]; 127,2 [C(1′)]; 131,2 [C(2′ / 6′)]; 146,6 [C(2)]; 161,3 [C(4′)]; 169,9 [C(4)]

cis-p-coumaric acid ethyl ester (**35a**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 294 nm

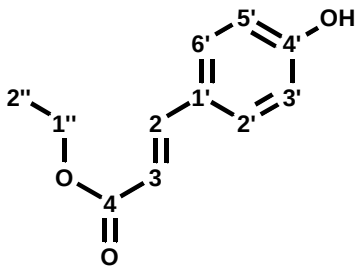
LC-TOF-MS (ESI-):
measured: m/z 191,0712; calculated for $[C_{11}H_{12}O_3\text{-}H^+]^-$: m/z 191,0708

LC-MS/MS (ESI^-):
m/z (%) 191 (100, $[M - H]^-$), 119 (16), 117 (41)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,26 [t, 3H, J = 7,0 Hz, H-C(2″)]; 4,18 [q, 2H, J = 7,0 Hz, H-C(1″)]; 5,75 [d, 1H, J = 12,7 Hz, H-C(3)]; 6,75 [m, 2H, J = 8,7 Hz, H-C(3′ / 5′)]; 6,84 [d, 1H, J = 12,7 Hz, H-C(2)]; 7,60 [m, 2H, J = 8.7 Hz, H-C(2′ / 6′)];

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 14,5 [C(2″)]; 61,2 [C(1″)]; 115,8 [C(3′ / 5′)]; 116,2 [C(3)]; 127,7 [C(1′)]; 133,5 [C(2′ / 6′)]; 144,7 [C(2)]; 160,0 [C(4′)]; 168,4 [C(4)]

trans-p-coumaric acid ethyl ester (**35b**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 294 nm

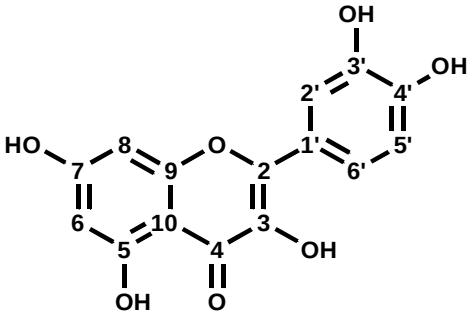
LC-TOF-MS (ESI-):
measured: m/z 191,0712; calculated for $[C_{11}H_{12}O_3\text{-}H^+]^-$: m/z 191,0708

LC-MS/MS (ESI^-):
m/z (%) 191 (100, $[M - H]^-$), 119 (16), 117 (41)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,30 [t, 3H, J = 7,3 Hz, H-C(2″)]; 4,21 [q, 2H, J = 7,3 Hz, H-C(1″)]; 6,31 [d, 1H, J = 16,1 Hz, H-C(3)]; 6,80 [m, 2H, J = 8,7 Hz, H-C(3′ / 5′)]; 7,45 [m, 2H, J = 8.7 Hz, H-C(2′ / 6′)]; 7,6 [d, 1H, J = 16,1 Hz, H-C(2)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 14,6 [C(2″)]; 61,5 [C(1″)]; 115,3 [C(3)]; 116,8 [C(3′ / 5′)]; 127,2 [C(1′)]; 131,1 [C(2′ / 6′)]; 146,4 [C(2)]; 161,3 [C(4′)]; 169,4 [C(4)]

Quercetin (**36**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 341 nm

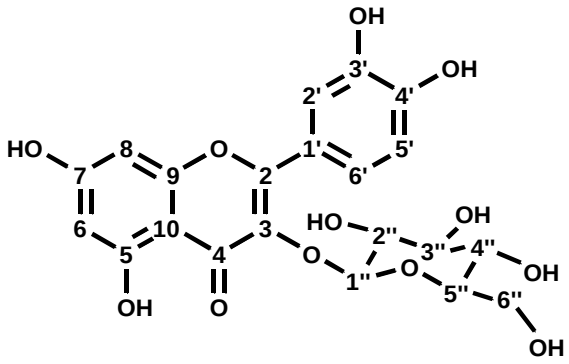
LC-TOF-MS (ESI-):
measured: m/z 301,0354; calculated for $[C_{15}H_{10}O_7\text{-}H^+]^-$: m/z 301,0348

LC-MS/MS (ESI^-):
m/z (%) 301 (100, $[M - H]^-$), 151 (63), 121 (27), 65 (55)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 6,19 [d, 1H, J = 2,0 Hz, H−C(6)]; 6,40 [d, 1H, J = 2,0 Hz, H-C(8)]; 6,90 [d, 1H, J = 8,5 Hz, H-C(5′)]; 7,63 [dd, 1H, J = 2,2 Hz & 8,5 Hz, H-C(6′)]; 7,73 [d, 1H, J = 2,2 Hz, H-C(2′)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 94,5 [C(8)]; 99,3 [C(6)]; 104,6 [C(10)]; 116,0 [C(2′)]; 116,3 [C(5′)]; 121,7 [C(6′)]; 124,1 [C(1′)]; 131,4 [C(3)]; 146,2 [C(3′)]; 148,1 [C(6′)]; 148,8 [C(4′)]; 158,2 [C(9)]; 162,5 [C(5)]; 165,5 [C(7)]; 177,4 [C(4)]

Quercetin-3-O-β-D-glucopyranoside (**37**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 353 nm

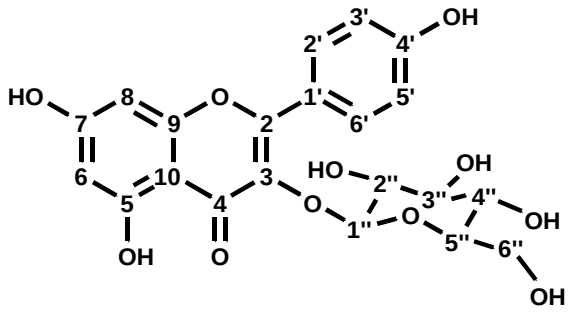
LC-TOF-MS (ESI-):
measured: m/z 463,0876; calculated for $[C_{21}H_{20}O_{12}\text{-}H^+]^-$: m/z 463,0877

LC-MS/MS (ESI^-):
m/z (%) 463 (60, $[M - H]^-$), 301 (53), 271 (100), 255 (52)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 3,22 [m, 1H, J = 2,4 Hz & 5,6 Hz & 9,5 Hz, H−C(5″)]; 3,35 [t, 1H, J = 8,7 Hz & 9,5 Hz, H−C(4″)]; 3,43 [t, 1H, J = 8,7 Hz & 9,2 Hz, H−C(3″)]; 3,48 [dd, 1H, J = 7,6 Hz & 9,2 Hz, H−C(2″)]; 3,57 [dd, 1H, J = 5,6 Hz & 11,8 Hz, H−C(6″a)]; 3,71 [dd, 1H, J = 2,4 Hz & 11,8 Hz, H−C(6″b)]; 5,24 [d, 1H, J = 7,6 Hz, H−C(1″)]; 6,21 [d, 1H, J = 2,2 Hz, H−C(6)]; 6,40 [d, 1H, J = 2,2 Hz, H-C(8)]; 6,87 [d, 1H, J = 8,6 Hz, H-C(5′)]; 7,59 [dd, 1H, J = 2,2 Hz & 8,6 Hz, H-C(6′)]; 7,71 [d, 1H, J = 2,2 Hz, H-C(2′)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 62,6 [C(6″)]; 71,2 [C(4″)]; 75,8 [C(2″)]; 78,1 [C(3″)]; 78,4 [C(5″)]; 94,7 [C(8)]; 99,9 [C(6)]; 104,3 [C(1″)]; 105,7 [C(10)]; 116,0 [C(2′)]; 117,6 [C(5′)]; 123,1 [C(6′)]; 123,2 [C(1′)]; 135,6 [C(3)]; 145,9 [C(4′)]; 149,8 [C(3′)]; 158,5 [C(2)]; 159,0 [C(9)]; 163,1 [C(5)]; 166,0 [C(7)]; 179,5 [C(4)]

174 Kaempferol-3-O-β-D-glucopyranoside (**38**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 347 nm

LC-TOF-MS (ESI-):
measured: m/z 447,0932; calculated for $[C_{21}H_{20}O_{11}\text{-}H^+]^-$: m/z 447,0927

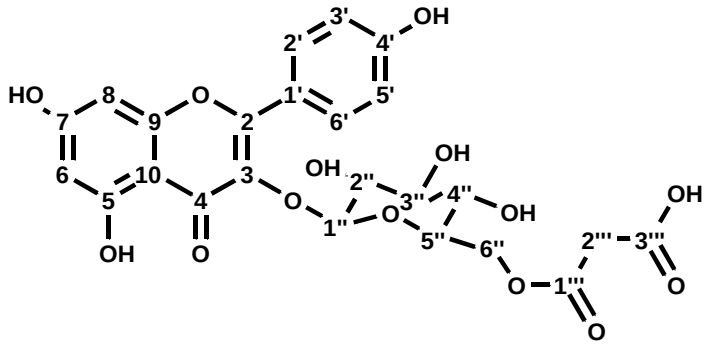
LC-MS/MS (ESI^-):
m/z (%) 447 (100, $[M - H]^-$), 284 (80), 255 (82), 226 (65)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 3,20 [dddd, 1H, J = 2,3 Hz & 5,6 Hz & 5,6 Hz, H−C(5″)]; 3,34 [dd, 1H, J = 5,6 Hz & 6,8 Hz, H−C(4″)]; 3,42 [dd, 1H, J = 5,6 Hz & 6,8 Hz, H−C(3″)]; 3,46 [dd, 1H, J = 5,6 Hz & 7,6 Hz, H−C(2″)]; 3,53 [dd, 1H, J = 5,6 Hz & 12,0 Hz, H−C(6″a)]; 3,70 [dd, 1H, J = 2,3 Hz & 12,0 Hz, H−C(6″b)]; 5,25 [d, 1H, J = 7,6 Hz, H−C(1″)]; 6,21 [d, 1H, J = 2,1 Hz, H−C(6)]; 6,41 [d, 1H, J = 2,1 Hz, H-C(8)]; 6,89 [d, 2H, J = 8,8 Hz, H-C(3′ / 5′)]; 8,06 [d, 2H, J = 8,8 Hz, H-C(2′ / 6′)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 62,6 [C(6″)]; 71,3 [C(4″)]; 75,7 [C(2″)]; 78,0 [C(3″)]; 78,4 [C(5″)]; 94,8 [C(8)]; 99,9 [C(6)]; 104,1 [C(1″)]; 105,8 [C(10)]; 116,1 [C(3′ / 5′)]; 122,8 [C(1′)]; 132,3 [C2′ / 6′)]; 135,5 [C(3)]; 158,5 [C(4′)]; 159,1 [C(2)]; 161,6 [C(9)]; 163,1 [C(5)]; 166,0 [C(7)]; 179,6 [C(4)]

175

176 Kaempferol-3-O-β-D-(6′-malonyl)-glucopyranoside (**39**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 346 nm

LC-TOF-MS (ESI-):
measured: m/z 533,0935; calculated for $[C_{24}H_{22}O_{14}\text{-}H^+]^-$: m/z 533,0937

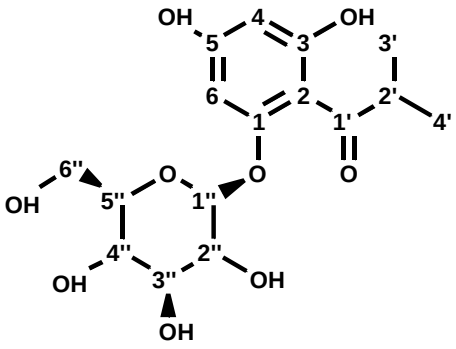
LC-MS/MS (ESI^-):
m/z (%) 533 (100, $[M - H]^-$), 489 (40), 447 (35), 244 (33)

^{1}H NMR (500 MHz, DMSO; COSY): δ [ppm]: 3,11 [s, 2H, H−C(2″)]; 3,15 [m, 1H, H−C(4″)]; 3,19 [dd, 1H, J = 3,7 Hz & 7,6 Hz, H−C(2″)]; 3,23 [dd, 1H, J = 3,7 Hz & 8,8 Hz, H−C(3″)]; 3,33 [m, 1H, H−C(5″)]; 4,00 [dd, 1H, J = 5,8 Hz & 11,9 Hz, H−C(6″a)]; 4,19 [dd, 1H, J = 1,7 Hz & 11,9 Hz, H−C(6″b)]; 5,36 [d, 1H, J = 7,5 Hz, H−C(1″)]; 6,21 [d, 1H, J = 2,1 Hz, H−C(6)]; 6,43 [d, 1H, J = 2,1 Hz, H-C(8)]; 6,88 [d, 2H, J = 8,8 Hz, H-C(3′ / 5′)]; 7,98 [d, 2H, J = 8,8 Hz, H-C(2′ / 6′)]; 10,14 [s, 1H, OH-C(4′)]; 10,85 [s, 1H, OH-C(7′)];12,53 [s, 1H, OH-C(5′)];

^{13}C NMR (125 MHz, DMSO; HSQC, HMBC): δ (ppm): 41,04 [C(2‴)]; 63,6 [C(6″)]; 69,5 [C(4″)]; 73,8 [C(5″)]; 74,0 [C(2″)]; 76,1 [C(3″)]; 93,7 [C(8)]; 98,7 [C(6)]; 101,2 [C(1″)]; 103,9 [C(10)]; 115,0 [C(3′ / 5′)]; 120,8 [C(1′)]; 130,8 [C2′ / 6′)]; 133,1 [C(3)]; 156,4 [C(4′)]; 156,7 [C(2)]; 160,0 [C(9)]; 161,2 [C(5)]; 164,2 [C(7)]; 166,4 [C(1‴)]; 167,7 [C(3‴)]; 177,4 [C(4)]

177

co-Multifidol-glucopyranoside (1-O-β-D-(2-Methyl-propanoyl)-phloroglucinol-glucopyranoside) (**40a**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 283 nm

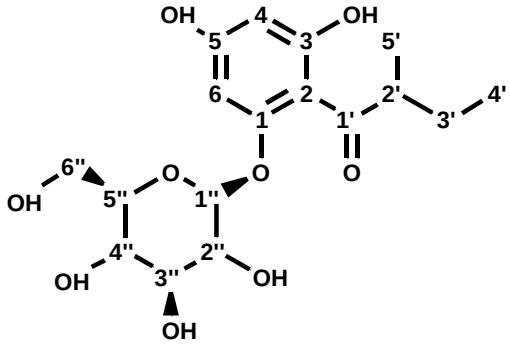
LC-TOF-MS (ESI-):
measured: m/z 357,1192; calculated for $[C_{16}H_{22}O_9\text{-}H^+]^-$: m/z 357,1186

LC-MS/MS (ESI^-):
m/z (%) 357 (100, $[M - H]^-$), 195 (50), 151 (16), 111 (8)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 1,13 [d, 3H, J = 6,7 Hz, H−C(3′)]; 1,15 [d, 3H, J = 6,7 Hz, H−C(4′)]; 3,40 [t, 1H, J = 9,1 Hz, H−C(4″)]; 3,46 [m, 1H, J = 9,1 Hz, H−C(3″)]; 3,46 [m, 1H, H−C(5″)]; 3,50 [dd, 1H, J = 7,5 Hz, H−C(2″)]; 3,72 [dd, 1H, J = 5,5 Hz & 12,1 Hz, H−C(6″a)]; 3,92 [dd, 1H, J = 2,1 Hz & 12,1 Hz, H−C(6″b)]; 3,99 [sept, 1H, J = 6,7 Hz, H−C(2′)]; 5,05 [d, 1H, J = 7,5 Hz, H−C(1″)]; 5,97 [d, 1H, J = 2,3 Hz, H-C(4)]; 6,18 [d, 1H, J = 2,3 Hz, H-C(6)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 19,4 [C(3′)]; 20,2 [C(4′)]; 40,4 [C(2′)]; 62,5 [C(6″)]; 71,2 [C(4″)]; 74,8 [C(2″)]; 78,3 [C(5″)]; 78,7 [C(3″)]; 95,5 [C(6)]; 98,3 [C(4)]; 101,5 [C(1″)]; 106,3 [C(2)]; 161,6 [C(1)]; 165,5 [C(5)]; 167,4 [C(3)]; 212,0 [C(1′)]

ad-Multifidol-glucopyranoside (1-O-β-D-(2-methylbutyryl)-phloroglucinol-glucopyranoside) (**40c**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 281 nm

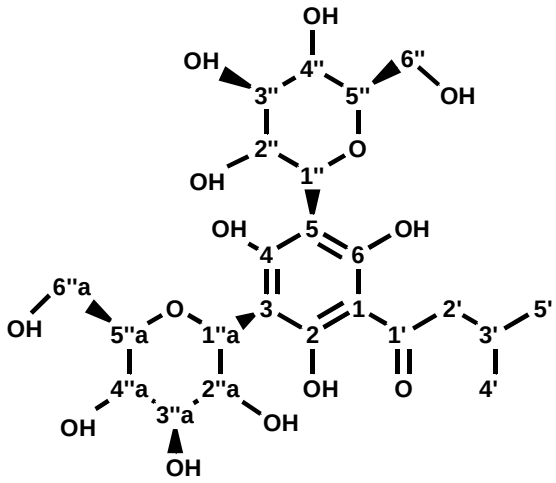
LC-TOF-MS (ESI-):
measured: m/z 371,1346; calculated for $[C_{17}H_{24}O_9\text{-}H^+]^-$: m/z 377,1342

LC-MS/MS (ESI^-):
m/z (%) 371 (100, $[M - H]^-$), 209 (34), 165 (7), 125 (6)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 0,87 [dd, 3H, J = 7,5 Hz & 9,3 Hz, H−C(4′)]; 1,13 [d, 3H, J = 7,0 Hz, H−C(5′)];1,38 [m, 1H, H−C(3′a)]; 1,13 [d, 1H, H−C(3′b)]; 3,38 [t, 1H, J = 9,0 Hz, H−C(5″)]; 3,45 [m, 1H, H−C(3″)]; 3,45 [m, 1H, H−C(5″)]; 3,50 [dd, 1H, J = 7,5 Hz & 9,0 Hz, H−C(2″)]; 3,71 [dd, 1H, J = 5,5 Hz & 12,3 Hz, H−C(6″a)]; 3,92 [dd, 1H, J = 2,1 Hz & 12,3 Hz, H−C(6″b)]; 3,92 [m, 1H, H−C(2′)]; 5,04 [d, 1H, J = 7,5 Hz, H−C(1″)]; 5,95 [d, 1H, J = 2,3 Hz, H-C(4)]; 6,18 [d, 1H, J = 2,3 Hz, H-C(6)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 12,1 [C(4′)]; 16,9 [C(5′)]; 28,3 [C(3′)]; 47,0 [C(2′)]; 62,5 [C(6″)]; 71,2 [C(4″)]; 74,8 [C(2″)]; 78,3 [C(5″)]; 78,7 [C(3″)]; 95,4 [C(6)]; 98,3 [C(4)]; 101,6 [C(1″)]; 106,7 [C(2)]; 161,7 [C(1)]; 165,5 [C(5)]; 167,4 [C(3)]; 211,9 [C(1′)]

n-Multifidol-Di-C-glucopyranoside (Phloroisovalerophenon-3,5-Di-C-ß-D-glucopyranoside) (**41b**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 283 nm

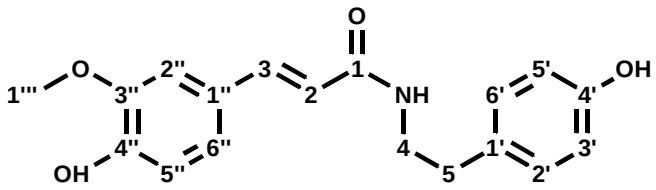
LC-TOF-MS (ESI-):
measured: m/z 533,1878; calculated for $[C_{23}H_{34}O_{14}\text{-}H^+]^-$: m/z 533,1870

LC-MS/MS (ESI^-):
m/z (%) 533 (60, $[M - H]^-$), 323 (50), 293 (100), 125 (30)

^{1}H NMR (400 MHz, MeOD; COSY): δ [ppm]: 0,94 / 0,96 [s, 2x 3H, H−C(4′ / 5′)]; 2,24 [m, 1H, J = 6,3 Hz & 6,5 Hz & 10,1 Hz, H−C(3′)]; 2,91 [dd, 1H, J = 7,0 Hz & 15,5 Hz, H−C(2′a)]; 3,03 [dd, 1H, J = 6,6 Hz & 15,5 Hz, H−C(2′b)]; 3,43 [m, 2H, H−C(5″ / 5″a)]; 3,49 / 3,53 [m, 4x 1H, H−C(3″ / 3″a / 4″ / 4″a)]; 3,61 [t, 2H, J = 9,8 Hz, H−C(2″ / 2″a)]; 3,80 [dd, 2H, J = 4,0 Hz & 12,0 Hz, H−C(6″-α / 6″a-α)]; 3,86 [dd, 2H, J = 2,5 Hz & 12,0 Hz, H−C(6″-β / 6″a-β)]; 4,93 [d, 2H, J = 9,8 Hz, H−C(1″ / 1″a)]

^{13}C NMR (100 MHz, MeOD; HSQC, HMBC): δ (ppm): 23,1 [C(4′)]; 23,2 [C(5′)]; 26,3 [C(3′)]; 54,3 [C(2′)]; 61,8 [C(6″ / 6″a)]; 71,1 [C(4″ / 4″a)]; 74,1 [C(2″ / 2″a)]; 76,7 [C(1″ / 1″a)]; 79,1 [C(3″ / 3″a)]; 82,7 [C(5″ / 5″a)]; 104,4 [C(3 / 5)]; 106,4 [C(1)]; 162,2 [C(2 / 6)]; 163,2 [C(4)]; 207,8 [C(1′)]

N-*trans*-Feruloyltyramine (**42**)



UV/Vis (ACN / Water; 0,1 % Formic acid):
λ_{max} = 320 nm

LC-TOF-MS (ESI-):
measured: m/z 207.1035; calculated for $[C_{17}H_{22}O_4N_1\text{-}H^+]^-$: m/z 207.1027

LC-MS/MS (ESI^-):
m/z (%) 312 (78, $[M - H]^-$), 177 (33), 148 (100), 147 (34), 135 (62)

^{1}H NMR (500 MHz, MeOD; COSY): δ [ppm]: 2.77 [t, 2H, J = 7,3 Hz, H−C(5)]; 3,48 [t, 2H, J = 7,3 Hz, H−C(4)]; 3,90 [s, 3H, H−C(1‴)]; 6,42 [d, 1H, J = 15,1 Hz, H−C(3)]; 6,74 [m, 2H, J = 8,5 Hz, H−C(3′ / 5′)]; 6,81 [d, 1H, J = 7,9 Hz, H−C(5″)]; 7,04 [dd, 1H, J = 2,0 Hz & 7,9 Hz, H−C(6″)]; 7,07 [m, 2H, J = 8,5 Hz, H−C(2′ / 6′)]; 7,13 [d, 1H, J = 2,0 Hz, H−C(2″)]; 7,45 [d, 2H, J = 15,1 Hz, H−C(2)]

^{13}C NMR (125 MHz, MeOD; HSQC, HMBC): δ (ppm): 35.8 [C(5)]; 42,5 [C(4)]; 56,4 [C(1‴)]; 111,6 [C(2″)]; 116,3 [C(2′ / 6′)]; 116,5 [C(5″)]; 118,7 [C(3)]; 123,2 [C(6″)]; 124,8 [C(1′)]; 128,3 [C(1″)]; 130,8 [C(2′ / 6′)]; 142,1 [C(2)]; 149,2 [C(4″)];149,8 [C(3″)];156,8 [C(4′)];169,2 [C(1)]

Table S1: Optimized Mass Spectrometric Parameters for the Quantitative Analysis of Taste-active Hop-Derived Compounds by Means of LC-MS/MS Using Negative Electrospray Ionization (ESI-).

compd no.[a]	mass transition Q1 → Q3	DP[b] [V]	CE[c] [V]	CXP[d] [V]
1a	*m/z* 347.1 → 277.9	-65	-28	-17
1b, 1c	*m/z* 361.2 → 292.0	-65	-28	-17
2a	*m/z* 399.2 → 286.9	-80	-38	-15
2b, 2c	*m/z* 413.2 → 301.2	-80	-38	-15
3a, 4a	*m/z* 347.0 → 251.0	-90	-22	-11
3b, 3c, 4b, 4c	*m/z* 361.0 → 265.0	-90	-22	-11
5, 6	*m/z* 352.9 → 118.8	-95	-42	-7
4, 8, 9	*m/z* 339.1 → 218.9	-105	-30	-13
10	*m/z* 421.2 → 118.9	-90	-42	-7
11	*m/z* 475.2 → 243.1	-120	-50	-15
12, 13, 14	*m/z* 353.0 → 119.0	-105	-38	-7
15, 16	*m/z* 399.1 → 119.0	-30	-42	-9
17	*m/z* 421.2 → 118.9	-105	-44	-9
18	*m/z* 421.2 → 118.8	-120	-44	-1
19	*m/z* 369.1 → 163.9	-105	-40	-9
20	*m/z* 369.1 → 118.8	-105	-36	-7
21	*m/z* 351.0 → 118.9	-90	-32	-7
22, 23	*m/z* 371.1 → 118.9	-100	-52	-5
24	*m/z* 353.0 → 163.0	-100	-44	-9
25	*m/z* 401.2 → 118.9	-120	-46	-7
26	*m/z* 369.3 → 119.0	-115	-38	-7
27	*m/z* 309.2 → 293.1	-105	-40	-19
28	*m/z* 369.1 → 119.0	-110	-40	-5
29, 30	*m/z* 385.1 → 118.9	-105	-52	-5
31	*m/z* 291.1 → 207.1	-105	-36	-3
32	*m/z* 207.1 → 136.8	-125	-28	-7
33a, 33b	*m/z* 163.0 → 119.1	-50	-20	-1
34a, 34b	*m/z* 177.0 → 118.0	-60	-24	-7
35a, 35b	*m/z* 191.0 → 117.0	-75	-44	-7
36	*m/z* 301.1 → 153.0	-105	-30	-9
37	*m/z* 463.1 → 299.9	-115	-38	-19
38	*m/z* 447.1 → 283.9	-100	-38	-17
39	*m/z* 533.2 → 489.2	-50	-18	-23
40a	*m/z* 357.2 → 194.8	-90	-22	-15
40c	*m/z* 371.1 → 208.9	-105	-24	-13
41b	*m/z* 533.2 → 323.2	-85	-34	-9
42	*m/z* 312.1 → 147.8	-95	-36	-7

[a]Compound numbering refers to the chemical structures given in Figure 1. [b]Declustering potential. [c]Collision energy. [d]Cell exit potential.