

Supplementary Data for **Synthesis of xanthohumol and xanthohumol-d₃ from naringenin**

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The MRM transitions of **1a** and **1b**

Table S1. Details of the MRM transitions of **1a** and **1b**

Compound	Ionization mode	Precursor ion	Product ion	Q1 [V] ^a	CE [eV] ^b	Q3 [V] ^c
1a	ESI(+)	355.0	178.9	-17.0	-27.0	-29.0
			299.0	-17.0	-13.0	-29.0
			113.0	-17.0	-48.0	-16.0
			150.9	-17.0	-44.0	-24.0
			93.0	-17.0	-55.0	-29.0
	ESI(-)	353.0	119.1	18.0	27.0	21.0
			233.0	18.0	19.0	23.0
			295.1	18.0	29.0	27.0
			218.2	18.0	25.0	21.0
			175.0	18.0	40.0	28.0
1b	ESI(+)	358.0	182.0	-26.0	-25.0	-30.0
			302.0	-26.0	-13.0	-29.0
			115.9	-26.0	-49.0	-18.0
			107.9	-26.0	-55.0	-16.0
			154.0	-26.0	-45.0	-25.0
	ESI(-)	356.0	119.1	10.0	29.0	21.0
			236.0	10.0	19.0	23.0
			295.2	10.0	28.0	27.0
			175.0	10.0	39.0	30.0
			218.1	10.0	25.0	21.0
		168.2	10.0	28.0	30.0	

^a voltage on 1st quadrupole; ^b collision energy; ^c voltage on 3rd quadrupole; highlighted transitions were used for preparation of analytical HPLC-MS method

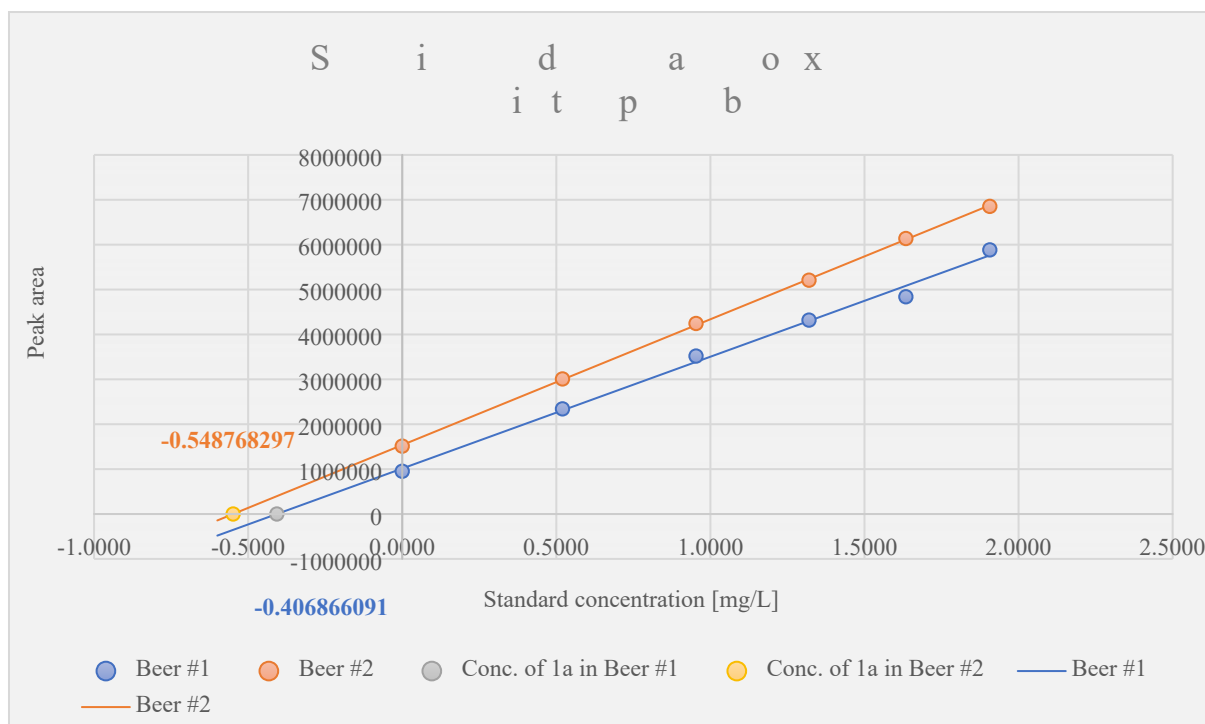
Stable isotope dilution assays

Stable isotope dilution assays were performed for two polish beers (Beer #1, Beer#2). A freshly opened beer was degassed for 30 min in ultrasonic cleaner. Then, to aliquots (1.0 mL) of degassed beer, samples of standard solution (**1b**, C = 5.720 mg/L) were added (0.1 mL, 0.2 mL, 0.3 mL, 0.4 mL, 0.5 mL). Prepared in such way samples together with beer samples were analyzed by HPLC-MS in MRM mode (Column: XB-C18, 100×3.0 mm, 2.6 μm, 100 Å; flow: 0.55 mL/min; oven: 35 °C; gradient MeOH/0.1% HCO₂H_(aq): from 50% MeOH to 95% MeOH). Plots of peak areas versus standard concentrations in samples were sketched and concentration of **1a** was determined from the plot as absolute value of zero point.

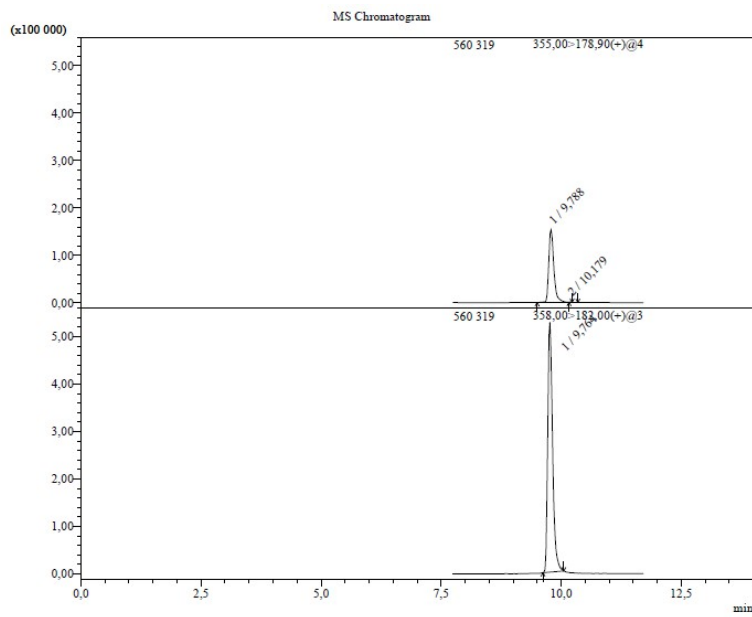
Table S2. Stable isotope dilution assays

Analysis	Standard volume [mL]	Std. conc. in sample [mg/L]	Peak area
Beer #1			Xanthohumol conc. [mg/L] 0.4069
1	0.0	0	952552
2	0.1	0.520	2342036
3	0.2	0.953	3518620
4	0.3	1.320	4319572
5	0.4	1.634	4839326
6	0.5	1.907	5883749
Beer #2			Xanthohumol conc. [mg/L] 0.5488
1	0.0	0	1512201
2	0.1	0.520	3008853
3	0.2	0.953	4244305
4	0.3	1.320	5208824
5	0.4	1.634	6137508
6	0.5	1.907	6853290

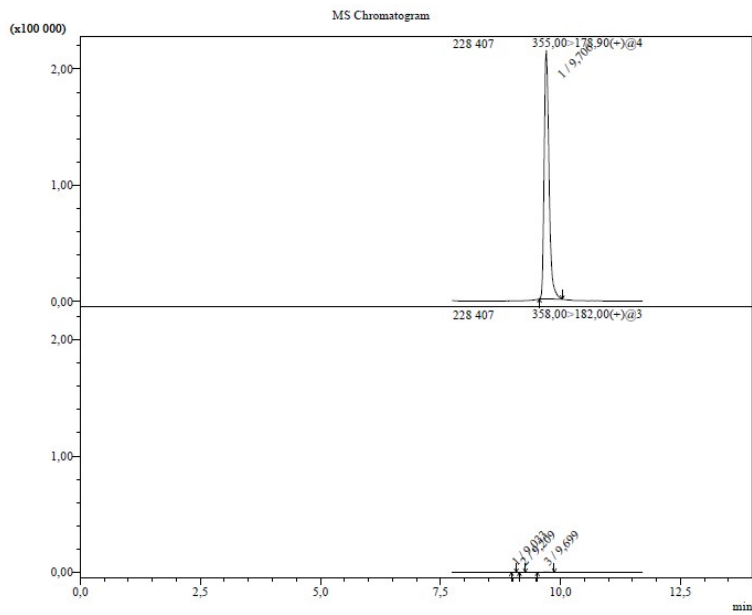
Calibration curves



Typical MS chromatogram for calibration points



Typical MS chromatogram for beer sample



^1H and ^{13}C NMR spectra

