Supplementary Data

Glycosylation of quercetin by selected entomopathogenic filamentous fungi and prediction of its products' bioactivity

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Content

Table S1. Identification of fungal strains on the basis of the sequence of the ITS1-ITS2 sequences and comparison with reference ITS sequences.

Name of fungal strain	Identified fungal species	Sequence identity	Sequence
CYS17	*Metapochonia bulbillosa*	99% identity to *Metapochonia bulbillosa*, Acc. Numbers: OK661050.1, DQ132810.1, MK164206.1	GGTCACTCTAAAAAGTTGGGCGTTTTACGGCAGTGGCCGCGTCGCG CTCccgctgcgagGTTGTGCTACTACGCAGAGGAGGCCGCGACGgggccg CCAATTCATTTCGGGGGCGGCGGACGCGCCGGGGGTGTTCCCCCGG GCGAGGTCGCCGGTCCCCAACACCAGGCCACTGGGGCTTGAGGGTT GAAATGACGCTCGAACAGGCATGCCCGCCAGAATACTGGCGGGCGC AATGTGCGTTCAAAGATTCGATGATTCACTGAATTCTGCAATTCACAT TACTTATCGCATTTCGCTGCGTTCTTCATCGATGCCAGAACCAAGAGA TCCGTTGTTGAAAGTTTTGATTCATTTGTTTATGATTCCACTCAGACAT GCTATAAAAAAGATACAAGAGTTTTGGTCCCCCGGCGGGCGCCTGG TTCCGGCGGCCCTCGCGGGCCTTCCGGGGCGTTaACCCGCCGAAGC AACAGTAAAGGTATAAGTTCACAGGGGTTTGGGAGTAGAATAACTC GGTAATGATCCCTCCGC
CYS30	*Isaria tenuipes*	100% identity to *Isaria tenuipes*, Acc. Numbers: MT966070.1, MT966058.1, MT966055.1	GTCAcGTTCAGAgGTTGGGGGTTTCACGGCGGGCCGCGTCGGGTTCC cgGtgcgaGTGCTTGTACTGCGCAGAGGTCGCCGCGGACGGGCCgCCA CTCCATTTCAGGGCCGGCGGGGTGCTGCCGGTCCCCAAGGCCGACG TCCCGGGGGACGTCGAGGGTTGAAATGACGCTCGAACAGGCATGCC CGCCAGAATGCTGGCGGGCGCAATGTGCGTTCAAAGATTCGATGAT TCACGGAATTCTGCAATTCACATTACGTATCGCATTTCGCTGCGTTCT TCATCGATGCCAGAACCAAGAGATCCGTTGTTGAAAGTTTTGATTCG TTTGTGTTGCCTTGCGGCGGATTCAGAGAGGCTGACAGATACAGGG TTGCGTGGTCCCCGGCGGCCGCCTGGGTCCAGGTCGCGGGCCGGCG CTGGGCCGTCCGGACGCTGGGGCGGGTCCGCCGAAGCAACTATGG GTAGGTTCACAGAAGGGTTGGGAGTTGTAAAACTCTGGTAATGATC CCTCCG
MU35	*Isaria tenuipes*	100% identity to *Isaria tenuipes*, Acc. Numbers: MT966070.1, MT966058.1, MT966055.1	GTCACGTTCAGAgGTTGGGGGTTTCACGGCGGGCCGCGTCGGGTTCc cggtgcgaGTGCTTGTACTGCGCAGAGGTCGCCGCGGACGGGCCGCCA CTCCATTTCAGGGCCGGCGGGGTGCTGCCGGTCCCCAAGGCCGACG TCCCGGGGGACGTCGAGGGTTGAAATGACGCTCGAACAGGCATGCC CGCCAGAATGCTGGCGGGCGCAATGTGCGTTCAAAGATTCGATGAT TCACGGAATTCTGCAATTCACATTACGTATCGCATTTCGCTGCGTTCT TCATCGATGCCAGAACCAAGAGATCCGTTGTTGAAAGTTTTGATTCG TTTGTGTTGCCTTGCGGCGGATTCAGAGAGGCTGACAGATACAGGG TTGCGTGGTCCCCGGCGGCCGCCTGGGTCCAGGTCGCGGGCCGGCG CTGGGCCGTCCGGACGCTGGGGCGGGTCCGCCGAAGCAACTATGG GTAGGTTCACAGAAGGGTTGGGAGTTGTAAAACTCTGGTAATGATC CCTCCGCAG
MU4	*Metarhizium anisopliae*	100% identity to *Metarhizium anisopliae*, Acc. Numbers: FJ177507.1, and 99%: FJ177475.1, EU307928.1	GTCACTATAAAaGTTGGGGGGTTTTACGGCAGTGGacCGCGCCGGG CTCCtgttGCGaGTGTTTTACTACTGCGCAGAGGAGGGCCACGGCgag ACCGCCAATTGATTTGAGGGACGGCTGCGCTGGAAAACCAGCCTCG CCGATCCCCAACACCAAGTCCACAGGGGACTTGAGGGGCGTAATGA CGCTCGAACAGGCATGCCCGCCAGAATACTGACGGGCGCAATGTGC GTTCAAAGATTCGATGATTCACTGAATTCTGCAATTCACATTACTTAT CGCATTTCGCTGCGTTCTTCATCGATGCCAGAACCAAGAGATCCGTT GTTGAAAGTTTTGATTCATTTTTTTAACCACTCAGAAGATACTTATTA AAAAATTCAGAAGGTTTGGGTCCCCGGCGGGCGCGAAGTCCCGCCG AAGCAACAATTAAAGGTATAATTCACAGGGGTTGGGAGtTGGATAA CTCGGTAATGATCCCTCCGCA

Figure S1. Structure of quercetin (**1**)

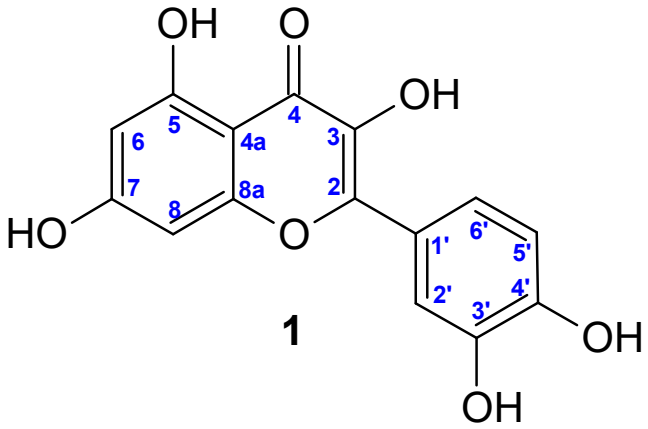
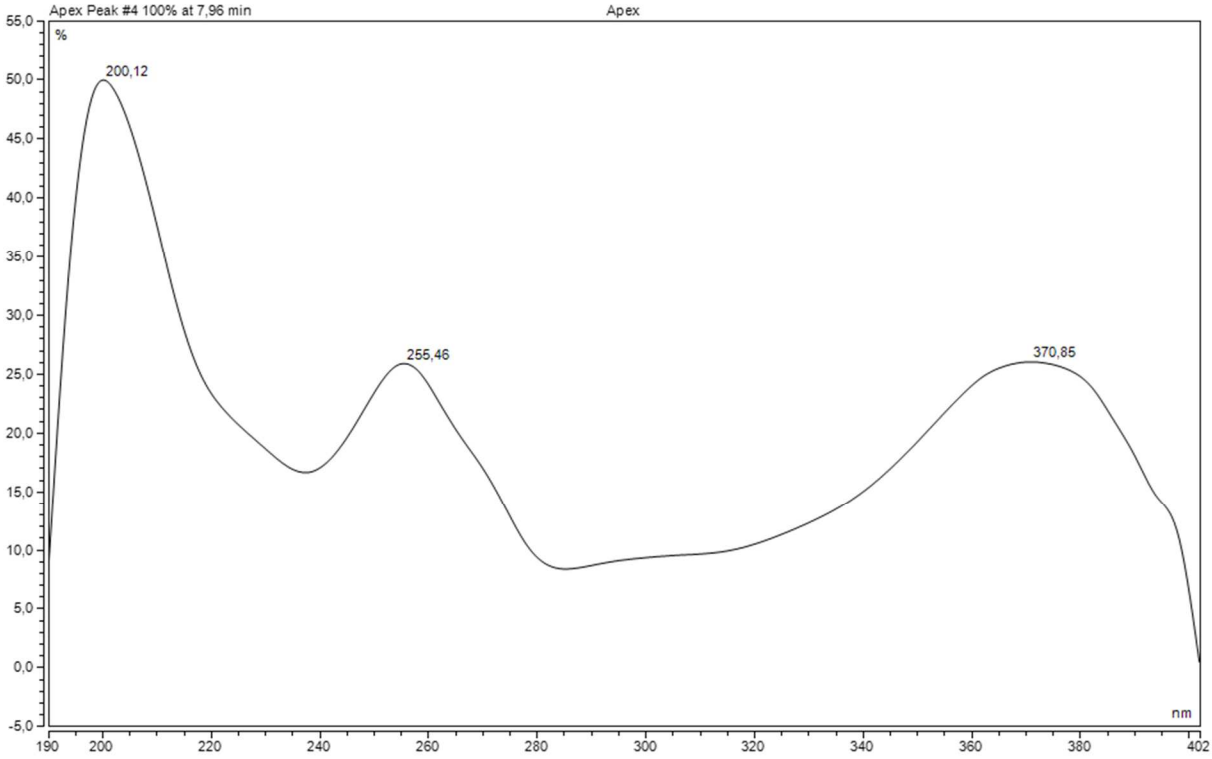


Figure S2. UV spectra of quercetin (**1**)



Supplementary Data 1. NMR Spectral data of quercetin (**1**): ^{1}H-NMR (DMSO-d_6) δ_H: 6.19 (1H, d, J = 2.1 Hz, H-6), 6.41 (1H, d, J = 2.1 Hz, H-8), 6.89 (1H, d, J = 8.5 Hz, H-5′), 7.54 (1H, dd, J = 8.5, 2.2 Hz, H-6′), 7.68 (1H, d, J = 2.2 Hz, H-2′). ^{13}C-NMR (DMSO-d_6) δ_C: 93.2 (C-8), 98.0 (C-6), 102.9 (C-10), 114.9 (C-2′), 115.4 (C-5′), 119.8 (C-6′), 121.8 (C-1′), 135.6 (C-3), 144.9 (C-3′), 146.6 (C-2), 147.5 (C-4′), 156.0 (C-9), 160.6 (C-5), 163.7 (C-7), 175.7 (C-4).

Figure S3. ^{1}H NMR spectra of quercetin (**1**) (600MHz, DMSO-d_6)

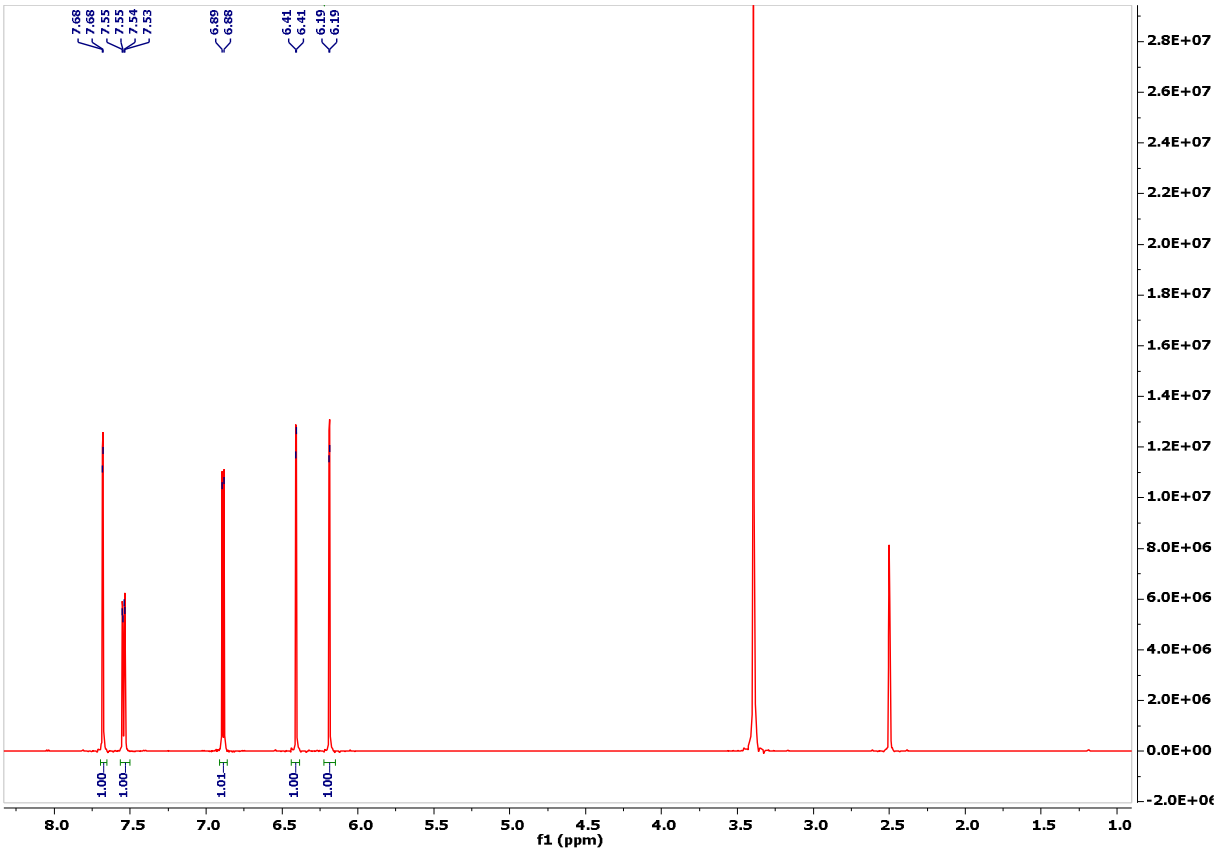


Figure S4. ^{13}C NMR spectra of quercetin (**1**) (151 MHz, DMSO-d_6)

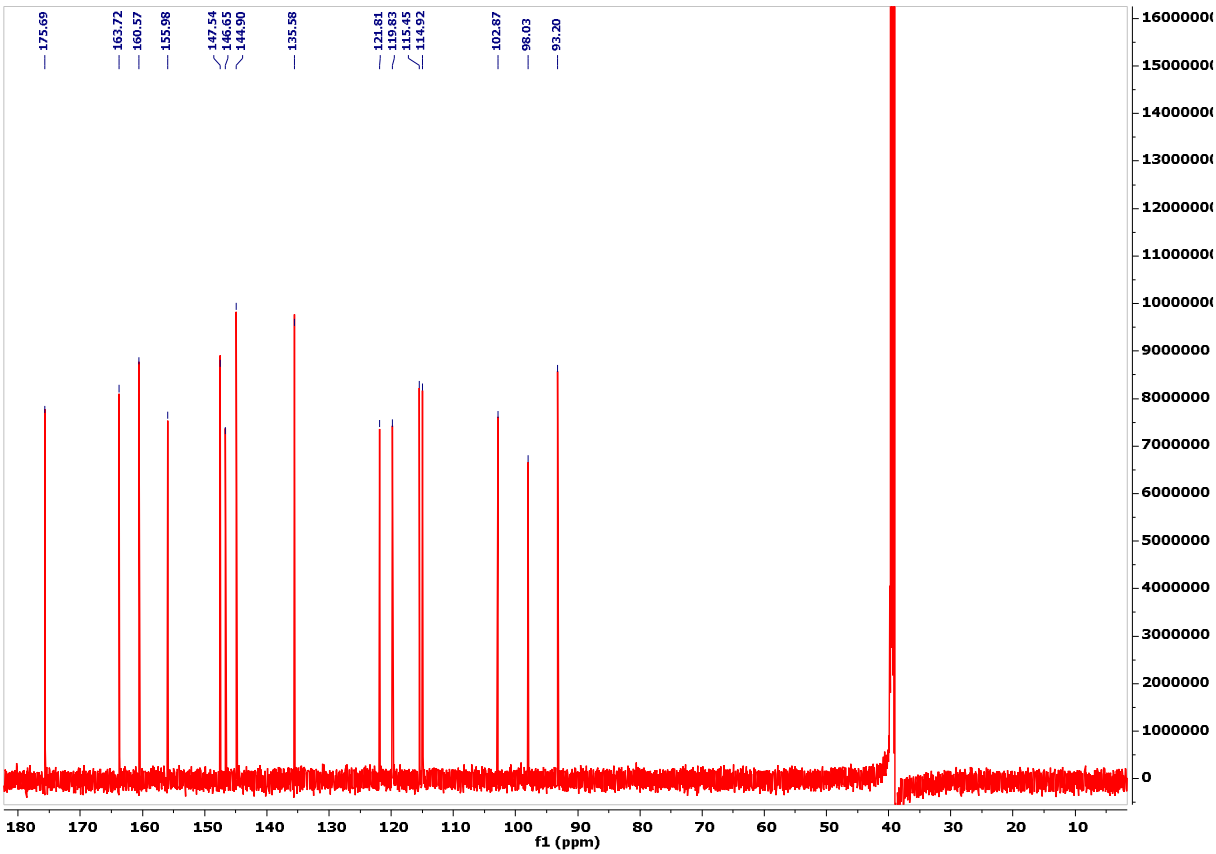


Figure S5. Structure of 7-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**2**)

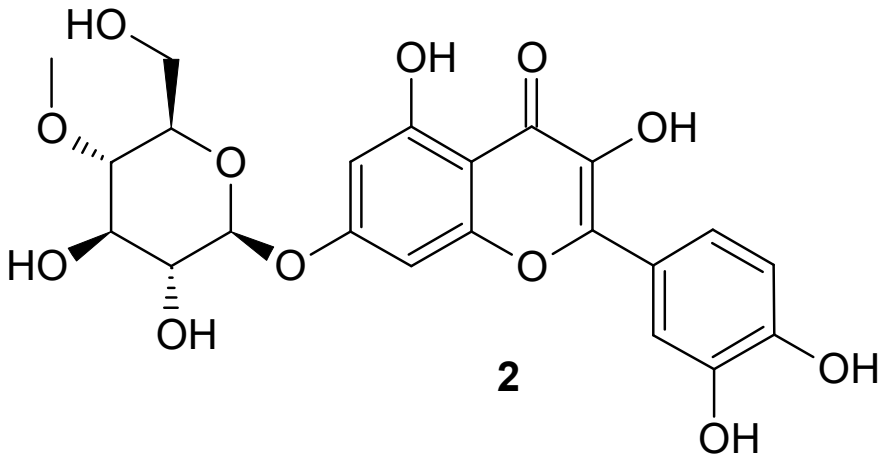
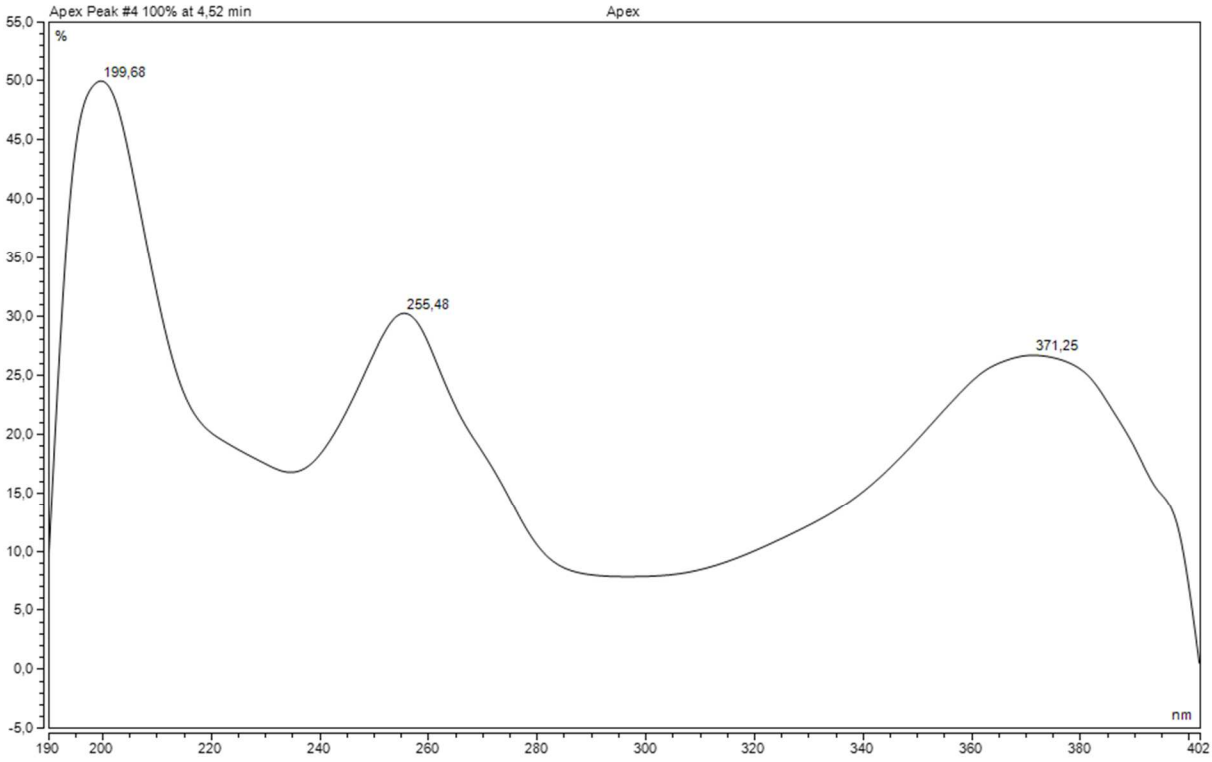


Figure S6. UV spectra of 7-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**2**)



Supplementary Data 2. NMR Spectral data of 7-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**2**): ^{1}H-NMR (DMSO-d_6) δH: 3.05 (1H, t, *J* = 9.0 Hz, H-4″), 3.26 (1H, dd, *J* = 9.0, 7.8 Hz, H-2″), 3.44 (1H, t, *J* = 9.0 Hz, H-3″), 3.46 (3H, s, C4″-OCH_3), 3.49–3.53 (1H, m, C-5″ overlapped on H-6″a), 3.49–3.53 (1H, m, H-1″a, overlapped on H-5″), 3.62–3.68 (1H, m, H-6″b), 5.10 (1H, d, *J* = 7.8 Hz, H-1″), 6.42 (1H, d, *J* = 2.2 Hz, H-6), 6.76 (1H, d, *J* = 2.2 Hz, H-8), 6.90 (1H, d, *J* = 8.5 Hz, H-5′), 7.55 (1H, dd, *J* = 8.5, 2.2 Hz, H-6′), 7.72 (1H, d, *J* = 2.2 Hz, H-2′). ^{13}C-NMR (DMSO-d_6) δC: 59.7 (C-4″-OCH_3), 60.1 (C-6″), 73.2 (C-2″), 75.6 (C-5″), 76.0 (C-3″), 78.8 (C-4″), 94.2 (C-8), 98.6 (C-6), 99.5 (C-1″), 104.6 (C-4a), 115.3 (C-2′), 115.5 (C-5′), 120.0 (C-6′), 121.8 (C-1′), 136.0 (C-3), 145.0 (C-3′), 147.5 (C-2), 147.8 (C-4′), 155.7 (C-8a), 160.1 (C-5) 162.6 (C-7), 175.9 (C-4).

Figure S7. ^{1}H NMR spectra of 7-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**2**) (600MHz, DMSO-d_6)

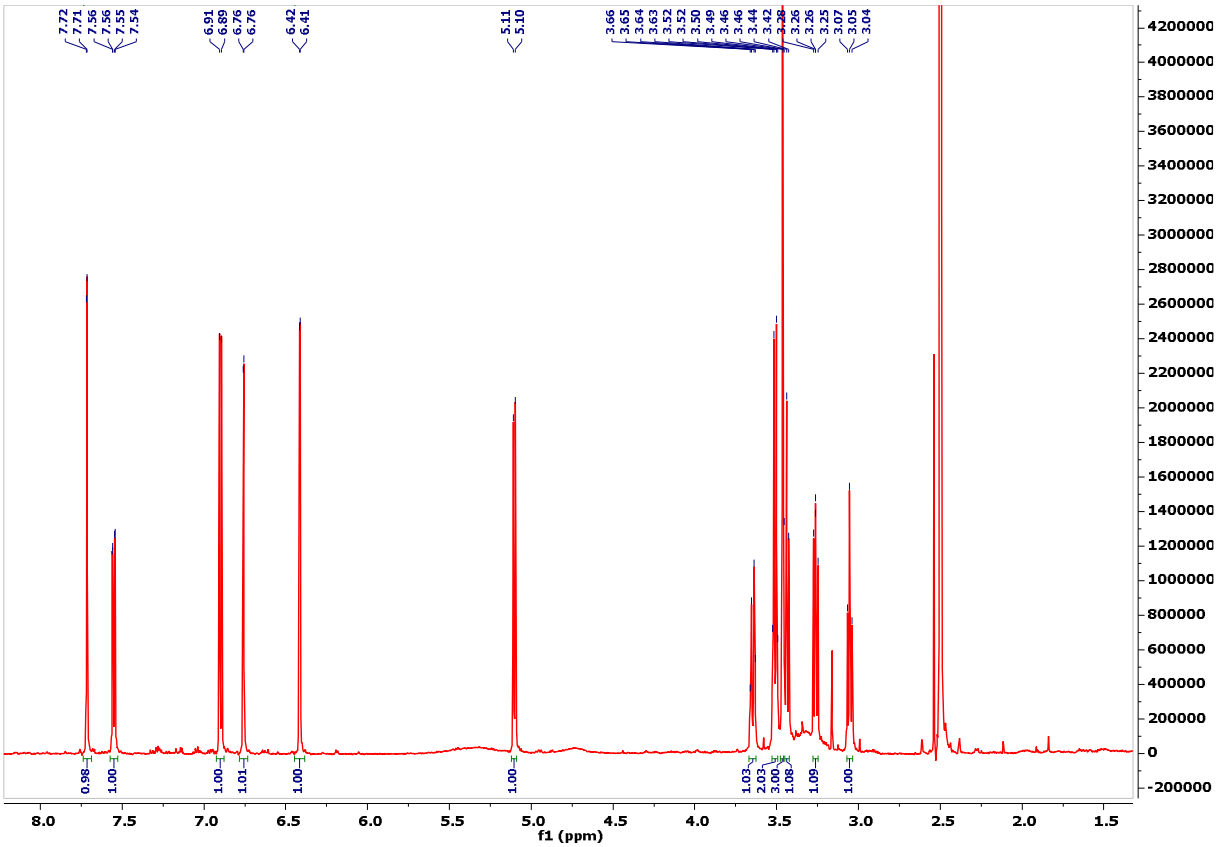


Figure S8. ^{13}C NMR spectra of 7-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**2**) (151 MHz, DMSO-d_6)

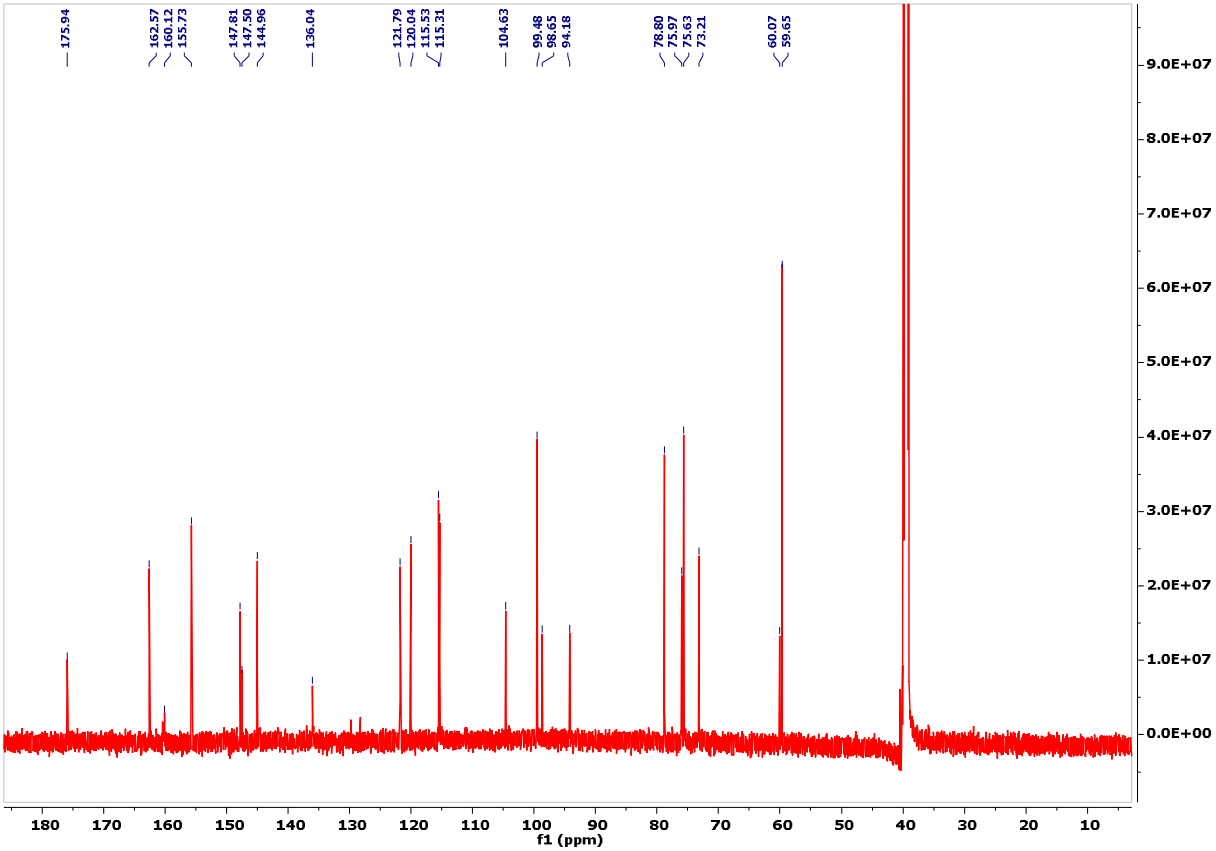


Figure S9. ^{1}H -^{1}H NMR (COSY) spectrum of quercetin 7-*O*-β-D-(4"-*O*-methyl)glucopyranoside (**2**) (600 /600 MHz, DMSO-d_6)

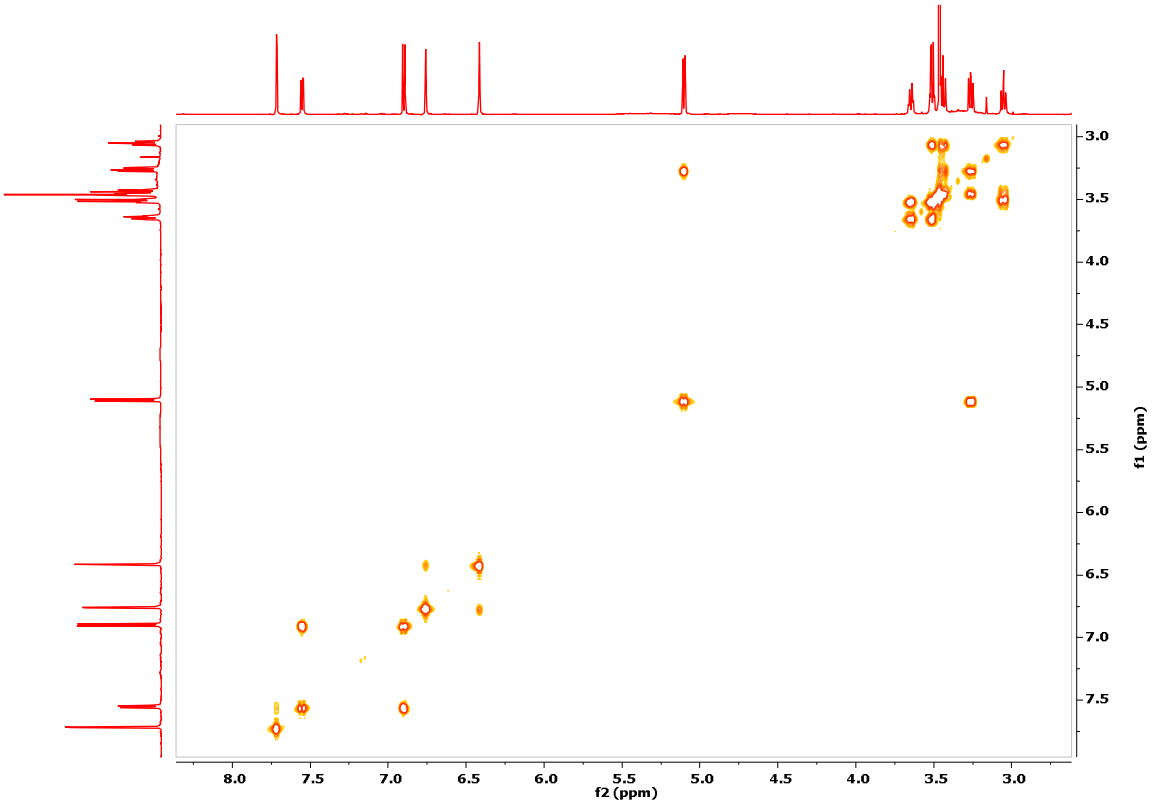


Figure S10. ^{1}H -^{13}C NMR (HSQC) spectrum of quercetin 7-*O*-β-D-(4"-*O*-methyl)glucopyranoside (**2**) (600 /151 MHz, DMSO-d_6)

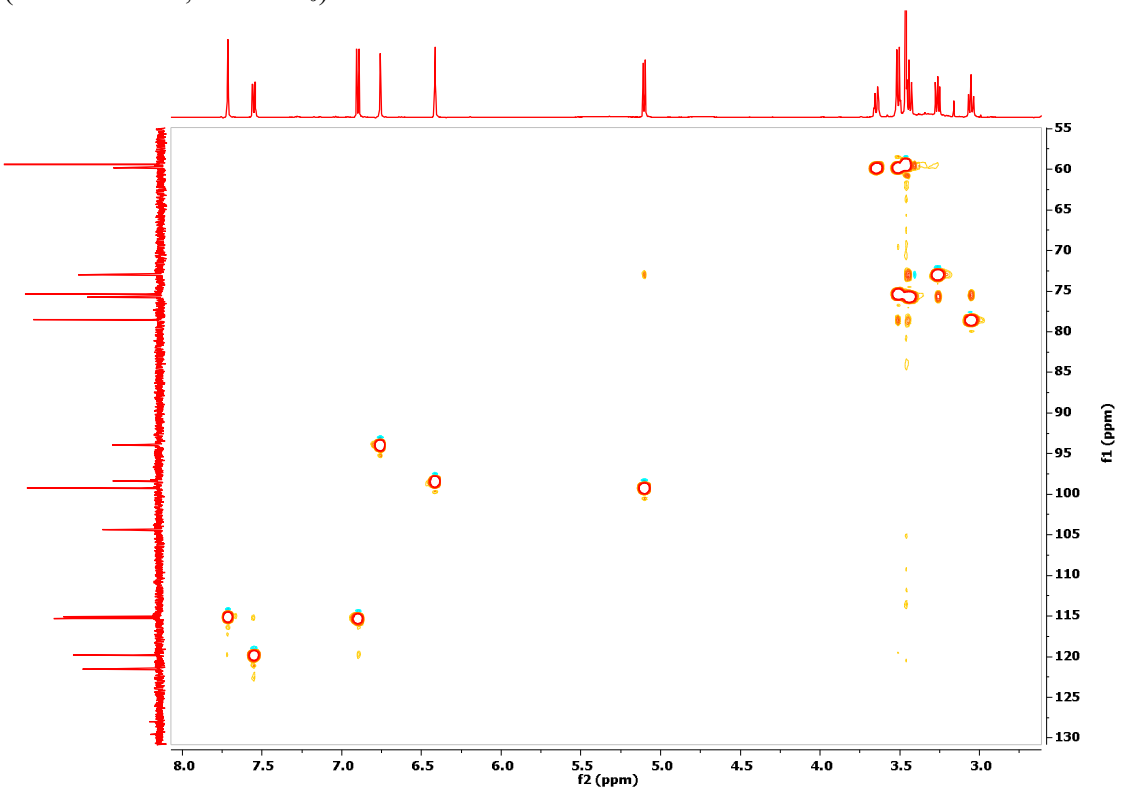
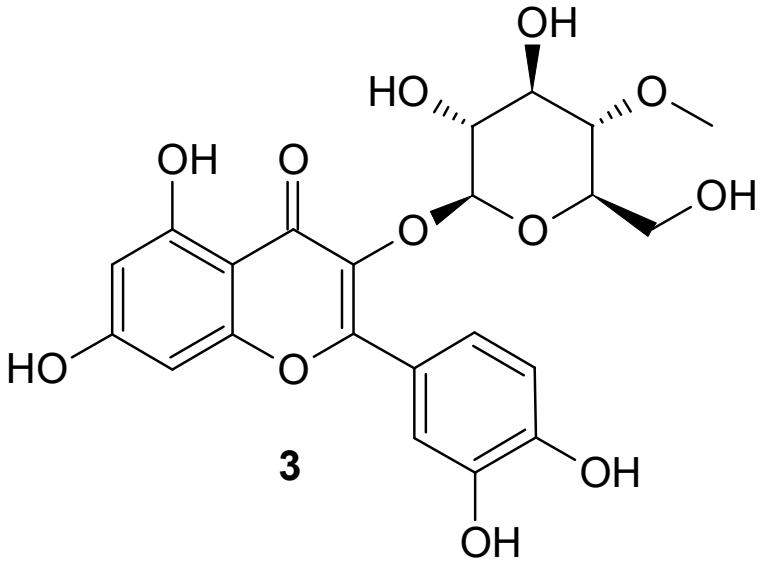
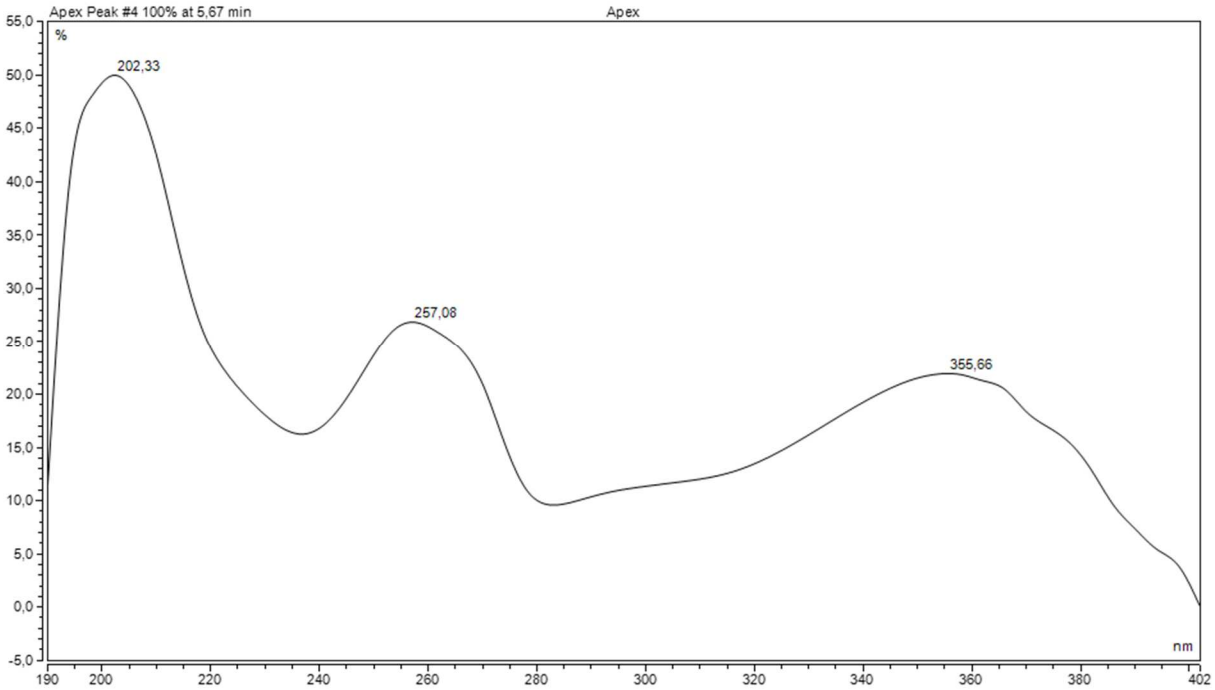


Figure S11. Structure of 3-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**3**)



3

Figure S12. UV spectra of 3-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**3**)



Supplementary Data 3. NMR Spectral data of 3-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**3**): ^{1}H-NMR (Acetone-d_6) δH: 3.**18** (1H, t, *J* = 9.0 Hz, H-4″), 3.34 (1H, ddd, *J* = 9.0, 5.0, 2.3 Hz, 5′-H), 3.50 (1H, t, *J* = 7.9 Hz, H-2″), 3.57 (3H, s, C4″-OCH$_3$), 3.60-3.66 (2H, m, H-3″ and one of H-6″), 3.73 (1H, dd, *J* = 12.0, 2.3 Hz, one of H-6″), 5.27 (1H, d, *J* = 7.9 Hz, H-1″), 6.32 (1H, d, *J* = 2.2 Hz, H-6), 6.55 (1H, d, *J* = 2.2 Hz, H-8), 7.00 (1H, d, *J* = 8.4 Hz, H-5′), 7.64 (1H, dd, *J* = 8.4, 2.2 Hz, H-6′), 8.04 (1H, d, *J* = 2.2 Hz, H-2′). ^{13}C-NMR (DMSO-d_6) δC: 60.5 (C-4″-OCH$_3$), 62.3 (C-6″), 75.7 (C-2″), 77.0 (C-5″), 78.2 (C-3″), 79.8 (C-4″), 94.7 (C-6), 99.8 (C-8), 104.8 (C-1″), 105.5 (C-4a), 115.9 (C-5′), 118.0 (C-2′), 122.7 (C-1′), 122.8 (C-6′), 135.6 (C-3), 145.3 (C-3′), 149.3 (C-4′), 158.0 (C-5), 158.8 (C-2), 162.9 (C-**8a**), 165.3 (C-7), 179.2 (C-4).

Figure S13. ^{1}H NMR spectra of 3-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**3**) (600MHz, Acetone-d_6)

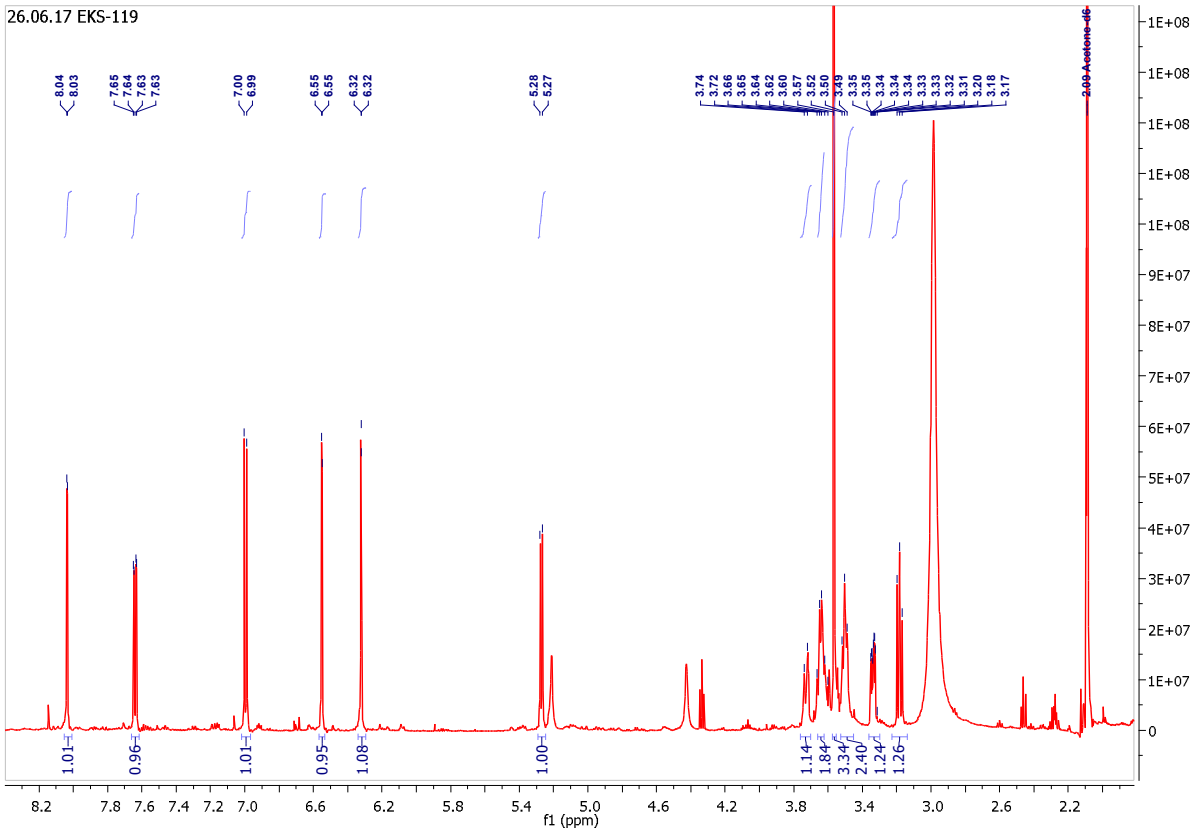


Figure S14. ^{13}C NMR spectra of 3-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**3**) (151 MHz, Acetone-d_6)

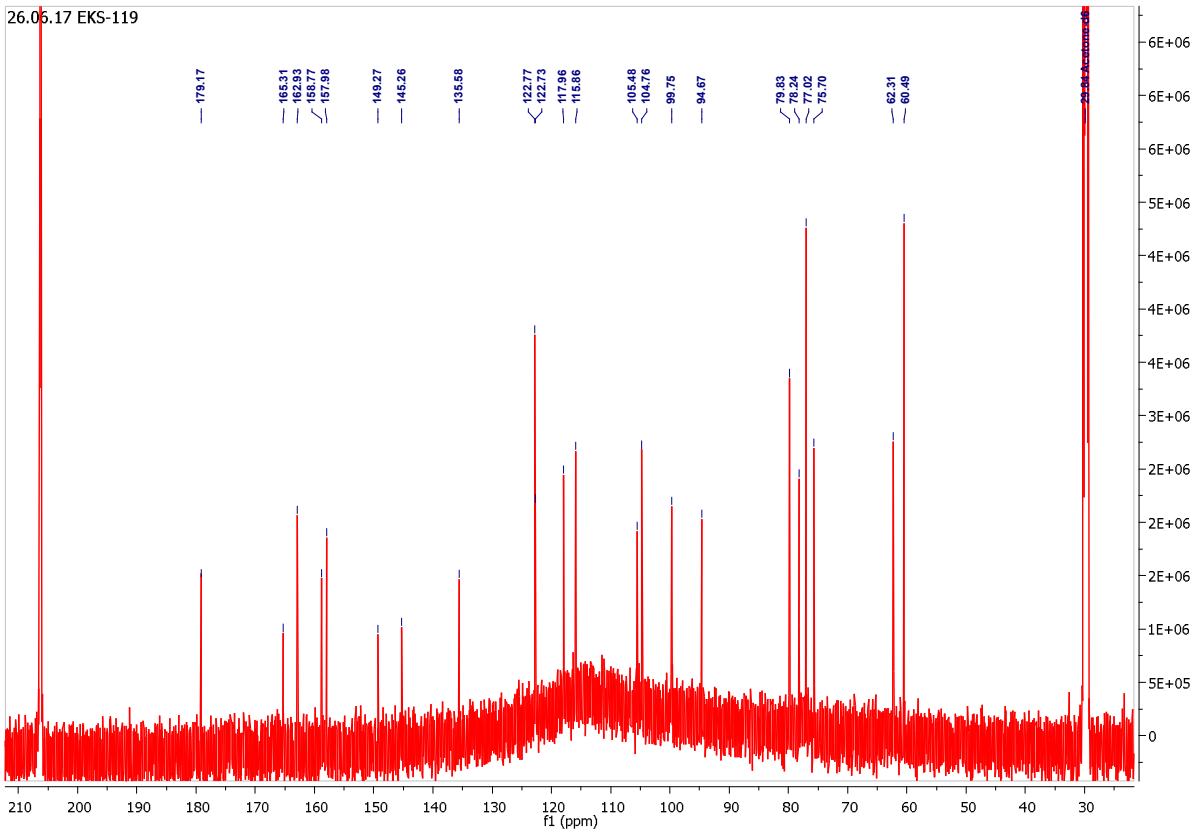


Figure S15. ^{1}H -^{1}H NMR (COSY) spectrum of quercetin 3-*O*-β-D-(4”-*O*-methylglucopyranosyl)-quercetin (**3**) (600 /600 MHz, Acetone-d_6)

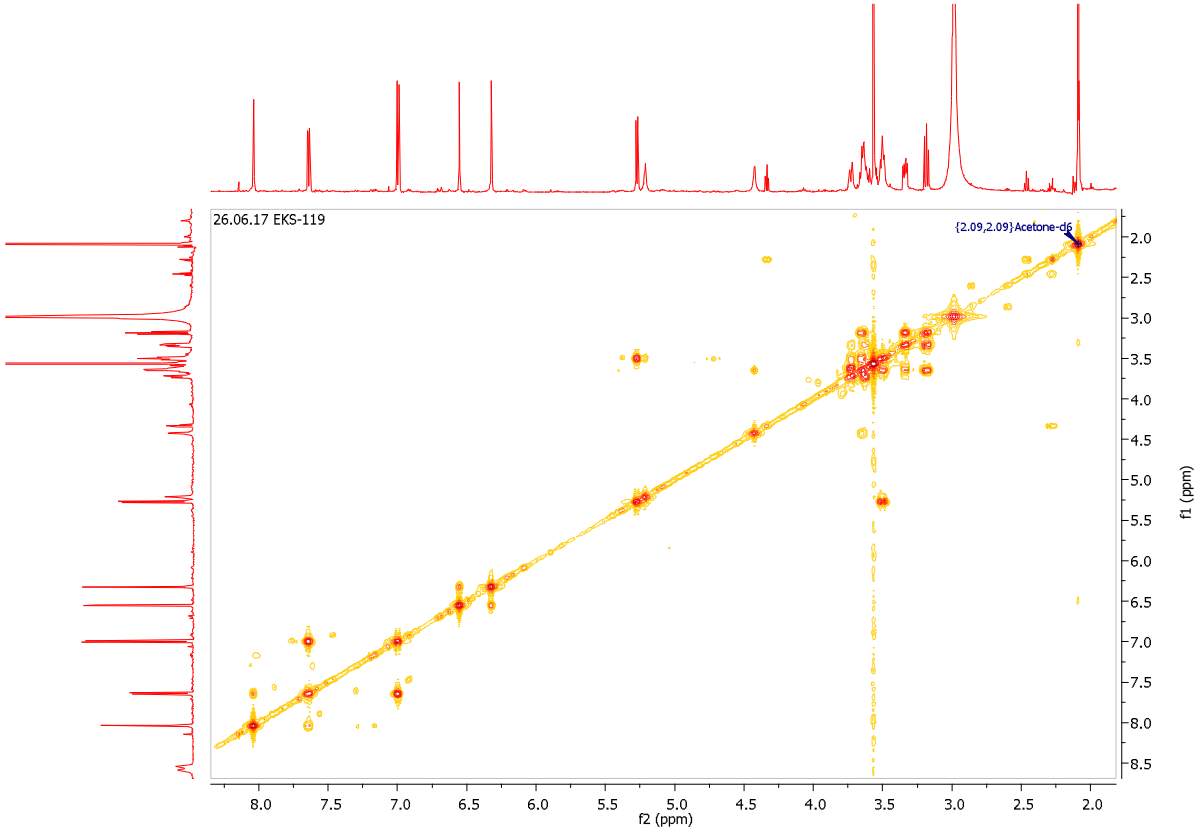


Figure S16. ^{1}H -^{13}C NMR (HSQC) spectrum of quercetin 3-*O*-β-D-(4”-*O*-methylglucopyranosyl)-quercetin (**3**) (600 /151 MHz, Acetone-d_6)

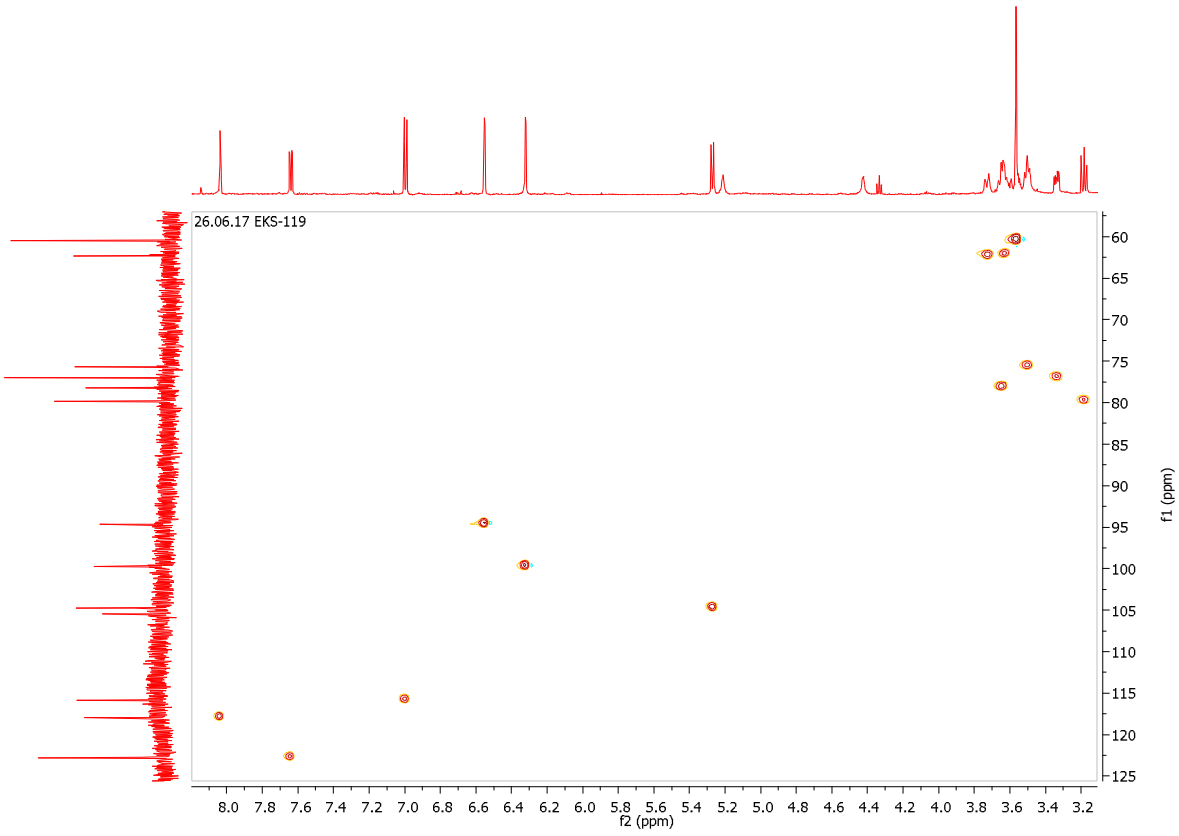


Figure S17. Structure of 3-*O*-β-D-(glucopyranosyl)-quercetin (**4**)

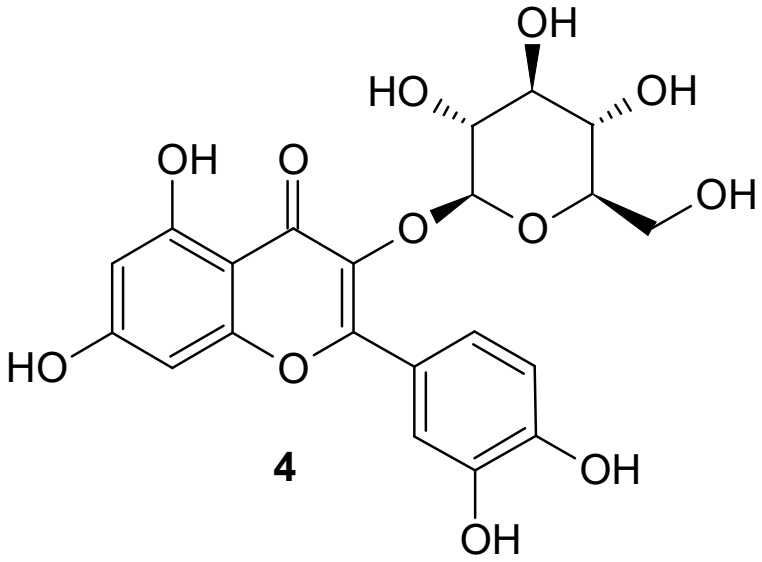
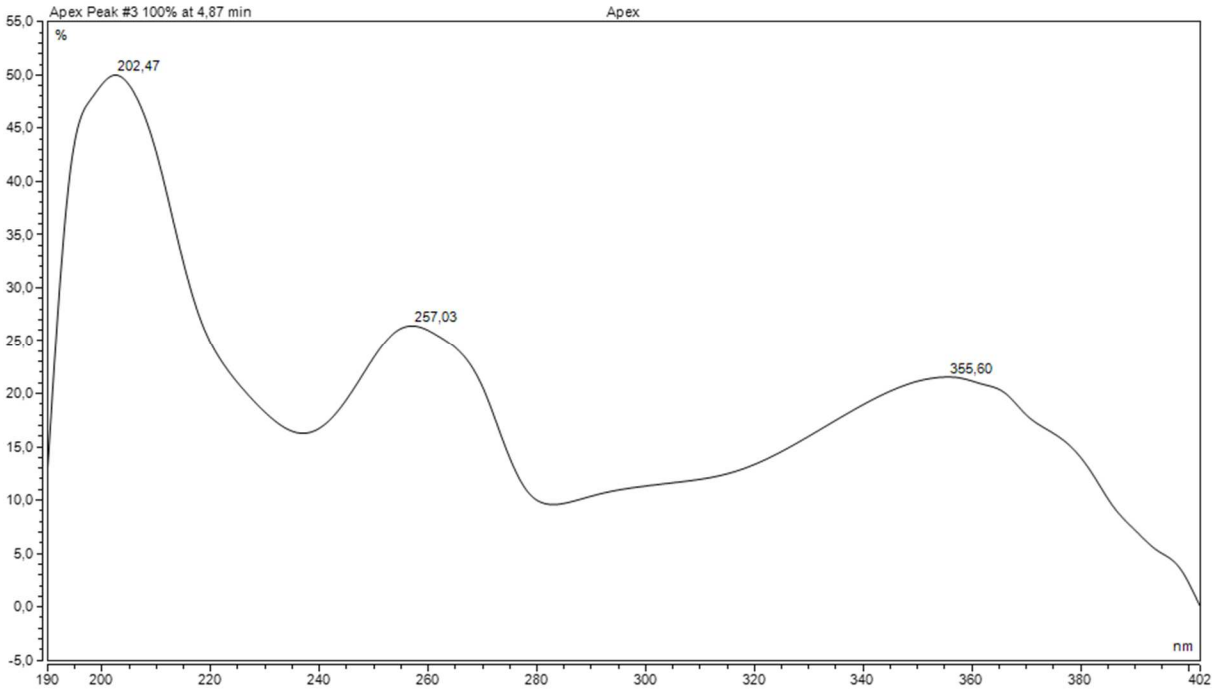


Figure S18. UV spectra of 3-*O*-β-D-(glucopyranosyl)-quercetin (**4**)



Supplementary Data 4. NMR Spectral data of 3-*O*-β-D-(glucopyranosyl)-quercetin (**4**): ^{1}H-NMR (Acetone-d_6) δH: 3.44 (1H, t, *J* = 8.8 Hz, H-4″), 3.32-3.37 (1H, m, 5′-H), 3.49-3.55 (2H, m, H-2″ and H-3″), 3.62-3.67 (1H, one of H-6″), 3.78 (1H, dd, *J* = 11.2, 2.3 Hz, one of H-6″), 5.30 (1H, d, *J* = 7.4 Hz, H-1″), 6.32 (1H, d, *J* = 2.1 Hz, H-6), 6.55 (1H, d, *J* = 2.1 Hz, H-8), 6.99 (1H, d, *J* = 8.4 Hz, H-5′), 7.62 (1H, dd, *J* = 8.4, 2.2 Hz, H-6′), 8.04 (1H, d, *J* = 2.2 Hz, H-2′). ^{13}C-NMR (DMSO-d_6) δC: 62.7 (C-6″), 75.5 (C-2″), 77.8 (C-5″), 78.1 (C-3″), 70.9 (C-4″), 94.7 (C-6), 99.7 (C-8), 105.0 (C-1″), 105.4 (C-4a), 115.8 (C-5′), 117.9 (C-2′), 122.6 (C-6′), 122.7 (C-1′), 135.6 (C-3), 145.3 (C-3′), 149.3 (C-4′), 158.0 (C-5), 158.8 (C-2), 162.9 (C-**8a**), 165.4 (C-7), 179.2 (C-4).

Figure S19. ^{1}H NMR spectra of 3-*O*-β-D-(glucopyranosyl)-quercetin (**4**) (600MHz, Acetone-d_6)

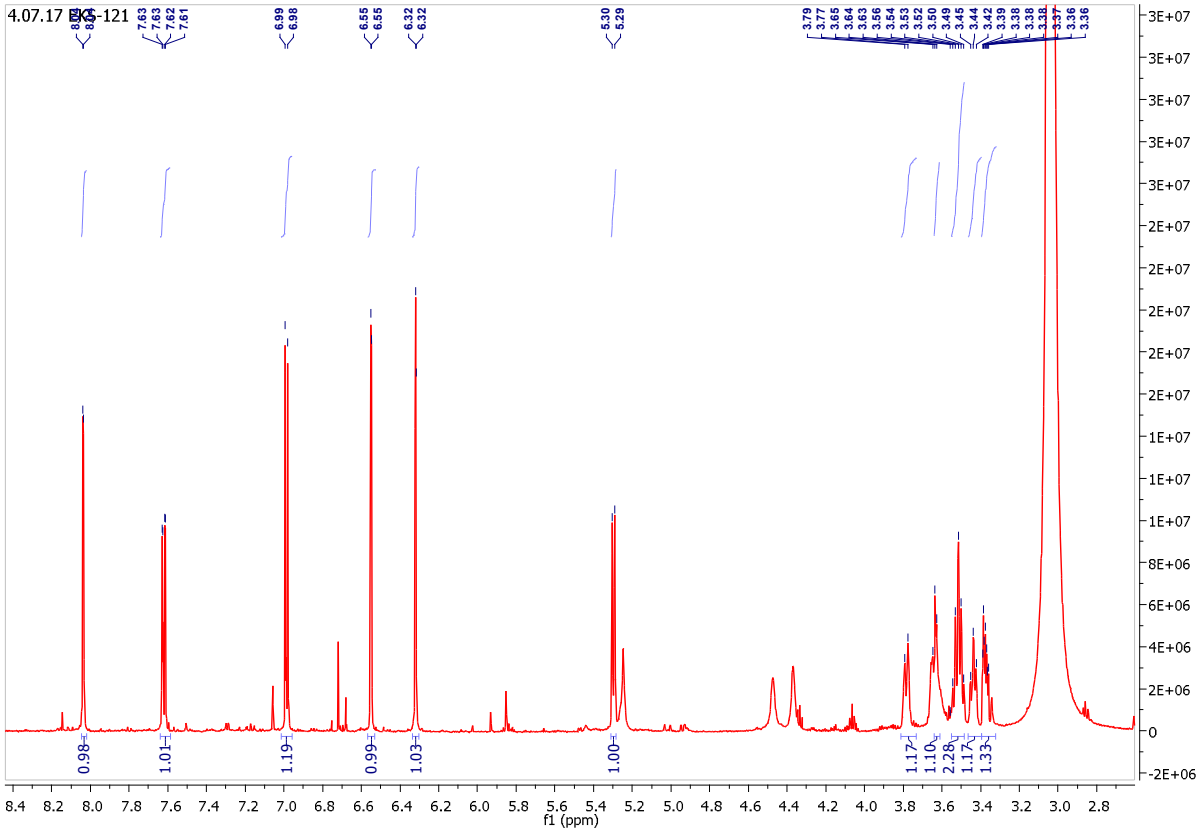


Figure S20. ^{13}C NMR spectra of 3-*O*-β-D-(glucopyranosyl)-quercetin (**4**) (151 MHz, Acetone-d_6)

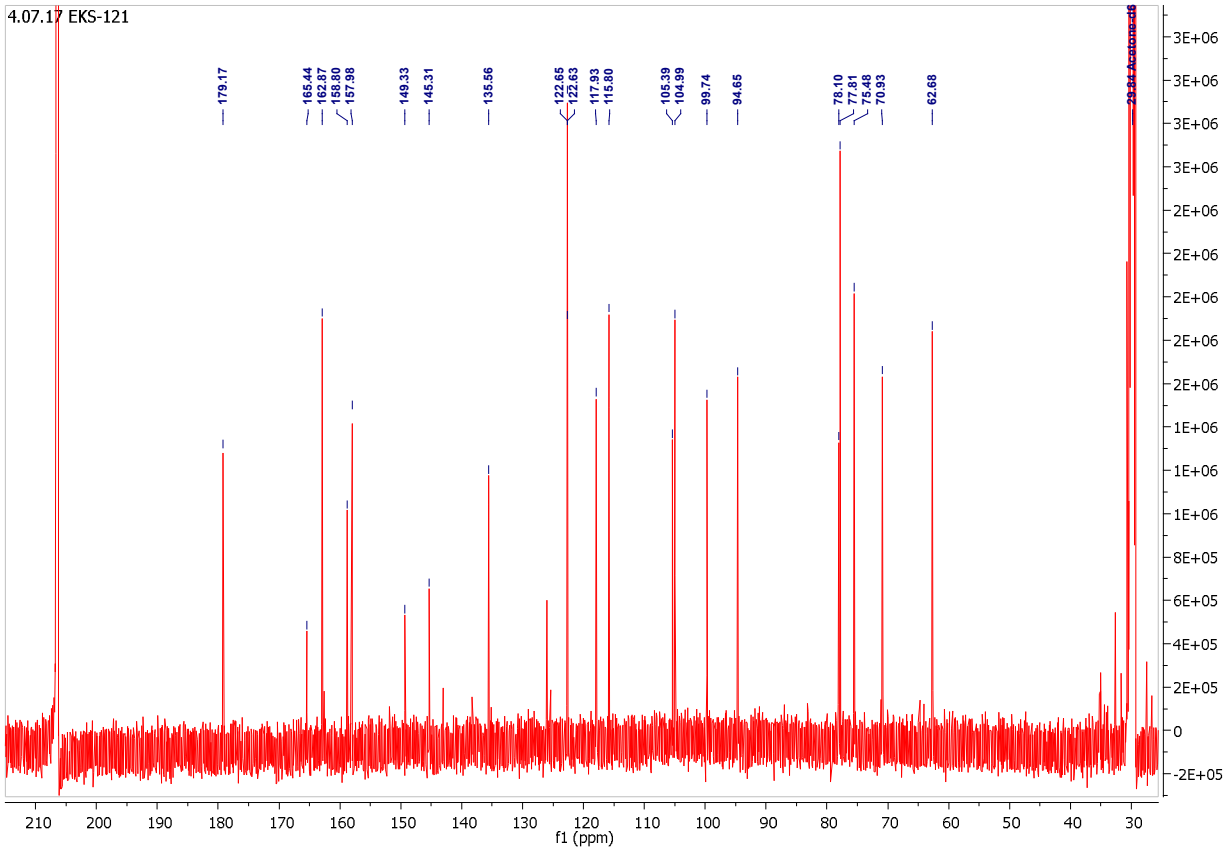


Figure S21. ^{1}H -^{1}H NMR (COSY) spectrum of quercetin 3-*O*-β-D-(glucopyranosyl)-quercetin (**4**) (600/600 MHz, Acetone-d_6)

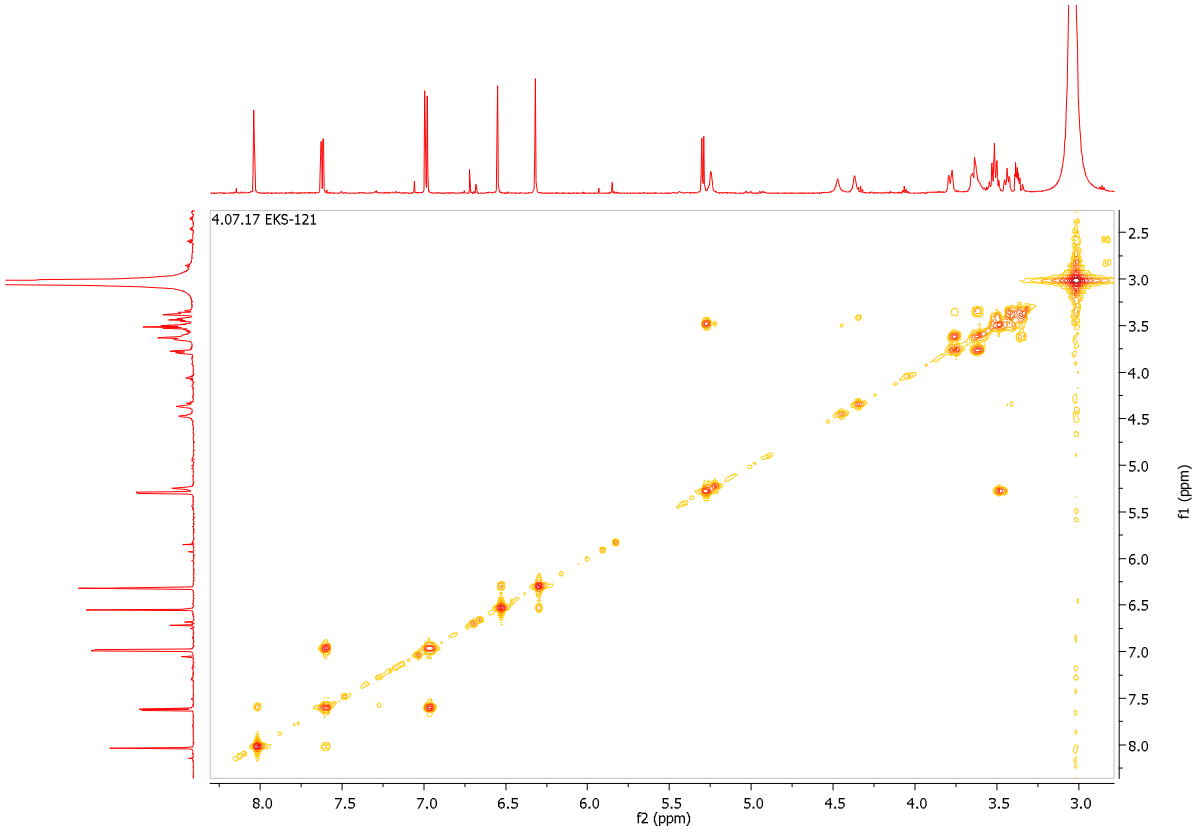


Figure S22. ^{1}H -^{13}C NMR (HSQC) spectrum of quercetin 3-*O*-β-D-(glucopyranosyl)-quercetin (**4**) (600/151 MHz, Acetone-d_6)

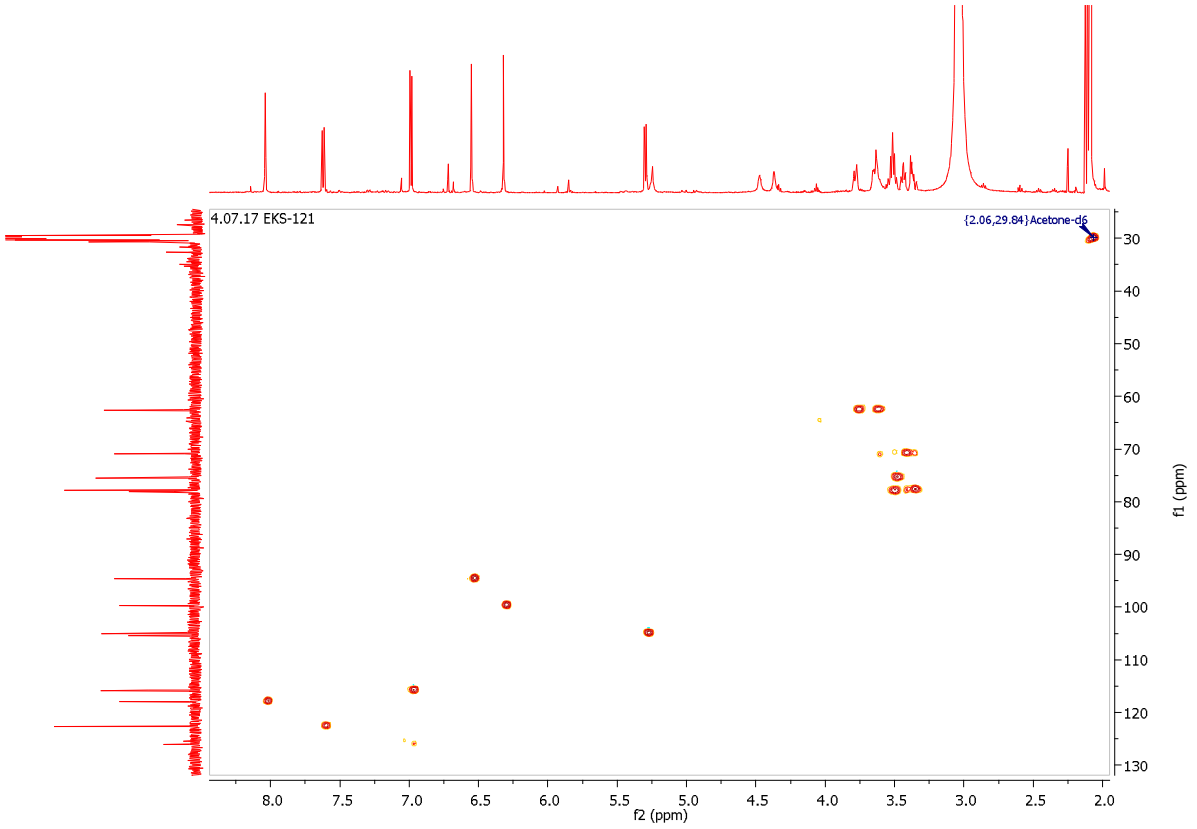
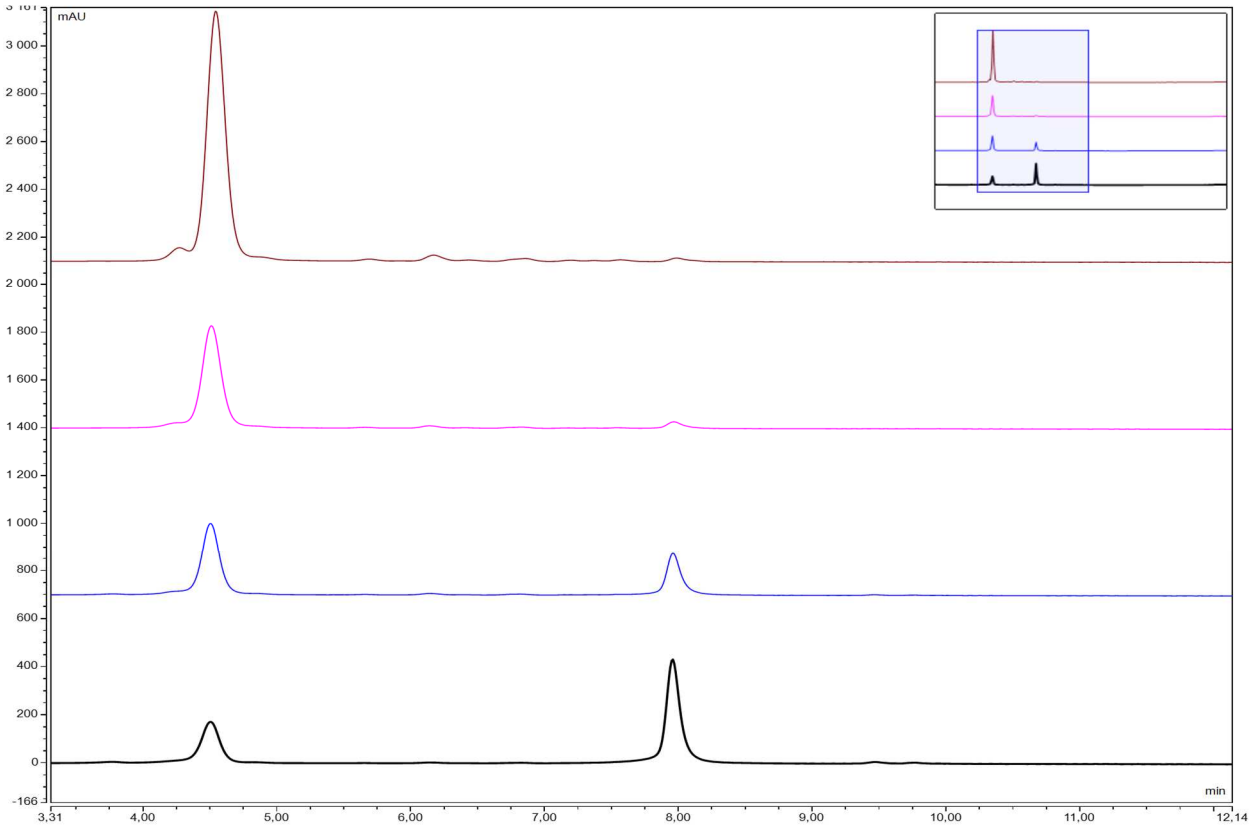


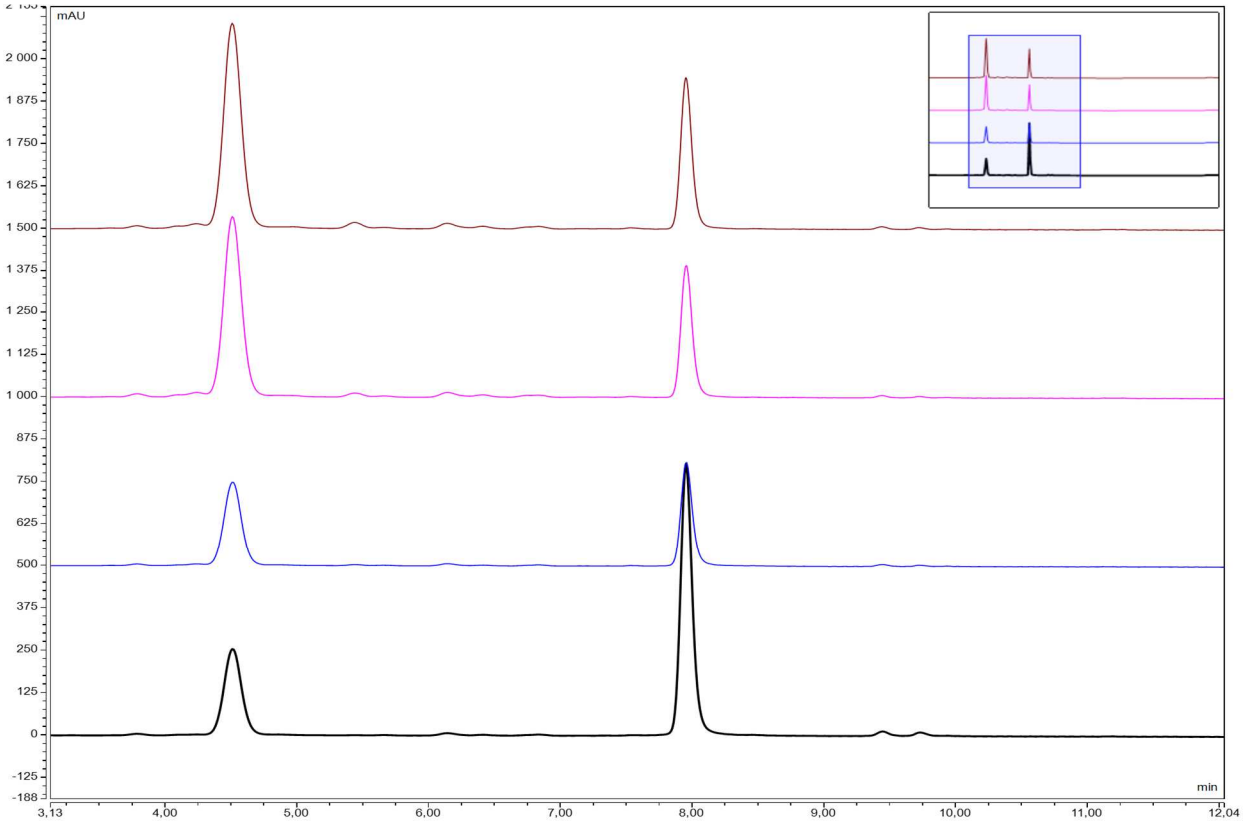
Figure S23. Selected chromatograms showing progress of quercetin (**1**) biotransformation in the cultures of entomopathogenic filamentous fungi.
Black - composition of products and unreacted substrate after the first day of biotransformation.
Blue - composition of products and unreacted substrate after the third day of biotransformation.
Pink - composition of products and unreacted substrate after the seventh day of biotransformation.
Brown - composition of products and unreacted substrate after the tenth day of biotransformation.

Retention time (t_R) of compounds **1-4**:
quercetin (**1**), t_R = 7.96 min;
7-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**2**) t_R = 4.52 min;
3-*O*-β-D-(4″-*O*-methylglucopyranosyl)-quercetin (**3**) t_R = 5.67 min;
3-*O*-β-D-(glucopyranosyl)-quercetin (**4**) t_R = 4.87 min;

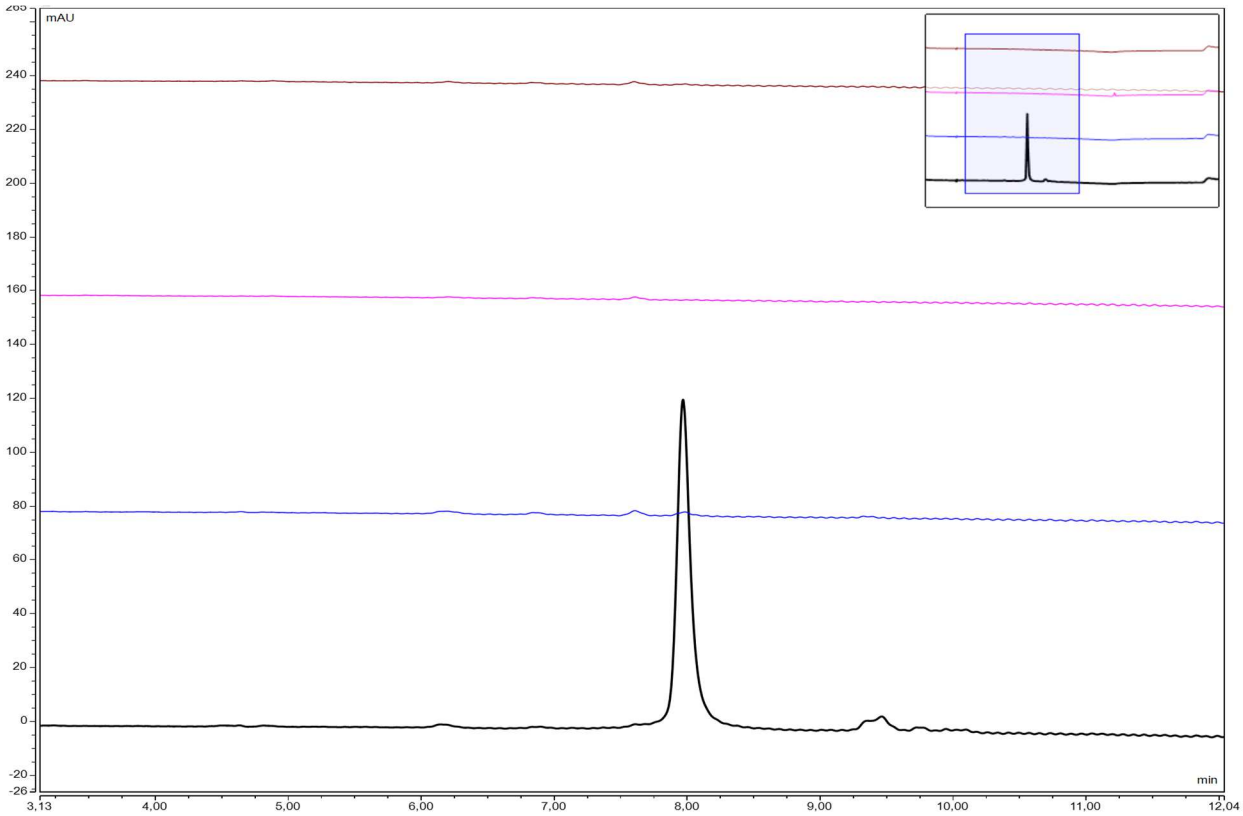
a) *Beauveria bassiana* KCh J1.5



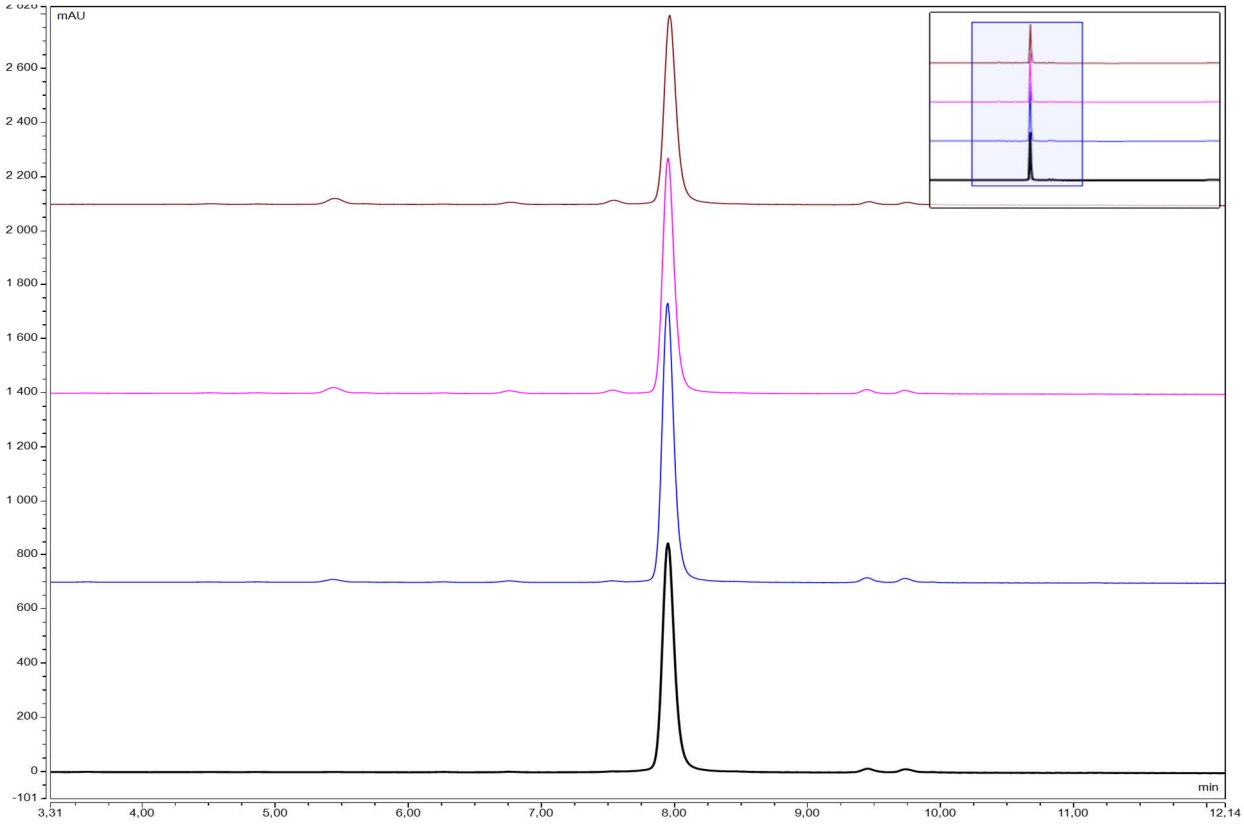
b) *Beauveria bassiana* KCh BBT



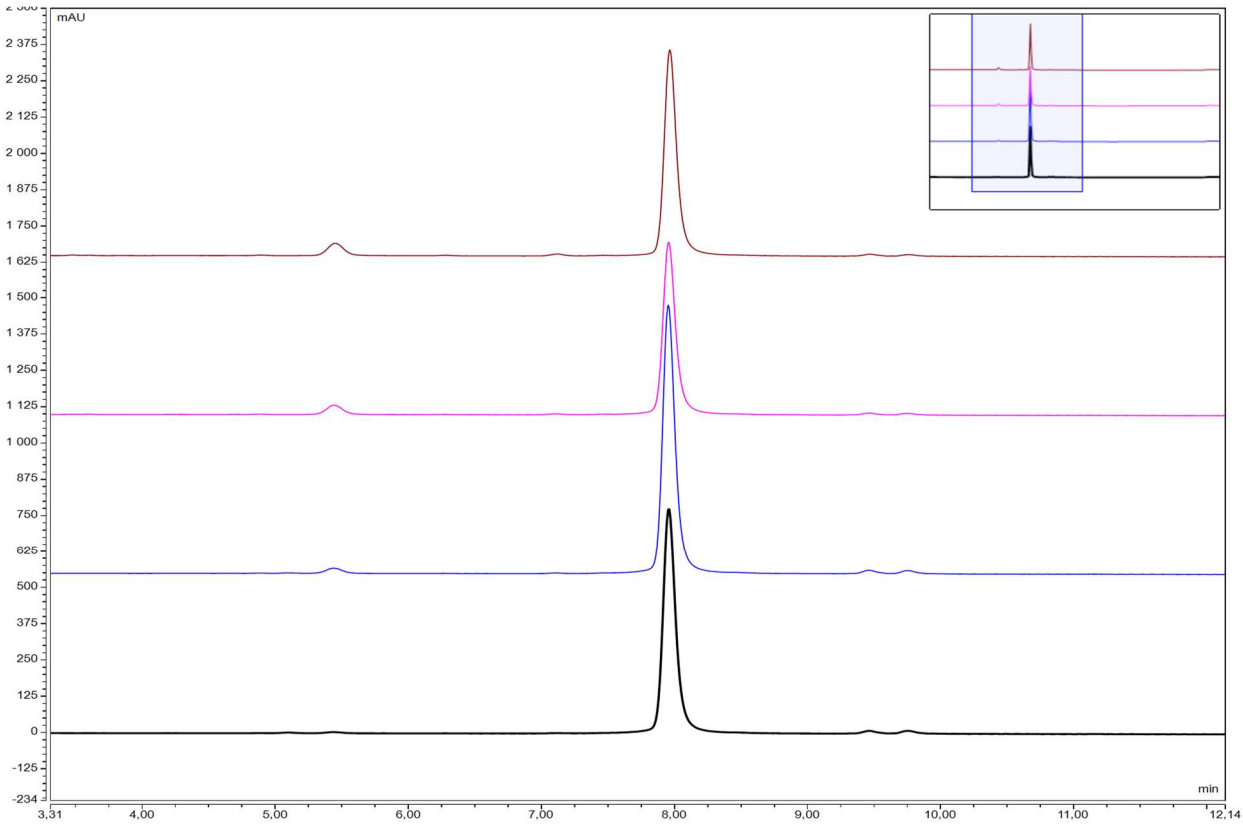
c) *Beauveria bassiana* KCh J3.2



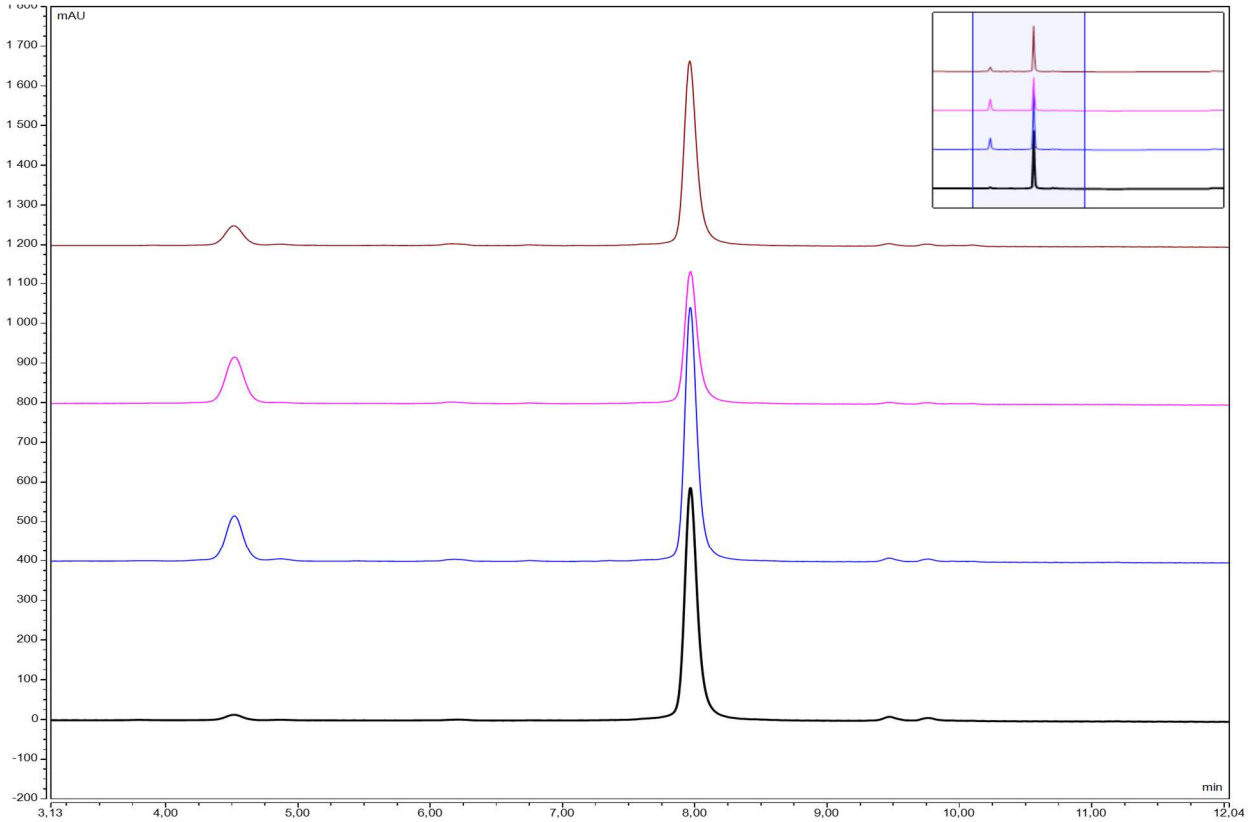
d) *Beauveria bassiana* KCh J2.1



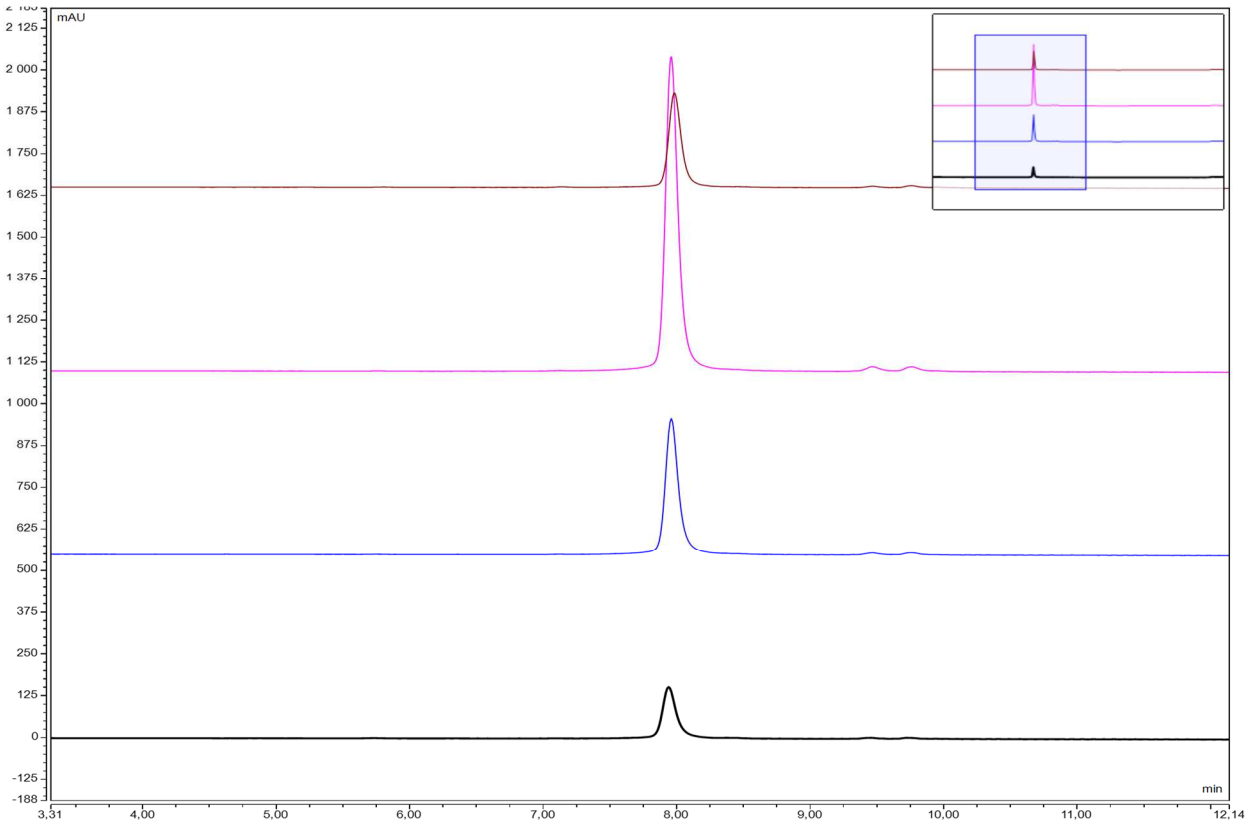
e) *Beauveria bassiana* KCh J1



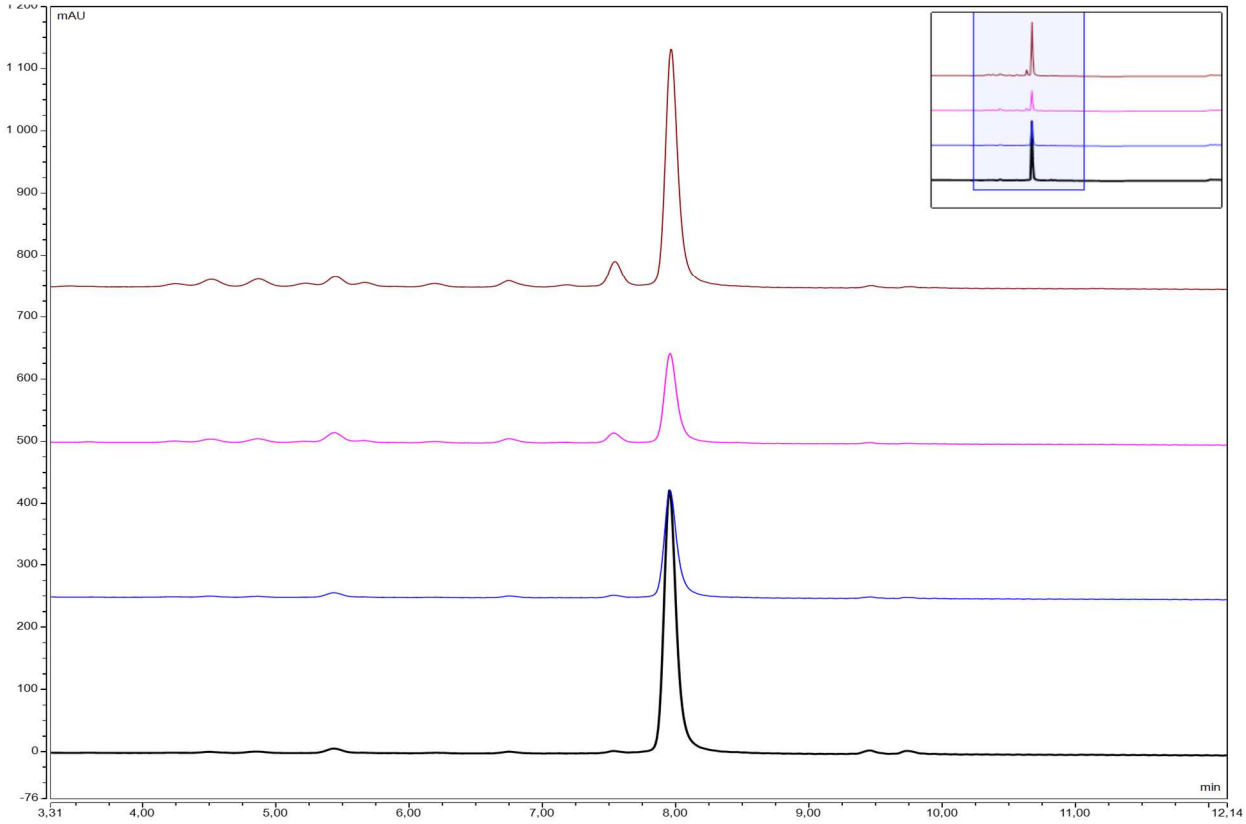
f) *Beauveria caledonica* KCh J3.3



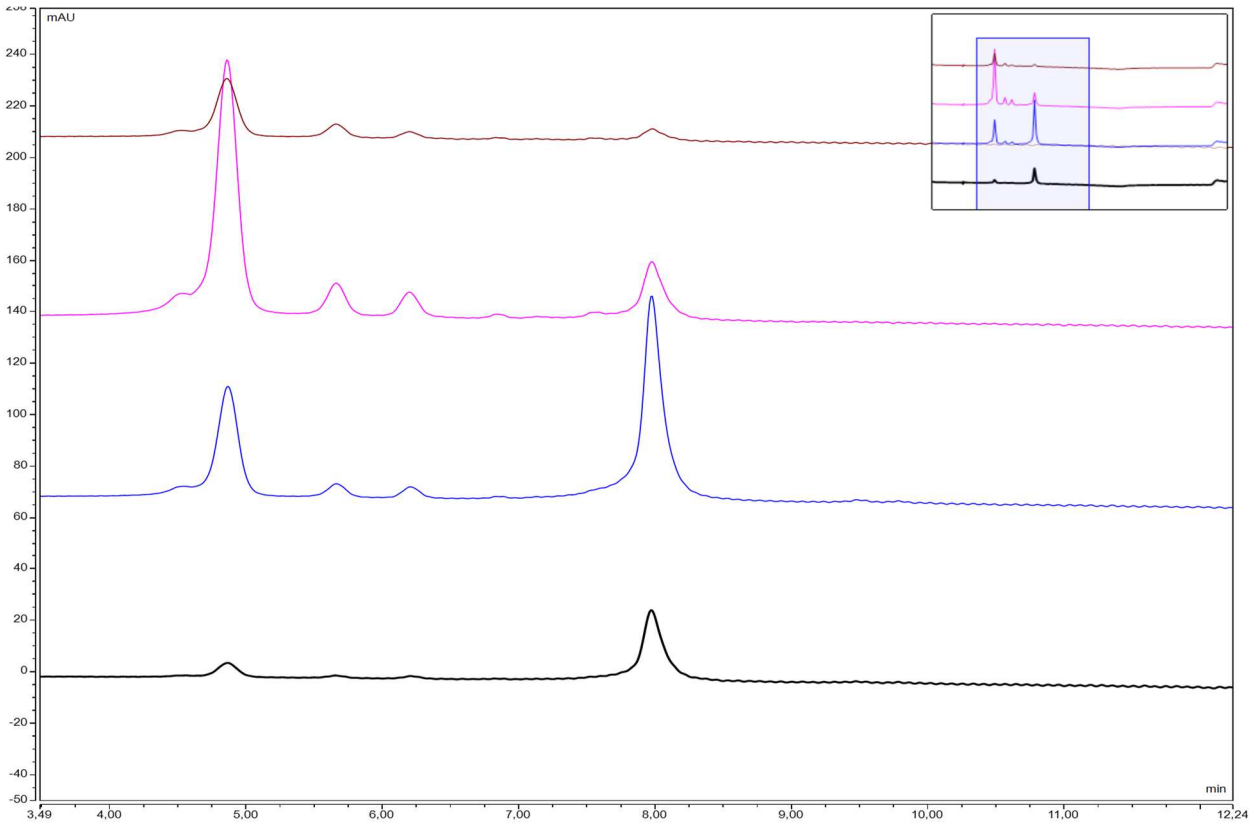
g) *Beauveria caledonica* KCh J3.4



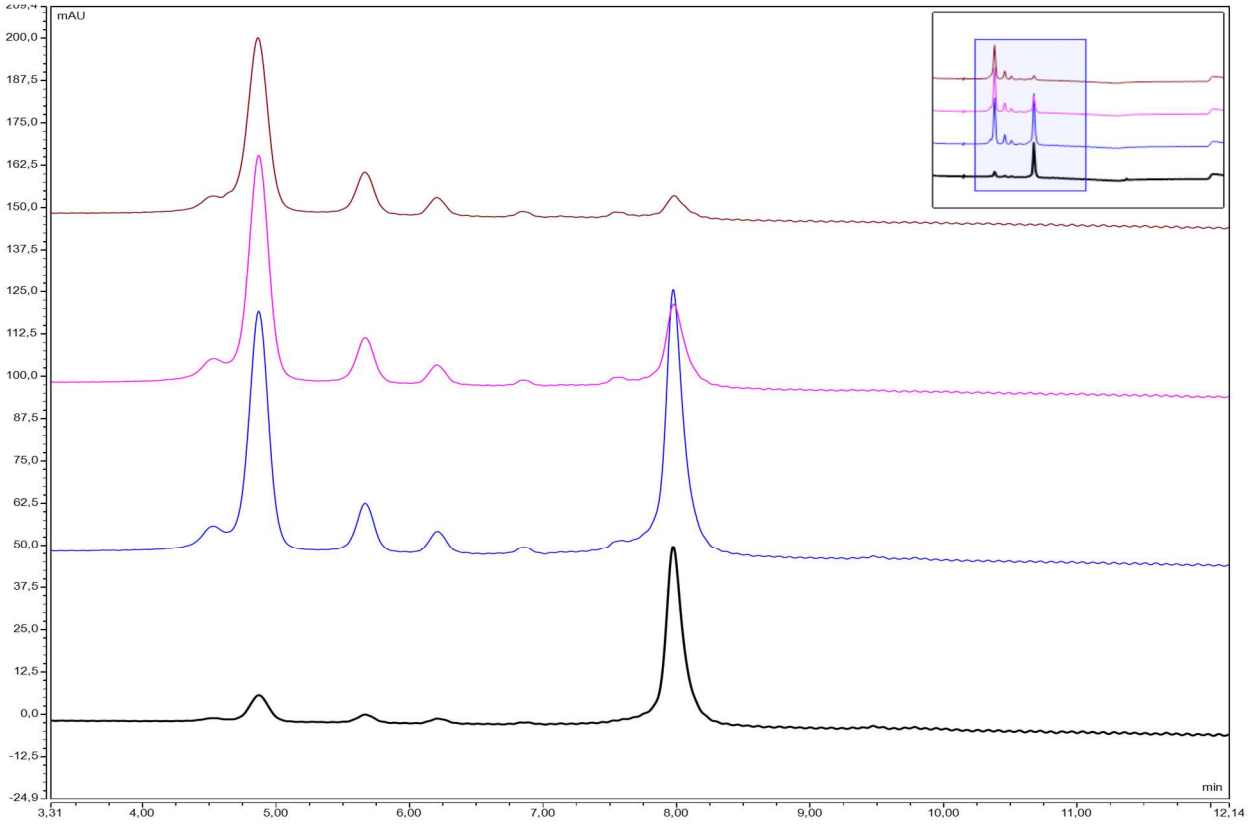
h) *Isaria farinosa* KCh KW 1.1



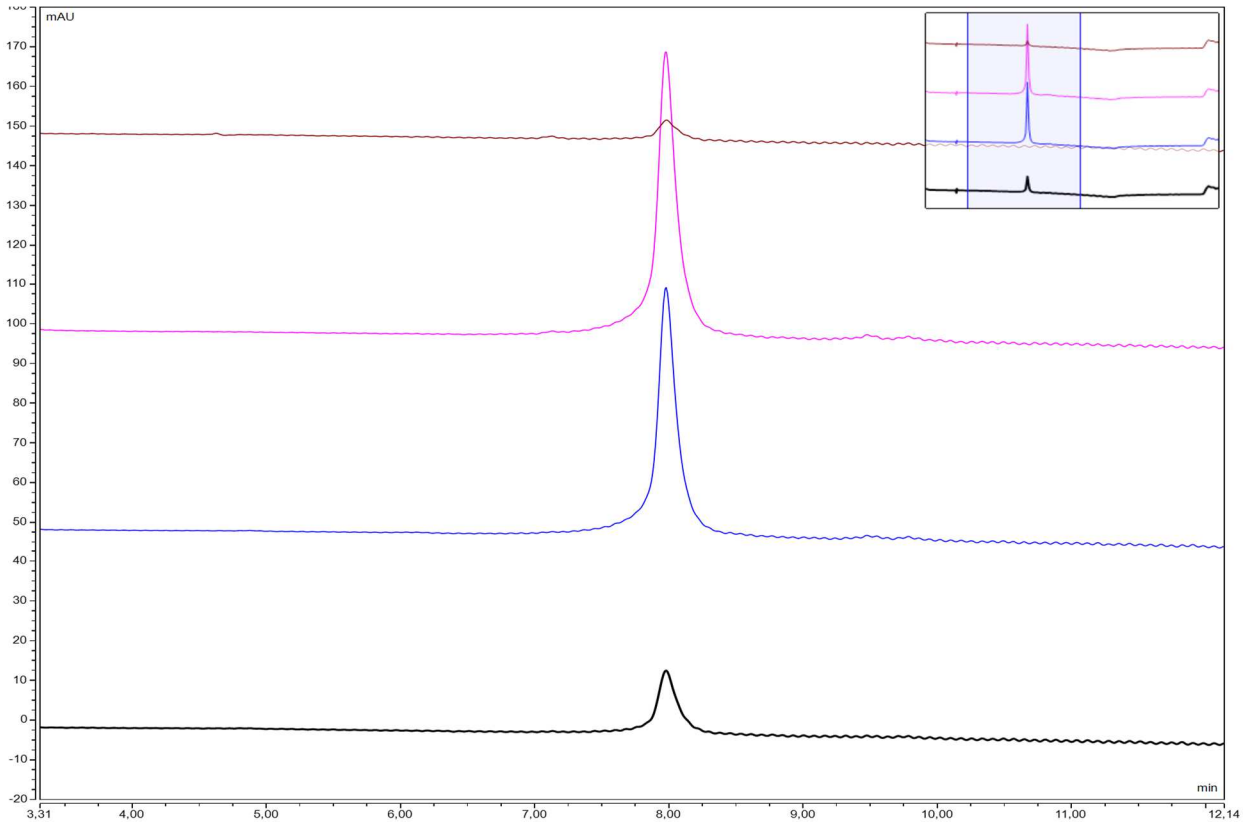
i) *Isaria tenuipes* MU35



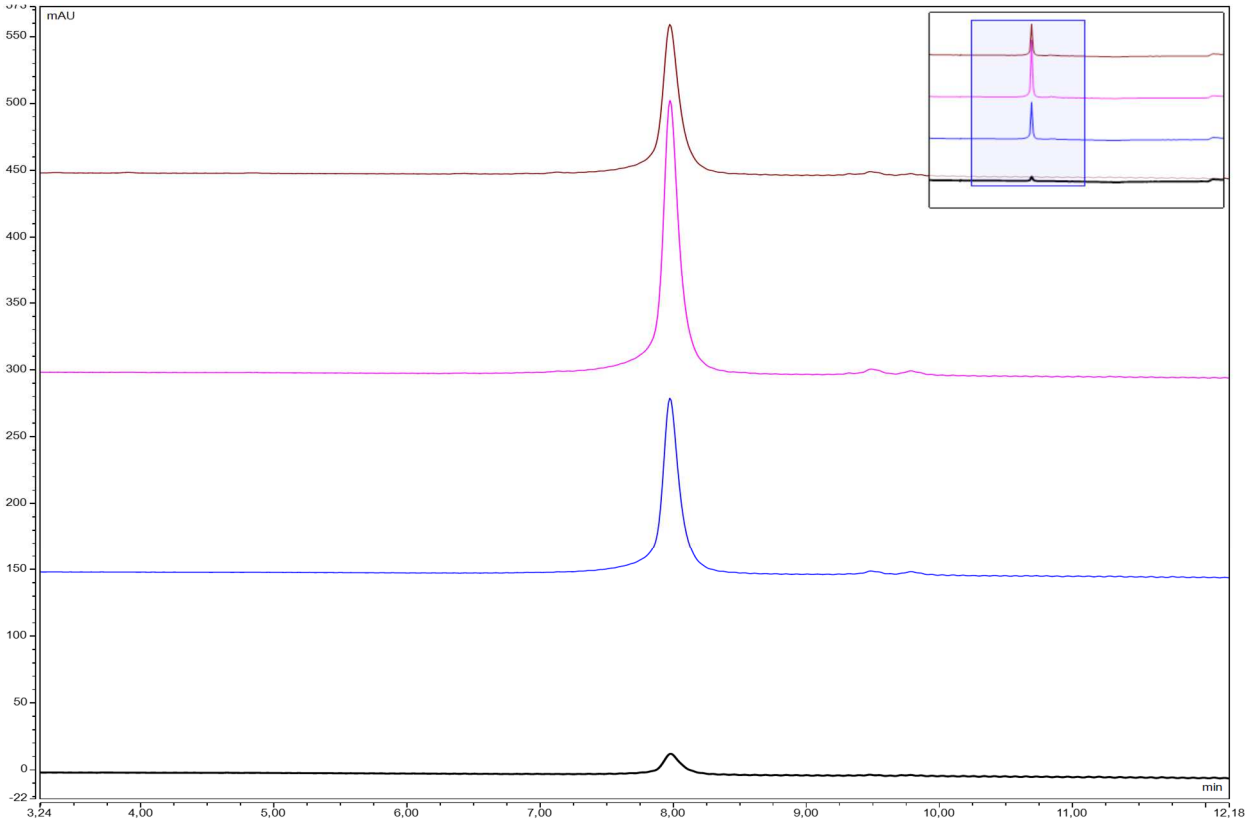
j) *Isaria tenuipes* CYS30



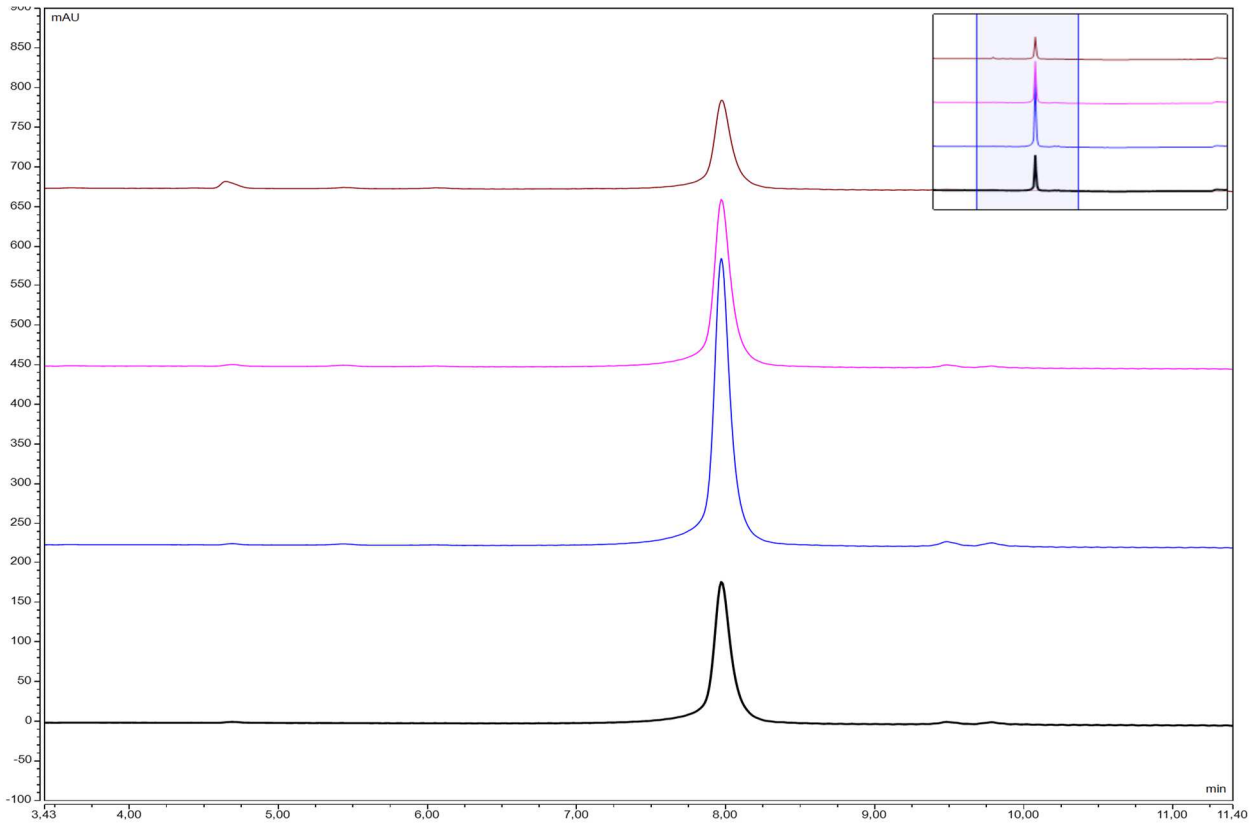
k) *Metapochonia bulbillosa* CYS17



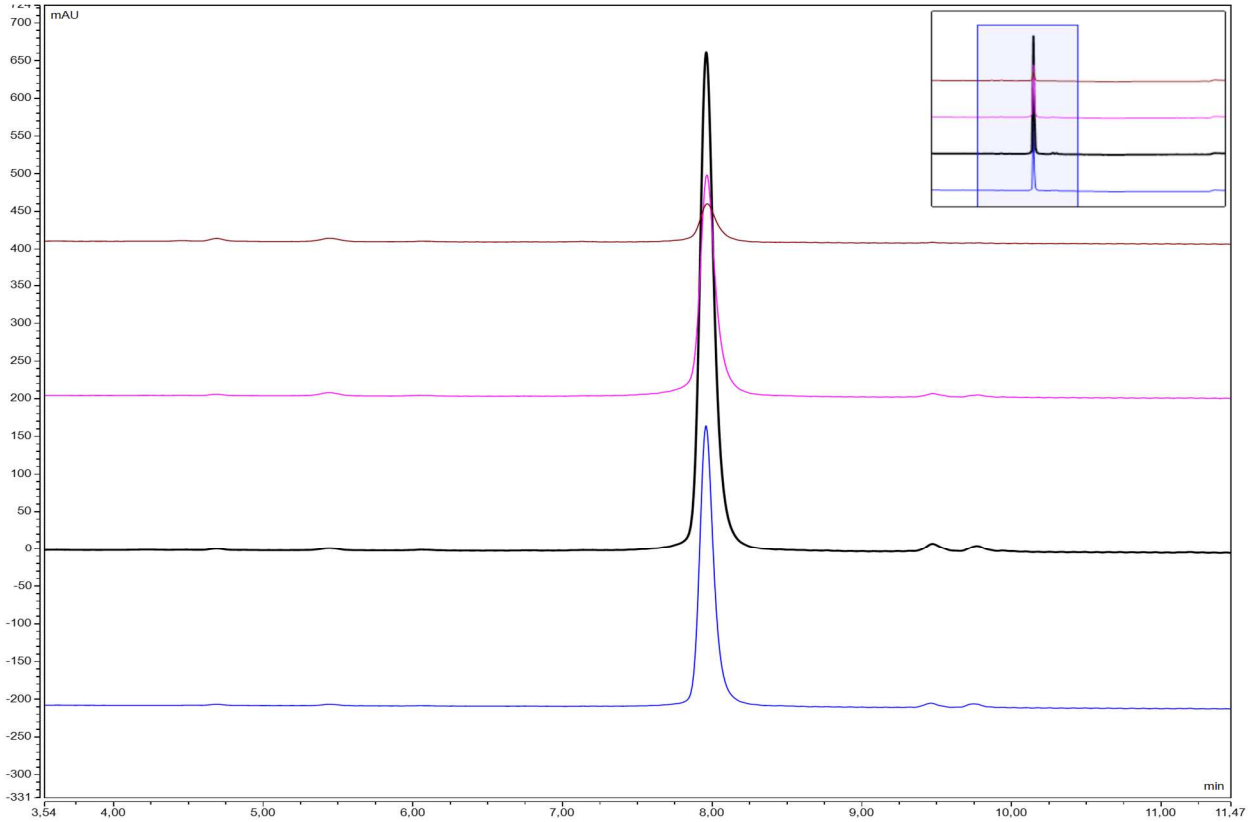
l) *Beauveria feline* ENC3



m) *Lecanicillium lecanii* DSM 63098



n) *Lecanicillium lecanii* NK3



o) *Metarhizium anisopliae* MU4

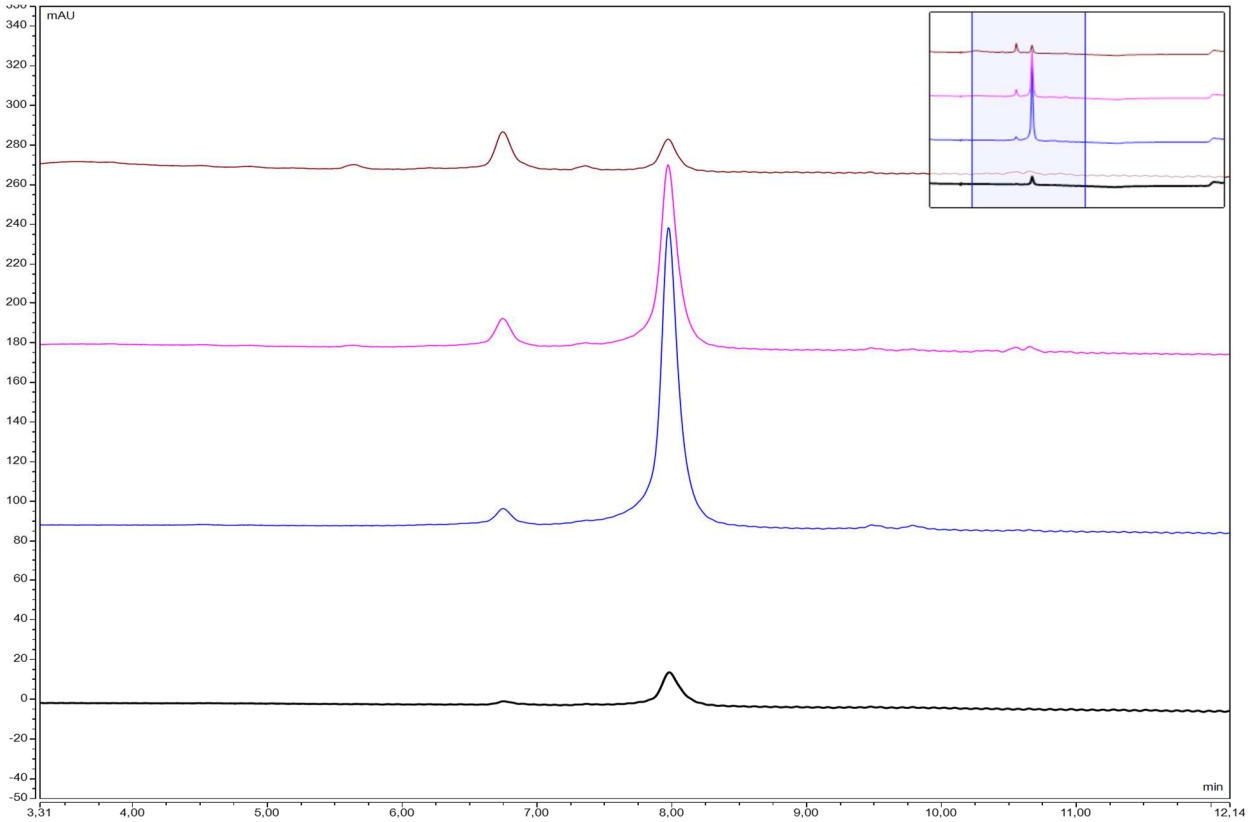


Table S2a. Microbial transformation of quercetin, HPLC conversion expressed by means and standard deviation.

Strain	Time of biotransformation [days]	Conversion [%] after 1, 3, 7 and 10 days of biotransformation				
		Substrate (1)	Products			Other products
			2	3	4	
Beauveria bassiana KCh J1.5	1	64.3 ± 3.7	35.7 ± 3.7	0 -	0 -	0 -
	3	30.2 ± 2.4	69.8 ± 2.4	0 -	0 -	0 -
	7	3.9 ± 0.3	96.1 ± 0.3	0 -	0 -	0 -
	10	0.7 ± 0.1	99.3 ± 0.1	0 -	0 -	0 -
Beauveria bassiana KCh BBT	1	68.3 ± 0.8	31.7 ± 0.8	0 -	0 -	0 -
	3	44.3 ± 2.5	55.7 ± 2.5	0 -	0 -	0 -
	7	31.9 ± 1.7	68.1 ± 1.7	0 -	0 -	0 -
	10	28.0 ± 2.5	72.0 ± 2.5	0 -	0 -	0 -
Beauveria bassiana KCh J3.2	1	95.0 ± 0.2	0 -	0 -	0 -	5.0 ± 0.2
	3	0.8 ± 0.8	4.4 ± 0.7	0 -	0 -	94.8 ± 1.5
	7	0 -	0 -	0 -	0 -	>99 -
	10	0 -	0 -	0 -	0 -	>99 -
Beauveria bassiana KCh J2.1	1	99.8 ± 0.1	0.0 -	0 -	0 -	0.2 ± 0.1
	3	98.3 ± 0.5	0.3 ± 0.2	0 -	0 -	1.4 ± 0.3
	7	95.9 ± 1.2	0.8 ± 0.3	0 -	0 -	3.4 ± 1.0
	10	91.4 ± 4.0	1.9 ± 1.2	0 -	0 -	6.7 ± 2.9
Beauveria bassiana KCh J1	1	98.7 ± 0.6	0 -	0 -	0 -	1.3 ± 0.6
	3	97.7 ± 0.7	0 -	0 -	0 -	2.3 ± 0.7
	7	96.8 ± 0.4	0 -	0 -	0 -	3.2 ± 0.5
	10	95.4 ± 0.6	0 -	0 -	0 -	4.6 ± 0.6
Beauveria caledonica KCh J3.3	1	96.9 ± 0.3	3.1 ± 0.3	0 -	0 -	0 -
	3	80.3 ± 2.4	19.6 ± 2.4	0 -	0 -	0 -
	7	67.6 ± 3.3	32.4 ± 3.3	0 -	0 -	0 -
	10	49.7 ± 4.0	13.0 ± 0.5	0 -	0 -	37.2 ± 4.1
Beauveria caledonica KCh J3.4	1	99.8 ± 0.1	0 -	0 -	0 -	0.2 ± 0.1
	3	99.6 ± 0.0	0 -	0 -	0 -	0.4 ± 0.1
	7	99.3 ± 0.2	0 -	0 -	0 -	0.7 ± 0.2
	10	99.0 ± 0.2	0 -	0 -	0 -	1.0 ± 0.2
Isaria farinosa KCh KW 1.1.	1	95.8 ± 0.9	0.4 ± 0.1	0.1 ± 0.0	0.6 ± 0.1	3.1 ± 0.8
	3	92.0 ± 1.5	1.5 ± 0.4	0.8 ± 0.3	1.9 ± 0.3	3.8 ± 0.7
	7	86.2 ± 0.1	2.9 ± 0.3	1.5 ± 0.3	3.4 ± 0.0	6.0 ± 0.3
	10	79.6 ± 0.8	2.8 ± 0.2	0.8 ± 0.1	3.5 ± 0.2	13.4 ± 0.9
Isaria tenuipes MU35	1	79.8 ± 1.6	1.7 ± 0.0	2.0 ± 0.3	16.4 ± 1.4	0 -
	3	61.0 ± 2.8	2.6 ± 0.2	3.3 ± 0.2	33.1 ± 2.4	0 -
	7	18.6 ± 5.1	4.2 ± 1.2	7.0 ± 1.1	70.2 ± 3.0	0 -
	10	10.4 ± 0.3	5.9 ± 0.9	12.1 ± 2.2	67.2 ± 0.8	4.4 ± 1.8
Isaria tenuipes CYS30	1	82.2 ± 1.6	1.5 ± 0.3	3.2 ± 0.7	13.2 ± 0.8	0 -
	3	43.3 ± 2.6	4.2 ± 0.8	6.8 ± 1.9	45.6 ± 3.4	0 -
	7	23.5 ± 6.1	5.9 ± 0.2	9.8 ± 2.1	60.8 ± 4.0	0 -
	10	11.0 ± 2.5	7.0 ± 0.8	13.1 ± 3.1	69.0 ± 1.7	0 -

Table S2b. Microbial transformation of quercetin, HPLC conversion expressed by means and standard deviation (continuation).

Strain	Time of biotransformation [days]	Conversion [%] after 1, 3, 7 and 10 days of biotransformation				
		Substrate (1)	Products			Other products
			2	3	4	
Metapochonia bulbillosa CYP17	1	98.9 ± 0.5	0 -	0 -	0 -	1.1 ± 0.5
	3	98.5 ± 0.4	0 -	0 -	0 -	1.8 ± 0.7
	7	97.0 ± 0.2	0 -	0 -	0 -	3.0 ± 0.2
	10	96.0 ± 0.6	0 -	0 -	0 -	4.0 ± 0.6
Beauveria felina ENC3	1	>99 -	0 -	0 -	0 -	<1 -
	3	>99 -	0 -	0 -	0 -	<1 -
	7	>99 -	0 -	0 -	0 -	<1 -
	10	>99 -	0 -	0 -	0 -	<1 -
Lecanicillium lecanii DSM 63098	1	>99 -	0 -	0 -	0 -	<1 -
	3	>99 -	0 -	0 -	0 -	<1 -
	7	>99 -	0 -	0 -	0 -	<1 -
	10	>99 -	0 -	0 -	0 -	<1 -
Lecanicillium lecanii NK3	1	>99 -	0 -	0 -	0 -	<1 -
	3	>99 -	0 -	0 -	0 -	<1 -
	7	>99 -	0 -	0 -	0 -	<1 -
	10	>99 -	0 -	0 -	0 -	<1 -
Metarhizium anisopliae MU4	1	96.6 ± 1.4	0 -	0 -	0 -	3.4 ± 1.4
	3	86.8 ± 6.3	0 -	0 -	0.1 ± 0.1	15.4 ± 6.8
	7	48.9 ± 8.2	0 -	0 -	0.6 ± 0.2	50.5 ± 8.2
	10	10.1 ± 2.4	0 -	0 -	4.2 ± 0.8	85.7 ± 2.5

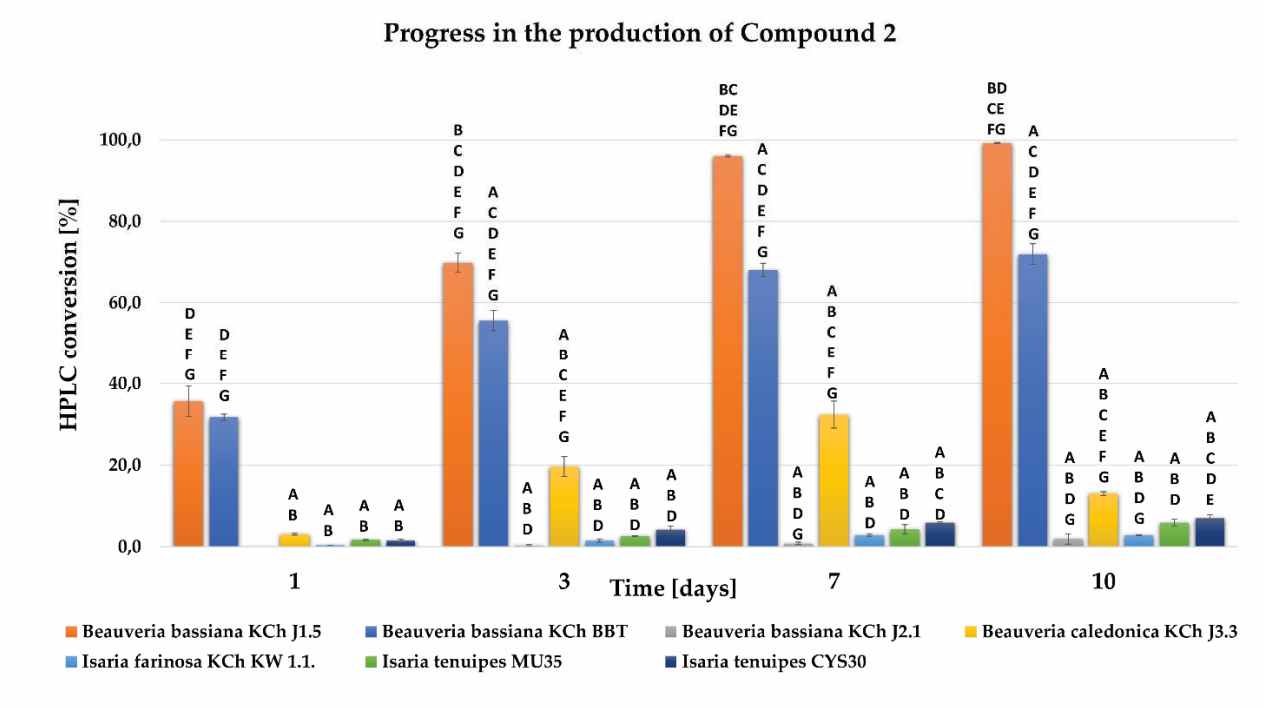


Figure S24. Progress in production of compound **2** by entomopathogenic fungi.

Statistically significant at *p* value < 0.05: **A** – vs obtaining of compound **2** by *Beauveria bassiana* KCh J1.5; **B** – vs obtaining of compound **2** by *Beauveria bassiana* KCh BBT; **C** – vs obtaining of compound **2** by *Beauveria bassiana* KCh J2.1; **D** – vs obtaining of compound **2** by *Beauveria caledonica* KCh J3.3; **E** – vs obtaining of compound **2** by *Isaria farinosa* KCh KW 1.1; **F** – vs obtaining of compound **2** by *Isaria tenuipes* MU35; **G** – vs obtaining of compound **2** by *Isaria tenuipes* CYS30

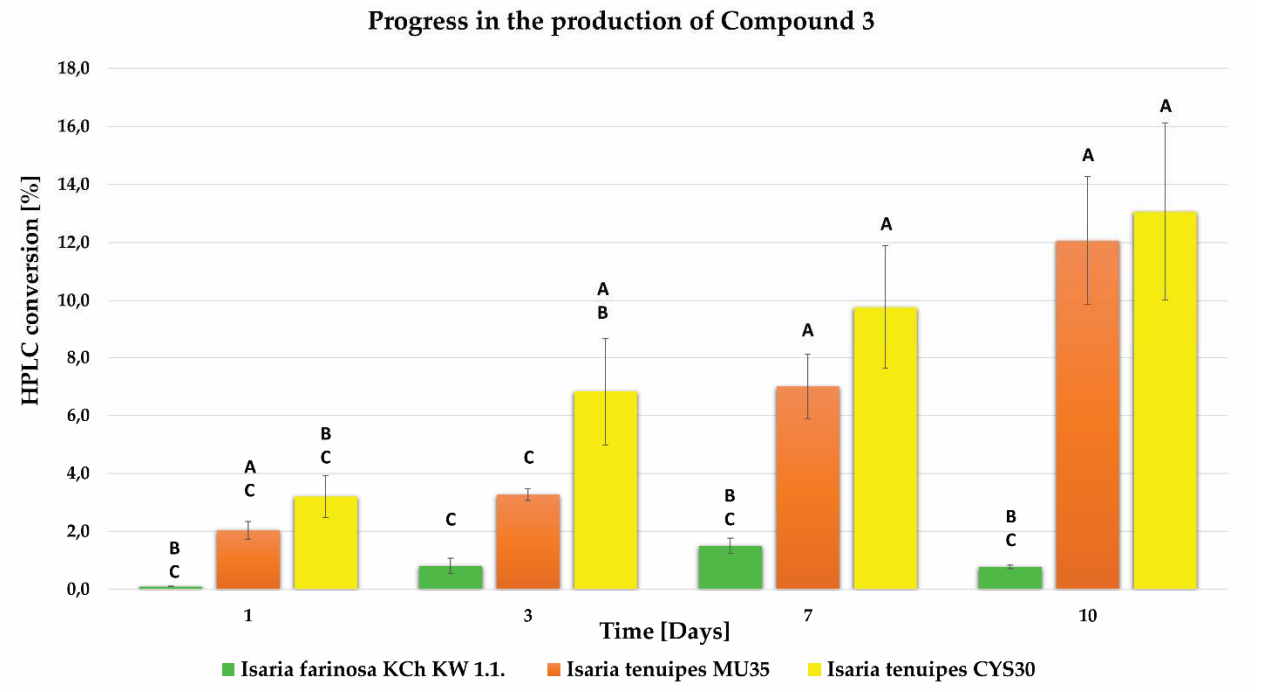


Figure S25. Progress in production of compound **3** by entomopathogenic fungi.

Statistically significant at *p* value < 0.05: **A** – vs obtaining of compound **3** by *Isaria farinosa* KCh KW 1.1; **B** – vs obtaining of compound **3** by *Isaria tenuipes* MU35; **C** – vs obtaining of compound **3** by *Isaria tenuipes* CYS30

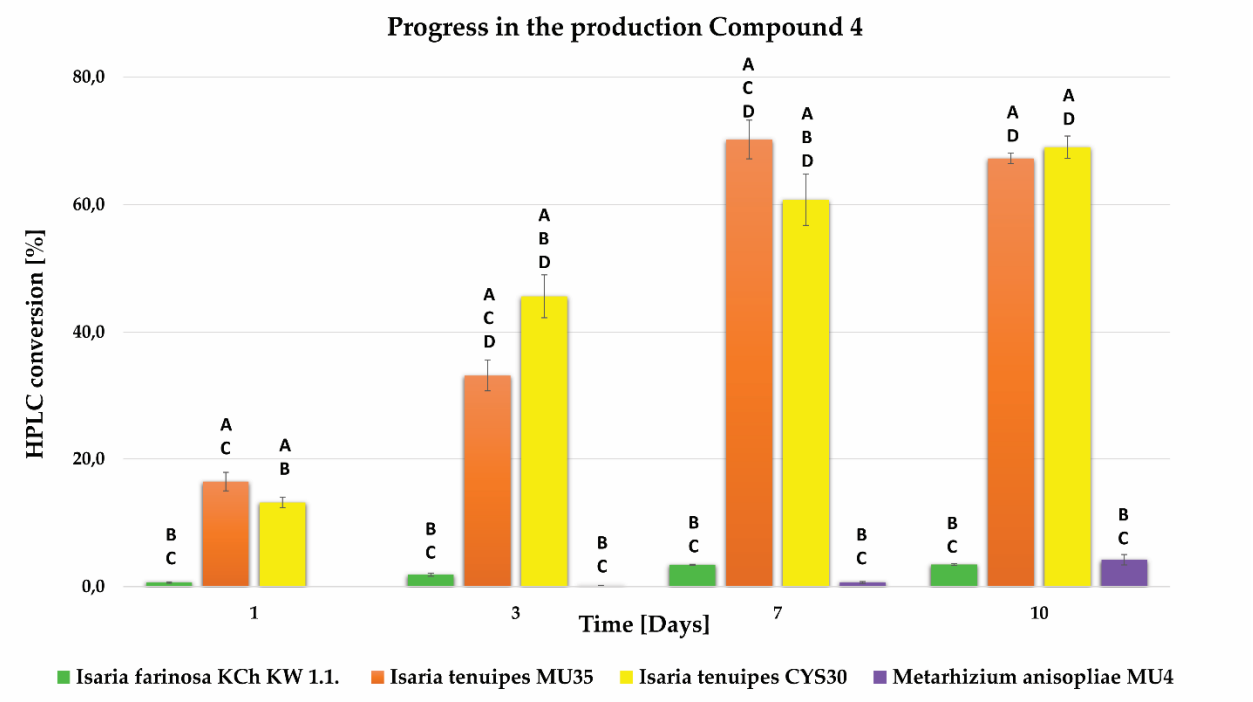


Figure S26. Progress in production of compound **4** by entomopathogenic fungi.

Statistically significant at p value < 0.05: **A** – vs obtaining of compound **4** by *Isaria farinosa* KCh KW 1.1; **B** – vs obtaining of compound **4** by *Isaria tenuipes* MU35; **C** – vs obtaining of compound **4** by *Isaria tenuipes* CYS30; **D** – vs obtaining of compound **4** by *Metarhizium anisopliae* MU4