Supplementary Information

Secondary Metabolites from an Infusion of *Lippia gracilis* Schauer Using LC-DAD-SPE/NMR Hyphenation Technique

Valéria R. S. Moraes,[a,b] Sérgio S. Thomasi,[b,c] Ricardo F. Sprenger,[b] Vilma M. J. Prado,[a] Elizangela M. O. Cruz,[d] Quezia B. Cass,[b] Antônio G. Ferreira[b] and Arie F. Blank[d]*

[a]*Departamento de Química, Universidade Federal de Sergipe, Av. Marechal Rondon s/n, 49100-000 São Cristovão-SE, Brazil*

[b]*Departamento de Química, Universidade Federal de São Carlos, Rodovia Washington Luiz, km 235, 13565-905 São Carlos-SP, Brazil*

[c]*Departamento de Química, Universidade Federal de Lavras, Av. Doutor Sylvio Menicucci, 1001, Kennedy 37200-000 Lavras-MG, Brazil*

[d]*Departamento de Agronomia, Universidade Federal de Sergipe, Av. Marechal Rondon s/n, 49100-000 São Cristovão-SE, Brazil*

*e-mail: valrsmoraes@uol.com.br

Table S1. ^{1}H NMR (600 MHz, CD_3OD) and ^{13}C NMR data [deduced by HSQC (heteronuclear single-quantum correlation) and HMBC (heteronuclear multiple-bond correlation)] for orientin **1**. Chemical shifts (δ, ppm) and coupling constants (J, Hz, in parenthesis)

Carbon	HSQC		HMBC		
	δ_C	δ_H	$^{2}J_{CH}$	$^{3}J_{CH}$	$^{4}J_{CH}$
2	168.2	–	6.54	7.56, 7.52	–
3	104.9	6.54 (s)		–	–
4	185.5	–	6.54	–	6.27
5	164.0	–	6.27	–	–
6	100.5	6.27 (s)	–	–	–
7	165.9	–	6.27	4.98	–
8	106.6	–	4.98	4.11	–
9	159.4	–	–	4.98	–
10	107.1	–	–	6.54 and 6.27	–
1’	125.6	–	–	6.91 and 6.54	–
2’	116.4	7.56 (s)	–	7.52	–
3’	148.4	–	7.56	6.91	–
4’	152.4	–	6.91	7.56, 7.52	–
5’	119.6	6.91 (d, 8.13)	–	–	–
6’	122.4	7.52 (d, 8.13)	–	7.56	–
1”	76.8	4.98 (d, 9.6)	4.11	–	–
2”	74.0	4.11 (t, 9.6)	4.98, 3.53	–	–
3”	81.8	3.53 (m)	4.11, 3.68	4.98	–
4”	78.1	3.68 (m)	–	4.11	–
5”	84.4	–	3.68	4.98	–
6”	64.8	3.97 (d, 12.7) 3.85 (m)	–	3.68	–

Table S2. ^{1}H NMR (600 MHz, CD_3OD) and ^{13}C NMR data [deduced by HSQC (heteronuclear single-quantum correlation) and HMBC (heteronuclear multiple-bond correlation)] for isoorientin **2**. Chemical shifts (δ, ppm) and coupling constants (J, Hz, in parenthesis)

Carbon	HSQC		HMBC	
	δ_C	δ_H	$^{2}J_{CH}$	$^{3}J_{CH}$
2	167.8	–	6.56	7.39
3	105.2	6.56 (s)	–	–
4	185.1	–	–	–
5	163.4	–	–	4.90
6	110.4	–	4.90	6.51
7	166.6	–	6.51	4.90
8	96.6	6.51 (s)	–	–
9	160.0	–	6.51	–
10	106.5	–	–	6.56 and 6.51
1’	125.0	–	–	6.91 and 6.56
2’	115.5	7.38 (s)	–	7.39
3’	148.3	–	7.38	6.91
4’	152.4	–	6.91	7.39
5’	118.1	6.91 (d, 8.3)	–	–
6’	121.5	7.39 (d, 8.3)	–	7.38
1”	76.5	4.90 (d, 9.5)	–	–
2”	73.8	4.16 (t, 9.5)	4.90	–
3”	81.3	3.48 (m)	4.16 and 3.48	4.90
4”	72.9	3.48 (m)	3.48	3.87
5”	83.7	3.42 (m)	3.74	–
6”	64.2	3.87 (dd, 2.2 and 12.2) 3.74 (dd, 5.4 and 12.2)	–	–

Table S3. ^{1}H NMR (600 MHz, CD_3OD) and ^{13}C NMR data [deduced by HSQC (heteronuclear single-quantum correlation) and HMBC (heteronuclear multiple-bond correlation)] for luteolin-4'-*O*-β-glucopyranoside **3**. Chemical shifts (δ, ppm) and coupling constants (J, Hz, in parenthesis)

Carbon	HSQC		HMBC	
	δ_C	δ_H	$^{2}J_{CH}$	$^{3}J_{CH}$
2	167.1	–	6.61	7.47, 7.46
3	106.4	6.61 (s)	–	–
4	185.1	–	6.61	–
5	164.9	–	6.22	–
6	101.6	6.22 (d, 2.1)	–	6.46
7	161.0	–	6.46	–
8	96.4	6.46 (d, 2.1)	–	6.22
9	NO	–	–	–
10	NO	–	–	–
1'	128.8	–	–	7.33
2'	116.1	7.46 (m)	–	7.47
3'	150.2	–	7.46	7.33
4'	151.2	–	7.33	7.47, 7.46, 4.94
5'	119.3	7.33 (d, 8.4)	7.47	–
6'	121.0	7.47 (d, 8.4)	7.33	7.46
1"	104.5	4.94 (d, 7.5)	3.55	–
2"	76.1	3.55 (m)	3.50	–
3"	79.0	3.50 (m)	3.55	–
4"	72.6	3.43 (m)	–	3.93
5"	79.4	3.50 (m)	3.74, 3.43	–
6"	63.8	3.93 (dd, 2.3 and 12.0) 3.74 (dd, 5.6 and 12.0)	–	3.43

NO: not observed.

Table S4. ^{1}H NMR (600 MHz, CD_3OD) and ^{13}C NMR data [deduced by HSQC (heteronuclear single-quantum correlation) and HMBC (heteronuclear multiple-bond correlation)] for carvacrol 2-*O*-β-glucopyranoside **4**. Chemical shifts (δ, ppm) and coupling constants (J, Hz, in parenthesis)

Carbon	HSQC		HMBC	
	δ_C	δ_H	$^{2}J_{CH}$	$^{3}J_{CH}$
1	127.4	–	7.01, 2.22	7.00, 6.78
2	158.5	–	–	7.01, 4.86, 2.22
3	115.5	7.00 (d, 1.8)	–	6.78, 2.84
4	150.4	–	2.84	7.01, 1.22
5	122.2	6.78 (dd, 8.0 and 1.8)	7.01	7.00, 2.84
6	132.5	7.01 (d, 8.0)	–	2.22
7	17.5	2.22 (s)	–	7.01
8	36.5	2.84 (sept, 6.9)	1.22	7.00, 6.78
9	25.8	1.22 (d, 6.9)	2.84	–
10	25.8	1.22 (d, 6.9)	2.84	–
1´	103.9	4.86 (d, 7.6)	3.47	–
2´	76.2	3.47 (m)	3.40	–
3´	79.3	3.40 (m)	3.47	–
4´	72.8	3.47 (m)	3.40	3.47
5´	79.3	3.48	3.69, 3.47	3.40
6´	63.9	3.88 (dd, 11.9 and 2.0) 3.69 (dd, 11.9 and 5.5)	–	–

Table S5. ^{1}H NMR (600 MHz, CD_3OD) and ^{13}C NMR data [deduced by HSQC (heteronuclear single-quantum correlation) and HMBC (heteronuclear multiple-bond correlation)] for 5,7,3',5'-tetrahydroxy flavanone **5**. Chemical shifts (δ, ppm) and coupling constants (J, Hz, in parenthesis)

Carbon	HSQC		HMBC	
	δ_C	δ_H	$^{2}J_{CH}$	$^{3}J_{CH}$
2	81.7	5.28 (dd, 12.7 and 3.1)	3.07	6.79
3	45.4	3.07 (dd, 17.1 and 12.7), 2.70 (dd, 17.1 and 3.1)	–	–
4	199.2	–	3.07, 2.70	–
5	NO	–	–	–
6	98.3	5.87 (d, 2.2)	–	5.89
7	166.4	–	5.87	–
8	97.4	5.89 (d, 2.2)	–	–
9	NO	–	–	–
10	104.9	–	–	5.87
1'	133.4	–	6.79	–
2'	117.5	6.79 (d, 1.7)	–	–
3'	148.3	–	6.91	–
4'	115.8	6.91 (d, 1.7)	–	6.79
5'	148.2	–	6.79	–
6'	120.4	6.79 (d, 1.7)	–	6.91

NO: not observed.

Table S6. ^{1}H NMR (600 MHz, CD_3OD) and ^{13}C NMR data [deduced by HSQC (heteronuclear single-quantum correlation) and HMBC (heteronuclear multiple-bond correlation)] for naringenin **6**. Chemical shifts (δ, ppm) and coupling constants (J, Hz, in parenthesis)

Carbon	HSQC		HMBC	
	δ_C	δ_H	$^2J_{CH}$	$^3J_{CH}$
2	81.8	5.34 (dd, 13.0 and 3.0)	3.11	7.32
3	45.5	3.11 (dd, 17.1 and 13.0) 2.69 (dd, 17.1 and 3.0)	–	–
4	NO	–	–	–
5	NO	–	–	–
6	98.2	5.87 (d, 2.2)	–	–
7	NO	–	–	–
8	97.5	5.89 (d, 2.2)	–	–
9	NO	–	–	–
10	NO	–	–	–
1’	132.5	–	–	6.82
2’/6’	130.3	7.32 (d, 8.7)	–	–
3’/5’	117.6	6.82 (d, 8.7)	–	–
4’	160.1	–	–	7.32

NO: not observed.

Table S7. ^{1}H NMR (600 MHz, CD_3OD) and ^{13}C NMR data [deduced by HSQC (heteronuclear single-quantum correlation) and HMBC (heteronuclear multiple-bond correlation)] for carvacrol **7**. Chemical shifts (δ, ppm) and coupling constants (J, Hz, in parenthesis)

Carbon	HSQC		HMBC	
	δ_C	δ_H	$^2J_{CH}$	$^3J_{CH}$
1	124.1	–	2.12	6.59, 6.61
2	157.7	–	–	6.93, 2.12
3	114.8	6.61 (d, 1.7)	–	6.59, 2.76
4	150.3	–	2.76	6.93, 1.19
5	119.6	6.59 (dd, 7.4 and 1.7)	–	6.61, 2.76
6	132.8	6.93 (dd, 7.4 and 0.5)	–	2.12
7	17.1	2.12 (s)	–	6.93
8	36.4	2.76 (sept, 7.0)	1.19	6.59, 6.61
9	25.9	1.19 (d, 7.0)	2.76	–
10	25.9	1.19 (d, 7.0)	2.76	–

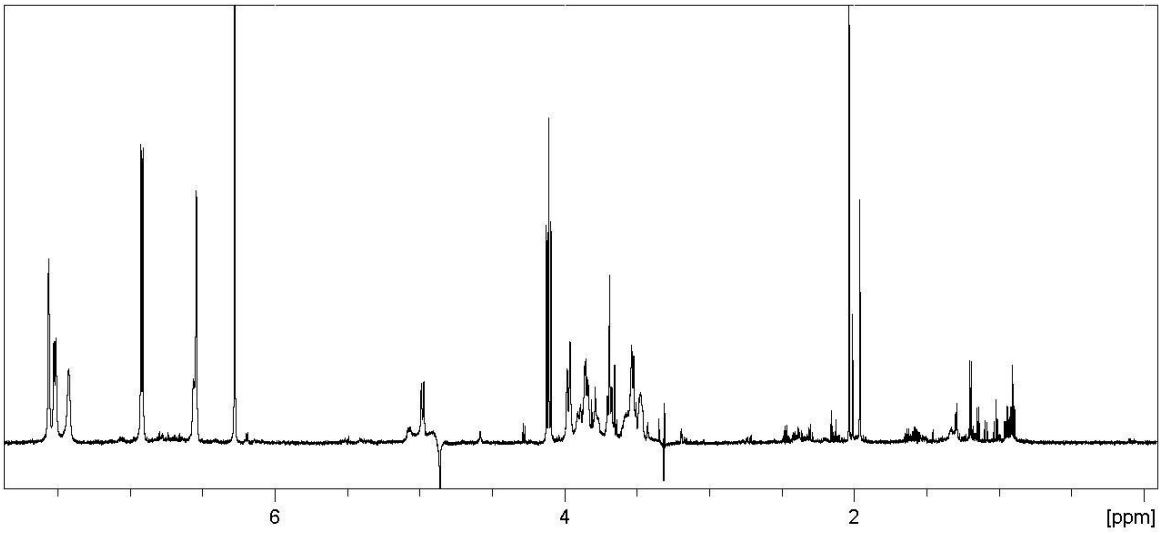

Figure S1. ^{1}H NMR spectrum (600 MHz, methanol-d_4) of orientin **1**.

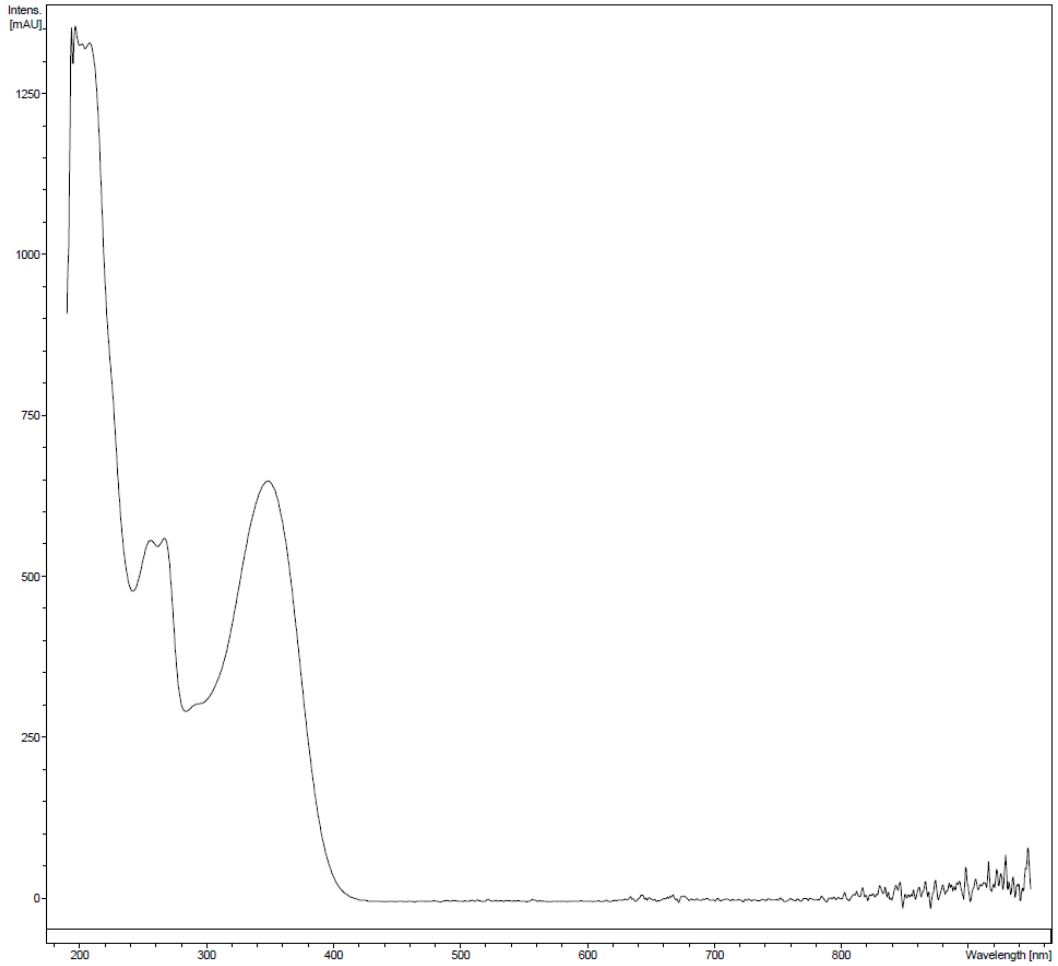

Figure S2. UV spectrum of orientin **1**.

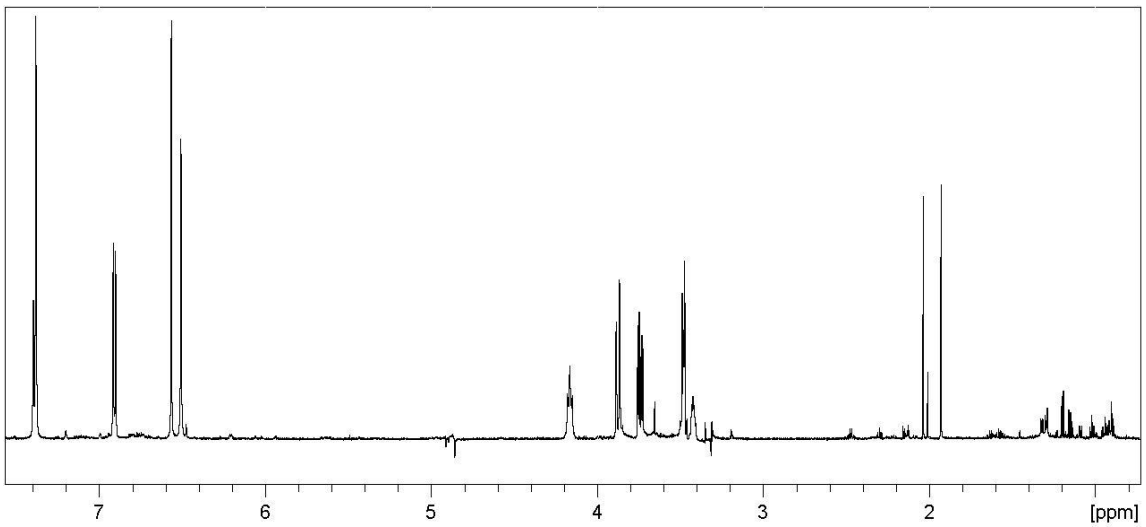

Figure S3. ^{1}H NMR spectrum (600 MHz, methanol-d_4) of isoorientin **2**.

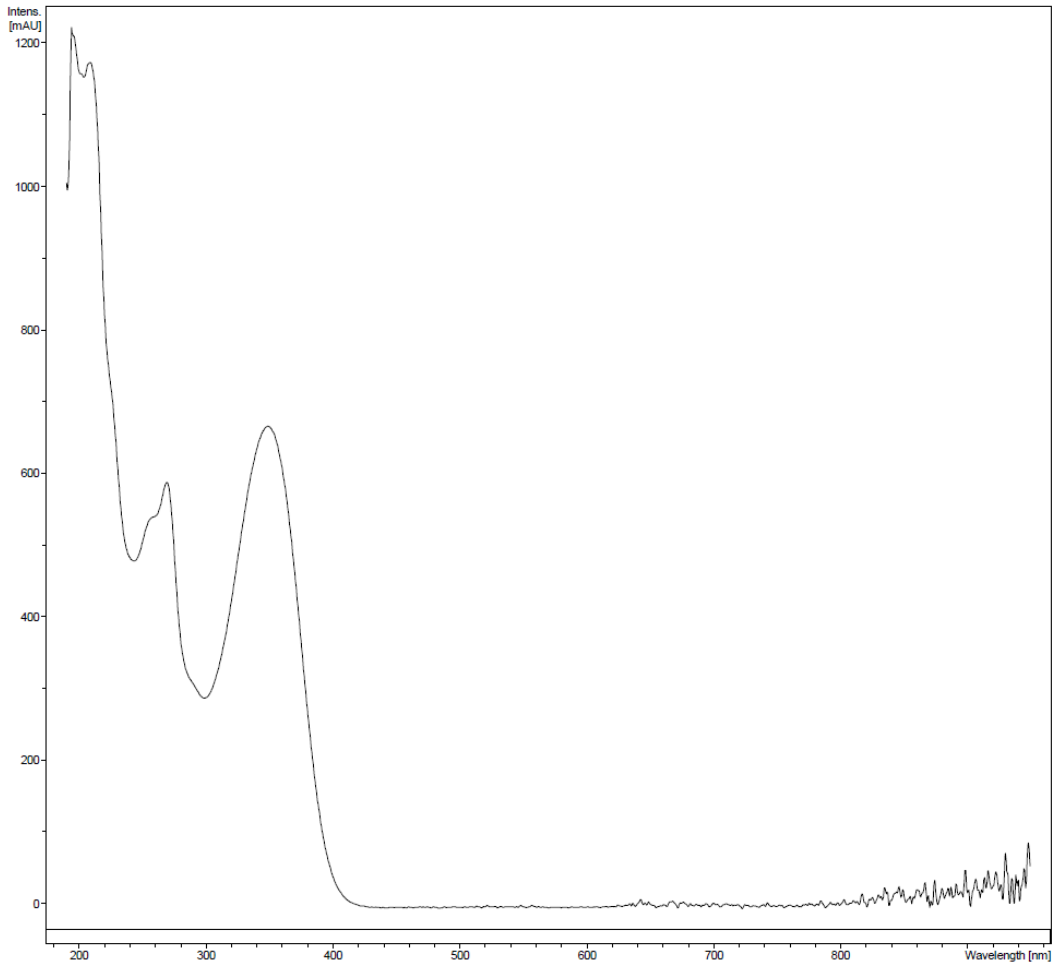

Figure S4. UV spectrum of isoorientin **2**.

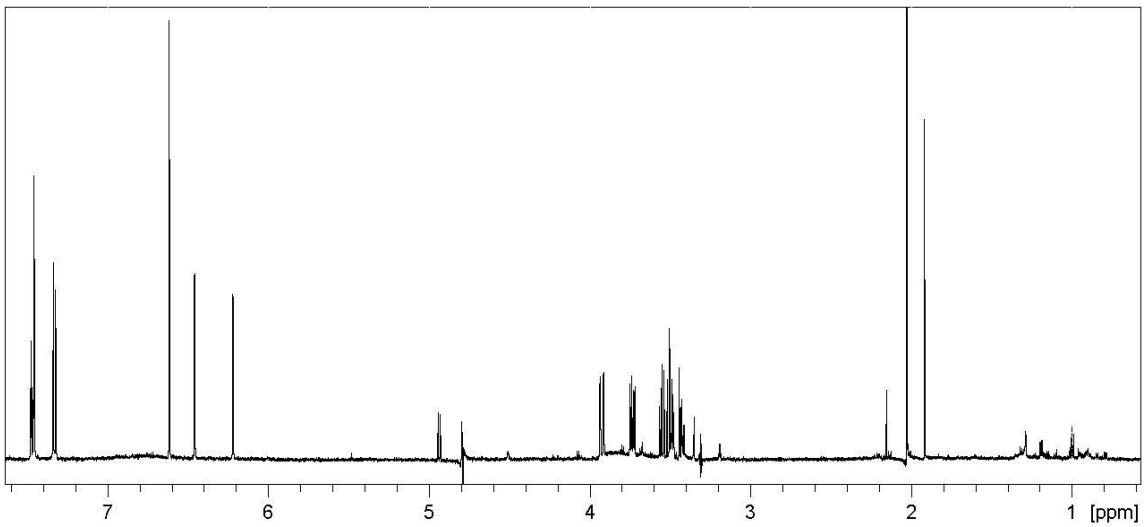

Figure S5. ^{1}H NMR spectrum (600 MHz, methanol-d_4) of 4'-*O*-β-glucopyranosyl luteolin **3**.

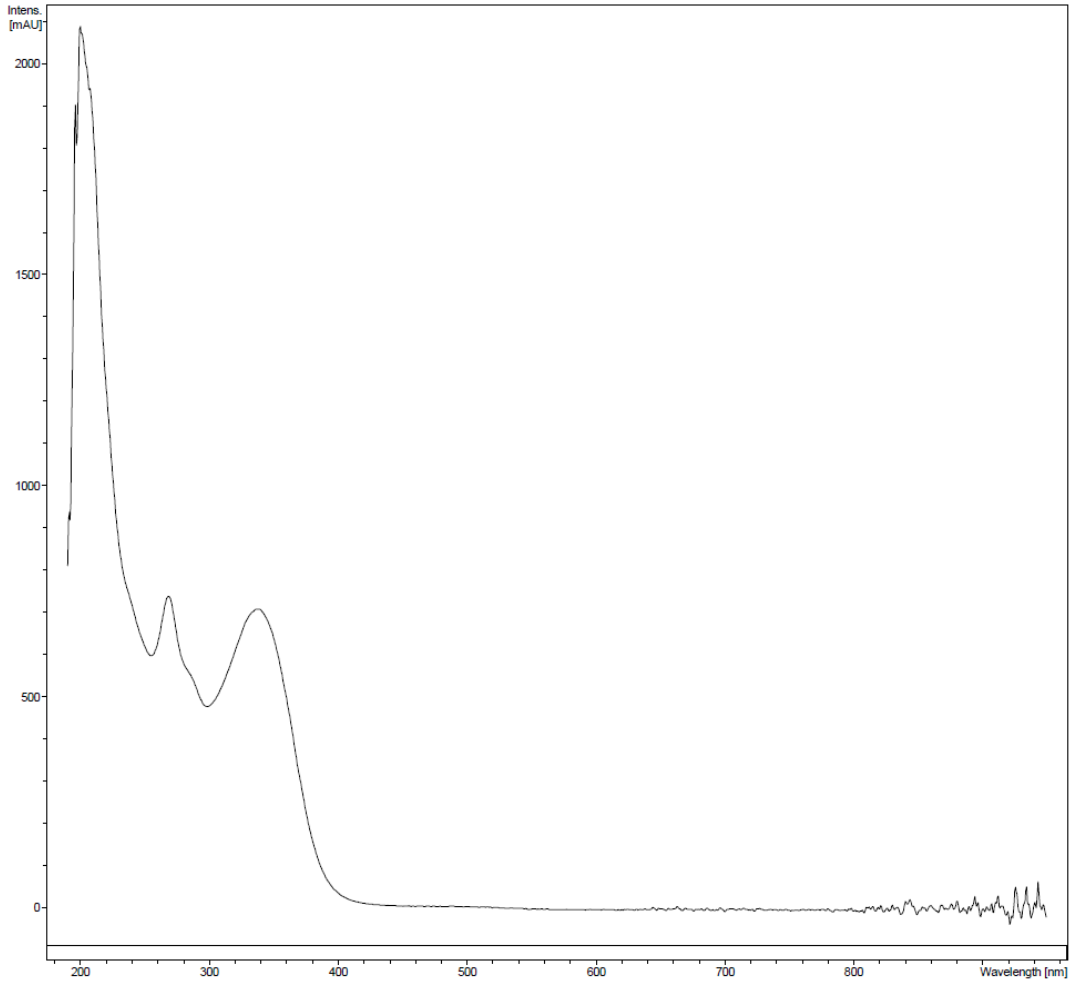

Figure S6. UV spectrum of 4'-*O*-β-glucopyranosyl luteolin **3**.

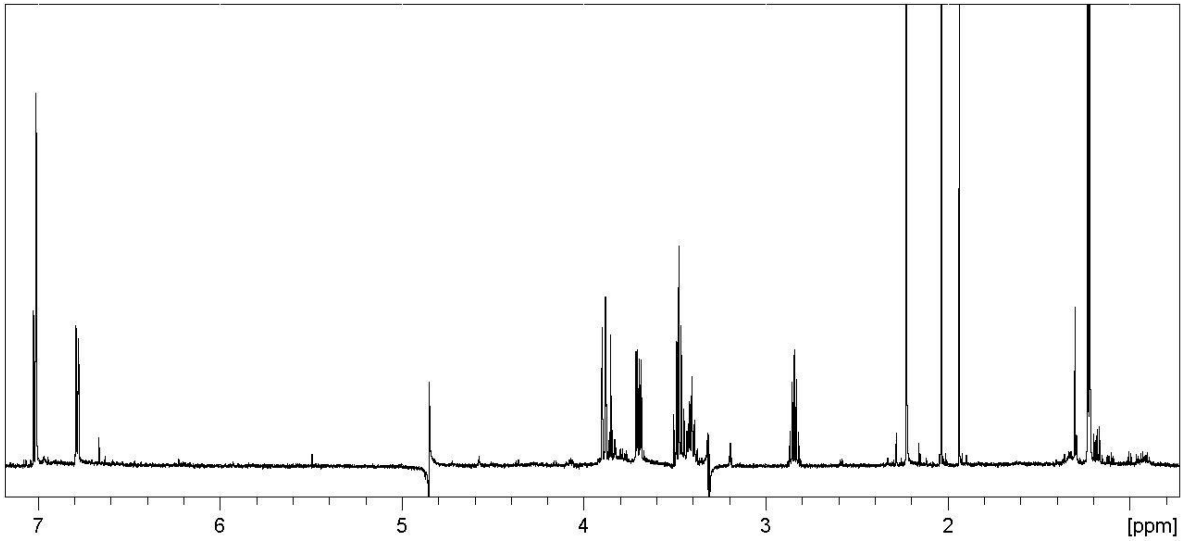

Figure S7. ^{1}H NMR spectrum (600 MHz, methanol-d_4) of 2-*O*-β-glucopyranosyl carvacrol **4**.

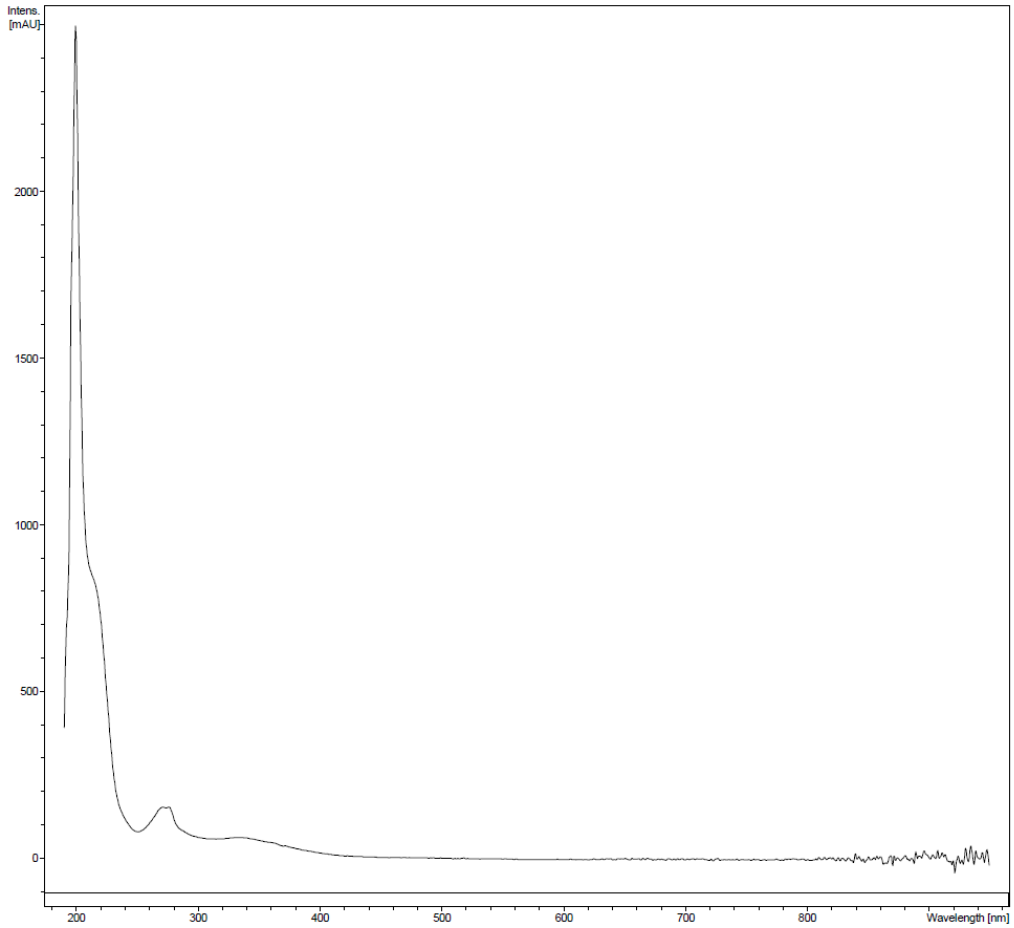

Figure S8. UV spectrum of 2-*O*-β-glucopyranosyl carvacrol **4**.

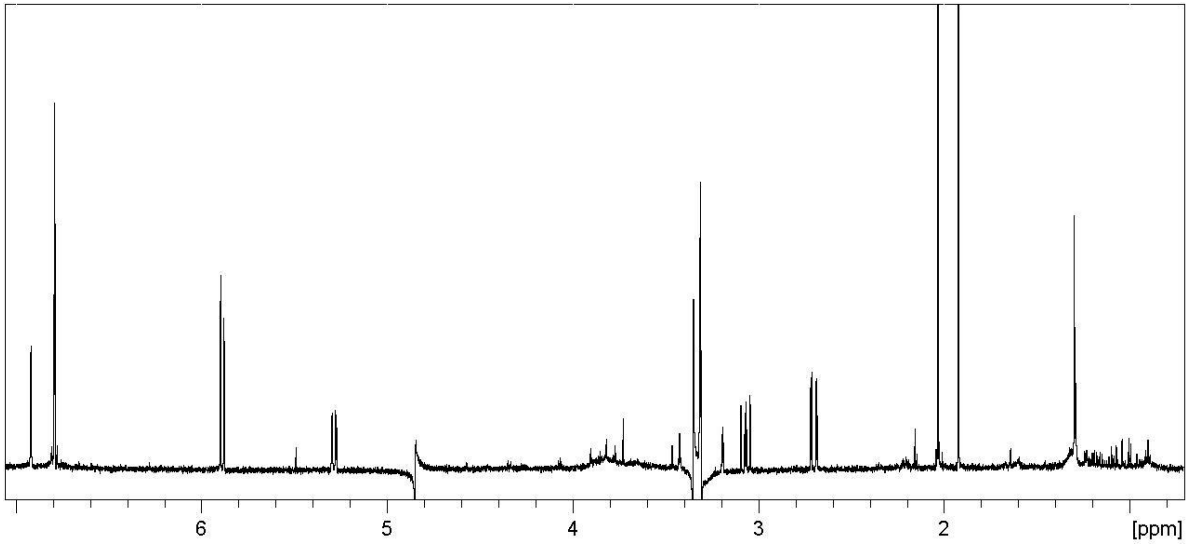

Figure S9. ^{1}H NMR spectrum (600 MHz, methanol-d_4) of 5,7,3',5'-tetrahydroxy flavanone **5**.

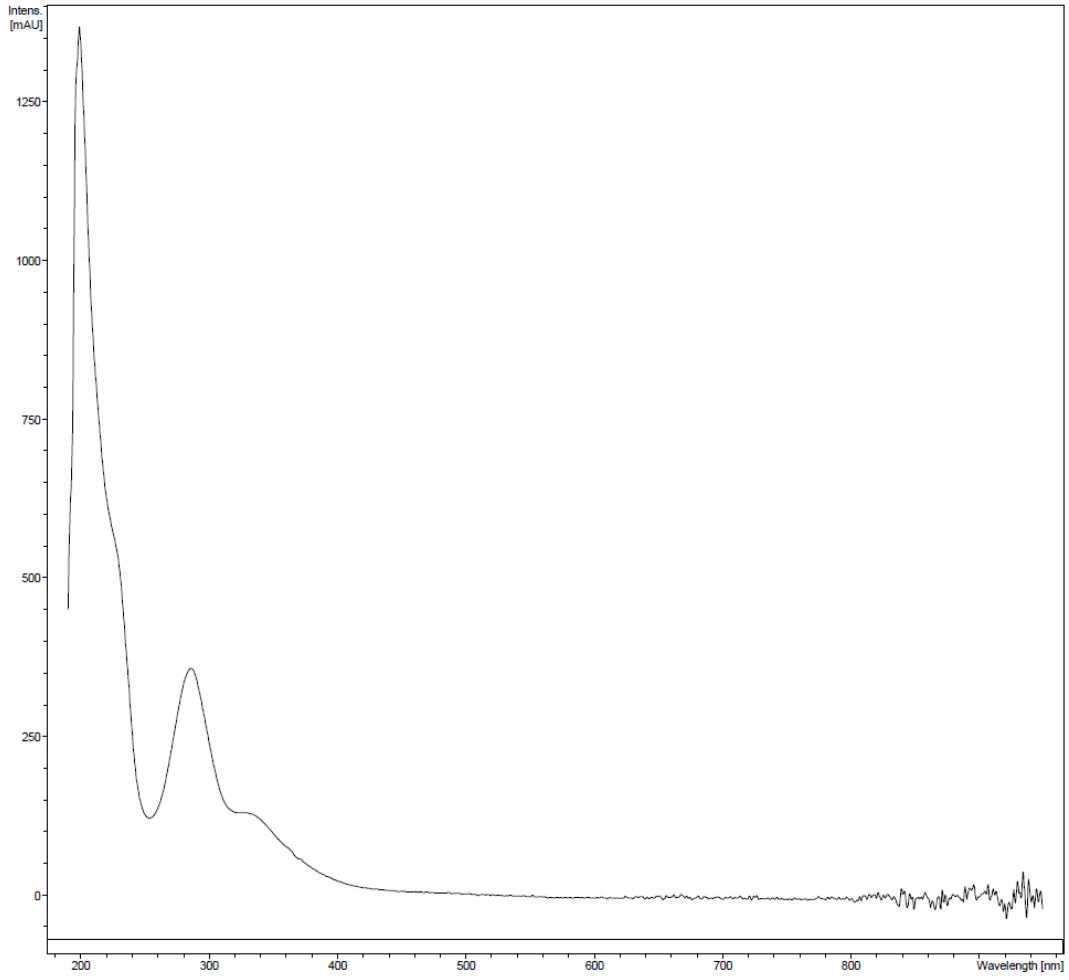

Figure S10. UV spectrum of 5,7,3',5'-tetrahydroxy flavanone **5**.

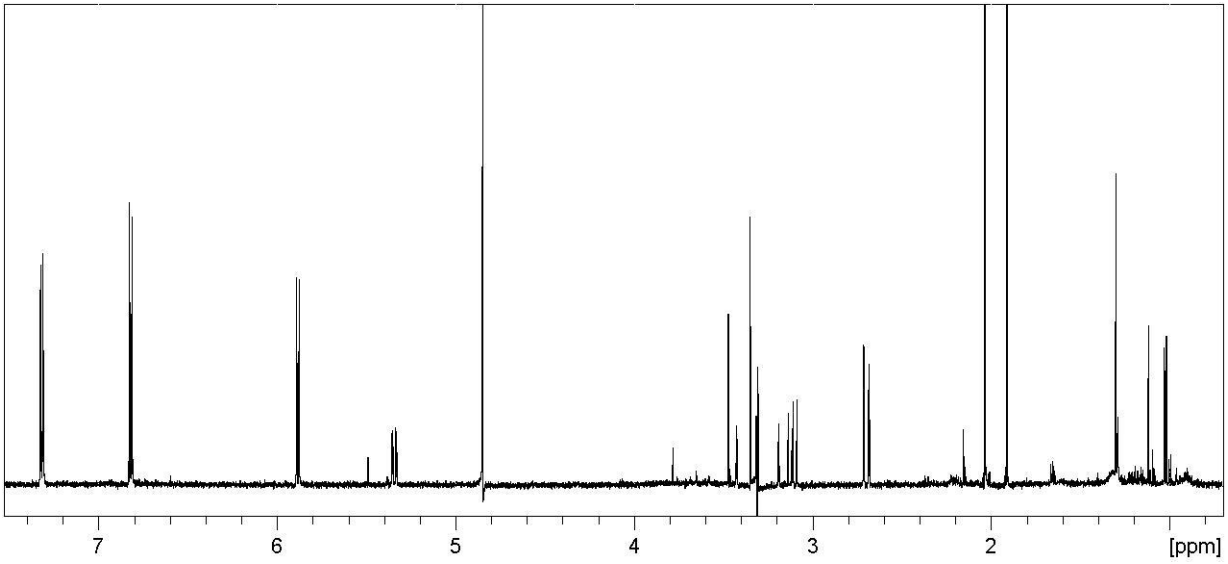

Figure S11. ^{1}H NMR spectrum (600 MHz, methanol-d_4) of naringenin **6**.

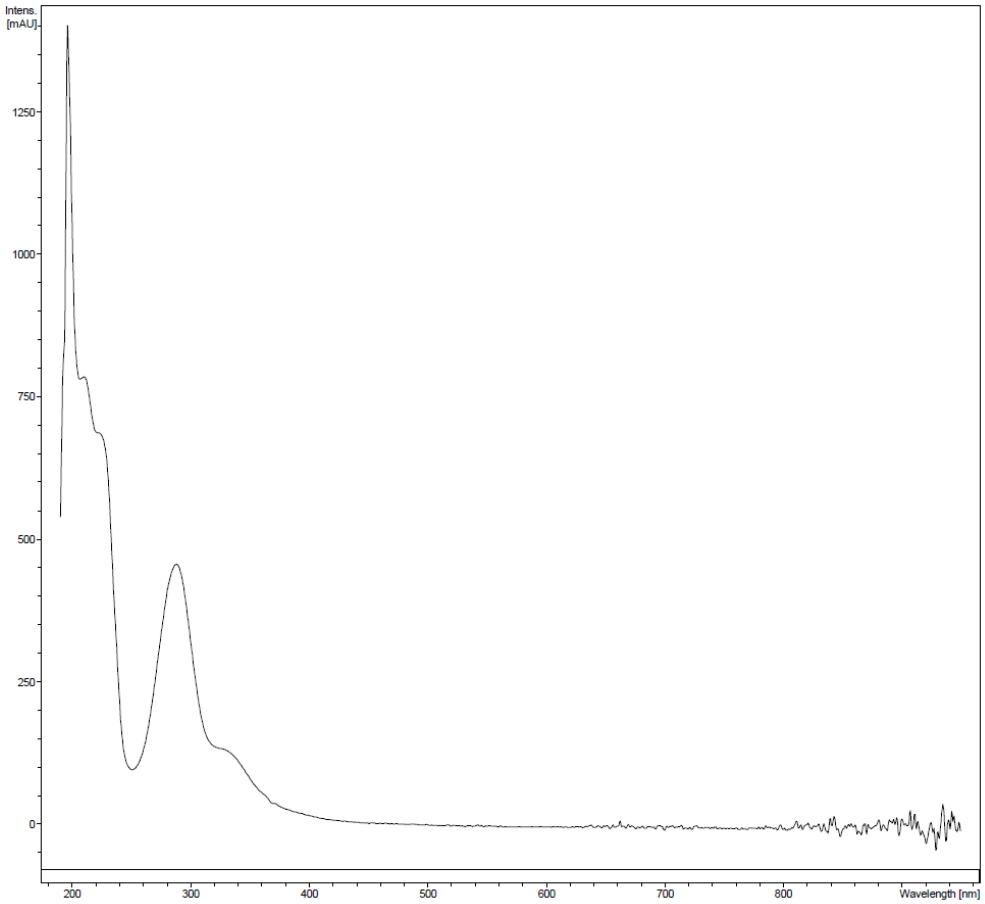

Figure S12. UV spectrum of naringenin **6**.

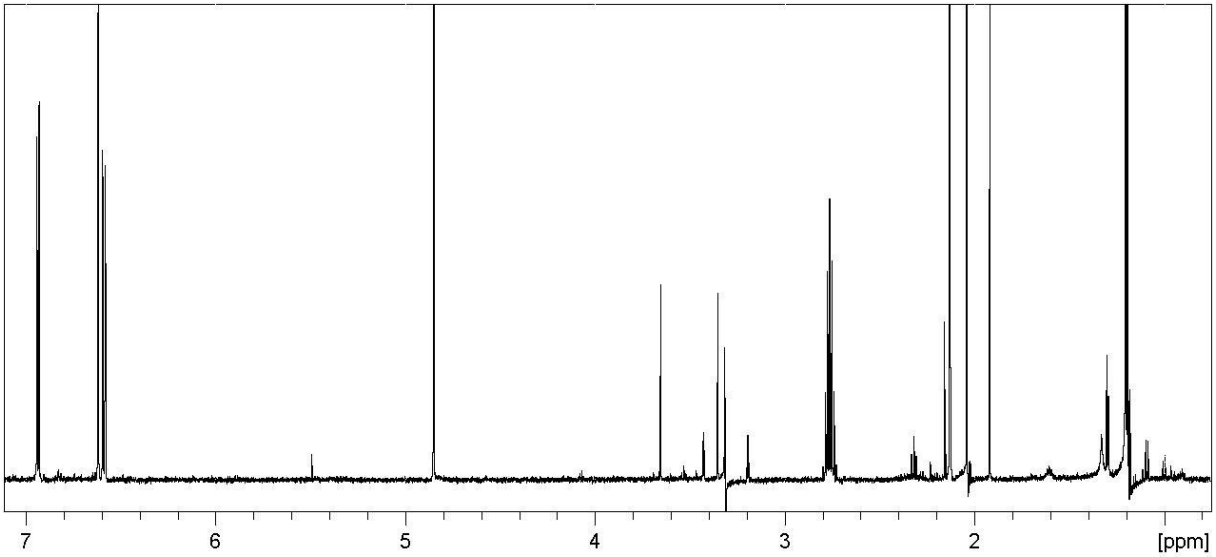

Figure S13. ^{1}H NMR spectrum (600 MHz, methanol-d_4) of carvacrol **7**.

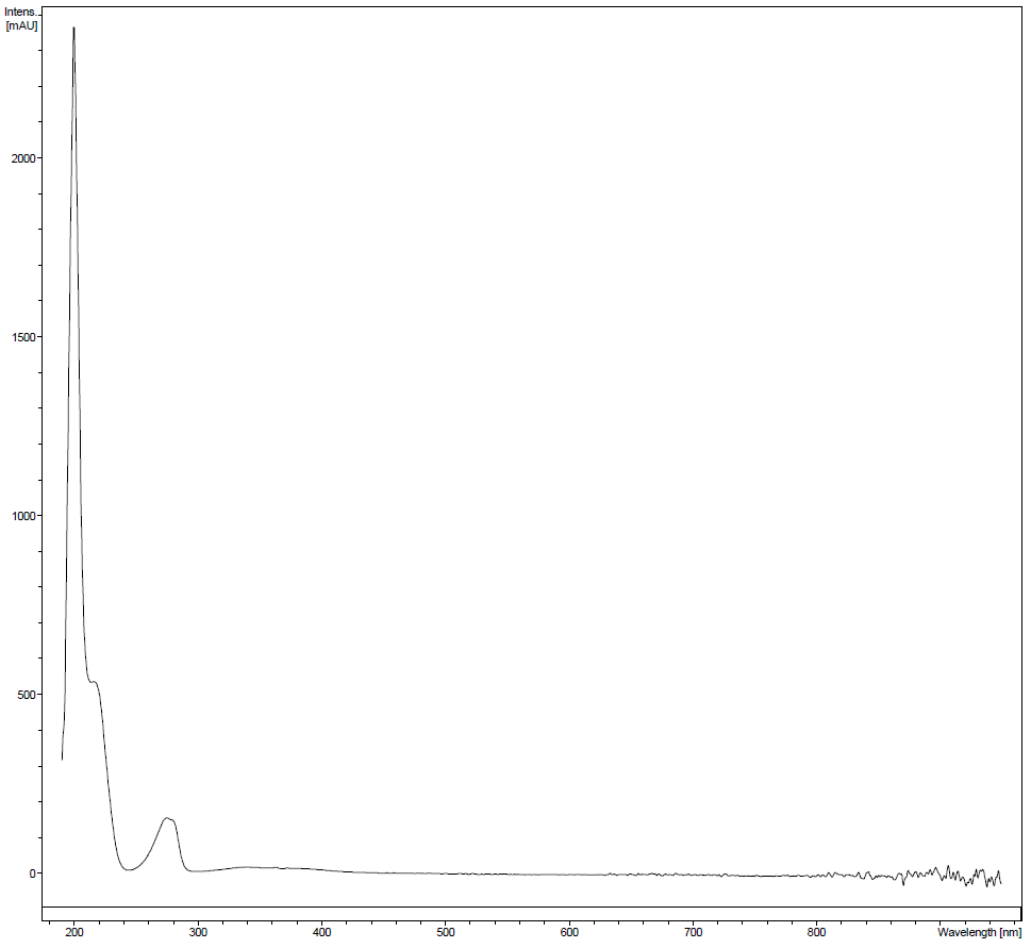

Figure S14. UV spectrum of carvacrol **7**.