SUPPLEMENTARY MATERIAL

New Coumarin from the Roots of *Prangos pabularia*

Sodik Numonov[a,b,c], Khayrulla Bobakulov[d], Mukhabbat Numonova[c], Farukh Sharopov[a,b], William N. Setzer[e], Qosimjon Khalilov[a], Nurmirza Begmatov[a], Maidina Habasi[a] and Haji Akber Aisa[a*]

[a]*Key Laboratory of Plant Resources and Chemistry in Arid Regions, Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi, 830011, P. R. China*
[b]*Chinese-Tajik Innovation Center of Natural Products, Dushanbe, 734063, Tajikistan*
[c]*State Scientifically-Experimental and Production Organization, Academy of Sciences of the Republic of Tajikistan, Dushanbe, 734063, Tajikistan*
[d]*Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, 100170, Tashkent, Uzbekistan*
[e]*Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL 35899, USA*

[*]Corresponding author: Prof. Dr. Haji Akber Aisa, Phone: +86 991 3835679; Fax: +86 991 3838957, E-mail: haji@ms.xjb.ac.cn

Abstract: The new coumarin **1**, yuganin A (7-methoxy-8-((1*S*,2*S*)-1,2,3-trihydroxy-3-methylbutyl)-2*H*-chromen-2-one) along with nine known coumarins, heraclenol 3′-*O*-β-D-glucopyranoside **(2)**, oxypeucedanin hydrate 3′-*O*-β-D-glucopyranoside **(3)**, heraclenol **(4),** oxypeucedanin hydrate **(5),** osthole **(6)**, oxypeucedanin **(7)**, heraclenin **(8)**, isoimperatorin **(9),** imperatorin **(10)** and the disaccharide sucrose **(11)**, have been isolated from the roots of *Prangos pabularia*, and the structures of these isolated compounds were elucidated by spectroscopic means, especially, UV, HR-ESIMS, and 1D and 2D NMR spectroscopy. Furthermore, the anti-melanogenic effect of yuganin A and its inhibitory effect on B16 cells were evaluated. Yuganin A may be useful in the treatment of hyperpigmentation and as a skin-whitening agent in the cosmetics industry.

Keywords: *Prangos pabularia*; coumarins; furanocoumarins; yuganin A; NMR; B16 melanoma cells

Supporting Information

Table S1. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectroscopic data and HMBC correlations of **1** in DMSO-d_6

Position	Chemical shift (δ) in ppm		HMBC
	^{1}H (J/Hz)	^{13}C	(from H to C atom)
Coumarin nucleus			
2	-	160.03	-
3	6.27, d (9.5)	112.17	C-2, C-10
4	7.97, d (9.5)	144.78	C-2, C-5, C-9
5	7.59, d (8.7)	128.32	C-4, C-7, C-9
6	7.06, d (8.7)	108.50	C-10, C-8
7	-	160.01	-
8	-	118.96	-
9	-	152.56	-
10	-	112.70	-
7-OCH_3	3.88, s	56.32	C-7
Prenyl unit			-
11	5.18, t (6.5)	64.70	C-7, C-8, C-9, C-12
12	3.78, dd (6.5; 4.6)	77.65	C-13, C-14
13	-	71.12	-
14	0.93, s	25.05	C-15, C-12, C-13
15	1.04, s	26.79	C-14, C-12, C-13
11-OH	4.74, d (6.5)	-	C-8, C-11
12-OH	4.70, d (4.6)	-	C-12, C-13
13-OH	3.88, m	-	C-12, C-13, C-14

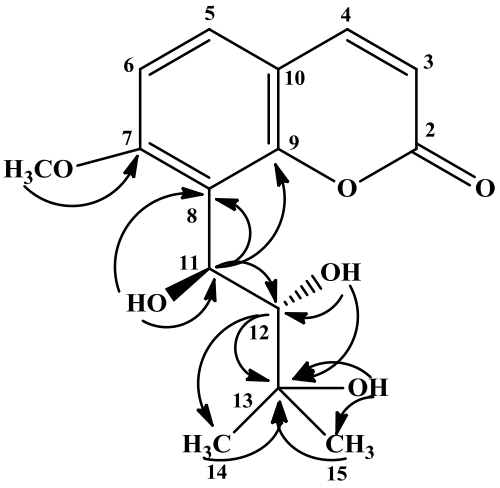

Figure S1. Structure of new coumarin **(1)** with key HMBC correlations

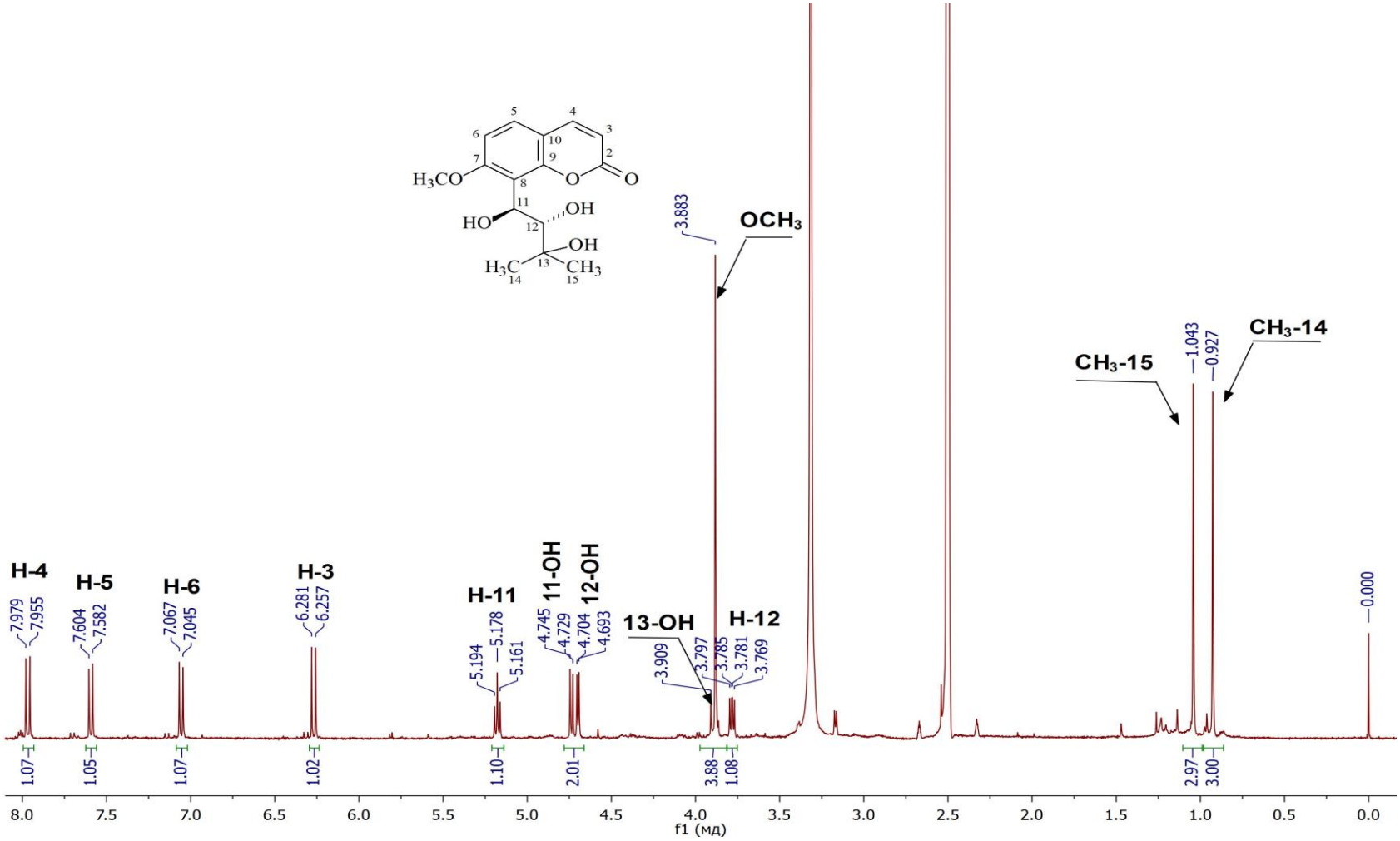

Figure S2. ^{1}H NMR spectrum of **1**

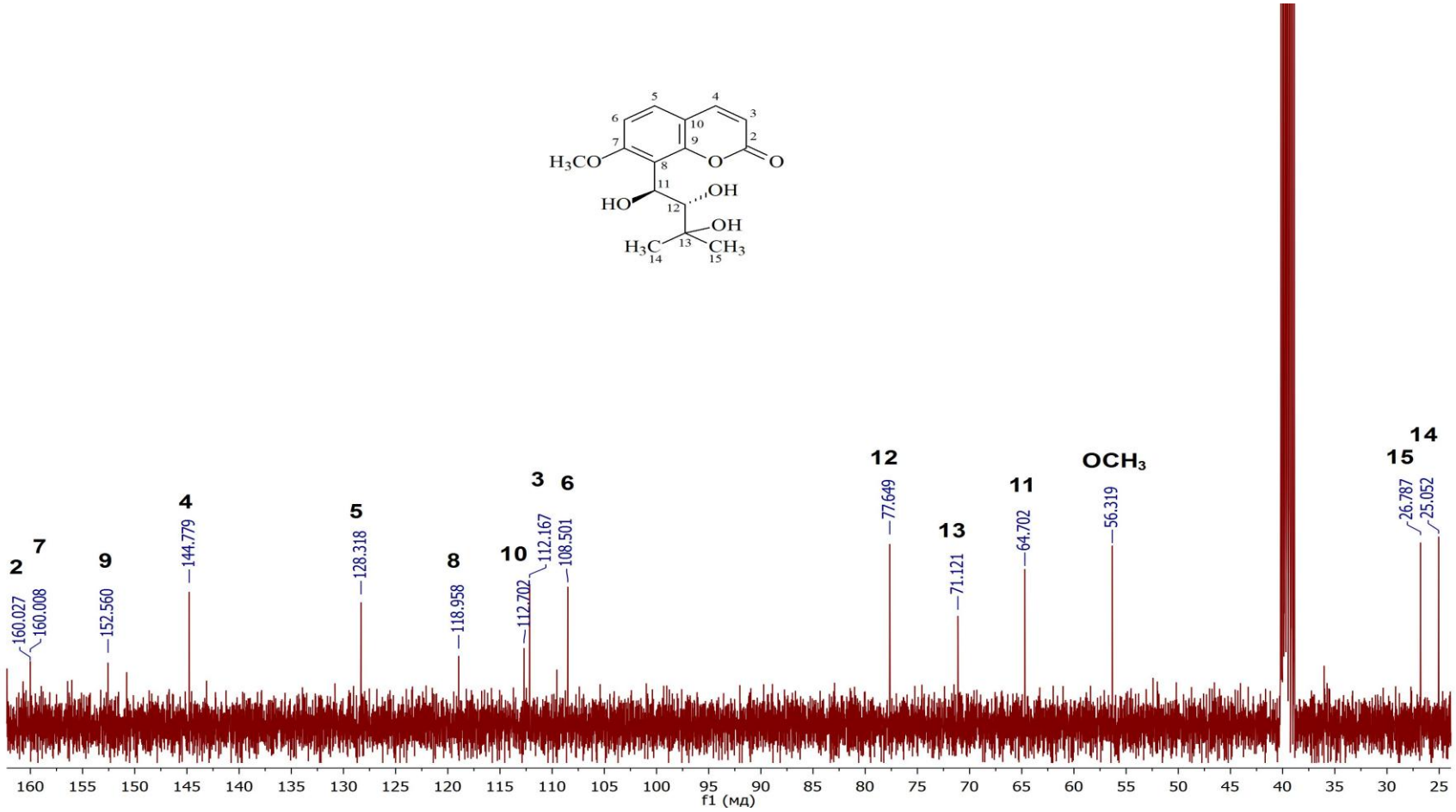

Figure S3. ^{13}C NMR spectrum of **1**

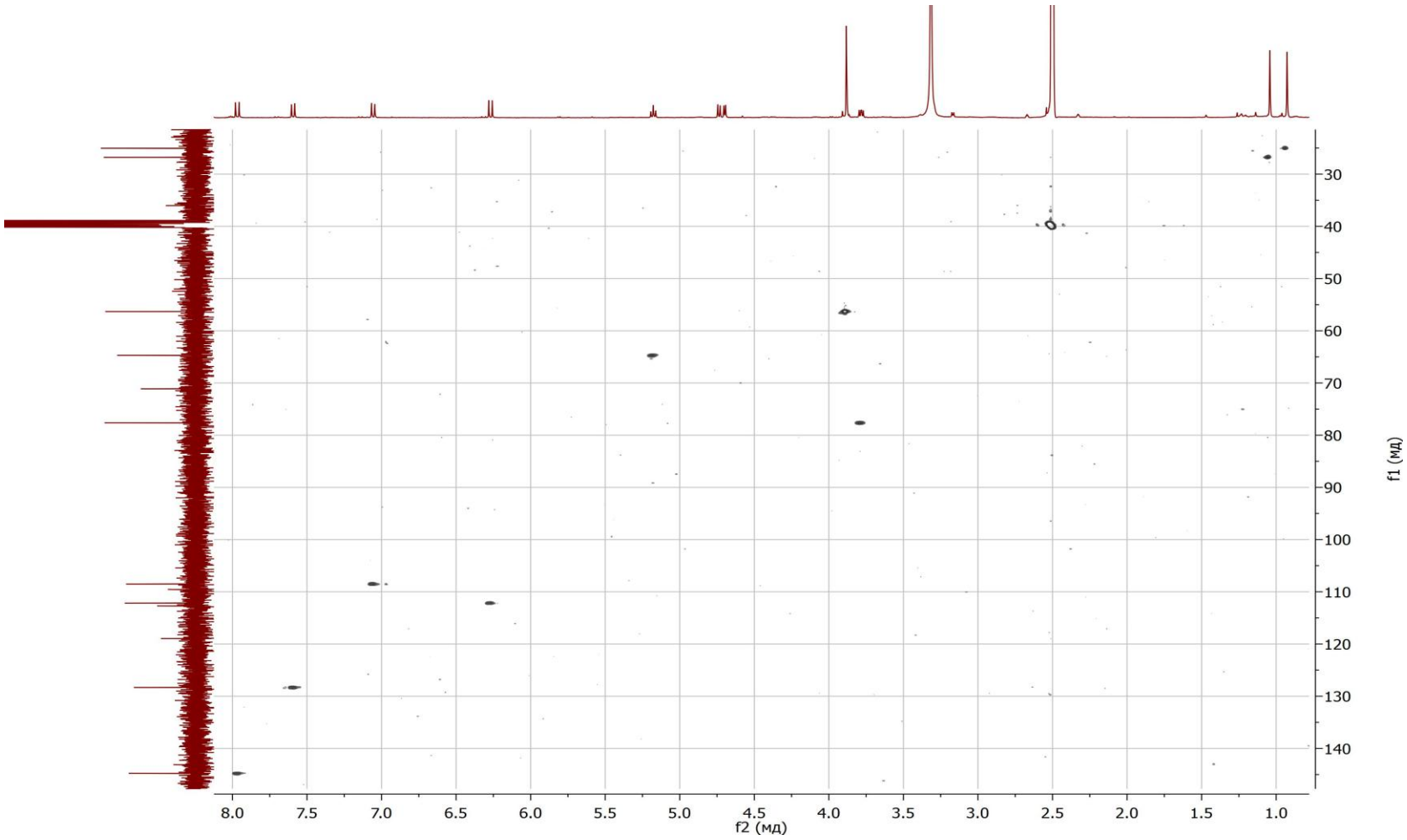

Figure S4. HSQC spectrum of **1**

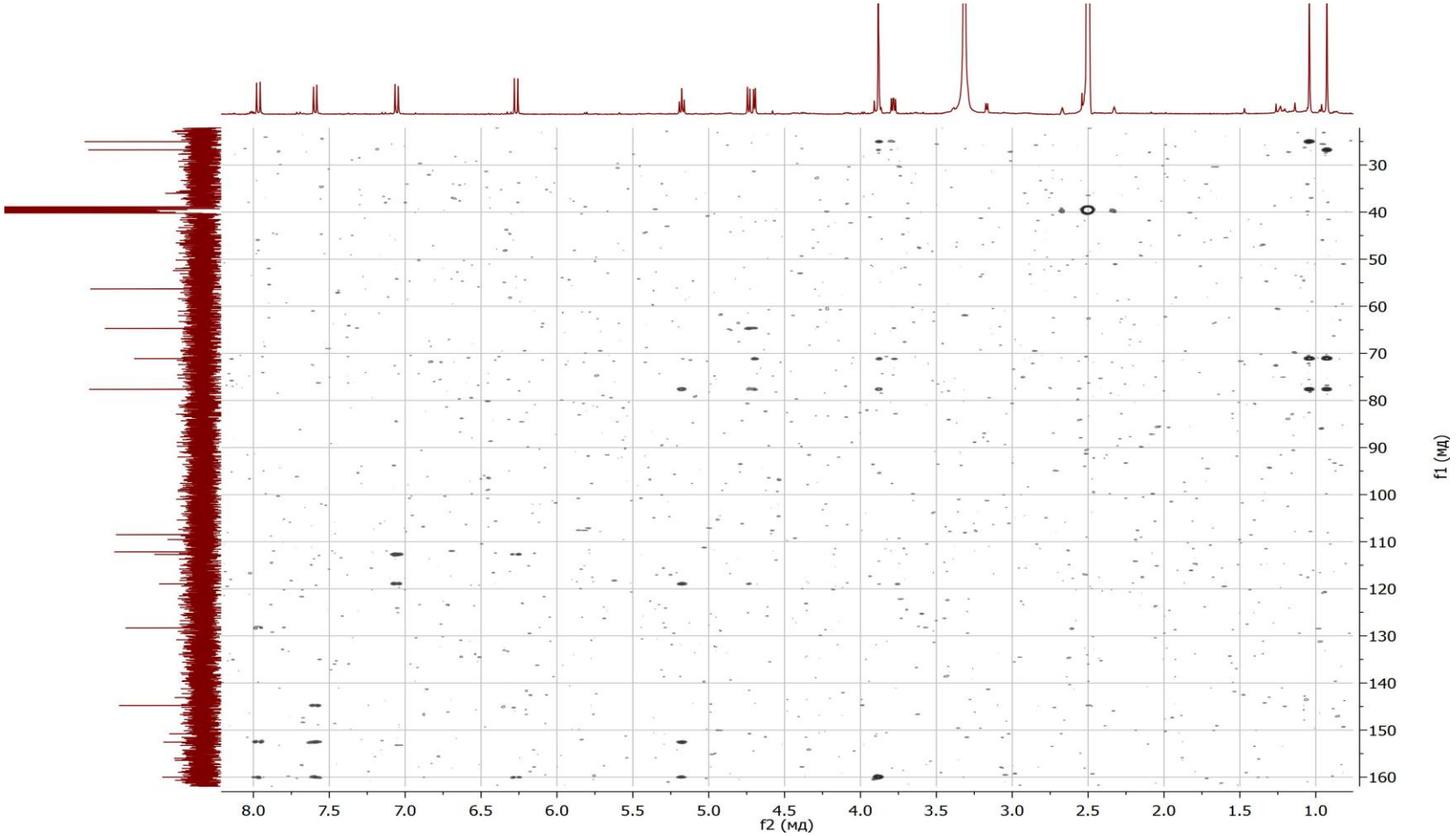

Figure S5. HMBC spectrum of **1**

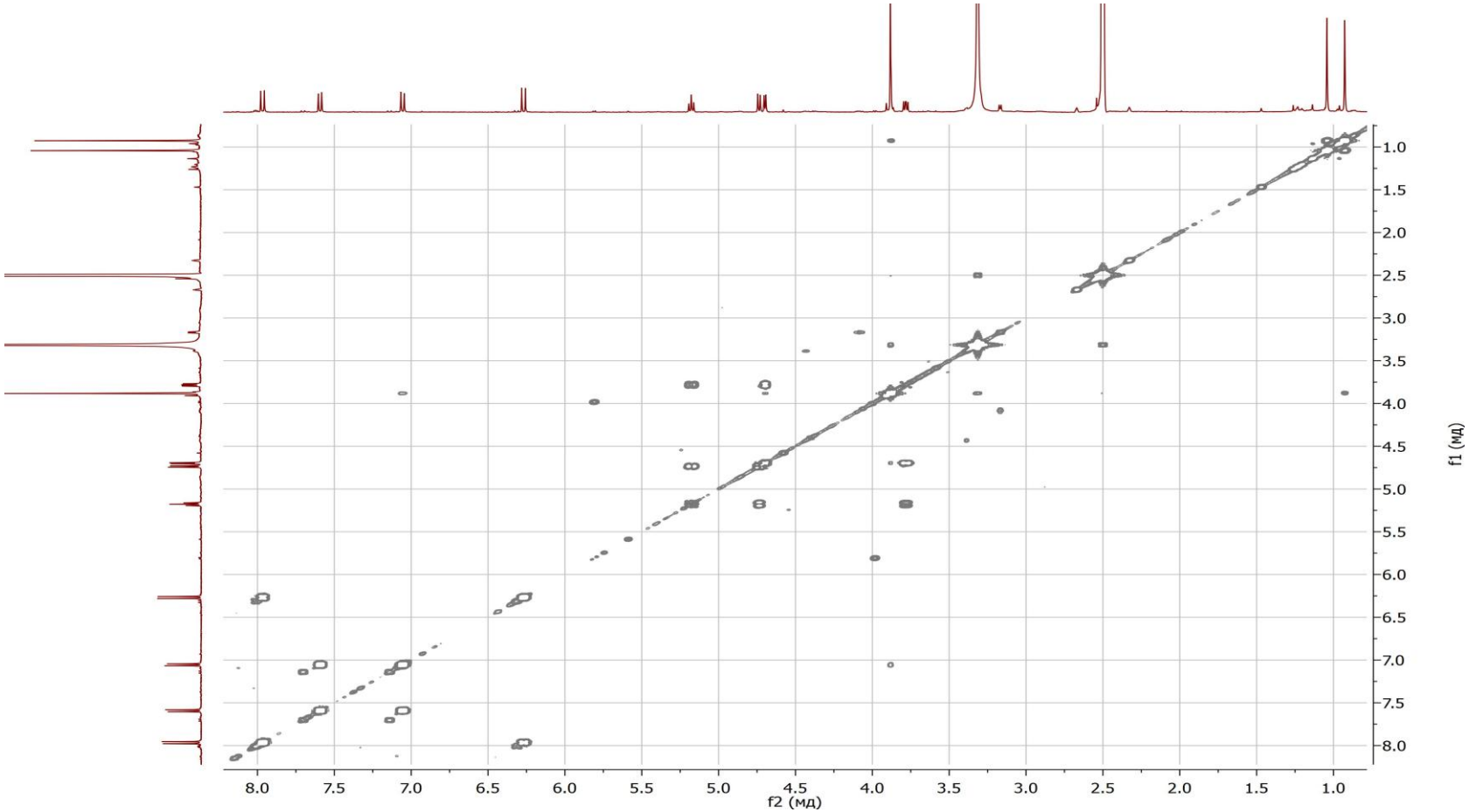

Figure S6. COSY spectrum of **1**

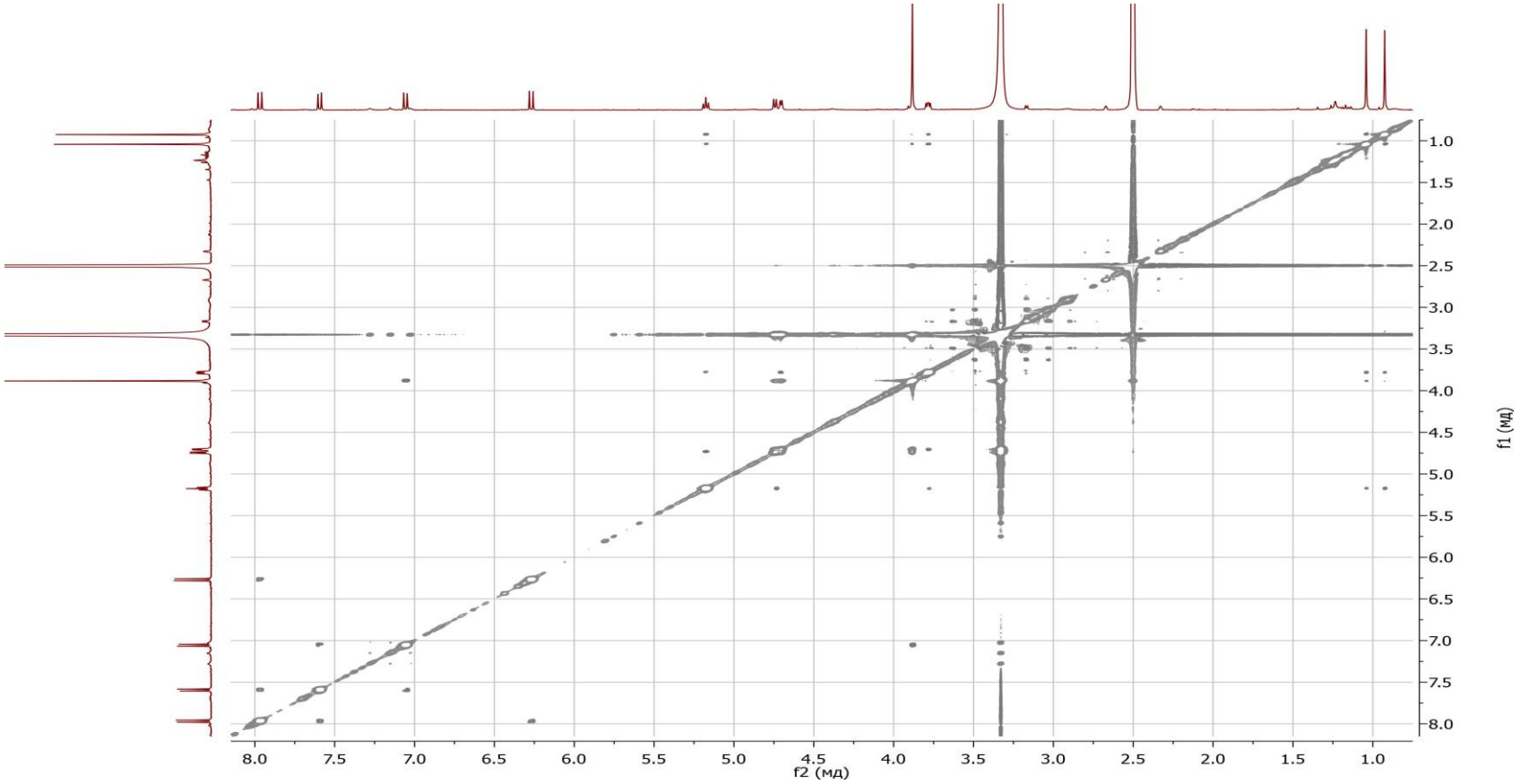

Figure S7. NOESY spectrum of **1**

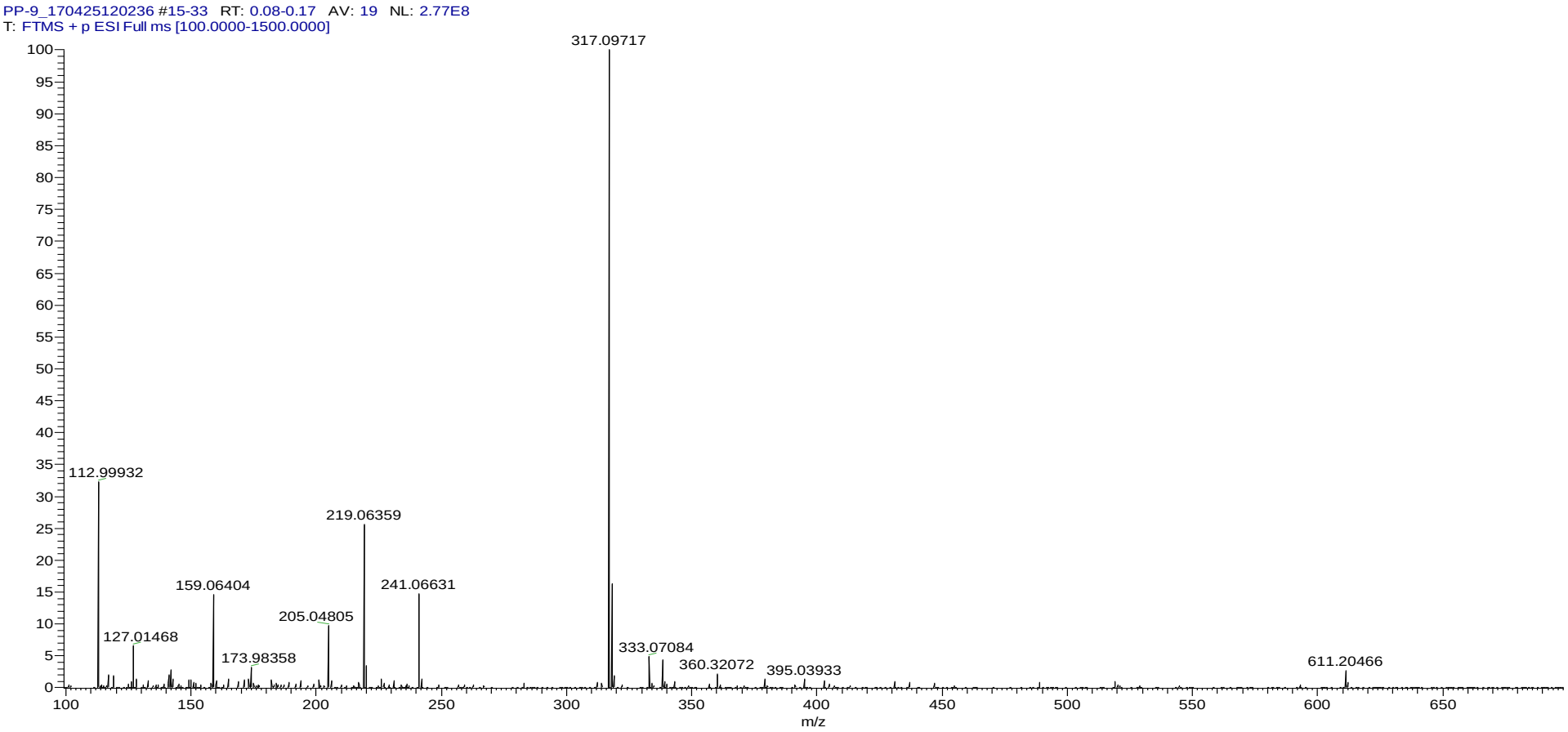

Figure S8. The positive mode HR-ESIMS spectrum of **1**

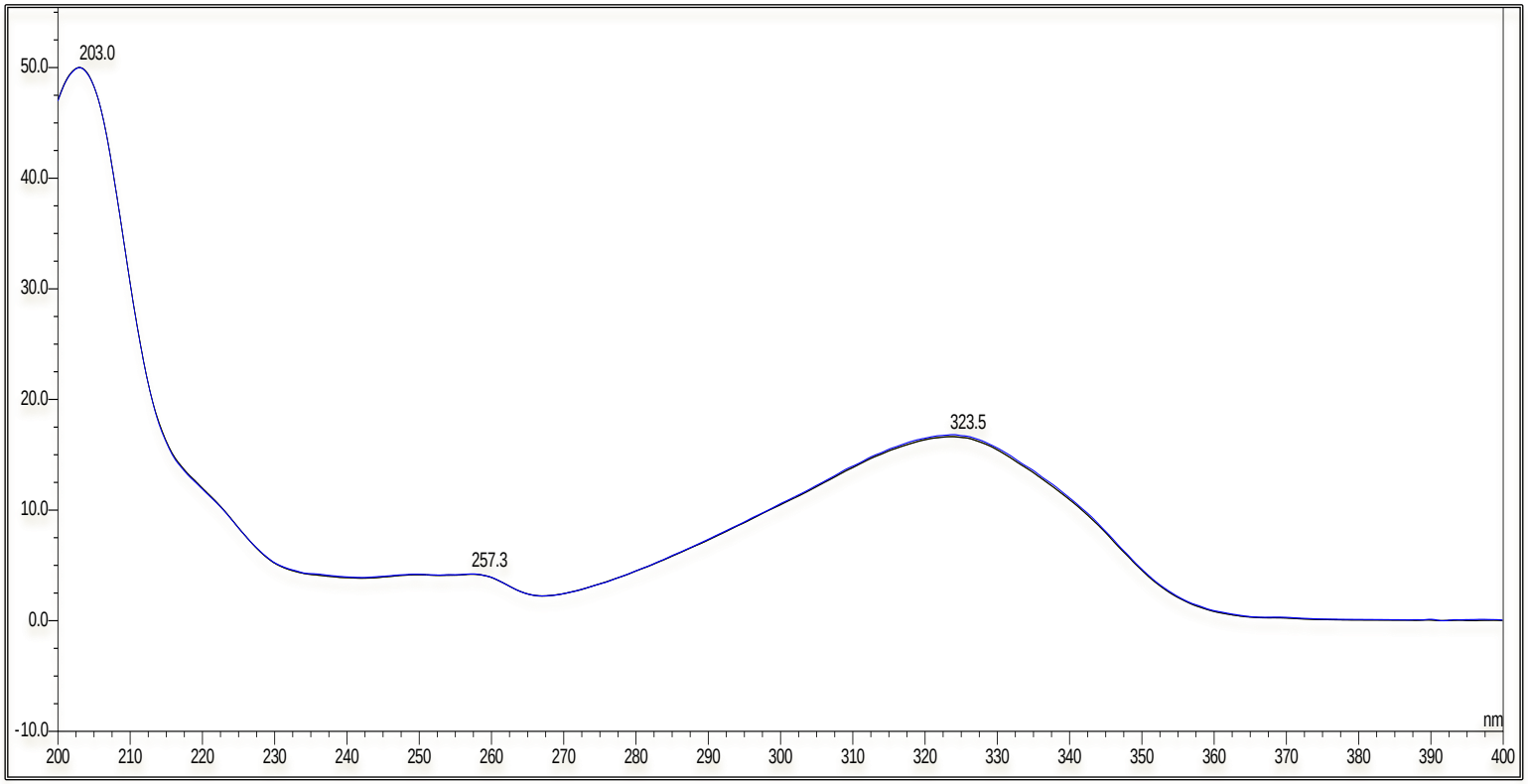

Figure S9. The UV spectrum of **1**

^{1}H and ^{13}C NMR dates of the isolated known compounds (2-11)

Heraclenol 3'-O-β-D-glucopyranoside (2)

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.35 (1H, d, , *J*=9.8 Hz, H-3), 8.37 (1H, d, *J*=9.8 Hz, H-4), 7.38 (1H, br.s, H-8), 7.34 (1H, dd, *J*=2.3 0.9 Hz, H-11), 8.03 (1H, d, *J*=2.3 Hz, H-12), 4.26 (1H, m, H-13a), 4.82 (1H, m, H-13b), 3.83 (1H, m, H-14), 1.22 (3H, s, H-16), 1.24 (3H, s, H-17), 4.43 (1H, d, *J*=7.7 Hz, H-1'), 2.93 (1H, m, H-2'), 3.17 (1H, m, H-3'), 3.03 (1H, m, H-4'), 3.12 (1H, m, H-5''), 3.38 (1H, m, H-6a'), 3.64 (1H, m, H-6b'); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.20 (C-2), 112.21 (C-3), 140.06 (C-4), 149. 22 (C-5), 113.73 (C-6), 157.53 (C-7), 93.48(C-8), 152.06 (C-9), 106.67 (C-10), 105.58 (C-11), 145.94 (C-12), 74.77 (C-13), 74.89 (C-14), 78.02 (C-15), 20.98 (C-16), 24.52 (C-17), 96.93 (C-1'), 73.69 (C-2'), 76.81 (C-3'), 70.24 (C-4'), 76.64 (C-5'), 61.19 (C-6').

Oxypeucedanin hydrate 3'-O-β-D-glucopyranoside (3)

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.44 (1H, d, , *J*=9.6 Hz, H-3), 8.15 (1H, d, *J*=9.6 Hz, H-4), 7.67 (1H, s, H-5), 7.09 (1H, d, *J*=2.0 Hz, H-11), 8.13 (1H, d, *J*=2.0 Hz, H-12), 4.38 (1H, d, *J*=10.03 Hz, H-13a), 4.61 (1H, dd, *J*=10.3; 2.5 Hz, H-13b), 3.89 (1H, m, H-14), 1.23 (3H, s, H-16), 1.20 (3H, s, H-17), 4.40 (1H, d, *J*=7.8 Hz, H-1'), 2.92 (1H, m, H-2'), 3.05 (1H, m, H-3'), 3.03 (1H, m, H-4'), 3.11 (1H, m, H-5'), 3.40 (1H, m, H-6a'), 3.60 (1H, m, H-6b'); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.81 (C-2), 114.15 (C-3), 145.28 (C-4), 113.67 (C-5), 125.82 (C-6), 147.10 (C-7), 131.47 (C-8), 142.57 (C-9), 116.39 (C-10), 107.00 (C-11), 147.75 (C-12), 74.95 (C-13), 75.03 (C-14), 78.06 (C-15), 21.52 (C-16), 23.65 (C-17), 96.67 (C-1'), 73.68 (C-2'), 76.74 (C-3'), 70.15 (C-4'), 76.73 (C-5'), 61.10 (C-6').

Oxypeucedanin hydrate (4)

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.45 (1H, d, , *J*=9.6 Hz, H-3), 8.15 (1H, d, *J*=9.6 Hz, H-4), 7.66 (1H, s, H-5), 7.10(1H, d, *J*=2.1 Hz, H-11), 8.14 (1H, d, *J*=2.1 Hz, H-12), 4.39 (1H, dd, *J*=10.1; 8.1 Hz, H-13a), 4.66(1H, dd, *J*=10.1; 2.2 Hz, H-13b), 3.69 (1H, dd, *J*=8.1; 2.2 Hz, H-

14), 1.16 (3H, s, H-16), 1.17 (3H, s, H-17); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.85 (C-2), 114.15 (C-3), 145.27 (C-4), 113.59 (C-5), 125.83 (C-6), 147.10 (C-7), 131.60(C-8), 142.56 (C-9), 116.39 (C-10), 107.02 (C-11), 147.72 (C-12), 75.44 (C-13), 76.70 (C-14), 70.80 (C-15), 24.46 (C-16), 27.27 (C-17).

Heraclenol (5)

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.35 (1H, d, , *J*=9.8 Hz, H-3), 8.39 (1H, d, *J*=9.8 Hz, H-4), 7.34 (1H, br.s, H-8), 7.31(1H, dd, *J*=2.4; 0.9 Hz, H-11), 8.02 (1H, d, *J*=2.4 Hz, H-12), 4.30 (1H, dd, *J*=9.8; 8.4 Hz, H-13a), 4.76(1H, dd, *J*=9.8; 2.2 Hz, H-13b), 3.66 (1H, m, H-14), 1.13 (3H, s, H-16), 1.20 (3H, s, H-17); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.51 (C-2), 112.27 (C-3), 140.31 (C-4), 149.43 (C-5), 113.56 (C-6), 157.75 (C-7), 93.49(C-8), 152.23 (C-9), 106.69 (C-10), 105.68 (C-11), 146.09 (C-12), 75.04 (C-13), 76.45 (C-14), 70.97 (C-15), 24.36 (C-16), 27.79 (C-17).

Osthole (6)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.23(1H, d, , *J*=9.4 Hz, H-3), 7.61 (1H, d, *J*=9.4 Hz, H-4), 7.28 (1H, d, , *J*=8.6 Hz, H-5), 6.83 (1H, d, , *J*=8.6 Hz, H-6), 3.53 (1H, d, *J*=7.3 Hz, H-11), 5.22 (1H, m, H-12), 1.67 (3H, s, H-14), 1.84 (3H, s, H-115), 3.92 (3H, s, OCH_3-7); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.49 (C-2), 113.11 (C-3), 143.87 (C-4), 126.32 (C-5), 107.47 (C-6), 160.34 (C-7), 118.10 (C-8), 152.95 (C-9), 113.14 (C-10), 22.06 (C-11), 121.25 (C-12), 132.75 (C-13), 18.06 (C-14), 25.91 (C-15), 56.17 (OCH_3-7).

Heraclenin (7)

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.38 (1H, d, , *J*=9.8 Hz, H-3), 8.26 (1H, d, *J*=9.8 Hz, H-4), 7.43 (1H, br.s., H-8), 7.33(1H, dd, *J*=2.4; 1.0 Hz, H-11), 8.06 (1H, d, *J*=2.4 Hz, H-12), 4.45 (1H, dd, *J*=11.1; 7.0 Hz, H-13a), 4.73(1H, dd, *J*=11.1; 7.0 Hz, H-13b), 3.27 (1H, dd, *J*=7.03; 3.9 Hz, H-14), 1.27 (3H, s, H-16), 1.31 (3H, s, H-17); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.02 (C-2), 112.80 (C-3), 139.33 (C-4), 148.30 (C-5), 114.11 (C-6), 157.38 (C-7), 94.16(C-8), 151.94 (C-9),

106.86 (C-10), 105.11 (C-11), 146.32 (C-12), 72.38 (C-13), 60.51 (C-14), 57.71 (C-15), 18.78 (C-16), 24.37 (C-17).

Oxypeucedanin (8)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.38 (1H, d, , *J*=9.6Hz, H-3), 7.77 (1H, d, *J*=9.6 Hz, H-4), 7.40 (1H, br.s., H-8), 6.83 (1H, d, *J*=2.2 Hz, H-11), 7.70 (1H, d, *J*=2.0 Hz, H-12), 4.57 (1H, dd, *J*=11.3; 5.4 Hz, H-13a), 4.60 (1H, dd, *J*=11.3; 6.7 Hz, H-13b), 3.32 (1H, t, *J*=5.6 Hz, H-14), 1.29 (3H, s, H-16), 1.35 (3H, s, H-17); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.44 (C-2), 114.97 (C-3), 144.41 (C-4), 114.00 (C-5), 126.12 (C-6), 148.47 (C-7), 131.62 (C-8), 143.78 (C-9), 116.66 (C-10), 106.95 (C-11), 146.94 (C-12), 72.62 (C-13), 61.47 (C-14), 58.30 (C-15), 19.01 (C-16), 24.70 (C-17).

Isoimperatorin (9)

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.33 (1H, d, , *J*=9.8 Hz, H-3), 8.17 (1H, d, *J*=9.8 Hz, H-4), 7.38 (1H, br.s., H-8), 7.34 (1H, dd, *J*=2.4; 1.0 Hz, H-11), 8.05 (1H, d, *J*=2.0 Hz, H-12), 4.99 (1H, br.d, *J*=7.0 Hz, H-13), 5.54 (1H, br.t, *J*=7.0 Hz, H-14), 1.67 (3H, s, H-16), 1.75 (3H, s, H-17); ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.09 (C-2), 112.41 (C-3), 139.60 (C-4), 148.59 (C-5), 113.89 (C-6), 157.47 (C-7), 93.60(C-8), 152.04 (C-9), 106.77 (C-10), 105.50 (C-11), 146.07 (C-12), 69.32 (C-13), 119.41 (C-14), 138.95 (C-15), 18.02 (C-16), 25.45 (C-17).

Imperatorin (10)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.39 (1H, d, , *J*=9.6 Hz, H-3), 7.76 (1H, d, *J*=9.6 Hz, H-4), 6.81(1H, d, *J*=2.2 Hz, H-11), 7.69 (1H, d, *J*=2.2 Hz, H-12), 5.00 (1H, d, *J*=7.2 Hz, H-13), 5.61 (1H, m, H-14), 1.72 (3H, s, H-16), 1.74 (3H, s, H-17); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.51 (C-2), 114.69 (C-3), 144.33 (C-4), 113.15 (C-5), 125.86 (C-6), 148.62 (C-7), 131.67(C-8), 143.83 (C-9), 116.49 (C-10), 106.71 (C-11), 146.61 (C-12), 70.16 (C-13), 119.78 (C-14), 139.67 (C-15), 18.12 (C-16), 25.81 (C-17).

Sucrose (11)

^{1}H NMR (400 MHz, D_2O): δ 5.42 (1H, d, , *J*=3.8 Hz, H-1), 3.56 (1H, dd, *J*=10.0; 3.9 Hz, H-2), 3.76 (1H, t, *J*=9.6 Hz, H-3), 3.47 (1H, t, *J*=9.8 Hz, H-4), 3.79-3.93 (1H, m, H-5), 3.79-3.93 (1H, m, H-6), 3.68 (1H, s, H-1'), 4.22 (1H, d, *J*=7.8 Hz H-3'), 4.05 (1H, t, *J*=8.5 Hz, H-4'), 3.79-3.93 (1H, m, H-5'), 3.79-3.93 (1H, m, H-6'); ^{13}C NMR (100 MHz, D_2O): δ 94.95 (C-1), 73.89 (C-2), 75.39 (C-3), 72.04 (C-4), 75.22 (C-5), 62.94 (C-6), 64.17 (C-1'), 106.50 (C-2'), 79.23 (C-3'), 76.81 (C-4'), 84.19 (C-5'), 65.19 (C-6').