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The chemical shift assignments of carbon and proton signals of **Dioscin G** (Compound **7**) in Pyridine-d_5.

Carbon NO.	**Dioscin G**	
	δ_C (ppm)	δ_C (ppm, J in Hz)
1	37.07	0.92 (H_2-1, m)
2	30.14	1.91 (H_1-2a, m), 2.14 (H_1-2b, m)
3	78.55	3.93 (H_1-3, m)
4	38.92	2.75 (H_1-4a, t, J=11.5 Hz), 2.81 (H_1-4b, dd, J=12.4, 3.8 Hz)
5	140.73	
6	121.72	5.29 (H_1-6, d, J=4.6 Hz)
7	32.27	1.91 (H_1-7a, m), 2.03 (H_1-7b, m)
8	31.61	1.45 (H_1-8, m)
9	50.25	0.92 (H_1-9, m)
10	39.86	
11	21.03	1.45 (H_2-11, m)
12	37.45	2.03 (H_2-12, m)
13	40.71	
14	56.52	1.13 (H_1-14, m)
15	32.41	1.45 (H_1-15a, m), 2.03 (H_1-15b, m)
16	81.03	4.98 (H_1-16, m)
17	63.77	1.91 (H_1-17, m)
18	16.4	0.9 (H_3-18, s)
19	19.35	1.05 (H_3-19, s)
20	40.62	2.22 (H_1-20, m)
21	16.4	1.33 (H_3-21, d, J=6.9 Hz)
22	110.57	
23	37.15	1.72 (H_1-23a, m), 2.03 (H_1-23b, m)
24	28.29	1.67 (H_1-24a, m), 2.03 (H_1-24b, m)
25	34.22	1.91 (H_1-25, m)
26	75.14	3.62 (H_1-26a, m), 4.29 (H_1-26b, m)
27	17.41	0.98 (H_3-27, d, J=6.7 Hz)
3-O-Glc-1'	100.28	5.05 (1H, d, J=7.7 Hz)
2'	77.71	4.29 (1H, m)
3'	78.24	4.29 (1H, m)
4'	71.6	4.24 (1H, m)
5'	78.44	4.19 (1H, m)
6'	62.57	4.38 (1H, m), 4.64 (1H, m)
Rha(1→2) 1''	102.01	6.4 (1H, s)
2''	71.72	4.24 (1H, m)
3''	72.54	4.64 (1H, m)
4''	72.78	4.64 (1H, m)
5''	69.44	4.98 (1H, m)
6''	18.63	1.78 (d, J=6.2 Hz)
26-O-Glc-1'''	104.89	4.81 (1H, d, J=7.7 Hz)

2'''	75.2	4.24 (1H, m)
3'''	79.61	4.29 (1H, m)
4'''	74.1	4.03 (1H, m)
5'''	77.84	4.29 (1H, m)
6'''	62.73	4.53 (1H, m), 4.64 (1H, m)

The chemical shift assignments of carbon and proton signals of **Dioscin H** (Compound **8**) in Pyridine-d_5.

	Dioscin H	
	δ_C (ppm)	δ_C (ppm)
1	37.07	0.92 (H_2-1, m)
2	30.14	1.91 (H_1-2a, m), 2.14 (H_1-2b, m)
3	78.55	3.93 (H_1-3, m)
4	38.92	2.75 (H_1-4a, t, *J*=11.5 Hz), 2.81 (H_1-4b, dd, *J*=12.4, 3.8 Hz)
5	140.73	
6	121.72	5.29 (H_1-6, d, *J*=4.6 Hz)
7	32.27	1.91 (H_1-7a, m), 2.03 (H_1-7b, m)
8	31.61	1.45 (H_1-8, m)
9	50.25	0.92 (H_1-9, m)
10	39.86	
11	21.03	1.45 (H_2-11, m)
12	37.45	2.03 (H_2-12, m)
13	40.71	
14	56.52	1.13 (H_1-14, m)
15	32.41	1.45 (H_1-7a, m), 2.03 (H_1-7b, m)
16	81.03	4.98 (H_1-16, m)
17	63.77	1.91 (H_1-17, m)
18	16.4	0.9 (H_3-18, s)
19	19.35	1.05 (H_3-19, s)
20	40.62	2.22 (H_1-20, m)
21	16.4	1.33 (H_3-21, d, *J*=6.9 Hz)
22	110.57	
23	37.15	1.72 (H_1-23a, m), 2.03 (H_1-23b, m)
24	28.29	1.67 (H_1-28a, m), 2.03 (H_1-28b, m)
25	34.22	1.91 (H_1-25, m)
26	75.14	3.62 (H_1-26a, m), 4.29 (H_1-26b, m)
27	17.41	0.98 (H_3-27, d, *J*=6.7 Hz)
3-O-Glu-1'	100.28	5.05 (1H, d, *J*=7.7 Hz)
2'	77.71	4.29 (1H, m)
3'	78.24	4.29 (1H, m)
4'	71.6	4.24 (1H, m)
5'	78.44	4.19 (1H, m)
6'	62.57	4.38 (1H, m), 4.64 (1H, m)

Rha(1→2) 1''	102.01	6.4 (1H, s)
2''	71.72	4.24 (1H, m)
3''	72.54	4.64 (1H, m)
4''	72.78	4.64 (1H, m)
5''	69.44	4.98 (1H, m)
6''	18.63	1.78 (d, J=6.2 Hz)
26-O-Glu-1'''	104.89	4.81 (1H, d, J=7.7 Hz)
2'''	75.2	4.24 (1H, m)
3'''	79.61	4.29 (1H, m)
4'''	74.1	4.03 (1H, m)
5'''	77.84	4.29 (1H, m)
6'''	62.73	4.53 (1H, m), 4.64 (1H, m)

The chemical shift assignments of carbon and proton signals of **Dioscin I** (Compound **9**) in Pyridine-d_5.

Carbon NO.	**Dioscin I**	
	δ_C (ppm)	δ_C (ppm)
1	37.38	1.69 (H_2-1, m)
2	30.02	2.08 (H_2-2, m)
3	78.14	4.25 (H_1-3, m)
4	38.8	2.73 (H_2-4, m)
5	140.63	
6	121.72	5.27 (H_1-6, br.s)
7	32.35	1.86 (H_1-7a, m), 2.03 (H_1-7b, m)
8	31.55	1.55 (H_1-8, m)
9	50.22	0.93 (H_1-9, m)
10	39.8	
11	20.98	1.45 (H_2-11, m)
12	37	2.03 (H_2-12, m)
13	40.55	
14	56.46	1.11 (H_1-14, m)
15	32.21	1.45 (H_1-15a, m), 2.03 (H_1-15b, m)
16	80.98	4.95 (H_1-16, m)
17	63.7	1.93 (H_1-17, m)
18	16.34	0.89 (H_3-18, s)
19	19.28	1.05 (H_3-19, s)
20	40.67	2.23 (H_1-20, m)
21	16.34	1.34 (H_3-21, d, J=6.8 Hz)
22	110.56	
23	37.06	1.74 (H_1-23a, m), 2.03 (H_1-23b, m)
24	28.23	1.69 (H_1-24a, m), 2.03 (H_1-24b, m)
25	34.15	1.93 (H_1-25, m)
26	75.15	3.62 (H_1-26a, m), 4.25 (H_1-26b, m)

27	17.35	0.99 (H_3-27, d, *J*=6.6 Hz)
3-O-Glu-1'	99.83	4.95 (1H, d, *J*=6.54 Hz)
2'	78.02	4.06 (1H, m)
3'	76.11	3.86 (1H, m)
4'	81.32	4.25 (1H, m)
5'	77.13	4.25 (1H, m)
6'	61.34	4.39 (1H, m), 4.56 (1H, m)
Glu(1→4) 1''	104.4	5.10 (1H, d, *J*=7.8 Hz)
2''	73.96	4.39 (1H, m)
3''	88.07	4.17 (1H, m)
4''	69.18	4.17 (1H, m)
5''	77.47	3.86 (1H, m)
6''	61.6	4.39 (1H, m), 4.56 (1H, m)
Glu(1→3) 1'''	105.72	5.30 (1H, d, *J*=7.2 Hz)
2'''	75.42	4.24 (1H, m)
3'''	77.84	3.86 (1H, m)
4'''	71.46	4.25 (1H, m)
5'''	78.54	4.06 (1H, m)
6'''	62.36	4.39 (1H, m), 4.56 (1H, m)
Rha(1→2)1''''	101.67	6.25 (1H, br.s)
2''''	72.3	4.74 (1H, br.s)
3''''	72.62	4.56 (1H, m)
4''''	73.65	4.06 (1H, m)
5''''	69.36	4.95 (1H, m)
6''''	18.53	1.77 (3H, d, *J*=6.1 Hz)
26-O-Glu-1'''''	104.78	4.82 (1H, d, *J*=7.6 Hz)
2'''''	75.05	4.06 (1H, m)
3'''''	78.45	4.25 (1H, m)
4'''''	71.55	4.25 (1H, m)
5'''''	78.33	4.06 (1H, m)
6'''''	62.67	4.39 (1H, m), 4.56 (1H, m)