The chemical shift assignments of carbon and proton signals of **Dioscin D** (Compound **4**) in Pyridine-d_5.

Carbon NO.	Dioscin D	
	δ_C (ppm)	δ_C (ppm)
1	37.42	1.73 (H_2-1, m)
2	30.08	2.09 (H_2-2, m)
3	78.04	3.87 (H_1-3, m)
4	38.86	2.73 (H_1-4, m)
5	140.67	
6	121.77	5.27 (H_1-6, br.s)
7	32.26	1.86 (H_1-7a, m), 2.03 (H_1-7b, m)
8	31.59	1.55 (H_1-8, m)
9	50.26	0.91 (H_1-9, m)
10	40.62	
11	21.03	1.46 (H_2-11, m)
12	37.05	2.03 (H_2-12, m)
13	39.84	
14	56.5	1.11 (H_1-14, m)
15	32.41	2.03 (H_2-15, m)
16	81.98	4.23 (H_1-16, m)
17	63.79	1.92 (H_1-17, m)
18	16.4	0.89 (H_3-18, s)
19	19.32	1.05 (H_3-19, s)
20	40.71	2.23 (H_1-20, dd, *J*=6.8 Hz, 13.4 Hz)
21	16.4	1.34 (H_3-21, d, *J*=6.8 Hz)
22	110.58	
23	37.15	1.73 (H_1-23a, m), 2.03 (H_1-23b, m)
24	28.30	1.68 (H-24a, m), 2.03 (H-24b, m)
25	34.22	1.92 (H_1-25, m)
26	75.21	3.61 (H_1-26a, m), 4.23 (H_1-26b, m)
27	17.41	0.98 (H_3-27, d, *J*=6.7 Hz)
3-O-Glu-1'	99.91	4.96 (1H, d, *J*=7.2 Hz)
2'	74.91	4.35 (1H, m)
3'	77.18	4.23 (1H, m)
4'	81.03	4.94 (1H, m)
5'	78.23	4.29 (1H, m)
6'	61.84	4.35 (1H, m), 4.56 (1H, m)
Glu(1→4)1"	105.19	5.14 (1H, d, *J*=7.9 Hz)
2"	78.56	4.23 (1H, m)
3"	77.68	4.23 (1H, m)
4"	72.7	4.56 (1H, m)
5"	78.44	4.23 (1H, m)
6"	61.99	4.35 (1H, m), 4.40 (1H, m)
Rha(1→2) 1"'	101.75	6.27 (1H, br.s)

2'''	71.12	4.29 (1H, m)
3'''	71.61	4.23 (1H, m)
4'''	74.07	4.05 (1H, m)
5'''	69.42	4.94 (1H, m)
6'''	18.61	1.77 (1H, d, *J*=6.2 Hz)
26-O-Glu-1''''	104.90	4.82 (1H, d, *J*=7.8 Hz)
2''''	75.15	4.05 (1H, m)
3''''	76.14	3.87 (1H, m)
4''''	72.41	4.56 (1H, m)
5''''	78.46	4.23 (1H, m)
6''''	62.74	4.40 (1H, m), 4.56 (1H, m)

The chemical shift assignments of carbon and proton signals of **Dioscin E** (Compound **5**) in Pyridine-d_5.

Carbon NO.	**Dioscin E**	
	δ_C (ppm)	δ_C (ppm, *J* in Hz)
1	37.35	1.68 (H_2-1, m)
2	29.99	2.09 (H_2-2, m)
3	78.1	4.24 (H_1-3, m)
4	38.76	2.73 (H_2-4, m)
5	140.61	
6	121.69	5.27 (H_1-6, br.s)
7	32.31	1.86 (H_1-7a, m), 2.03 (H_1-7b, m)
8	31.51	1.55 (H_1-8, m)
9	50.19	0.93 (H_1-9, m)
10	39.77	
11	20.95	1.46 (H_2-11, m)
12	36.96	2.03 (H_2-12, m)
13	40.51	
14	56.42	1.11 (H_1-14, m)
15	32.18	1.46 (H_1-15a, m), 2.09 (H_1-15b, m)
16	80.96	4.94 (H_1-16, m)
17	63.63	1.93 (H_1-17, m)
18	16.3	0.89 (H_3-18, s)
19	19.24	1.05 (H_3-19, s)
20	40.64	2.23 (H_1-20, m)
21	16.29	1.34 (H_3-21, d, *J*=6.8 Hz)
22	110.55	
23	36.96	1.73 (H_1-23a, m), 2.03 (H_1-23b, m)
24	28.18	1.68 (H_1-24a, m), 2.03 (H_1-24b, m)
25	34.12	1.93 (H_1-25, m)
26	75.12	3.62 (H_1-26a, m), 4.07 (H_1-26b, m)
27	17.3	0.99 (H_3-27, d, *J*=6.6 Hz)

3-O-Glu-1'	99.81	4.94 (1H, d, *J*=7.8 Hz)
2'	75.39	4.06 (1H, m)
3'	76.07	3.86 (1H, m)
4'	81.27	4.24 (1H, m)
5'	77.15	4.24 (1H, m)
6'	61.3	4.39 (1H, m), 4.55 (1H, m)
Glu(1→4) 1''	104.31	5.1 (1H, d, *J*=7.8 Hz)
2''	73.91	4.39 (1H, m)
3''	87.94	4.17 (1H, m)
4''	69.17	4.17 (1H, m)
5''	77.42	3.86 (1H, m)
6''	61.59	4.24 (1H, m), 4.39 (1H, m)
Glu(1→3) 1'''	105.62	5.30 (1H, d, *J*=7.9 Hz)
2'''	78.01	4.24 (1H, m)
3'''	77.8	3.86 (1H, m)
4'''	71.44	4.24 (1H, m)
5'''	78.5	4.06 (1H, m)
6'''	62.34	4.39 (1H, m), 4.55 (1H, m)
Rha(1→2)1''''	101.65	6.25 (1H, br.s)
2''''	72.25	4.74 (1H, br.s)
3''''	72.58	4.55 (1H, m)
4''''	73.65	4.06 (1H, m)
5''''	69.33	4.94 (1H, m)
6''''	18.48	1.77 (3H, d, *J*=6.1 Hz)
26-O-Glu-1'''''	104.72	4.82 (1H, d, *J*=7.7 Hz)
2'''''	75.01	4.06 (1H, m)
3'''''	78.4	4.24 (1H, m)
4'''''	71.51	4.24 (1H, m)
5'''''	78.27	4.06 (1H, m)
6'''''	62.63	4.39 (1H, m), 4.55 (1H, m)

The chemical shift assignments of carbon and proton signals of **Dioscin F** (Compound **6**) in Pyridine-d_5.

Carbon NO.	**Dioscin F**	
	δ_C (ppm)	δ_C (ppm)
1	37.39	1.64 (H_2-1, m)
2	30.02	2.05 (H_2-2, m)
3	78.02	4.21 (H_1-3, m)
4	38.81	2.71 (H_2-4, m)
5	140.64	
6	121.74	5.27 (H_1-6, br.s)
7	32.36	1.89 (H_1-7a, m), 2.01 (H_1-7b, m)
8	31.55	1.47 (H_1-8, m)

9	50.22	0.92 (H_1-9, m)
10	39.81	
11	20.99	1.47 (H_2-11, m)
12	37.01	2.05 (H_2-12, m)
13	40.57	
14	56.47	1.09 (H_1-14, m)
15	32.23	1.46 (H_1-15a, m), 2.09 (H_1-15b, m)
16	81	4.96 (H_1-16, m)
17	63.71	1.89 (H_1-17, m)
18	16.36	0.88 (H_3-18, s)
19	19.29	1.03 (H_3-19, s)
20	40.67	2.22 (H_1-20, m)
21	16.36	1.32 (H_3-21, d, *J*=6.87 Hz)
22	110.57	
23	37.09	1.74 (H_1-23a, m), 2.01 (H_1-23b, m)
24	28.25	1.68 (H_1-24a, m), 2.01 (H_1-24b, m)
25	34.18	1.89 (H_1-25, m)
26	75.17	3.61 (H_1-26a, m), 3.9 (H_1-26b, m)
27	17.36	0.97 (H_3-27, d, *J*=6.6 Hz)
3-O-Glu-1'	100.11	4.93 (1H, d, *J*=7.54 Hz)
2'	77.88	4.21 (1H, m)
3'	76.14	3.90 (1H, m)
4'	81.35	4.21 (1H, m)
5'	77.14	4.21 (1H, m)
6'	61.33	4.45 (1H, m), 4.55 (1H, m)
Glu(1→4)1"	104.43	5.09 (1H, d, *J*=6.87 Hz)
2"	73.99	4.36 (1H, m)
3"	88.12	4.21 (1H, m)
4"	69.19	4.21 (1H, m)
5"	77.18	3.90 (1H, m)
6"	61.61	4.21 (1H, m), 4.36 (1H, m)
Glu(1→3)1"'	105.76	5.29 (1H, d, *J*=7.9 Hz)
2"'	76.09	4.21 (1H, m)
3"'	77.51	3.90 (1H, m)
4"'	71.56	4.21 (1H, m)
5"'	78.59	4.05 (1H, m)
6"'	62.39	4.36 (1H, m), 4.55 (1H, m)
Glu(1→2)1""	99.84	4.92 (1H, d, *J*=6.87 Hz)
2""	75.46	4.05 (1H, m)
3""	78.49	4.21 (1H, m)
4""	71.48	4.21 (1H, m)
5""	78.38	4.05 (1H, m)
6""	62.69	4.45 (1H, m), 4.55 (1H, m)
Rha(1→2) 1"""	101.71	6.23 (1H, s)

2"''	72.34	4.55 (1H, m)
3"''	72.66	4.45 (1H, m)
4"''	73.65	4.05 (1H, m)
5"''	69.38	4.93 (1H, m)
6"''	18.55	1.78 (1H, d, *J*=6.45 Hz)
26-O-Glu-1"'''	104.82	4.81 (1H, d, *J*=7.7 Hz)
2"'''	75.08	4.05 (1H, m)
3"'''	78.42	4.21 (1H, m)
4"'''	71.62	4.21 (1H, m)
5"'''	78.19	4.05 (1H, m)
6"'''	62.39	4.36 (1H, m), 4.55 (1H, m)