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Two New C – 21 Steroidal Glycosides from *Cynanchum aurichulatum*

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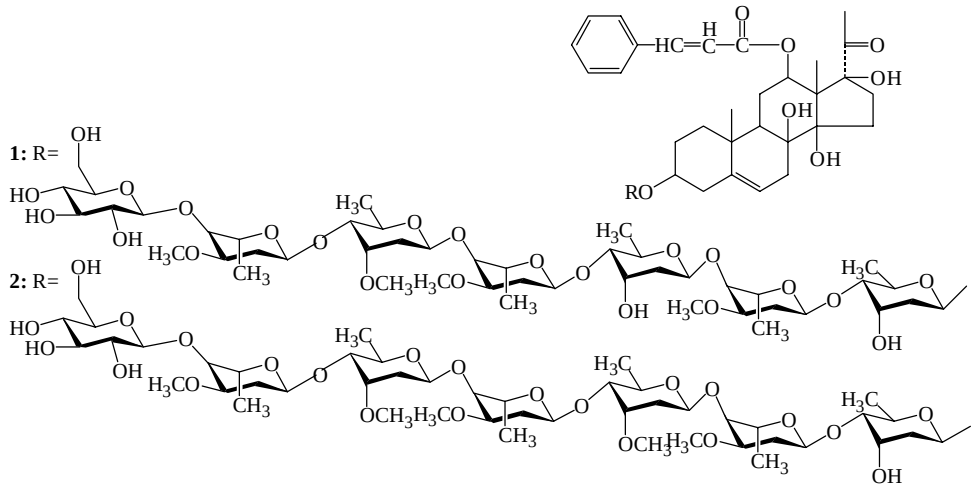
Abstract: Two new C–21 steroidal glycosides, cynanauriculoside I and cynanauriculoside II, were isolated from the roots of *Cynanchum aurichulatum*. Their structures were established using spectroscopic methods including one and two-dimensional NMR.

Keywords: *Cynanchum aurichulatum*, C–21 steroidal glycoside, cynanauriculoside I, cynanauriculoside II.

The roots of *Cynanchum aurichulatum* Royle ex Wight have been used in traditional medicine for the prevention and treatment of geriatric diseases and prolonging life. The active constituents against hepatocarcinoma of the root of *Cynanchum aurichulatum* are studied and two new active steroidal glycosides named cynanauriculoside I and cynanauriculoside II (**Figure 1**) are obtained and elucidated.

Figure 1 The structures of **1** and **2**



The positive ESI-MS spectrum of compound **1** showed the molecular ion at *m/z* 1531.87$(M+Na)^+$ in agreement with the molecular formula $C_{76}H_{116}O_{30}$. Compared

^{1}HNMR and ^{13}CNMR data for compound **1** with those in literature[1] (**Table 1**), the aglycone of **1** is confirmed to be kidjoranin. In the ^{13}CNMR spectrum of **1**, comparing with ^{13}CNMR chemical shifts of kidjoranin, the glycosidation shifts[1] were observed at C-2(-2.11 ppm), C-3(+5.95 ppm) and C-4(-4.14 ppm) indicating the attachment of the sugar chain at the C-3 hydroxyl group of the aglycone.

In the ^{13}C NMR spectrum of **1**, seven anomeric carbon signals were observed at δ (ppm) 95.91, 98.35, 96.27, 98.29, 95.86, 98.87 and 102.21, corresponding to seven ano-

Table 1 ^{1}H and ^{13}CNMR of compound **1** (in C_5D_5N, δ ppm)

C	^{13}CNMR	^{1}HNMR	C	^{13}CNMR	^{1}HNMR
1	38. 84	1. 08, 1. 80	3	73. 55	3. 73
2	29. 89	2. 06, 1. 78	4	77. 23	3. 85
3	77. 55	3. 84	5	66. 03	4. 57
4	39. 16	2. 50, 2. 39	6	18. 07	1. 40
5	139. 29		OMe	56. 95	3. 35
6	119. 06	5. 28	D-digito-1	96. 27	5. 40
7	34. 67	2. 31, 2. 46	2	38. 78	2. 39, 1. 95
8	74. 22	5. 16	3	67. 57	4. 47
9	44. 43	1. 73	4	81. 24	3. 45
10	37. 33		5	68. 86	4. 16
11	25. 00	2. 30, 2. 16	6	18. 39	1. 37
12	73. 50	5. 18	L - cym-1	98. 29	5. 04
13	58. 04		2	32. 43	2. 29, 1. 85
14	89. 41	6. 19	3	73. 48	3. 74
15	33. 72	2. 12	4	77. 12	3. 82
16	33. 00	3. 26, 2. 03	5	66. 31	4. 55
17	92. 35	6. 46	6	18. 17	1. 37
18	10. 60	2. 01	OMe	56. 97	3. 33
19	18. 08	1. 32	D-cym-1	95. 86	5. 21
20	209. 79		2	36. 53	2. 30, 1. 77
21	27. 61	2. 48	3	77. 60	3. 88
1′	165. 74		4	82. 24	3. 43
2′	119. 14	6. 81	5	68. 86	4. 16
3′	144. 85	7. 99	6	18. 43	1. 33
4′	135. 10		OMe	58. 15	3. 54
5′	128. 51	7. 62	L - cym-1	98. 87	4. 94
6′	129. 23	7. 33	2	32. 20	2. 34, 1. 78
7′	130. 52	7. 33	3	73. 28	3. 93
8′	129. 23		4	78. 76	3. 94
9′	128. 51		5	65. 11	4. 69
D-digito - 1	95. 91	5. 39	6	18. 43	1. 46
2	38. 73	2. 37, 1. 98	OMe	56. 67	3. 42
3	65. 57	4. 47	D-glu-1	102. 21	4. 99
4	81. 24	3. 45	2	75. 23	3. 97
5	68. 86	4. 16	3	78. 29	4. 23
6	18. 39	1. 39	4	71. 71	4. 20
L – cym-1	98. 35	5. 04	5	78. 43	3. 97
2	32. 43	2. 29, 1. 82	6	62. 90	4. 55, 4. 36

meric proton signals at δ (ppm) 5.39 (dd, 1H, J=9. 5, 1. 6Hz), 5.04 (br d, 1H, J=3. 2Hz), 5.40 (dd, 1H, J=9. 5, 1. 5Hz), 5.04 (br d, 1H, J=3. 2Hz), 5.21 (dd, 1H, J=9. 4, 1. 6Hz), 4.94

(dd, 1H, J=4. 4, 1. 8Hz) and 4.99 (d, 1H, J=7. 7Hz) as revealed in HSQC spectrum, which indicated that there were seven sugar units in **1**. Detailed analysis of the proton and carbon chemical shifts and splitting pattern in NMR showed that **1** contained one D-cymarose, three L-cymaroses, two D-digitoxoses, and one D-glucose, of which the che-mical shifts were consistent with those in literatures[2-6]. Many NOE correlations were

Table 2 ^{1}H and ^{13}CNMR of compound **2** (in C_5D_5N, δ ppm)

C	^{13}CNMR	^{1}HNMR	C	^{13}CNMR	^{1}HNMR
1	38.79	1. 08, 1. 80	3	73. 48	3. 73
2	29. 78	2. 06, 1. 78	4	77. 23	3. 85
3	77. 55	3. 84	5	66. 10	4. 55
4	39. 16	2. 50, 2. 40	6	18. 06	1. 38
5	139. 29		OMe	56. 77	3. 35
6	119. 06	5. 28	D-cym-1	95. 62	5. 21
7	34. 67	2. 31, 2. 46	2	36. 57	2. 30, 1. 78
8	74. 22	5. 16	3	77. 60	3. 87
9	44. 43	1. 73	4	82. 33	3. 42
10	37. 33		5	69. 27	4. 15
11	25. 00	2. 29, 2. 16	6	18. 43	1. 33
12	73. 55	5. 18	OMe	58. 27	3. 51
13	58. 04		L – cym-1	98. 85	4. 93
14	89. 41	6. 19, 6. 19	2	32. 24	2. 30, 1. 81
15	33. 72	2. 12	3	73. 17	3. 74
16	33. 00	3. 26, 2. 03	4	77. 60	3. 83
17	92. 35	6. 46	5	65. 26	4. 63
18	10. 60	2. 01	6	18. 55	1. 49
19	18. 08	1. 32	OMe	56. 77	3. 35
20	209. 79		D-cym-1	95. 78	5. 20
21	27. 61	2. 48	2	36. 58	2. 28, 1. 76
1′	165. 74		3	77. 63	3. 87
2′	119. 14	6. 81	4	82. 33	3. 42
3′	144. 85	7. 99	5	69. 27	4. 17
4′	135. 10		6	18. 43	1. 34
5′	128. 51	7. 62	OMe	58. 23	3. 53
6′	129. 23	7. 33	L - cym-1	98. 97	4. 95
7′	130. 52	7. 33	2	32. 20	2. 34, 1. 77
8′	129. 23	7. 33	3	73. 27	3. 93
9′	128. 51	7. 62	4	78. 84	3. 94
D - digito-1	96. 23	5. 40	5	65. 10	4. 68
2	38. 75	2. 37, 1. 99	6	18. 46	1. 45
3	67. 70	4. 47	OMe	56. 88	3. 42
4	81. 32	3. 45	D-glu-1	102. 23	4. 99
5	68. 73	4. 16	2	75. 39	3. 96
6	18. 15	1. 39	3	78. 35	4. 23
L- cym -1	98. 28	5. 04	4	71. 77	4. 19
2	32. 38	2. 29, 1. 82	5	78. 66	3. 96
			6	62. 90	4. 55

observed in the 2D NOESY spectrum of **1**. These linkages were also confirmed by long-range correlation observed in HMBC spectrum.

Therefore, compound **1** was concluded to be kidjoranin-3-O-β-D-glucopyranosyl- (1→4)-α-L-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-α-L-cymaropyrano-syl -(1→4)-β-D-digitoxopyranosyl-(1→4)-α-L- cymaropyranosyl-(1→4)-β-D-digitoxo-

pyranoside and named cynanauriculoside I.

In ESI-MS, **2** showed the molecular ion $(M+Na)^+$ at *m/z* 1545.94, suggesting the molecular formula of compound **2** to be $C_{77}H_{118}O_{30.}$ **2** had the same aglycone moiety as that in **1** as indicated by the **c**omparison of their ^{1}HNMR and ^{13}CNMR assignments presented in **Table 2**. Similar to **1**, cynanauriculoside **2** also contains seven sugar units, as revealed by seven anomeric carbon signals at δ_C (ppm) 96.23, 98.28, 95.62, 98.85, 95.78, 98.97 and 102.23, corresponding to seven anomeric proton signals at δ_H 5.40, 5.04, 5.21, 4.93, 5.20, 4.95 and 4.99 as observed in HSQC spectrum. The same methods were used for the elucidation of sugar linkages of **2**. Similar NOE effect and HMBC spectrum of **2** to those of **1** were observed. Consequently, the structure of **2** was assigned askidjoranin-3-O-β-D-glucopyranosyl-(1→4)-α-L-cymaropyranosyl-(1→4)-β-D-cymaro -pyranosyl-(1→4)-α-L-cymaropyranosyl-(1→4)-β-D-cymaropyranosyl-(1→4)-α-L-cy -maropyranosyl-(1→4)-β-D-digitoxopyranoside and named cynanauriculoside II.

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