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大叶吊兰甙 A 和 B 的 NMR
化学位移全归属

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摘 要: 应用 2D NMR 实验技术进一步研究确定了从百合科植物大叶吊兰中分离到的两个新的 C-27 甙体皂甙类化合物, 大叶吊兰甙(chloromaloside) A 和 B 的化学结构, 并对其¹H 和¹³C NMR 信号进行了全归属。

关键词: Chloromaloside A; Chloromaloside B; 甙体皂甙; NMR 信号全归属

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大叶吊兰甙

中药

化学位移

大叶吊兰甙(chloromaloside) A(1) 和 B(2) 为我们研究组数年前从百合科吊兰属植物大叶吊兰(*Chlorophytum malayense* Ridley) 中分离得到的两个新的 C-27 甙体皂甙^[1]。鉴于这两个化合物的糖基部分结构复杂, 根据经验及与文献比较的方法, 难以准确地得到每个糖基相应的¹³C NMR 信号; 应用配糖位移效应的经验规律不一定能准确推定糖链的连接。尽管进行了化学降解, 但其 NMR 化学位移的指定仍不完全确定, 为了进一步证实其化学结构, 本文应用 2D NMR 技术, 对其¹H 和¹³C NMR 信号进行全归属。

1 结果与讨论

1.1 大叶吊兰甙 A(1)

$[\alpha]_D^{20} = -68.5^{\circ}$ (c 0.40; pyridine). FAB-MS 出现准分子离子峰 $m/z: 1047[M-H]^{-}$; 结合¹³C NMR(DEPT) 谱, 推定分子式为 C₅₀H₈₀O₂₃, 这与文献的结果吻合^[1]。甙元的结构通过与文献中 neohecogenin 的¹³C NMR 数据比较而确定^[1](表 1)。

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表 1 大叶吊兰甙 A(1)和 B(2) 甙元部分的¹H(500MHz)和¹³C(125MHz)
NMR 数据(溶剂:吡啶-d₅, 偶合常数:Hz)

Tab.1 ¹H(500MHz) and ¹³C(125MHz)NMR data of aglycon moiety of chloromaloside
A(1) and B(2) (δ in pyridine-d₅, J:Hz)

位置	1			2		
	δ_C ref. [1]	δ_C	δ_H	δ_C ref. [1]	δ_C	δ_H
1	36.6	36.8	1.29(m);0.70(m)	36.7	36.7	1.30(m);0.71(m)
2	29.6	29.8	1.97(br.d,9.90);1.51(m)	29.7	29.7	1.98(m);1.54(m)
3	77.3	77.4	4.05(m)	77.3	77.3	3.85(m)
4	34.6	34.8	1.59(m);1.31(m)	34.7	34.5 ^a	1.77(m);1.33(m)
5	44.5	44.6	0.84(m)	44.5	44.6	0.87(m)
6	28.6	28.7	1.13(m);1.05(m)	28.6	28.7	1.15(m);1.08(m)
7	31.4	31.5	2.09(m);1.58(m)	31.4	31.5	2.03(m);1.53(m)
8	34.3	34.5	1.57(m)	34.4	34.5 ^a	1.72(m)
9	55.6	55.6	0.90(m)	55.7	55.8	0.90(m)
10	36.3	36.4		36.3	36.4	
11	38.0	38.2	2.36(t,13.78); 2.19(dd,13.78,4.47)	37.9	38.0	2.34(t,14.31); 2.20(dd,14.31,4.94)
12	212.9	213.3		212.8	213.0	
13	55.3	55.5		55.5	55.6 ^b	
14	55.9	56.1	1.34(m)	55.9	55.9	1.32(m)
15	31.7	31.8	1.56(m);0.77(m)	31.7	31.8	1.57;0.78
16	79.8	80.0	4.44(m)	79.8	80.0	4.38
17	54.1	54.3	2.72(dd,8.54,7.00)	55.3	55.6 ^b	2.66(dd,7.87,7.17)
18	16.3	16.4	1.07(s) [1.080(s)]	16.0	16.2	1.05(s) [1.056(s)]
19	11.7	11.9	0.65(s) [0.646(s)]	11.7	11.8	0.66(s) [0.666(s)]
20	43.1	43.2	1.86(m)	41.1	41.2	2.19(m)
21	13.7	13.9	1.34(d,6.99) [1.369(d,6.9)]	15.0	15.2	1.37(d,6.30) [1.390(d,6.4)]
22	109.8	109.9		112.8	112.9	
23	26.4	26.5	2.11(m);1.89(m)	30.9	31.0	1.93(m);1.81(m)
24	26.1	26.3	1.89(dd,13.78,4.66); 1.38(m)	28.2	28.2	1.70(m);1.36(m)
25	27.5	27.6	1.59(m)	34.4	34.4	1.87(m)
26	65.2	65.4	4.03(m); 3.37(dd,9.30,7.12)	74.6	75.0	4.06(m); 3.52(dd,9.12,7.03)
27	16.1	16.3	1.06(d,7.12) [1.071(d)]	17.5	17.6	1.03(d,7.03) [1.048(d,6.9)]
OMe				47.4	47.6	3.25(s) [3.265(s)]

注:^a-^b信号重叠;[]内为文献¹H NMR 数据

表 2 大叶吊兰甙 A(1)和 B(2)糖基部分的¹H(500MHz)和¹³C(125MHz)NMR 数据(溶剂:吡啶-d₅, 偶合常数:Hz)Tab.2 ¹H(500MHz) and ¹³C(125MHz)NMR data of sugar moieties of chloromaloside A(1) and B(2) (δ in pyridine-d₅, J:Hz)

糖基	1			2		
	δ _C ref. [1]	δ _C	δ _H	δ _C ref. [1]	δ _C	δ _H
A-1	102.4	102.6	4.84(d, 7.38) [4.874(d, 7.5)]	102.5	102.5	4.85(d, 7.52) [4.835(d, 8.0)]
2	73.1	73.2	4.37(m)	73.1	73.2	4.39(m)
3	75.5	75.7	4.11(m)	75.6	75.7	4.11(m)
4	79.8	80.0	4.58(br.s)	79.9	80.0	4.58(br.s)
5	76.0	75.4	3.99(m)	76.1	75.4	4.00(m)
6	60.7	60.8	5.64(t, 9.71); 4.18(m)	60.7	60.8	4.65(t, 9.77); 4.20(m)
B-1	104.8	105.1	5.14(d, 7.77) [5.198(d, 7.9)]	105.0	105.1	5.16(d, 7.35) [5.156(d, 7.6)]
2	81.2	81.4	4.35(m)	81.2	81.4	4.37(m)
3	87.0	87.0	4.12(m)	87.2	86.9	4.13(m)
4	70.4	70.5	3.78(t, 9.51)	70.4	70.5	3.79(t, 9.27)
5	77.7	77.6	3.83(m)	77.5	77.7	3.85(m)
6	62.4	63.1	4.49(m); 4.02(m)	62.5	63.1	4.54(m); 4.03(m)
C-1	104.8	104.9	5.53(d, 7.77) [5.241(d, 7.6)]	105.0	104.9	5.55(d, 7.17) [5.218(d, 8.1)]
2	75.0	76.2	4.03(m)	75.2	76.3	4.02(m)
3	78.5	77.9	4.10(m)	78.6	77.8	4.08(m)
4	71.1	71.2	4.17(m)	71.1	71.1	4.15(m)
5	77.7	78.7 ^a	3.87(m)	77.8	78.8	3.87(m)
6	62.9	62.6	4.52(m); 4.34(m)	62.9	62.5	4.56(m); 4.36(m)
D-1	104.6	105.0	5.19(d, 7.96) [5.578(d, 7.0)]	104.7	105.0	5.21(d, 7.87) [5.558(d, 7.0)]
2	75.3	76.2	3.95(m)	75.3	75.1	3.92(m)
3	78.5	78.7 ^a	4.09(m)	78.6	78.7 ^b	4.05(m)
4	70.7	70.9	4.07(m)	70.7	70.8	4.09(m)
5	67.3	67.4	4.21(m); 3.66(t, 10.87)	67.3	67.4	4.21(m); 3.64(t, 10.32)
E-1				105.0	105.2	4.82(d, 7.87) [4.857]
2				75.0	75.3	3.99(m)
3				78.5	78.7 ^b	4.17(m)
4				71.8	71.8	4.19(m)
5				78.4	78.6	3.92(m)
6				62.9	63.0	4.51(m); 4.34(m)

注: ^a、^b信号重叠, []内为文献的¹H NMR 数据

^{13}C NMR 谱提示化合物 **1** 具有四个端基碳, 化学位移分别为: $\delta 102.56(\text{A}_{\text{C}1})$, $104.85(\text{C}_{\text{C}1})$, $105.01(\text{D}_{\text{C}1})$ 和 $105.11(\text{B}_{\text{C}1})$; HMQC 实验显示四个端基质子的化学位移分别为: $\delta 4.84(\text{A}_{\text{H}1})$, $5.14(\text{B}_{\text{H}1})$, $5.53(\text{C}_{\text{H}1})$ 和 $5.19(\text{D}_{\text{H}1})$. HMQC-TOCSY 谱提示 A, B 和 C 为六碳糖, 而 D 为五碳糖. 由于半乳糖 H-4 处于 e 键, H-3 和 H-4 以及 H-4 和 H-5 之间的 $^3J_{\text{HH}}$ 较小, 磁化矢量转移效果大为降低, 在 HMQC-TOCSY 实验中, 即使混合时间达到 180ms 也不能建立糖基偶合网络内的全相关; 但可以建立糖基内端基到 4 位的相关以及 6 位到 5 位的相关; 而葡萄糖和木糖当混合时间为 180ms 时, 可以建立糖基偶合网络内的从端基到末位的全相关^[2]. HMQC-TOCSY ($t_m = 180\text{ms}$) (图 2) 出现 $\text{A}_{\text{C}1}$ 至 $\text{A}_{\text{C}4}$ 相关提示 A 为半乳糖; B, C 和 D 出现端基碳至末位碳的全相关提示它们分别为葡萄糖、葡萄糖和木糖. 从四个糖基端基氢的偶合常数 $^3J_{\text{H}1, \text{H}2}$ 在 7-8Hz, 说明它们皆为 β -构型. ROESY 谱中, 四个糖都出现了端基氢与 H-3 和 H-5 的 NOE 相关, 证实它们均为 β -构型^[3]. 在 HMQC-TOCSY 技术获得每个糖基内所有氢和所有碳的信息基础上, 结合 TOCSY, COSY, HMQC 等 2D NMR 实验, 对皂甙 **1** 的四个糖基氢与碳的信号进行了全归属^[4-6], 指定结果经 HMBC 和 ROESY 验证(表 2).

皂甙 **1** 的 HMBC 谱出现以下 H, C 远程相关信号, 从而确定了糖基之间及糖基与甙元之间的连接: $\text{A}_{\text{H}1}$ ($\delta 4.84$) 与甙元 C-3 ($\delta 77.41$), $\text{B}_{\text{H}1}$ ($\delta 5.14$) 与 $\text{A}_{\text{C}4}$ ($\delta 79.99$), $\text{C}_{\text{H}1}$ ($\delta 5.53$) 与 $\text{B}_{\text{C}3}$ ($\delta 87.00$), $\text{D}_{\text{H}1}$ ($\delta 5.19$) 与 $\text{B}_{\text{C}2}$ ($\delta 81.38$). ROESY 实验出现 $\text{A}_{\text{H}1}$ ($\delta 4.84$) 与甙元 H-3 ($\delta 4.05$), $\text{B}_{\text{H}1}$ ($\delta 5.14$) 与 $\text{A}_{\text{H}4}$ ($\delta 4.58$), $\text{C}_{\text{H}1}$ ($\delta 5.53$) 与 $\text{B}_{\text{H}3}$ ($\delta 4.12$), $\text{D}_{\text{H}1}$ ($\delta 5.19$) 与 $\text{B}_{\text{H}2}$ ($\delta 4.35$) 的 NOE 相关信号也进一步证实了推定结构的合理性(图 1).

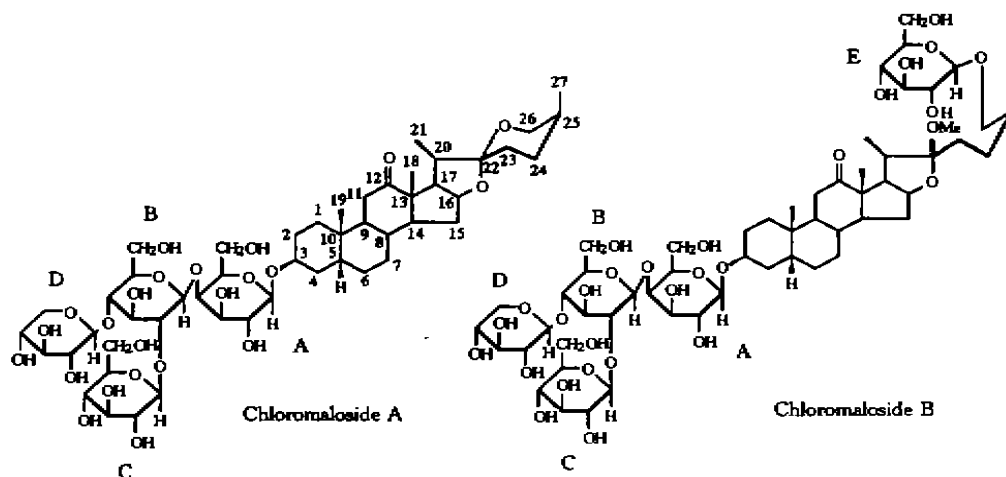


图 1 Chloromaloside A 和 B 的结构

Fig. 1 The structures of chloromaloside A and B

1.2 大叶吊兰甙 B(2)

$[\alpha]_{\text{D}}^{20} = -31.0^{\circ}$ (c 0.50; pyridine). FAB-MS 出现准分子离子峰 $m/z: 1242[\text{M}-\text{H}]^{-}$; 结合核磁 ^{13}C NMR (DEPT) 谱, 推定分子式为 $\text{C}_{57}\text{H}_{94}\text{O}_{29}$, 与文献的结果吻合^[1]. 该化合物为

neohecogenin 的呋甙烷型皂甙, 甙元的结构通过与文献中的 ^{13}C NMR 数据比较而确定^[7] (表 1).

^{13}C NMR 谱提示化合物 2 具有五个端基碳, 化学位移分别为: $\delta 102.55(\text{A}_{\text{C}1})$, $104.88(\text{C}_{\text{C}1})$, $105.00(\text{D}_{\text{C}1})$, $105.10(\text{B}_{\text{C}1})$ 和 $105.16(\text{E}_{\text{C}1})$; 五个端基氢的化学位移系由 HMQC 实验得到指定, 分别为: $\delta 4.85(\text{A}_{\text{H}1})$, $5.16(\text{B}_{\text{H}1})$, $5.55(\text{C}_{\text{H}1})$, $5.21(\text{D}_{\text{H}1})$ 和 $4.82(\text{E}_{\text{H}1})$. 用 HMQC-TOCSY(图 3) 技术获得每个糖基内所有氢和所有碳的信息后, 发现 2 与 1 具有四个相同的糖基, 即: A、B、C 和 D. 但 2 多一个糖基 E, 其 ^{13}C 化学位移($\delta 105.16, 78.69, 78.55, 75.28, 71.84, 62.96$)表明为 β -D-葡萄糖吡喃糖基^[8]; 其端基质子信号($\delta 4.82, d, J = 7.87\text{Hz}$)证明应为 β -构型^[3]. 与 1 相比较, 并结合 HMQC-TOCSY、COSY、HMQC 等 2D NMR 实验, 对皂甙 2 的氢和碳的 NMR 化学位移进行了全归属, 并经 HMBC 验证, 结果见表 2. 可以看出, 在化合物 1 和 2 中, 四个相同的糖基 A、B、C 和 D 的氢和碳的化学位移非常接近, 进一步证实了两个化合物结构推定和糖基化学位移归属的准确性.

皂甙 2 的糖基与甙元之间以及糖基之间的连接由 HMBC 实验进一步得以确定. HMBC 谱观察到下列 H、C 远程相关信号: $\text{A}_{\text{H}1}(\delta 4.85)$ 与甙元 C-3($\delta 77.29$), $\text{B}_{\text{H}1}(\delta 5.16)$ 与 $\text{A}_{\text{C}4}(\delta 80.01)$, $\text{C}_{\text{H}1}(\delta 5.55)$ 与 $\text{B}_{\text{C}3}(\delta 86.89)$, $\text{D}_{\text{H}1}(\delta 5.21)$ 与 $\text{B}_{\text{C}2}(\delta 81.40)$, $\text{E}_{\text{H}1}(\delta 4.82)$ 与甙元 C-26($\delta 75.01$). 所以 2 的结构与文献中的结构相符, 如图 1 所示.

鉴于所有的 NMR 均在 500MHz 超导核磁共振谱仪上测定, 两个皂甙的 NMR 化学位移值与原来用 400MHz NMR 谱仪测定的略有差异. 本次实验的结果还对个别碳化学位移(如糖基部分的 C-1 与 D-1, B-6 与 C-6)和氢化学位移(如 C-1 与 D-1)的指定进行了纠正.

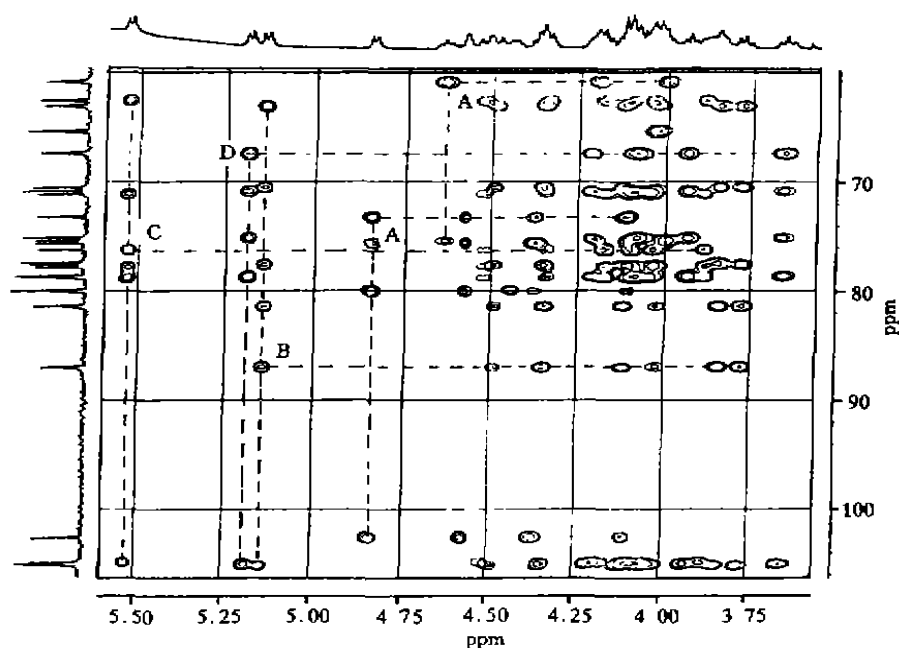


图 2 大叶吊兰甙 A 的 HMQC-TOCSY 图谱

Fig. 2 HMQC-TOCSY spectrum of chloromaloside A

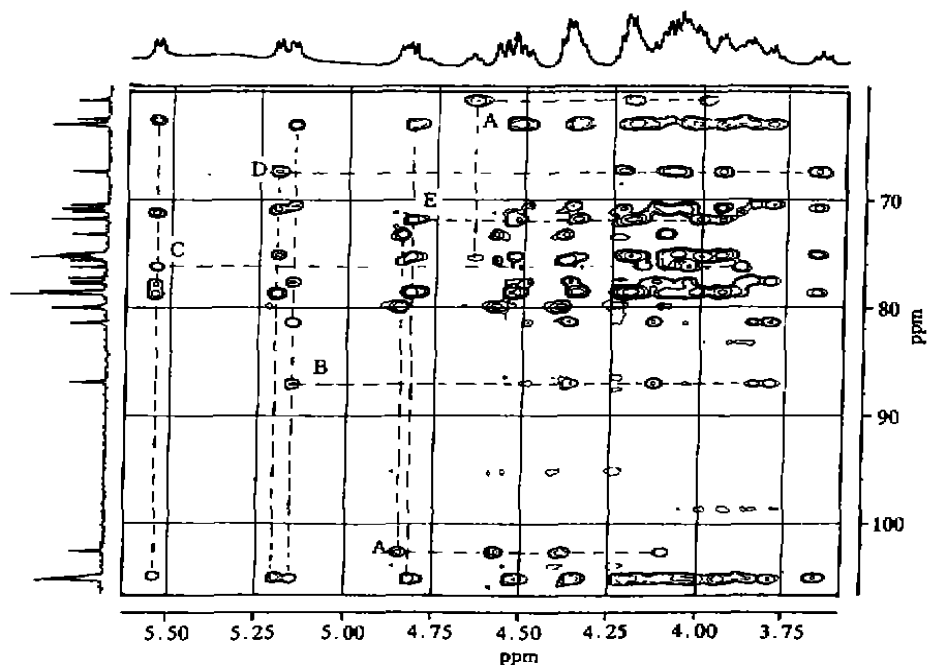


图 3 大叶吊兰贰 B 的 HMQC-TOCSY 图谱

Fig. 3 HMQC-TOCSY spectrum of chloromaloside B

2 实验与仪器

FAB-MS 在 VG Autospec-3000 质谱仪测定;旋光在日本 HORIBA SEPA-300 数字旋光仪上测定。

所有核磁共振实验在 Bruker DRX 500MHz 超导核磁共振谱仪上测定. 1(约 40mg)与 2(约 52mg)溶于 99.5% 的 C_5D_5N (约 0.4mL)于室温下在 500.13MHz(1H)和 125.76MHz(^{13}C)下用 $\phi 5mm$ 反相探头(BBI)进行测定. 溶剂提供氘锁信号并以其最低场的 $C(\delta_c 149.9)$ 、 $H(\delta_H 8.71)$ 信号作为内标,采用正交检测. DQF COSY, HMQC 和 HMBC 都是 Z-梯度脉冲实验, HMBC 取 62.5ms 以得到 H、C 远程相关. HMQC-TOCSY 实验混合时间取 180ms 以分别获得各糖基内 H、C 的相关. ROESY 实验的自旋锁定时间为 300ms. TOCSY 取混合时间 180ms 得到每个糖基从端基氢至末位氢的全相关。

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COMPLETE ASSIGNMENT OF NMR CHEMICAL SHIFTS OF CHLOROMALOSIDE A AND B

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Abstract

By means of 2D NMR techniques, such as HMQC-TOCSY, TOCSY, ROESY, HMQC, HMBC and COSY, the structures of chloromaloside A and B, two new C-27 steroidal saponins from *Chlorophytum malayense* were confirmed. Their complete assignment of ^1H and ^{13}C NMR chemical shifts were also obtained.

Key words: Steroidal saponins; Chloromaloside A; Chloromaloside B; complete assignment

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