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CHAMAECHROMONE, A NOVEL REARRANGED BIFLAVONOID FROM STELLERA CHAMAEJASME L.

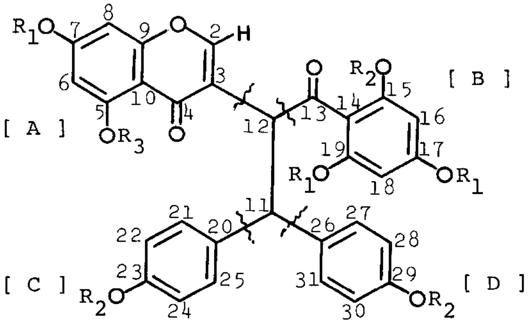
Masatake Niwa,* Guo-Quan Liu,[1] Hiroshi Tatematsu, and Yoshimasa Hirata
Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

Summary: A novel biflavonoid, chamaechromone was isolated from *Stellera chamaejasme* L. (Thymelaeaceae) and its structure elucidated by spectroscopic and chemical methods.

Our previous studies on the constituents of the roots of *Stellera chamaejasme* L. (Thymelaeaceae) resulted in the isolation and structural elucidation of five C-3/C-3''-biflavanones.[2,3] We now describe the isolation and structure of a novel rearranged biflavonoid named chamaechromone (**1**) from the same plant.

According to essentially the same procedure as described in the previous paper,[3] the ethyl acetate fraction obtained from the methanolic extract was roughly separated by column chromatography on silica gel (Merck 7734) using a gradient solution of chloroform-ethyl acetate. The fraction obtained after elution of biflavanones, neochamaejasmin A (**2**) and neochamaejasmin B (**3**) was further separated by medium pressure chromatography on reversed phase silica gel (Merck Lobar column RP-8) using methanol-water (75 : 25) to afford chamaechromone (**1**) as amorphous powder : $C_{30}H_{22}O_{10}$ [m/z 542.1244; calcd. 542.1212]; $[\alpha]_D$ +80.0° (c 0.5, MeOH), UV (MeOH) λ 225 (ε 40600), 260 (ε 19900), and 296 nm (ε 21700); IR (KBr) ν 3350, 1650, and 1620 cm^{-1}; ^{1}H NMR (CD$_3$OD) δ 4.64 (1H, d, J=12Hz), 5.80 (2H, s), 6.13 (1H, d, J=2Hz), 6.20 (1H, d, J=2Hz), 6.36 (1H, d, J=12Hz), 6.57 (2H, d, J=7Hz), 6.64 (2H, d, J=7Hz), 7.07 (2H, d, J=7Hz), 7.20 (2H, d, 7Hz), and 7.94 ppm (1H, s).

The ^{13}C NMR spectrum of **1** accommodates the signals corresponding to genistein (**4**),[4] trihydroxyacetophenone (**5**),[5] and bis(p-hydroxyphenyl)methane (**6**),[6] strongly suggesting the presence of the partial structures A, B, C, and D in **1** (Table 1), which was also supported by ^{1}H NMR spectrum of **1**. In addition, ^{1}H NMR [δ 4.64 (1H, d, J=12Hz) and 6.36 (1H, d, J=12Hz)] and ^{13}C NMR spectra [δ 48.7 (d) and 52.8 (d)] also indicated the presence of the partial structure $>$CH-CH$<$ in **1**. On the basis of the data mentioned above, the structure of chamaechromone can be represented by **1a** or **1b**. Of these two possible structures, however, the former (**1a**) must be given to chamaechromone, as judged from the mass spectra of the derivatives of **1**.

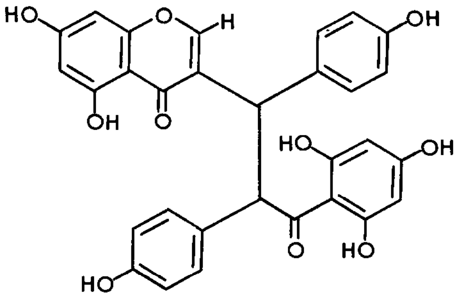


1a ; $R_1=R_2=R_3=H$

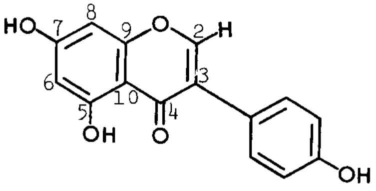
7 ; $R_1=CH_3$, $R_2=R_3=H$

8 ; $R_1=CH_3$, $R_2=COCH_3$, $R_3=H$

9 ; $R_1=CH_3$, $R_2=R_3=COCH_3$



1b



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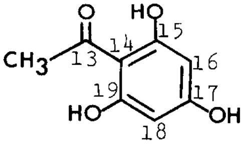

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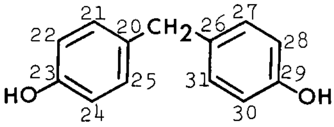

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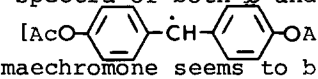
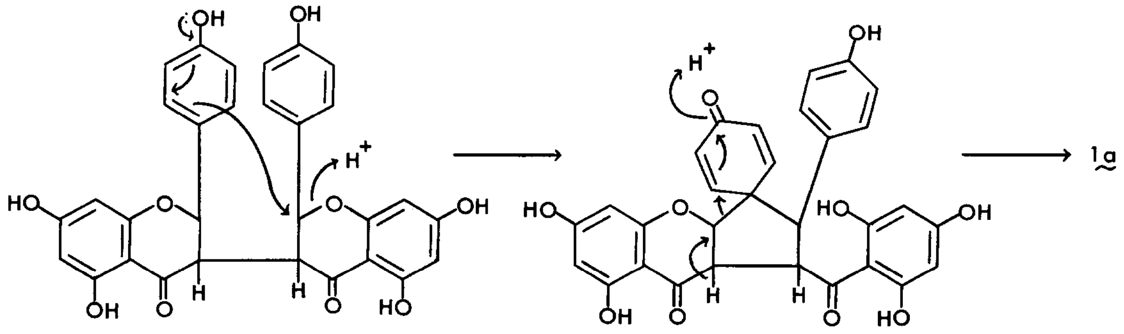
Table 1. ^{13}C NMR Spectra of 1a, 4, 5 and 6

Position	1a	4
2	156.7(d)	153.6(d)
3	120.7(s)	122.4(s)
4	181.3(s)	180.2(s)
5	161.9(s)	162.1(s)
6	99.7(d)	98.6(d)
7	164.6(s)	164.3(s)
8	94.5(d)	93.7(d)
9	158.2(s)	157.5(s)
10	104.9(s)	104.6(s)
11	48.7(d)	
12	52.8(d)	5
13	203.4(s)	204.6(s)
14	106.9(s)	105.6(s)
15	163.7(s)	165.7(s)
16	96.2(d)	95.6(d)
17	165.2(s)	166.2(s)
18	96.2(d)	95.6(d)
19	163.7(s)	165.7(s)

Position	1a	6
20	134.4(s)	134.2(s)
21	129.0(d)	130.6(d)
22	115.5(d)	116.1(d)
23	155.0(s)	156.3(s)
24	115.5(d)	116.1(d)
25	129.0(d)	130.6(d)
26	133.9(s)	134.2(s)
27	129.5(d)	130.6(d)
28	115.4(d)	116.1(d)
29	155.4(s)	156.3(s)
30	115.4(d)	116.1(d)
31	129.5(d)	130.6(d)

Chamaechromone (1) was treated with diazomethane (room temp., 30 min.) to afford the corresponding trimethyl ether (7)[7] and then acetylated with acetic anhydride-pyridine (room temp., overnight) to give two products, triacetate (8)[8] and tetraacetate (9).[9] In the mass spectra of both 8 and 9, the fragment peak at m/z 283 corresponding to $C_{17}H_{15}O_4$ [] was observed.

From a biogenetic point of view, chamaechromone seems to be derived from C-3/C-3''-biflavanone[3,10] as seen below.



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References and Notes

1. Present address: Institute of Chemistry, Chinese Academy of Science, Beijing, China.
2. G.-Q. Liu, H. Tatematsu, M. Kurokawa, M. Niwa and Y. Hirata, Chem. Pharm. Bull., 32, 362 (1984).
3. M. Niwa, H. Tatematsu, G.-Q. Liu and Y. Hirata, Chem. Lett., 539 (1984).
4. a) K.R. Markham and V.M. Chari, "The Flavonoids : Advances in Research", edited by J.B. Harborne and T.J. Mabry, Chapman and Hall, 1982, p. 19.
   b) A.K. Granguly and O.Z. Sarre, Chem. & Ind., 1970, 201.
   ^1H NMR (DMSO-d_6) δ 6.2 (1H, d, J=2Hz), 6.4 (1H, d, J=2Hz), 6.8 (2H, d, J=10Hz), 7.45 (2H, d, J=10Hz), 8.3 (1H, s), and 12.96 ppm (1H, s).
5. 5: ^1H NMR (CD_3OD) δ 2.60 (3H, s) and 5.80 ppm (2H, s).
6. 6: ^1H NMR (CD_3OD) δ 3.74 (2H, s), 6.68 (4H, d, J=8Hz), and 6.96 ppm (4H, d, J=8Hz).
7. 7: $C_{33}H_{28}O_{10}$ [m/z 584 (M^+)]; ^1H NMR (CD_3OD) δ 3.72 (3H, s), 3.76 (3H, s), 3.84 (3H, s), 4.60 (1H, d, J=12Hz), 5.88 (1H, d, J=2Hz), 5.96 (1H, d, J=2Hz), 6.26 (2H, s), 6.36 (1H, d, J=12Hz), 6.60 (2H, d, J=7Hz), 6.67 (2H, d, J=7Hz), 7.05 (2H, d, J=7Hz), 7.16 (2H, d, J=7Hz), and 7.93 ppm (1H, s);

^{13}C NMR (CD_3OD) δ 49.0(d), 55.9(d), 55.9(q), 56.2(q), 56.3(q), 91.7(d), 92.8(d), 94.5(d), 99.0(d), 106.3(s), 107.5(s), 115.7(d), 115.7(d), 115.9(d), 115.9(d), 122.2(s), 129.9(d), 129.9(d), 131.0(d), 131.0(d), 134.8(s), 136.0(s), 156.4(s), 156.4(s), 156.9(d), 158.6(s), 162.8(s), 163.8(s), 166.6(s), 167.8(s), 168.0(s), 181.1(s), and 205.1 ppm (s).

8. **8**: $C_{39}H_{34}O_{13}$ [m/z 710 (M^+)]; ^{1}H NMR ($CDCl_3$) δ 2.01 (3H, s), 2.14 (3H, s), 2.20 (3H, s), 3.64 (3H, s), 3.72 (3H, s), 3.76 (3H, s), 4.70 (1H, d, J=12 Hz), 5.70 (1H, d, J=12Hz), 6.03 (1H, d, J=2Hz), 6.22 (1H, d, J=2Hz), 6.24 (2H, s), 6.82 (2H, d, J=7Hz), 6.90 (2H, d, J=7Hz), 7.22 (2H, d, J=7Hz), 7.34 (2H, d, J=7Hz), 7.88 (1H, s), and 12.50 ppm (1H, s); ^{13}C NMR ($CDCl_3$) δ 20.5(q), 21.1(q), 21.1(q), 49.3(d), 54.5(d), 55.5(q), 55.7(q), 55.7(q), 92.4(d), 96.3(d), 98.2(d), 100.9(d), 105.4(s), 116.0(s), 119.7(s), 121.3(d), 121.3(d), 121.3(d), 121.3(d), 129.1(d), 129.1(d), 129.3(d), 129.3(d), 139.0(s), 139.9(s), 149.2(s), 150.4(s), 155.1(d), 157.5(s), 159.7(s), 162.1(s), 162.7(s), 165.4(s), 169.1(s), 169.1(s), 169.1(s), 169.1(s), 179.8(s), and 198.9 ppm (s).
9. **9**: $C_{41}H_{36}O_{13}$ [m/z 752 (M^+)]; ^{1}H NMR ($CDCl_3$) δ 2.01 (3H, s), 2.14 (3H, s), 2.21 (3H, s), 2.36 (3H, s), 3.63 (3H, s), 3.71 (3H, s), 3.77 (3H, s), 4.67 (1H, d, J=12Hz), 5.69 (1H, d, J=12Hz), 6.01 (1H, d, J=2Hz), 6.20 (1H, d, J=2Hz), 6.42 (1H, d, J=2Hz), 6.58 (1H, d, J=2Hz), 6.79 (2H, d, J=8Hz), 6.87 (2H, d, J=8Hz), 7.14 (2H, d, J=8Hz), 7.33 (2H, d, J=8Hz), and 7.77 ppm (1H, s); ^{13}C NMR ($CDCl_3$) δ 20.5(q), 21.1(q), 21.1(q), 21.1(q), 49.6(d), 54.2(d), 55.5(q), 55.7(q), 55.8(q), 96.3(d), 98.8(d), 100.7(d), 108.5(d), 111.0(s), 116.1(s), 121.1(d), 121.1(d), 121.1(d), 121.1(d), 121.7(s), 129.2(d), 129.2(d), 129.4(d), 129.4(d), 139.1(s), 140.3(s), 149.2(s), 150.2(s), 150.6(s), 153.3(d), 158.4(s), 159.7(s), 162.6(s), 163.1(s), 169.2(s), 169.2(s), 169.2(s), 169.2(s), 169.2(s), 173.2(s), and 199.2 ppm (s).
10. W.-K. Hwang and C.-C. Chang, K'o Hsueh Tung Pao, 24, 24 (1979); Chem. Abstr., 90, 135086m (1979).

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