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STRUCTURE OF ISOCHAMAEJASMIN FROM STELLERA CHAMAEJASME L.

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A new C-3/C-3''-biflavanone named isochamaejasmin has been isolated from Stellera chamaejasme L. (Thymelaeaceae) and its structure has been elucidated by spectroscopic and chemical methods. Furthermore, the stereochemistry of some C-3/C-3''-biflavanones including isochamaejasmin was discussed.

Our previous studies on the constituents of the roots of Stellera chamaejasme L. (Thymelaeaceae) resulted in the isolation of five C-3/C-3''-biflavanones[1,2] and one rearranged biflavonoid being a kind of chromone.[3] We now describe the isolation and structure of a new C-3/C-3''-biflavanone named isochamaejasmin (1) from the same plant.

According to the same procedure as described in the previous paper,[2] the fraction obtained before elution of neochamaejasmin A (2) was further separated by high performance liquid chromatography on reversed phase silica gel (Develosil ODS-5, ϕ10 mm x 250 mm) using methanol - water (70 : 30) to afford isochamaejasmin (1) as amorphous powder. The physical data of isochamaejasmin are : $[\alpha]_D \pm 0°$ (c 0.4, MeOH); $C_{30}H_{22}O_{10}$ [m/z 271 (1/2 M^+)]; UV (MeOH) 296 nm(ε 30200); IR (KBr) 3350 and 1620 cm^{-1}; ^{1}H NMR (CD_3OD)[4]: δ 3.72 (2H, d, J=12 Hz), 4.90 (2H, d, J=12 Hz), 5.74 (2H, s), 5.88 (2H, s), 6.75 (4H, d, J=8 Hz), and 7.00 ppm (4H, d, J=8 Hz); ^{13}C NMR

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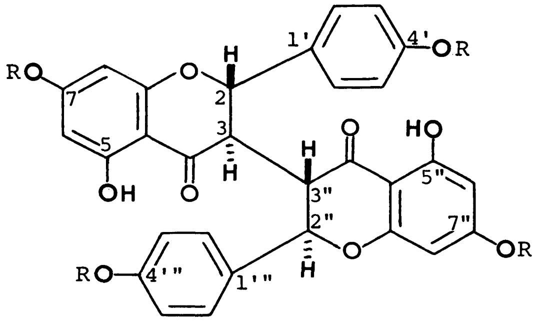
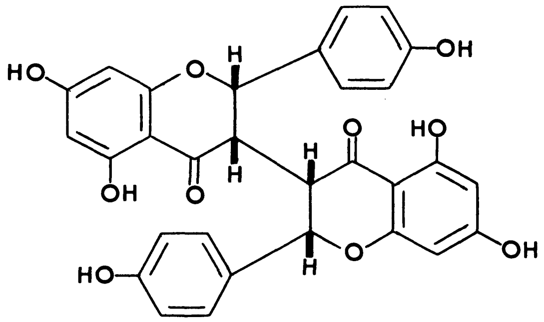
(CD_3OD): δ 49.0 (d), 82.4 (d), 96.1 (d), 97.3 (d), 102.8 (s), 116.5 (d), 116.5 (d), 129.0 (s), 130.8 (d), 130.8 (d), 159.5 (s), 164.3 (s), 165.3 (s), 168.1 (s), and 196.8 ppm (s).

The mass and ^{13}C NMR spectra of isochamaejasmin (**1**) indicate that **1** is a C-3/C-3''-biflavanone similar to neochamaejasmin A (**2**) except for the stereochemistry.[2)] Furthermore, the J-values (12 Hz and 12 Hz) of the protons observed at δ 3.72 and 4.90 in the ^1H NMR spectrum indicate that **1** has the trans - trans geometry at the C-2/C-3 and C-2''/C-3'' positions. Isochamaejasmin is optically inactive, although all natural C-3/C-3''-biflavanones reported by us are optically active.[1,2)] On methylation with CH_2N_2, natural isochamaejasmin was converted into optically inactive 7,4',7'',4'''-tetramethylisochamaejasmin (**3**).[5)] This product was clearly different from optically active 7,7''-dimethylchamaejasmenin A (**4**)[2,6)] which was obtained by methylation of natural chamaejasmenin A (**5**)[1)] with CH_2N_2. But, **3** was isomerized with 10% NaOH (room temp , 5 h) to give a mixture of two compounds.[7)]



1 R = H

3 R = CH_3



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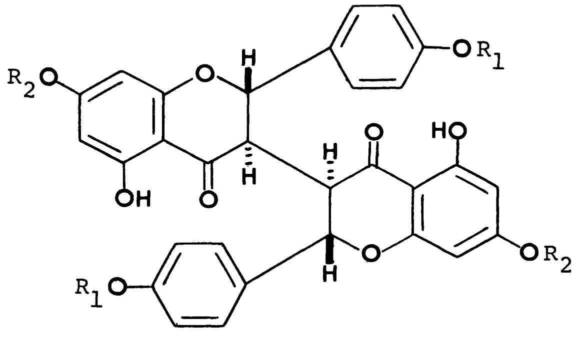
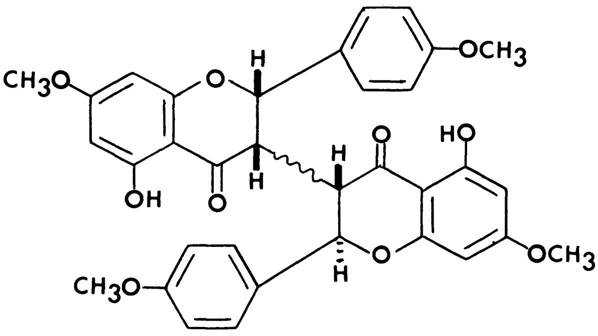


4 $R_1 = R_2 = CH_3$

5 $R_1 = CH_3$, $R_2 = H$

6 $R_1 = R_2 = H$



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The same mixture was also obtained on treatment of neochamaejasmin B tetramethyl ether (7) with 10% NaOH (room temp , 5 h).[7] Both compounds were optically inactive. One of them was the starting material (3) and the other was completely identical with 4 except for the value in the optical rotation. The above results strongly suggest that 3 derived from natural 1 has a symmetrical plane as seen in the case of meso-tartaric acid and 4 derived from natural 5 has no symmetrical plane as seen in the case of d- or l-tartaric acid. Therefore, isochamaejasmin and chamaejasmenin A can be represented as the meso-form (1) and the d- or l-form (5), respectively. Neochamaejasmin A can be also represented as 2 or its antipode.

In 1979, Hwang and Chang reported the isolation and structure of chamaejasmine from the same plant as ours.[8] Chamaejasmine (6) is a C-3/C-3''-biflavanone having the geometry of trans - trans at C-2/C-3 and C-2''/C-3'' positions and the chirality at C-3/C-3'' positions of 6 remains still unsettled. But, chamaejasmine is clearly different from isochamaejasmin (1) by comparison of their ^{1}H NMR data.[4,8]

Table 1. Chemical shift values of H-3, 3'' and H-2, 2'' protons of trans-trans-C-3/C-3''-biflavanones, 1, 5, and 6

	Isochamaejasmin (1)[4]	Chamaejasmenin A (5)[1]	Chamaejasmine (6)[8]
H - 3, 3''	3.72 (3.84)[a]	2.78	2.97[a]
H - 2, 2''	4.90 (4.92)[a]	5.90	5.84 - 5.99[a]

[a] Measured in acetone-d_6.

As judged from the data shown in Table 1, chamaejasmine is similar to chamaejasmenin A (5) which is optically active. Therefore, the former should be represented as 6, but it is a racemate because of having no optical rotation. We have not yet isolated optically active or inactive chamaejasmine from the plant.
Probably, their isolation procedure using aqueous NaOH[8] results in isomerization of neochamaejasmin A and neochamaejasmin B to racemic chamaejasmine or in racemization of optically active chamaejasmine, even if it is included in the plant, in the course of isolation. On these points, further study is in progress.

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References

1) G.-Q. Liu, H. Tatematsu, M. Kurokawa, M. Niwa, and Y. Hirata, Chem. Pharm. Bull., 32, 362 (1984).

2) M. Niwa, H. Tatematsu, G.-Q. Liu, and Y. Hirata, Chem. Lett., 1984, 539.

3) M. Niwa, G.-Q. Liu, H. Tatematsu, and Y. Hirata, Tetrahedron Lett., in press.

4) **1** : ^{1}H NMR (acetone-d_6) δ 3.84 (2H, d, J=12 Hz), 4.92 (2H, d, J=12 Hz), 5.80 (2H, s), 5.94 (2H, s), 6.86 (4H, d, J=8 Hz), 7.12 (4H, d, J=8 Hz), and 11.92 ppm (2H, s).

5) **3** : amorphous powder; $[\alpha]_D \pm 0°$ (c 0.7, $CHCl_3$); $C_{34}H_{30}O_{10}$ [m/z 598 (M^+), and 299]; IR ($CHCl_3$) 1630, 1570, 1510, and 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.76 (6H, s), 3.84 (6H, s), 3.86 (2H, d, J=12 Hz), 5.02 (2H, d, J=12 Hz), 5.90 (2H, d, J=2 Hz), 6.08 (2H, d, J=2 Hz), 6.94 (4H, d, J=8 Hz), 7.18 (4H, d, J=8 Hz), and 11.90 ppm (2H, s); ^{13}C NMR ($CDCl_3$) δ 47.6 (d), 55.3 (q), 55.6 (q), 81.0 (d), 94.0 (d), 95.2 (d), 102.5 (s), 114.3 (d), 114.3 (d), 128.6 (s), 129.5 (d), 129.5 (d), 160.5 (s), 162.6 (s), 164.2 (s), 168.0 (s), and 195.6 ppm (s).

6) **4** : $[\alpha]_D$ -145° (c 0.75, $CHCl_3$).

7) A ring-opened compound such as a chalcone or a rearranged compound such as chamaechromone[3)] could not be found in the reaction mixture.

8) W.-K. Hwang and C.-C. Chang, K'o Hsueh Tung Pao, 24, 24 (1979); Chem. Abstr., 90, 135086m (1979). The physical data of chamaejasmine (**6**) reported is shown here: mp 309 °C; $[\alpha]_D \pm 0°$ (EtOH); $C_{30}H_{22}O_{10}$ [m/z 542 (M^+), and 271]; UV (EtOH) 293 nm(logε 4.59); IR (KBr) 3425 and 1637 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 2.97 (2H, d, J=12 Hz), 5.84 - 5.99 (6H, m), 6.85 and 6.99 (total 8H, d, J=9 Hz), and 11.23 ppm (2H, s).

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