# Neo-clerodane Diterpenes from *Ajuga decumbens*

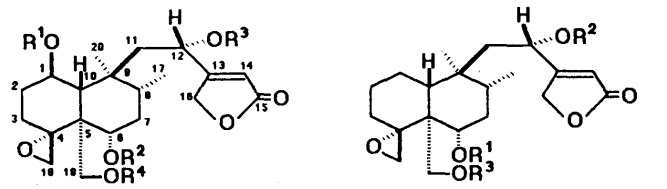
Hiroko SHIMOMURA, Yutaka SASHIDA* and Kazunori OGAWA

*Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan.* *Received September 7, 1988*

**From the whole plants of *Ajuga decumbens*, four new neo-clerodane diterpenes, ajugamarins A2, G1, H1 and F4, and a previously known ajugamarin B2 have been isolated. The structures were elucidated on the basis of spectral data and chemical correlations.**

**Keywords** neo-clerodane; diterpene; bitter principle; *Ajuga decumbens* Labiatae; adjugamarin

*Ajuga decumbens* THUNB. is a common perennial plant growing in China, Korea and Japan.[1] It is used as a folk medicine for treatment of inflammation and infectious disease in China and Japan.[2] As a part of a continuing study on the chemical constituents of the *Ajuga* species growing in Japan,[3] we have now investigated the whole plants of *A. decumbens*. The bitter taste of the leaves suggested the existence of neo-clerodane diterpenes in view of the known chemotaxonomy. As a result, we have isolated four new neo-clerodanes, ajugamarins A2 (**1**), G1 (**2**), H1 (**3**) and F4 (**4**), and one previously known neo-clerodane ajugamarin B2 (**5**),[3b] from the plant. The structures of these compounds have been elucidated on the basis of the combined spectral and physical evidence, and chemical correlation.



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| **1** | Tig | Ac | Ac | Ac |
| **2** | Tig | Ac | MeBu | Ac |
| **3** | MeBu | Ac | Tig | Ac |
| **5** | MeBu | Ac | Ac | Ac |
| **6** | Tig | Ac | H | Ac |
| **7** | H | Ac | MeBu | H |
| **8** | MeBu | Ac | H | Ac |

| | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| **4** | Ac | MeBu | Ac |
| **9** | H | MeBu | H |

Ac: acetyl
Tig: tigloyl
MeBu: (2*S*)-2-methylbutanoyl

Chart 1

TABLE I. $^1$H-NMR Spectral Data[a]

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| H-1α | 5.71 (ddd, 11.0, 11.0, 4.8) | 5.73 (ddd, 10.8, 10.8, 4.8) | 5.55 (ddd, 10.8, 10.8, 4.8) | 1.70—1.50[b] |
| H-1β | — | — | — | 1.87 (br d, 13) |
| H-2α | 2.16[b] | 2.16 (dddd, 12.4, 5.2, 4.8, 2.4) | 2.17 (dddd, 12.4, 5.2, 4.8, 2.4) | 1.98 (br d, 13) |
| H-2β | 1.47[b] | [b] | 1.41 (dddd, 13.6, 12.4, 10.8, 5.2) | 1.37 (ddddd, 13.0, 13.5, 13.5, 4.8, 4.8) |
| H-3α | 2.41 (dddd, 14.0, 14.0, 4.4, 2.3) | 2.41 (dddd, 13.6, 12.4, 10.8, 5.2) | 2.36 (dddd, 13.6, 12.4, 10.8, 5.2) | 2.12 (dddd, 13.5, 13.5, 4.8, 2.4) |
| H-3β | 1.15 (ddd, 14.0, 4.4, 2.8) | 1.14 (ddd, 13.6, 5.2, 2.4) | 1.08 (ddd, 13.6, 5.2, 2.4) | 1.05 (br d, 13.5) |
| H-6β | 5.67 (dd, 10.8, 4.0) | 4.67 (dd, 11.2, 4.8) | 4.61 (dd, 11.2, 4.2) | 4.71 (dd, 10.4, 4.8) |
| H-7α | 1.71 (ddd, 12, 12, 11) | 1.72 (ddd, 13.2, 11.2, 12) | 1.69 (ddd, 13.2, 11.2, 12) | |
| H-7β | 1.54[b] | [b] | [b] | 1.70—1.50[b] |
| H-8β | 1.79[b] | [b] | 1.80 (m) | |
| H-10 | 2.13 (d, 11.0) | 2.15 (d, 10.8) | 2.18 (d, 10.8) | 1.57 (dd, 12.5, 2.8) |
| $H_A$-11 | 2.69 (dd, 16.0, 9.2) | 2.74 (dd, 16.0, 10.8) | 2.80 (dd, 16.0, 10.8) | 2.12 (dd, 16.4, 9.4) |
| $H_B$-11 | 1.50 (dd, 16.0, 2.4) | 1.45 (dd, 16.0) | [b] | 1.53 (br d, 16.4) |
| H-12 | 5.85 (br d, 9.2) | 5.75 (br d, 10.8) | 5.99 (br d, 10.8) | 5.62 (br d, 9.4) |
| H-14 | 5.88 (ddd, 1.8, 1.8, 1.2) | 5.85 (ddd, 1.8, 1.8, 1.2) | 5.93 (ddd, 1.8, 1.8, 1.2) | 5.93 (ddd, 1.8, 1.8, 1.8) |
| $H_A$-16 | 4.78 (dd, 17.7, 1.8) | 4.79 (dd, 17.6, 1.8) | 4.82 (dd, 17.6, 1.8) | 4.86 (dd, 17.6, 1.8) |
| $H_B$-16 | 4.72 (dd, 17.7, 1.8) | 4.69 (dd, 17.6, 1.8) | 4.75 (dd, 17.6, 1.8) | 4.71 (dd, 17.6, 1.8) |
| $H_3$-17 | 0.85 (d, 6.1) | 0.85 (d, 6.2) | 0.87 (d, 6.2) | 0.83 (d, 5.9) |
| $H_A$-18 | 3.00 (dd, 3.8, 2.3) | 2.98 (dd, 4.0, 2.2) | 2.89 (dd, 4.0, 2.2) | 2.94 (dd, 3.8, 2.4) |
| $H_B$-18 | 2.28 (d, 3.8) | 2.24 (d, 4.0) | 2.11 (d, 4.0) | 2.16 (d, 3.8) |
| $H_A$-19 | 4.97 (d, 12.7) | 4.97 (d, 12.5) | 4.93 (d, 12.5) | 4.82 (d, 12.1) |
| $H_B$-19 | 4.44 (br d, 12.7) | 4.44 (br d, 12.5) | 4.38 (br d, 12.5) | 4.35 (d, 12.1) |
| $H_3$-20 | 0.79 (s) | 0.80 (s) | 0.79 (s) | 0.75 (s) |
| H-3′ | 6.95 (qq, 7.1, 1.4) | 6.96 (qq, 7.1, 1.4) | 7.06 (qq, 7.1, 1.4) | — |
| $H_3$-4′ | 1.80 (dd, 7.1, 1.2) | 1.80 (dd, 7.1, 1.2) | 1.86 (dd, 7.1, 1.2) | — |
| $H_3$-5′ | 1.87 (dd, 1.4, 1.2) | 1.88 (dd, 1.4, 1.2) | 1.92 (dd, 1.4, 1.2) | — |
| H-2″ | — | 2.45 (qdd, 6.9, 6.9, 6.9) | 2.29 (qdd, 6.9, 6.9, 6.9) | 2.37 (qdd, 6.9, 6.9, 6.9) |
| $H_2$-3″ | — | 1.70—1.50[b] | 1.70—1.50[b] | 1.70—1.50[b] |
| $H_3$-4″ | — | 0.96 (t, 7.5) | 0.90 (t, 7.5) | 0.91 (t, 7.5) |
| $H_3$-5″ | — | 1.23 (d, 6.9) | 1.14 (d, 6.9) | 1.16 (d, 6.9) |
| Ac | 2.18 | 2.13 | 2.12 | 2.10 |
| | 2.13 | 1.95 | 1.94 | 1.95 |
| | 1.96 | | | |

*a*) Spectra were measured in $CDCl_3$ at 400.1 MHz. Chemical shifts (in δ values) and coupling constants were obtained by first-order approximation. *b*) Chemical shifts or parameters of these protons were unidentified.

TABLE II. $^{13}$C-NMR Spectral Data[a)]

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| C-1 | 70.3[b)] | 70.3[b)] | 70.6[b)] | 21.5 |
| C-2 | 32.1 | 32.3 | 31.6 | 24.8 |
| C-3 | 30.4 | 30.5 | 30.4 | 32.5[b)] |
| C-4 | 64.3 | 64.2 | 64.1 | 64.9 |
| C-5 | 46.1 | 46.2 | 46.0 | 45.5 |
| C-6 | 71.4[b)] | 71.5[b)] | 71.3[b)] | 71.8 |
| C-7 | 32.6 | 32.7 | 32.6 | 32.9[b)] |
| C-8 | 35.2 | 35.3 | 34.9 | 35.6 |
| C-9 | 39.1 | 39.2 | 39.2 | 39.5 |
| C-10 | 51.2 | 51.5 | 50.4 | 48.2 |
| C-11 | 40.5 | 40.7 | 40.9 | 41.1 |
| C-12 | 66.8 | 66.8 | 66.6 | 66.2 |
| C-13 | 168.4 | 168.8 | 169.2 | 168.6 |
| C-14 | 116.1 | 116.0 | 115.8 | 116.0 |
| C-15 | 172.3 | 172.3 | 173.0 | 172.4 |
| C-16 | 70.6 | 70.8 | 70.7 | 70.5 |
| C-17 | 15.4 | 15.4 | 15.4 | 15.5 |
| C-18 | 48.6 | 48.9 | 48.6 | 49.2 |
| C-19 | 61.6 | 61.9 | 61.7 | 61.6 |
| C-20 | 16.9 | 17.1 | 17.2 | 17.0 |
| C-1′[c)] | 166.7 | 166.7 | 166.4 | |
| C-2′ | 129.4 | 129.6 | 128.3 | |
| C-3′ | 138.2 | 138.1 | 139.6 | |
| C-4′ | 12.3 | 12.3 | 12.2 | |
| C-5′ | 14.5 | 14.5 | 14.6 | |
| C-1″[c)] | | 175.6 | 175.6 | 175.6 |
| C-2″ | | 41.1 | 41.7 | 40.8 |
| C-3″ | | 27.0 | 27.1 | 26.9 |
| C-4″ | | 11.6 | 11.5 | 11.5 |
| C-5″ | | 15.8 | 16.2 | 15.8 |
| Ac | 170.4 | 170.3 | 170.4 | 170.9 |
| | 169.7 | 169.7 | 169.7 | 169.9 |
| | 169.5 | 21.2 | 21.2 | 21.2 |
| | 21.2 | 21.1 | 21.1 | 21.1 |
| | 21.1 | | | |
| | 21.0 | | | |

*a*) Spectral data were measured in $CDCl_3$ at 100.6 MHz. Chemical shifts are given in $\delta$ values. *b*) These assignments may be interchanged. *c*) C-1′—5′ tigloyl moiety; C-1″—5″, 2-methylbutanoyl moiety.

Ajugamarin A2 (**1**), $C_{31}H_{42}O_{11}$, showed an $[M]^+$ peak at *m/z* 590 in the electron impact mass spectrum (EI-MS). The clerodane structure[4)] of **1** was concluded from the $^1$H-nuclear magnetic resonance ($^1$H-NMR) spectral data to resemble closely that of ajugamarin A1 (**6**) isolated from *A. nipponensis*.[3a,b)] An additional acetyl group and the $^1$H-NMR signal of H-12 in **6** were different from those of **1**. The identity of **1** with the 12-acetate of **6** was assumed from the above, and was confirmed. Thus, the structure of **1** was (12*S*)-6α,12,19-triacetoxy-1β-tigloyl-4,18-epoxyneo-clerod-13(14)-en-15,16-olide.

Ajugamarin G1 (**2**), $C_{34}H_{48}O_{11}$, showed the $[M]^+$ peak at *m/z* 632 in the EI-MS. Its $^1$H- and $^{13}$C-NMR spectra were closely related to those of **1** and **6**, suggesting that **2** had a neo-clerodane structure corresponding to that of **1** except for the positions of four acyl groups, one tigloyl, one 2-methylbutanoyl and two acetyls. The $^1$H-NMR signal of H-1α ($\delta$ 5.71) in **1** appeared at lower field than that ($\delta$5.55) in **5**. The H-12 signals of **1** and **5** were observed at $\delta$ 5.85, whereas that of the 1,19-diacetate of ajugamarin E1 (**7**)[3c)] appeared at $\delta$ 5.75. By analogy with the above, the locations of the 1β-tigloyloxyl and the 12-(2-methylbutanoyloxyl) groups in **2** were deduced. To obtain the complete structure of **2**, the 12-[(2*S*)-2-methylbutanoate] of **6** was prepared (see Experimental). The identity between the derivative and **2** demonstrated that **2** was (12*S*)-6α,19-diacetoxy-12-[(2*S*)-2-methylbutanoyloxy]-1β-tigloyloxy-4,18-epoxyneo-clerod-13(14)-en-15,16-olide.

Ajugamarin H1 (**3**), $C_{34}H_{48}O_{11}$, showed the same $[M]^+$ peak as **2** at *m/z* 632 in the EI-MS. The $^1$H- and $^{13}$C-NMR spectral data of **3**, which closely resembled those of **2**, suggested that **3** contained the neo-clerodane structure of **2** and the same ester moieties. The difference between **2** and **3** was attributable to positional changes of the esters. Significant differences of the H-1α and H-12 signals in the $^1$H-NMR spectra between **2** and **3** suggested the 1-position for the 2-methylbutanoyloxyl group and the 12-position for the tigloyl group in **3**. Confirmation of the structure of **3** was obtained by chemical correlation with the 12-tiglate of ajugamarin B1 (**8**)[3a,b)] (see Experimental). The structure of **3** was (12*S*)-6α,19-diacetoxy-1β-[(2*S*)-2-methylbutanoyloxyl]-12-tigloyloxy-4,18-epoxyneo-clerod-13(14)-en-15,16-olide.

Ajugamarin F4 (**4**), $C_{29}H_{42}O_9$, showed an $[M+H]^+$ peak at *m/z* 535 in the EI-MS. In the $^1$H-NMR spectrum of **4**, the major signals showed almost identical chemical shifts and couplings with those of ajugamarin F1 (**9**) previously isolated from *A. ciliata* var. *villosior*[3c)] except for two acetoxyl groups at the 6α- and 19-positions. The diacetate of **9** was identical with **4**. Thus, the structure of **4** was (12*S*)-6α,19-diacetoxy-12-[(2*S*)-2-methylbutanoyloxy]-4,18-epoxyneo-clerod-13(14)-en-15,16-olide.

Three Japanese species, *A. nipponensis*,[3a,b)] *A. ciliata* var. *villosior*[3c)] and *A. decumbens*, contain neo-clerodanes having the α,β-unsaturated γ-lactone structure. Neo-clerodanes having the α,β-unsaturated γ-lactone structure were also isolated from an African species, *A. remota*.[5)] European *Ajuga* species[6)] contain neo-clerodanes characterized by furofuran structure, except for two minor constituents from *A. reptans*.[7)] Thus, it appears that *Ajuga* species containing neo-clerodanes can probably be divided into those containing furofuran type neo-clerodanes and those containing α,β-unsaturated γ-lactone type neo-clerodanes.

## Experimental

Melting points are uncorrected. The $^1$H- and $^{13}$C-NMR spectra were measured on a Bruker AM400 spectrometer. Chemical shifts are given in $\delta$ values (tetramethylsilane as an internal standard). Optical rotations were measured with a Jasco DIP-360 polarimeter. Infrared (IR) spectra were recorded with a Perkin-Elmer 1710 FT-IR instrument. Mass spectrum (MS) measurements were recorded with a Hitachi M-80 spectrometer.

**Extraction and Isolation** The dried whole plants (500 g) of *A. decumbens* (crude drug purchased from Tochimoto-tenkaido, Osaka) were extracted with hot EtOAc. Repeated column chromatography of the concentrated EtOAc extract on silica gel (Fuji gel BW300) with $CHCl_3$–$Me_2CO$ (8 : 2) and $C_6H_{12}$–EtOAc (5 : 5) systems afforded four new neo-clerodanes, ajugamarins A2 (**1**, 28.7 mg), G1 (**2**, 13.1 mg), H1 (**3**, 4.0 mg) and $F_4$ (**4**, 5.2 mg), together with a known neo-clerodane ajugamarin B2 (**5**, 9.8 mg). The previously known ajugamarin B2 was shown to be identical with an authentic sample by spectroscopic ($^1$H-NMR, $^{13}$C-NMR, IR and MS) and physical (thin layer chromatography (TLC), melting point, mixed melting point and $[\alpha]_D$) comparisons.

**Ajugamarin A2 (1)** Amorphous solid. $[\alpha]_D^{25}$ −38° (*c*=2.8, $CHCl_3$). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 2970, 2930, 1780, 1740, 1640, 1370, 1250, 1230, 1150, 1130, 1080, 1060, 1040, 1020. EI-MS *m/z*(%): 590 $[M]^+$ (3), 560 (3), 547 (2), 530 (1), 517 (4), 475 (10), 375 (14), 371 (10), 345 (12), 311 (12), 201 (25), 187 (25), 171 (20), 83 (100), 55 (100). CI-MS *m/z*(%): 591 $[M+H]^+$ (3), 560 (1), 531 (1), 517 (1), 490 (1), 475 (3), 449 (2), 431 (3), 371 (10), 311 (15), 201 (20), 83 (100).

**Preparation of 1 from Ajugamarin A1** Acetylation of ajugamarin A1

(53.0 mg) with $Ac_2O$ and pyridine in the usual manner afforded the 12-acetate (57.5 mg). This was identical with naturally occurring **1**.

**Ajugamarin G1 (2)** Colorless crystals from EtOH. mp 165—167 °C. *Anal.* Calcd for $C_{34}H_{48}O_{11} \cdot 1/2\ C_2H_5OH$: C, 64.10; H, 7.84. Found: C, 64.10; H, 7.64. $[\alpha]_D^{25}$ −37° ($c$=1.1, $CHCl_3$). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 2970, 2930, 2860, 1780, 1760, 1730, 1700, 1640, 1460, 1370, 1250, 1130, 1080, 1060, 1030. EI-MS $m/z$(%): 632 $[M]^+$ (0.2), 602 (0.3), 589 (0.2), 559 (0.4), 517 (2), 431 (10), 417 (2), 311 (6), 201 (11), 187 (10), 85 (13), 83 (100), 57 (30), 55 (35). CI-MS $m/z$(%): 633 $[M+H]^+$ (23), 573 (8), 533 (12), 473 (15), 431 (25), 433 (28), 395 (30), 371 (23), 329 (32), 311 (100), 201 (86), 83.

**Preparation of 2 from Ajugamarin A1** Ajugamarin A1 (28.0 mg) was added to (2*S*)-2-methylbutanoyl chloride (50 $\mu$l) and 4-dimethylaminopyridine (DMAP, 4 mg) in pyridine (0.2 ml). The mixture was refluxed for 10 h, then the solvent was removed from the reaction mixture *in vacuo*. The residue was subjected to silica gel column chromatography. Elution with $C_6H_{12}$–EtOAc (6:4) gave the chlorohydrin of the 12-[(2*S*)-2-methylbutanoate] of ajugamarin A1 (13.6 mg). The chlorohydrin (6.0 mg in 1 ml of MeOH) was treated with 1% aqueous sodium bicarbonate (0.5 ml). The mixture was left at room temperature for 10 min. The $CHCl_3$ extract of the mixture was chromatographed over silica gel with $C_6H_{12}$–EtOAc (6:4), affording the 12-[(2*S*)-2-methylbutanoate] of ajugamarin A1 (3.2 mg). The ester was identical ($^1$H-NMR, $^{13}$C-NMR, IR, MS, melting point, mixed melting point, $[\alpha]_D$ and TLC) with natural **2**.

**Ajugamarin H1 (3)** Colorless needles from $C_6H_{12}$–$Me_2CO$. mp 75—79 °C. $[\alpha]_D^{25}$ −11° ($c$=1.2, $CHCl_3$). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 2970, 2930, 2850, 1780, 1750, 1730, 1640, 1450, 1370, 1250, 1170, 1150, 1130, 1080, 1030, 880. EI-MS $m/z$(%): 632 $[M]^+$ (0.1), 602 (1), 589 (1), 559 (1), 517 (7), 415 (3), 297 (9), 201 (15), 187 (23), 85 (40), 83 (100), 57 (90), 55 (45). CI-MS $m/z$(%): 633 $[M+H]^+$ (6), 602 (3), 589 (2), 559 (4), 531 (3), 517 (10), 449 (4), 430 (3), 415 (4), 311 (15), 201 (30), 83 (100).

**Preparation of 3 from Ajugamarin B1** Ajugamarin B1 (52.0 mg) was added to tigloyl chloride (50 $\mu$l) and DMAP (4 mg) in pyridine (0.5 ml). After being refluxed for 24 h, the reaction mixture was concentrated *in vacuo*. The residue was subjected to silica gel column chromatography. Elution with $C_6H_{12}$–EtOAc (6:4) gave the chlorohydrin of the 12-tiglate of ajugamarin B1 (10.6 mg). The chlorohydrin (10.6 mg in 1 ml of MeOH) was treated with 1% aqueous sodium bicarbonate (1 ml). The mixture was left at room temperature for 10 min. The $CHCl_3$ extract of the mixture was chromatographed over silica gel with $C_6H_{12}$–EtOAc (6:4), yielding the 12-tiglate of ajugamarin B1 (2.8 mg). The ester was identical ($^1$H-NMR, $^{13}$C-NMR, IR, MS, melting point, mixed melting point, $[\alpha]_D$ and TLC) with natural **3**.

**Ajugamarin F4 (4)** Colorless crystals from $C_6H_{12}$–$Me_2CO$. mp 160—163 °C. $[\alpha]_D^{25}$ −32° ($c$=0.9, $CHCl_3$). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 2980, 2950, 2890, 1780, 1730, 1640, 1460, 1390, 1380, 1370, 1260, 1240, 1370, 1090, 1040, 900, 880, 870, 860, 800. EI-MS $m/z$ (%): 504 $[M-CH_2O]^+$ (3), 491 (12), 461 (13), 419 (100), 389 (10), 299 (20), 203 (58). CI-MS $m/z$(%): 535 $[M+H]^+$ (4), 490 (5), 475 (12), 461 (7), 419 (25), 313 (48), 203 (100).

**Preparation of 4 from Ajugamarin F1** Acetylation of ajugamarin F1 (35.2 mg) with $Ac_2O$ and pyridine in the usual manner afforded the 6,19-diacetate (7.7 mg), the 6-acetate (3.8 mg) and the 19-acetate (7.7 mg). The 6,19-diacetate was identical with naturally occurring **4**.

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