# Cynanformosides A and B, Two New Pregnane Glycosides, from the Aerial Part of *Cynanchum formosanum*

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**Two new pregnane glycosides, cynanformosides A and B, together with α-amyrin acetate, taraxerol, chrysoeriol, and isorhamnetin were isolated from the aerial part of *Cynanchum formosanum*. The structures of the new pregnane glycosides have been elucidated by spectroscopic and chemical methods.**

**Keywords** *Cynanchum formosanum*; Asclepiadaceae; steroid; cynanformoside A; cynanformoside B; pregnane glycoside

Extensive studies on the constituents[1-6] of some species of *Cynanchum* (*C.*), as well as the immunopotentiating activities[6b,7] of C/D-*cis*-polyoxypregnane glycosides, have been reported. In connection with our interest in pregnane-type steroids, chemical studies on the constituents of *C. formosanum* (MAXIM.) HEMSL. ex FORBES *et* HEMSL., a folk medicine used as an expectorant,[8] were undertaken in our laboratory.

The methanol extract of the aerial part of *C. formosanum* was partitioned between petroleum ether and 80% aqueous methanol. The aqueous methanol layer was evaporated under reduced pressure to afford an aqueous solution which was extracted successively with chloroform and butanol. After repeated purification on silica gel and Sephadex LH-20 columns, triterpenoids(α-amyrin acetate[9] and taraxerol[10]), pregnane glycosides [cynanformosides A (**1a**) and **B** (**1b**)], and flavonoids (chrysoeriol[11] and isorhamnetin[12])were isolated from the petroleum ether extract, chloroform extract, and butanol extract, respectively. This paper deals with the structural elucidation of cynanformosides A (**1a**) and B (**1b**).

Cynanformoside A (**1a**), mp 183 °C (dec.), $[\alpha]_D^{24}$ −15.5° ($c$=1.00 in $CHCl_3$), has the molecular formula $C_{28}H_{46}O_8$ on the basis of elemental analysis and its infrared (IR) spectrum shows hydroxyl group (3407 $cm^{-1}$) and olefinic group (3053 and 1636 $cm^{-1}$) absorptions. The presence of a steroidal glycoside with a 2-deoxysugar was indicated by the positive Liebermann–Burchard and Keller–Kiliani reactions.[13] The proton nuclear magnetic resonance ($^1$H-NMR) spectrum of **1a** (Table I) showed seven methine proton signals at δ 3.10—3.62 (5H, m, 3-, 12-, 3′-, 4′-, and 5′-H), 4.04 (1H, q, $J$=6.4 Hz, 20-H), and 4.57 (1H, dd, $J$=9.1, 1.3 Hz, 1′-H), four methyl signals at δ 0.98 and 1.13 (each 3H, s, 18- and 19-H), 1.17 (3H, d, $J$=6.4 Hz, 21-H), and 1.30 (3H, d, $J$=6.0 Hz, 6′-H), one methoxyl signal at 3.36 (3H, s), and one olefinic proton signal at δ 5.38 (1H, br s, 6-H). The coupling constant of the anomeric proton (1′-H) revealed that the sugar is β-linkage. The mass spectrum (MS) of **1a** exhibited the ($M^+$ − sugar) peak at $m/z$ (%) 348 (20) and other fragment peaks at 330 ($M^+$ − sugar − $H_2O$, 13), 312 ($M^+$ − sugar − $2H_2O$, 29), 303 ($M^+$ − sugar − $CH_3CHOH$, 46), 145 [(sugar − OH)$^+$, 100], 113 [(sugar − OH−$CH_3OH$)$^+$, 47]. The peaks at 303, 145, and 113 suggested the presence of a 1-hydroxyethyl group at C-17[14] and oleandrose[15] (or cymarose). The carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectroscopic data (Table II) of **1a** were also consistent with the proposed structure. The acetylation of **1a** with $Ac_2O$ and pyridine at room temperature for 1 d afforded a triacetate (**1c**) [mp 211—214 °C; IR $\nu_{max}^{KBr}$: 3441 and 1731 $cm^{-1}$; $^1$H-NMR δ: 1.95, 2.05, 2.06 (each 3H, s)]. The result shows that the structure of **1a** contains three secondary hydroxyl groups. A comparison of the physical data of **1a** and utendin-3-*O*-β-D-cymaropyranoside (**1d**) isolated from *Marsdenia formosana*[16] showed that they are different compounds with similar structures except for oleandrosyl instead of cymarosyl at 3-C. The existence of the oleandrosyl moiety in **1a** was confirmed by comparison of the chemical shifts of 1′-H (δ 4.57) and $CH_3O$- (δ 56.5) with those (δ 4.80, 59.0)[3a,6b,17] in cymarosyl. In addition, the signal of 4′-H

TABLE I. $^1$H-NMR Data (δ-Value) for **1a**, **1b** and **1d** ($CDCl_3$)

| H | 1a[a] | 1b[a] | 1d[b] |
|---|---|---|---|
| 3 | 3.46—3.60 m | 3.54 m | |
| 6 | 5.38 br s | 5.38 br s | 5.40 br s |
| 12 | 3.46—3.60 m | 3.41 dd (9.9, 5.7) | |
| 18 | 0.98 s | 0.96 s | 1.00 s |
| 19 | 1.13 s | 1.16 s | 1.14 s |
| 20 | 4.04 q (6.4)[c] | 5.15 q (6.5) | |
| 21 | 1.16 d (6.0) | 1.24 d (7.5) | 1.20 d (6.0) |
| 1′ | 4.57 dd (9.1, 1.3) | 4.57 dd (8.4, 1.9) | 4.80 dd (9.0, 3.0) |
| 6′ | 1.30 d (6.4) | 1.29 d (6.0) | 1.28 d (6.0) |
| $CH_3O$– | 3.36 s | 3.38 s | 3.42 s |
| $CH_3CO$– | | 2.02 s | |

*a*) 300 MHz. *b*) 60 MHz. *c*) Figures in parentheses are coupling constants in Hz.

TABLE II. $^{13}$C-NMR Data (δ-Value) for **1a** and **1b** (75 MHz, $CDCl_3$)

| C | 1a | 1b | C | 1a | 1b |
|---|---|---|---|---|---|
| 1 | 37.2 t | 38.6 t | 16 | 29.4 t | 29.5 t |
| 2 | 31.0 t | 31.1 t | 17 | 87.7 s | 87.5 s |
| 3 | 75.5 d | 75.6 d | 18 | 8.1 q | 7.0 q |
| 4 | 38.5 t | 38.6 t | 19 | 19.4 q | 19.3 q |
| 5 | 139.0 s | 139.2 s | 20 | 72.4 d | 75.2 d |
| 6 | 122.0 d | 122.0 d | 21 | 16.7 q | 14.8 q |
| 7 | 31.4 t | 31.7 t | $CH_3CO$– | | 21,3 q |
| 8 | 35.6 d | 36.1 d | $CH_3CO$– | | 169.8 s |
| 9 | 42.6 d | 42.8 d | 1′ | 97.6 d | 97.7 d |
| 10 | 36.8 s | 36.7 s | 2′ | 35.6 t | 35.7 t |
| 11 | 26.1 t | 26.1 t | 3′ | 80.8 d | 80.8 d |
| 12 | 71.6 d | 71.6 d | 4′ | 77.4 d | 77.6 d |
| 13 | 56.2 s | 56.8 s | 5′ | 70.4 d | 69.8 d |
| 14 | 88.3 s | 88.0 s | 6′ | 17.9 q | 17.8 q |
| 15 | 32.3 t | 32.1 t | $CH_3O$– | 56.5 q | 56.1 q |

Assignments established by DEPT and off-resonance methods. s, singlet; d, doublet; t, triplet; q, quartet.

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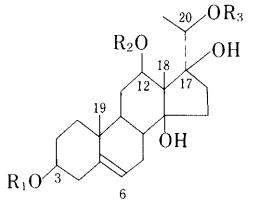
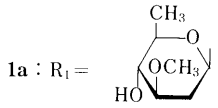
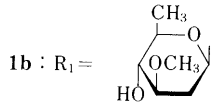
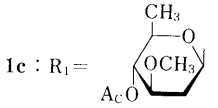




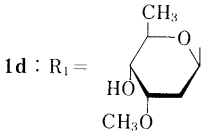
**1a** : $R_1$ = $R_2=R_3=H$



**1b** : $R_1$ = $R_2=H$, $R_3=Ac$



**1c** : $R_1$ = $R_2=R_3=Ac$



**1d** : $R_1$ = $R_2=R_3=H$

**1e** : $R_1=R_2=R_3=H$

in **1c** appears at $\delta$ 4.63 with a large coupling constant (t, $J=9.3$ Hz). On acid hydrolysis with aqueous 0.025 M $H_2SO_4$–1,4-dioxane, **1a** gave an aglycone and a sugar. The resulting aglycone (mp 248—250 °C) was identical co-thin layer chromatography ((co-TLC) and mixed melting point) with an authentic sample of natural utendin (**1e**)[18] which was obtained by the acidic hydrolysis of **1d**.[16] The sugar fraction was also identified as oleandrose by comparison of the thin-layer chromatographic (TLC) behavior with that of an authentic sample. As a result of the above experiments, cynanformoside A is proved to be utendin-3-*O*-$\beta$-oleandropyranoside.

Cynanformoside B (**1b**), mp 212—214 °C, $[\alpha]_D^{20}$ −17.5° ($c=1.00$ in $CHCl_3$), has the molecular formula $C_{30}H_{48}O_9$ on the basis of elemental analysis its IR spectrum, which showed the presence of hydroxyl group (3400 $cm^{-1}$), olefinic group (3051 and 1637 $cm^{-1}$), and acetoxyl group (1720 $cm^{-1}$) absorptions. It also exhibited positive Liebermann–Burchard and Keller–Kiliani reactions. Prominent MS peaks indicative of a 1-acetoxyethyl group were observed at *m/z* 43 (acetyl cation) and 87 (acetoxyethyl cation). Further substantiation was obtained from the MS peaks of this compound at 390 ($M^+$ − oleandrose), 372 ($M^+$ − oleandrose − $H_2O$), 354 ($M^+$ − oleandrose − $2H_2O$), 330 ($M^+$ − oleandrose − AcOH), 303 ($M^+$ − oleandrose − $CH_3CHOAc$), 145 [(oleandrose − OH)$^+$], and 113 [oleandrose − OH–$CH_3OH$)$^+$]. The peaks at *m/z* 303, 145, and 113 suggested the presence of acetoxyl at C-20[14] and oleandrosyl.[15] The $^1$H-NMR spectrum of **1b** (Table I) also showed seven methine signals, four methyl signals, one acetoxyl signal, one methoxyl signal, and one olefinic signal. Compound **1b** showed similar $^1$H-NMR signals to **1a** except for the low-field shift of the quartet signal at $\delta$ 5.15 (20-H) and an additional acetyl group. This fact suggests that **1b** is a monoacetate derivative of **1a**, and the acetoxyl group of **1b** must be located at C-20. Hydrolysis of **1b** with 5% methanolic sodium hydroxide afforded **1a** as a neutral product. The $^{13}$C-NMR data (Table II) of **1b** were also consistent with the structure of **1b**. On the basis of the above evidence, the structure of cynanformoside B can be assigned as 20-*O*-acetylutendin-3-*O*-$\beta$-oleandropyranoside (**1b**).

## Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter at room temperature. IR spectra were recorded on a JASCO A-102 spectrophotometer. $^1$H- and $^{13}$C-NMR spectra were run on a Bruker AM 300 in $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in $\delta$ values and coupling constants ($J$) are given in hertz (Hz). Electron impact mass spectrum (EI-MS) was taken on a JEOL JMS-100 spectrometer.

**Extraction and Isolation** The air dried aerial parts of *C. formosanum* (2.3 kg) were extracted with methanol (5 l) five times (6 h for every time) under reflux. The combinded extracts were evaporated under reduced pressure to give a residue, which was partitioned between petroleum ether (500 ml) and 80% aqueous methanol (500 ml). The latter layer was evaporated to about 100 ml of aqueous solution, then 200 ml of water was added. The aqueous solution was partitioned with choloroform (300 ml) and butanol (300 ml), successively. Every fraction was evaporated to give a residue, and the weights of the petroleum ether fraction, chloroform fraction, butanol fraction, and the last aqueous fraction were 36.1 g, 14.6 g, 43.7 g, and 59.3 g, respectively. After repeated purification on silica gel and Sephadex LH-20 columns, $\alpha$-amyrin acetate (202 mg) and taraxerol (13 mg) from the petroleum ether fraction, cynanformoside B (**1b**, 11 mg) and cynanformoside A (**1a**, 15 mg) from the chloroform fraction, and chrysoerial (18 mg) and isorhamnetin (8 mg) from the butanol fraction were isolated.

**Cynanformoside A (1a)** mp 183 °C (dec.) (from chloroform–hexane), $[\alpha]_D^{24}$ −15.5° ($c=1.00$ in $CHCl_3$). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3407, 3053, 1636, 1407, 1365, 1272, 1069, 988, 962, 806, 737. MS *m/z* (%): 348 ($M^+$ − oleandrose, 20), 330 (13), 312 (29), 303 (46), 285 (24), 268 (19), 145 (100), 113 (47). *Anal.* Calcd for $C_{28}H_{46}O_8$: C, 65.85; H, 9.08. Found C, 65.75; H, 9.05.

**Cynanformoside B (1b)** mp 212—214 °C (from chloroform–hexane), $[\alpha]_D^{20}$ −17.5° ($c=1.00$ in $CHCl_3$). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3415, 3051, 1720, 1637, 1260, 1160, 1100, 1065, 1030, 980, 963, 845. MS *m/z* (%): 390 ($M^+$ − oleandrose, 5), 372 (2), 354 (12), 330 (11), 303 (11), 297 (14), 294 (13), 276 (16), 251 (13), 224 (19), 145 (100), 113 (65), 95 (6), 87 (11), 43 (8). *Anal.* Calcd for $C_{30}H_{48}O_9$: C, 65.19; H, 8.75. Found C, 65.24; H, 8.69.

**α-Amyrin Acetate**[9] mp 228 °C (from chloroform–methanol). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1730, 1450, 1370, 1250. MS *m/z* (%): 468 (9.5, $M^+$), 408 (3), 218 (100), 203 (36), 189 (31.5), 175 (10.5), 161 (21), 147 (28.4), 133 (35.7), 122 (26.3), 107 (23.1). $^1$H-NMR ($CDCl_3$) $\delta$: 0.77 (3H, s), 0.84 (3H, s), 0.89 (9H, s), 0.95 (3H, s), 0.98 (3H, s), 1.04 (3H, s), 2.02 (s, OAc), 4.47 (dd, $J=7.4$, 9.1 Hz, 3α-H), 5.11 (t, $J=3.0$ Hz, 12-H). $^{13}$C-NMR ($CDCl_3$) $\delta$: 38.5 (C-1), 23.6 (C-2), 80.9 (C-3), 37.7 (C-4), 55.3 (C-5), 18.3 (C-6), 32.9 (C-7), 40.0 (C-8), 47.6 (C-9), 36.8 (C-10), 17.5 (C-11), 124.3 (C-12), 139.6 (C-13), 42.1 (C-14), 26.6 (C-15), 26.6 (C-16), 33.7 (C-17), 59.1 (C-18), 39.6 (C-19), 39.6 (C-20), 31.2 (C-21), 41.5 (C-22), 28.9 (C-23), 16.7 (C-24), 15.7 (C-25), 16.9 (C-26), 23.3 (C-27), 28.1 (C-28), 23.4 (C-29), 21.4 (C-30), 170.9 (MeC=O), 21.3 (MeC=O).

**Taraxerol**[10] mp 280—282 °C (from chloroform–methanol). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3500, 1480, 1390, 1380, 1040. MS *m/z* (%): 426 (9.1, $M^+$), 411 (12.7), 393 (4.6), 302 (34.5), 287 (54.5), 269 (34), 257 (19.1), 245 (15.5), 231 (13.6), 218 (21.8), 204 (100), 189 (50), 175 (25.5), 161 (23.6), 147 (36.4), 135 (80), 121 (56.4), 107 (59.1). $^1$H-NMR ($CDCl_3$) $\delta$: 0.79 (3H, s), 0.89 (3H, s), 0.91 (6H, s), 0.93 (3H, s), 0.95 (3H, s), 1.01 (3H, s), 1.25 (3H, s), 3.18 (m, 3-H), 5.51 (dd, $J=3.2$, 8.1 Hz, 15-H).

**Chrysoeriol**[11] mp 280—282 °C (from chloroform–methanol). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3600—3349, 1644, 1617, 1593, 1559, 1501, 1429. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 241 sh (3.89), 249 (3.9), 268 (3.9), 345 (4.0); +NaOMe: 265, 405; +$AlCl_3$: 276, 358, 386; +$AlCl_3$/HCl: 276, 355, 383, +NaOAc: 274, 320, 362; +NaOAc/$H_3BO_3$: 252, 269, 347. MS *m/z* (%): 300 (100), 285 (0.3), 272 (8.2), 257 (19.5), 229 (11.7), 153 (6.5), 148 (3.4), 124 (2.1), 105 (4.3). $^1$H-NMR (DMSO-$d_6$) $\delta$: 12.4 (5-OH), 8.1 (OH), 7.49 (2H, d, $J=8.6$ Hz),

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6.92 (1H, d, $J$=8.6 Hz), 6.72 (1H, s), 6.43 (1H, d, $J$=2.0 Hz), 6.16 (1H, d, $J$=2.0 Hz), 3.89 (3H, s).

**Isorhamnetin**[12] mp 308—310 °C (from chloroform–methanol). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3229, 1650, 1609, 1552, 1501. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 254 (3.2), 262 sh (3.1), 294 (4.0), 340 sh (3.2), 367 (3.6); +NaOMe: 275, 323, 413; +$AlCl_3$: 266, 304, 358, 428; +$AlCl_3$/HCl: 266, 302, 357, 426; +NaOAc: 255, 274, 320, 379; +NaOAc/$H_3BO_3$: 254, 294, 369. MS $m/z$ (%): 316 (100), 301 (10.5), 287 (10), 273 (8), 257 (4), 245 (11), 217 (4.5), 153 (2.5), 123 (4.5), 108 (4). $^1$H-NMR (DMSO-$d_6$) $\delta$: 12.43 (5-OH), 10.7 (OH), 9.69 (OH), 9.37 (OH), 7.73 (d, $J$=2.0 Hz, 2′-H), 7.68 (dd, $J$=8.4, 2.0 Hz, 6′-H), 6.92 (d, $J$=8.4 Hz, 5′-H), 6.45 (d, $J$=2.0 Hz, 8-H), 6.17 (d, $J$=2.0 Hz, 6-H), 3.84 (3H, s, Me).

**Acetylation of Cynanformoside A (1a)** A solution of cynanformoside A (**1a**, 5 mg) in pyridine (0.2 ml) and acetic anhydride (0.2 ml) was left for 1d at room temperature. The reaction mixture was treated by the usual method and purified by silica gel column chromatography (10% EtOAc in hexane as the eluent) to give a triacetate (**1c**) (5 mg) [mp 211—214 °C (from MeOH). IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3441, 1731, 1259, 1238, 1105, 1060, 1035, 1018, 973, 802. $^1$H-NMR ($CDCl_3$) $\delta$: 0.95 (3H, s, 18-H), 1.16 (3H, d, $J$=6.2 Hz, 6′-H), 1.20 (3H, s 19-H), 1.21 (3H, d, $J$=6.0 Hz, 21-H), 1.95, 2.05, 2.06 (each 3H, s, -OCOMe), 3.29 (3H, s, -OMe), 4.49—4.61 (3H, m, 1′-, 12-, 20-H), 4.63 (1H, t, $J$=9.3 Hz, 4′-H), 5.37 (1H, br s, 6-H)].

**Mild Hydrolysis of Cynanformoside A (1a) with Acid** Cynanformoside A (**1a**) (10 mg) in 80% aqueous 1,4-dioxane (1.2 ml) was mixed with 0.05 M $H_2SO_4$ (1.2 ml) and warmed for 30 min at 50 °C.[18] Dioxane was then removed under reduced pressure. The aqueous concentrate was repeatedly extracted with chloroform and the organic layer washed in turn with $H_2O$, 3% $Na_2CO_3$, and $H_2O$, dried over $Na_2SO_4$, and evaporated to afford utendin (**1e**) (colorless needles from $CHCl_3$–MeOH, mp 248—250 °C)[19] (5 mg). The aqueous layer of the hydrolysate was neutralized with Amberlite IR-45 and concentrated to dryness under reduced pressure. The residue was identified as oleandrose by TLC comparison ($CHCl_3$ : MeOH = 9 : 1), with an authentic sample.

**Alkaline Hydrolysis of Cynanformoside B (1b)** Cynanformoside B (**1b**) (10 mg) was dissolved in 5% methanolic NaOH (1 ml) at room temperature overnight. After addition of $H_2O$ (1 ml), MeOH was removed under reduced pressure. The aqueous concentrate was extracted with $CHCl_3$, dried over $Na_2SO_4$, filtered and evaporated to dryness, yielding a product (7 mg) which was identical with cynanformoside A (**1a**).

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