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The Constituents of *Schizandra chinensis* Baill. The Structures of Two New Lignans, Gomisin F and G, and the Absolute Structures of Gomisin A, B, and C

Two new schizandrin type lignans, gomisin F(I) and G(II), were isolated from the fruits of *Schizandra chinensis* Baill. (Schizandraceae). Their structures including the absolute configurations were established by chemical and spectral evidences.

The absolute structures of gomisin A(V), B(VI), and C(VII), whose relative structures have already elucidated, were also established by circular dichroism spectral studies.

Keywords——*Schizandra chinensis* Baill; Schizandraceae; lignan; gomisin A; gomisin B; gomisin C; gomisin F; gomisin G; CD spectrum

In the previous papers, we reported the relative structures of gomisin A, B, C, and the absolute structure of gomisin D isolated from the fruits of *Schizandra chinensis* Baill. (Schizandraceae).[1,2]

This paper concerns with the structures of two new schizandrin type lignans, gomisin F(I, yield, 0.004%) and G(II, 0.016%) isolated from the same source, and the absolute structures of gomisin A, B, and C.

Gomisin F(I), $C_{28}H_{34}O_9$, colourless needles, mp 119.5—120.5°, $[\alpha]_D^{23} \simeq 0°$. Ultraviolet (UV) spectrum: λ_{max}^{EtOH} nm (log ε): 220 (4.77), 256 (sh, 4.13), 288 (sh, 3.42). Infrared (IR) spectrum ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1715 (ester). Proton magnetic resonance (PMR) spectrum (δ in C_6D_6): 1.10 (3H, d, $J=7$ Hz, $C\underline{H}_3\text{-}\overset{|}{\underset{|}{C}}H$), 1.25 (3H, s, $C\underline{H}_3\text{-}\overset{|}{\underset{|}{C}}\text{-}OH$), 2.05 (1H, q, $J=14/1$ Hz, H-9β), 2.52 (1H, q, $J=14/9$ Hz, H–9α), 3.53, 3.67, 3.83, 3.85 (each 3H, s, 4×$-OCH_3$), 5.36 (2H, q, $-OCH_2O-$) 5.88 (1H, s, H–6), 6.48 (1H, s, H–11), 6.82 (1H, s, H–4), 1.33 (3H, q, $J=1$ Hz), 1.82 (3H, d, q, $J=7/1$ Hz), and 5.63 (1H, q, q, $J=7/1$ Hz) (angeloyl). Mass Spectrum *m/e* (%): 514 (62, M^+), 414 (48, $M^+-CH_3CH=C(CH_3)COOH$), 83 (91, $CH_3CH=C(CH_3)CO$), 55(100, 83-CO).

Gomisin G(II), $C_{30}H_{32}O_9$, colourless prisms, mp 97—98°, $[\alpha]_D^{25}$ −126° ($c=0.43$, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 224 (4.72), 255 (sh, 4.08), 280 (sh, 3.61), 290 (sh, 3.35). IR ν_{max}^{KBr} cm^{-1}: 3430 (OH), 1715 (ester), 927, 722 (aromatic). PMR (δ in $CDCl_3$): 1.17 (3H, d, $J=7$ Hz, $C\underline{H}_3\text{-}\overset{|}{\underset{|}{C}}H$), 1.33 (3H, s, $C\underline{H}_3\text{-}\overset{|}{\underset{|}{C}}\text{-}OH$), 1.57 (1H, s, OH), 2.07 (1H, m, $-\overset{|}{\underset{|}{C}}H$), 2.0—2.6 (2H, m, C_9–H), 3.15, 3.43, 3.82, 3.98 (each 3H, s, 4×$-OCH_3$), 5.90 (1H, s, H–6), 6.00 (2H, q, $J=1.5$ Hz, $-OCH_2O-$), 6.70 (1H, s, H–11), 6.78 (1H, s, H–4) and 7.35 (5H, m, aromatic protons).

These spectral data suggested that two compounds are schizandrin type lignans having a methylenedioxy group, four methoxyl groups, attached to the aromatic ring and also have a tertiary hydroxyl group and an ester linkage.[1–4] The PMR spectral data of I and II closely resemble those of gomisin B(VI) and C(VII), respectively, and show that I has an angeloyl group and II has a benzoyl group.

On hydrolysis with 3% ethanolic potassium hydroxide, I and II gave the same deacyl-derivative (III), $C_{23}H_{28}O_8$, mp 222.5—224°, $[\alpha]_D^{25}$ −73.1° ($c=0.22$, $CHCl_3$). UV λ_{max}^{EtOH} nm (log ε): 220 (4.76), 253 (sh, 4.19), 284 (sh, 3.58). IR ν_{max}^{KBr} cm^{-1}: 3560, 3460 (OH). PMR (δ in $CDCl_3$): 1.13 (3H, d, $J=7$ Hz, $C\underline{H}_3\text{-}\overset{|}{\underset{|}{C}}H$), 1.39 (3H, s, $C\underline{H}_3\text{-}\overset{|}{\underset{|}{C}}\text{-}OH$), 1.58 (1H, d, $J=11$ Hz, OH), 1.70 (1H, s, OH), 2.08 (1H, q, $J=14/1$ Hz, H–9β), 2.43 (1H, q, $J=14/8$ Hz, H–9α), 3.68 (3H), 3.85 (3H), 3.90 (6H) (each s, 4×$-OCH_3$), 4.53 (1H, d, $J=11$ Hz, H–6, singlet after the addition

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of D_2O), 6.00 (2H, s, $-OCH_2O-$), 6.53 (1H, s, H-11) and 6.57 (1H, s, H-4). II also gave benzoic acid by the above hydrolysis. Oxidation of III with chromium trioxide in pyridine afforded a carbonyl compound (IV), $C_{23}H_{26}O_8$, mp 227.5—229.5°, $[\alpha]_D^{23}$ $-93.6°$ (c=0.24, $CHCl_3$), UV λ_{max}^{EtOH} nm (log ε): 218 (4.56), 247 (sh, 4.23). IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 1695 (>C=O). Mass Spectrum, m/e (%): 430 (100, M^+), 412 (6.3, M^+-H_2O), 358 (39, $M^+-CH_3-CH=C(OH)CH_3$). The spectral data of III and IV also closely resemble those of VIII[1] and IX[$C_{23}H_{26}O_8$, mp 129—130°, $[\alpha]_D^{23}$ $-88.5°$ (c=0.38, $CHCl_3$), UV λ_{max}^{EtOH} nm (log ε): 217 (sh, 4.58), 249 (sh, 4.18), 256 (sh, 4.11), 291—295 (sh, 3.48). IR ν_{max}^{KBr} cm^{-1}: 3420 (OH), 1690 (>C=O). Mass Spectrum m/e (%): 430 (100), 412 (8.7), 358 (69)] derived from gomisin B by the same procedure, suggesting that III has the same structure as VIII without regard to the positions of the functional groups attached to the aromatic rings.

Finally, the structures of I and II were thus confirmed by the measurements of intramolecular nuclear Overhauser effects (NOE) in I (in C_6D_6).[1-3] As shown in Fig. 2, irradiation of a methoxyl signal (δ 3.53) and a higher field proton of methylene signal (δ 2.05) caused in 10% and 13% increase in integrated intensity of the aromatic proton signal at δ 6.48 (H-11), respectively. The lower aromatic proton (δ 6.82) was effected by irradiation of C_6 proton signal (δ 5.88), while no effect was shown by irradiation of each methoxyl signal. Irradiation of a ter-

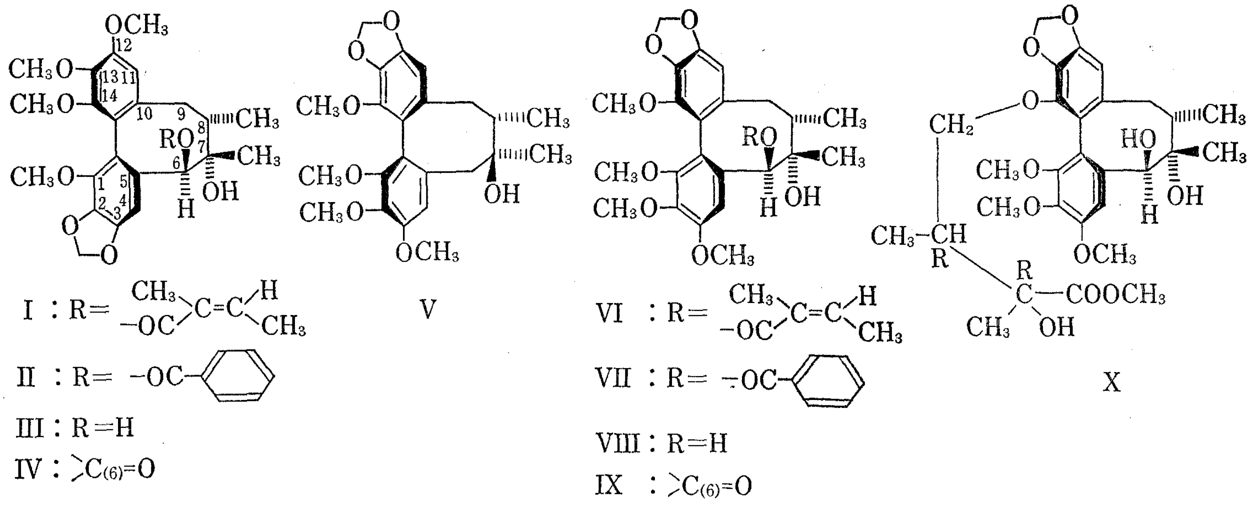

Fig. 1

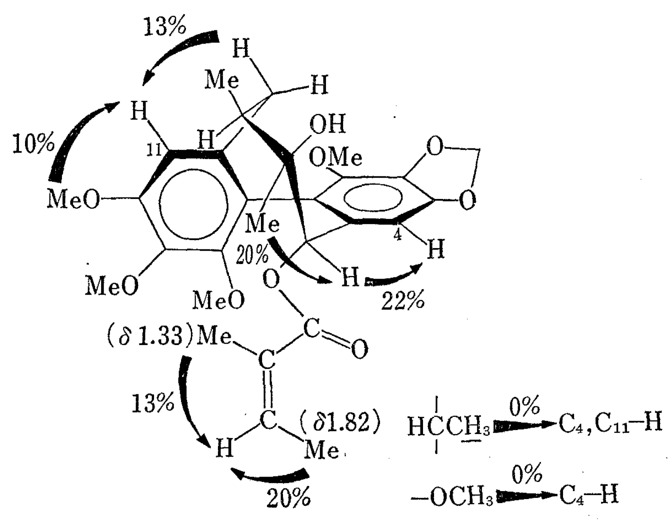

Fig. 2. NOE in I

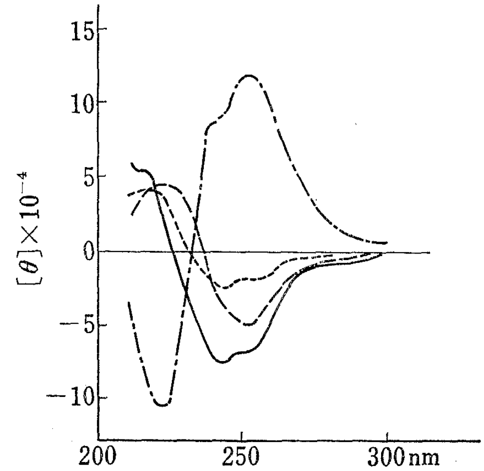

Fig. 3. CD Curves of Gomisin A (V), B (VI), F (I) and (X)

——: X, ------: VI, --------: I, —-—: V

tiary methyl signal caused 20% increase in integrated intensity of C_6 proton signal. On the other hand, the both aromatic protons showed no effect by irradiation of a secondary methyl signal.

From the above results and the Dreiding model examination, the relative structures of gomisin F and G must be expressed by the formulae I and II, respectively. These facts agree with J value between C_8 proton and C_9 methylene protons in the PMR spectra of I and II ($J_{8,9\alpha}=8$—9 Hz, $\Phi_{8,9\alpha}\fallingdotseq 150°$; $J_{8,9\beta}\fallingdotseq 1$ Hz, $\Phi_{8,9\beta}\fallingdotseq 90°$).

The configurational correlations of biphenyl part in gomisin A (V), B, C, F, and G were carried out by the comparisons of circular dichroism (CD) spectra with that of X derived from gomisin D, whose absolute structure has been established by X-ray analysis and shown to have S-configuration of biphenyl part,²⁾ as in the case of Lythraceae alkaloids series.⁵⁾ The CD spectrum of X showed two negative Cotton effects at 249 nm ([θ], -72400 sh), 240 nm ([θ], -78500) and a positive at 216 nm ([θ], $+54000$)($c=0.0229$).⁶⁾ Gomisin B ($c=0.0119$, [θ](nm), -52000 (252), $+46000$ (223)), C($c=0.0135$, [θ](nm), -89500(242), $+19000$ (223)), F($c=0.015$, [θ](nm), -25000 (240), $+41000$ (217)), and G($c=0.045$, [θ](nm), -77000 (239), $+38000$ (222)) also showed a negative and a positive Cotton effects in the same region as that of X, while gomisin A showed two positive effects at 253([θ], $+120000$) and 242 ($+88000$, sh) and a negative at 222 nm (-110000) (Fig. 3).

These data indicate that gomisin B, C, F, and G possess the S-biphenyl configurations same as gomisin D and gomisin A possesses a R-configuration. Consequently, the absolute structures of gomisin A, B, C, F, and G are expressed by the formulae V, VI, VII, I, and II, respectively.

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6) All CD spectra were measured as methanolic solutions.