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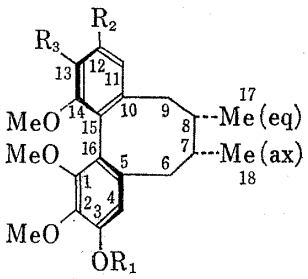
The Constituents of *Schizandra chinensis* Baill. The Structures of Two New Lignans, Gomisin N and Tigloylgomisin P

Two new lignans, gomisin N(**1**) and tigloylgomisin P (**2**), have been isolated from the fruits of *Schizandra chinensis* Baill. (Schizandraceae). Their structures were established by chemical and spectral evidence.

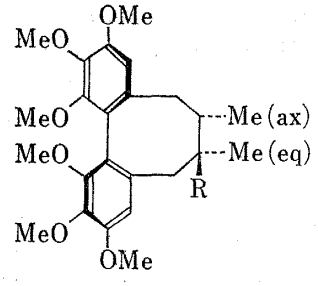
Keywords——*Schizandra chinensis* Baill.; Schizandraceae; dibenzocyclooctadiene lignan; gomisin N; tigloylgomisin P; ^{13}C NMR; ^{1}H NMR

In our previous communications, we reported the structures of the eleven new lignans isolated from the fruits of *Schizandra chinensis* Baill. (Schizandraceae).[1] This paper deals with the structure elucidation of two new dibenzocyclooctadiene lignans, gomisin N (**1**, yield 0.31%) and tigloylgomisin P (**2**, 0.0013%) isolated from the same source.

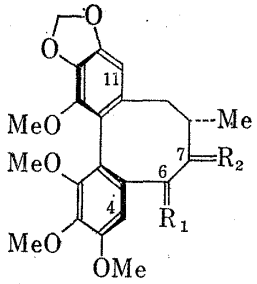
Gomisin N(**1**) was isolated as colourless prisms (ether–*n*-hexane), $C_{23}H_{28}O_6$, mp 105—107°, $[\alpha]_D^{23}$ −84.7° (c=2.17, $CHCl_3$), UV λ_{max}^{EtOH} nm (log ε): 217 (4.73), 251 (sh 4.14), 275—280 (sh 3.61); IR ν_{max}^{KBr} cm^{-1}: 1615, 1595, 1570 (aromatic). The proton nuclear magnetic resonance

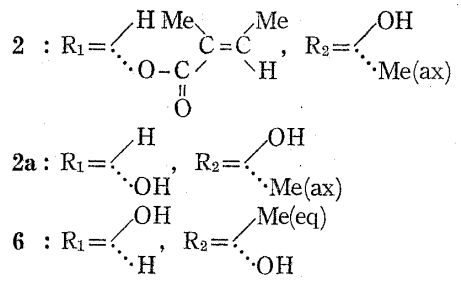


1 : R_1=Me, R_2, R_3=OCH_2O
1a: R_1=Me, R_2=R_3=OH
1b: R_1=Me, R_2=R_3=OMe[3]
5 : R_1=H, R_2=OH, R_3=OMe

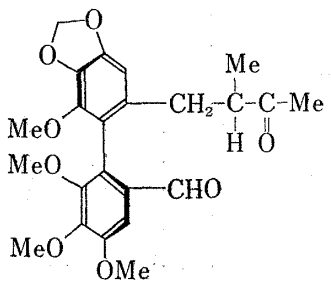


3: R=H[3]
4: R=OH

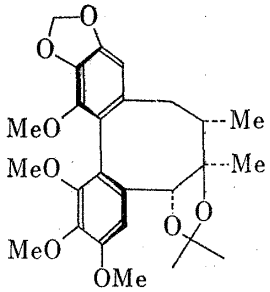




2 : R_1=, R_2=
2a : R_1=, R_2=
6 : R_1=, R_2=



2b



2c

Chart 1 (ax=axial, eq=equatorial)

1) *a*) H. Taguchi and Y. Ikeya, *Chem. Pharm. Bull.* (Tokyo), **23**, 3296 (1975); *b*) *Idem, ibid.*, **25**, 364 (1977); *c*) Y. Ikeya, H. Taguchi and Y. Iitaka, *Tetrahedron Lett.*, **1976**, 1357; *d*) Y. Ikeya, H. Taguchi and I. Yosioka, *Chem. Pharm. Bull.* (Tokyo), **26**, 328 (1978); *e*) *Idem, ibid.*, **26**, 682 (1978).

(^{1}H NMR) and the carbon (^{13}C) NMR[2] spectral analysis of **1** comparing with those of lignans [deoxyschizandrin (**3**), schizandrin (**4**), gomisin J (**5**) and deacylgomisin B (**6**)] isolated from the same source (Table I) indicated that **1** must be a dibenzocyclooctadiene lignan having a methylenedioxyl and four methoxyls on the aromatic rings, and also has a *cis*-dimethyl (^{13}C NMR, ax-CH_3: δ 12.9, eq-CH_3: δ 21.5). The appearance of more shielded protonated aromatic carbon signal at δ 102.9 in the ^{13}C NMR spectrum indicated that methylenedioxyl must link to C-(2-3) or C-(12-13) position.

Treatment of **1** with $Pb(OAc)_4$ in benzene gave a diphenol (**1a**), mp 184.5—188°, $[\alpha]_D^{23}$ −129° (c=0.52, $CHCl_3$), IR ν_{max}^{KBr} cm^{-1}: 3525, 3275 (OH). Methylation of **1a** [$(CH_3)_2SO_4/K_2CO_3$ in acetone] afforded a dimethyl ether (**1b**), mp 116—117°, $[\alpha]_D^{22}$ −100° (c=0.34, $CHCl_3$), as colourless prisms, which was identified with dimethyl-gomisin J(**1b**) by the direct comparison (infrared (IR) and mixed mp)).[1e,3] These facts indicate that **1** possesses the same cyclooctadiene moiety as **1b** and S-biphenyl configuration. Finally, the structure of gomisin N was elucidated as **1** by the measurements of intramolecular nuclear Overhauser effects (NOE) in the ^{1}H NMR spectrum (in $CDCl_3$) as shown in Fig. 1.

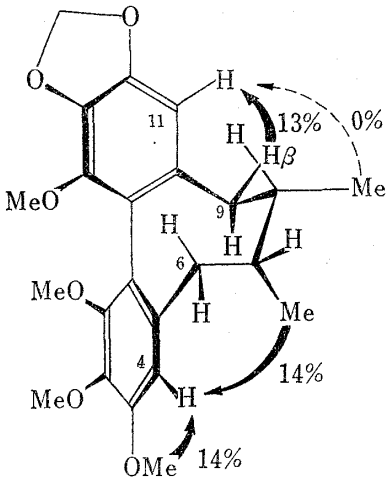
Tigloylgomisin P (**2**) was isolated as an amorphous powder (ether–*n*-hexane), $C_{28}H_{34}O_9$ (M^+, *m/e*, Calcd., 514.2208; Found: 514.2180), $[\alpha]_D^{22}$ −64.2° (c=0.463, $CHCl_3$), UV λ_{max}^{EtOH} nm (log ε): 217 (4.68), 255 (sh, 3.99), 282 (3.51); IR ν_{max}^{KBr} cm^{-1}: 3480 (OH), 1712 (C=O), 1645 (C=C);

Table I. ^{13}C NMR and ^{1}H NMR Spectral Data [δ in $CDCl_3$, ^{13}C: 15.04 MHz; ^{1}H: 100 MHz (J=Hz), at 25°]

Carbon	Biphenyl *R*-configuration		Biphenyl *S*-configuration			
	3[a]	**4**	**5**	**6**	**1** (^{1}H NMR)	**2a**(^{1}H NMR)
1	151.5[b]	151.9[b]	148.8[b]	151.9	147.6[b]	150.9
2	140.0[c]	140.8[c]	137.5[c]	140.7	140.1	140.8
3	151.3[b]	152.0[d]	147.6[d]	152.1	151.6	152.4
4	107.0	110.5[e]	113.3[e]	110.3	110.7(6.55, s)	106.4(7.10, s)
5	138.8	131.8[f]	134.9	133.6[b]	134.0[c]	136.9[b]
6	39.1	40.9	35.3	86.0	35.6(2.57, 2H, m)	75.0(4.32, 1H, s)
7	33.7	71.8	41.0	73.6	40.7(1.83, 2H, m)	76.2
8	40.7	41.8	33.8	41.6	33.6	46.6(1.77, 1H, m)
9	35.5	34.4	38.9	36.3	39.2 (2.10, 2H, ABX)[g]	36.9(2.10, 2H, m)
10	133.5	133.8[f]	140.2	135.0[b]	137.7[c]	135.4[b]
11	110.3	110.1[e]	110.2[e]	103.2	102.9(6.47, s)	102.7(6.47, s)
12	152.7	152.3[d]	147.3[d]	149.9	148.6[b]	149.2
13	139.6[c]	140.3[c]	137.7[c]	135.5	134.6[c]	134.9[b]
14	151.5[b]	151.6[b]	153.4[b]	141.5	141.1	141.1
15	122.2	122.8	121.5	119.6	123.3	122.2
16	123.3	124.2	122.5	122.1	121.4	119.5
17	12.7	15.9	21.7	18.8	21.5(0.97, d, J=7)	18.8(1.07, d, J=7)
18	21.8	29.7	12.6	28.5	12.9(0.73, d, J=7)	16.0(1.00, s)
OMe C-1,14	60.4(×2)	60.5(×2)	60.1(×2)	59.8	59.6	59.6
OMe C-2,13	60.8(×2)	60.9(×2)	61.0(×2)	60.7 60.8	60.5 61.0 (3.82, s)	60.5 60.9 (3.83, s)
OMe C-3,12	55.7(×2)	56.0(×2)	—	56.0	55.9 (3.93, s(×2))	56.0 (3.92, s(×2))
OCH_2O	—	—	—	101.0	100.7(5.93, s)	100.8(5.93, s)

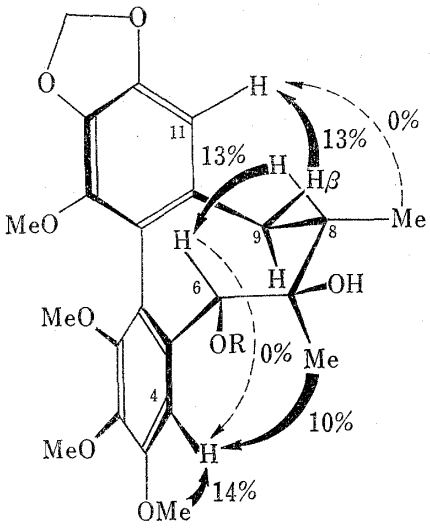
a) Measured at 25.15 MHz.
b, c, d, e, f) Signals within any vertical column may be reversed.
g) $J_{14\alpha,\beta}$=14; $J_{8,9\beta}$=2; $J_{8,9\alpha}$=8.

2) E. Wenkert, H.E. Gottlieb, O.R. Gottlieb, M.O.Da.S. Pereira and M.D. Formiga, *Phytochemistry*, **15**, 1547 (1976).
3) **3**=(*R*)-(+)-deoxyschizandrin, **1b**=(*S*)-(−)-deoxyschizandrin.



OMe ---0%---→ $C_{(11)}$-H

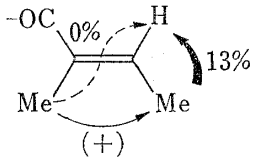
Fig. 1. NOE in **1** (in $CDCl_3$)



OMe ····0%····→ $C_{(11)}$-H

H-$C_{(8)}$-Me ····0%····→ $C_{(4)}$-H

Fig. 2. NOE in **2** (in C_6D_6)

R= 

^{1}H NMR (δ in C_6D_6): 1.10 (3H, d, J=7 Hz, C$\underline{H}_3$–CH), 1.13 (3H, s, C$\underline{H}_3$–C–OH), 1.98 (1H, m, -CH), 2.10 (center) (2H, m, Ar–C$\underline{H}_2$–), 3.53, 3.70, 3.83, 3.92 (each 3H, s, 4×OCH_3), 5.37 (1H, s, $C_{(6)}$–H), 5.90 (2H, s, OCH_2O), 6.13 (1H, s, $C_{(11)}$–H), 6.95 (1H, s, $C_{(4)}$–H), 1.38 (3H, d, q, J= 7/1 Hz), 1.68 (3H, m), 6.85 (1H, m) (tigloyl group); Mass Spectrum, *m/e* (%): 514 (M^+, 12), 414 (M^+—CH_3CH=$C(CH_3)$-COOH, 19), 83 (CH_3CH=$C(CH_3)CO$, 100), 55 (CH_3CH=$C(CH_3)$, 90).

These spectral data suggested that **2** must be a dibenzocyclooctadiene lignan having a tigloyl group.[4] Hydrolysis of **2** with 3% ethanolic potassium hydroxide afforded tiglic acid (mp 63—64°, identified by gas–liquid chromatography (GLC), IR and mixed mp) and a diol (**2a**), $C_{23}H_{28}O_8$, amorphous powder (ether–*n*–hexane), $[\alpha]_D^{25}$ −94.3° (*c*=0.53, $CHCl_3$), CD $[\theta]^{23}$ (nm) (*c*=0.0183, MeOH): +62000 (221), −66000 (sh 242), −76000 (253) (biphenyl: S-configuration); UV λ_{max}^{EtOH} nm (log ε): 220 (4.59), 254 (sh 4.02), 283 (sh 3.49), 294 (sh 3.37); IR ν_{max}^{KBr} cm^{-1}: 3440 (OH), 1615, 1595 (aromatic); Mass Spectrum, *m/e* (%): 432 (M^+, 91), 414 (M^+–H_2O, 66), 371 (14), 343 (100). From the ^{1}H and ^{13}C NMR spectra of **2a** (Table I), comparing with those of deacyl-gomisin B (**6**), it was assumed that **2a** should be a diastereomer of **6** at the C-6 and C-7 positions as mentioned below. In the ^{1}H NMR spectrum, the tertiary methyl of **2a** appeared at higher field than that of **6** (δ 1.40, lit. 1*a*) indicating that it should be shielded by an aromatic ring and one of the aromatic protons appeared at lower field than that of **6** (δ 6.62), suggesting the presence of a C-6α-oriented hydroxyl group. The ^{13}C NMR spectrum also suggested that electronic environment at C-6 and C-7 in **2a** is different from **6**. Oxidation of **2a** (CrO_3 in pyridine or MnO_2 in acetone) afforded a ketoaldehyde (**2b**),[5] $C_{23}H_{26}O_8$ (M^+, *m/e*, 430) as an colourless oil, which was identified with **2b** prepared from **6** by oxidation with CrO_3 in AcOH. This fact supports the above assumption. On the other hand, treatment of **2a** with $CuSO_4$ and 0.25% H_2SO_4 in dry acetone afforded an acetonide (**2c**), $C_{26}H_{32}O_8$ (M^+,

4) Presence of a tigloyl group in **2** was indicated by the chemical shift of olefinic proton at δ 6.87 (*cf.*, angeloyl, around δ 6.00).

5) **2b**: UV λ_{max}^{EtOH} nm (log ε): 218 (sh 4.59), 280 (4.01), 320 (sh 3.57). IR ν_{max}^{KBr} cm^{-1}: 1710 (C=O), 1685 (CHO), 1610, 1583 (aromatic). ^{1}H NMR (δ in $CDCl_3$): 0.89 (3H, d, J=6 Hz, C$\underline{H}_3$–CH), 1.87 (3H, s, CH_3CO–), 2.0—2.93 (2H, m, Ar–C$\underline{H}_2$–), 2.53 (1H, m, –CH), 3.69 (3H, s), 3.85 (3H, s), 3.98 (6H, s) (4×OCH_3), 5.97 (2H, s, OCH_2O), 6.48 (1H, s, $C_{(11)}$–H), 7.37 (1H, s, $C_{(4)}$–H), 9.57 (1H, s, CHO).

m/e, 472) as an amorphous powder, $[\alpha]_D^{22}$ −135° (*c*=0.615, $CHCl_3$).[6] The Dreiding model examination indicated that the structure of the acetonide is only expressed by the formula **2c** and the structure of tigloylgomisin P is expressed as **2**. Finally, the structure of **2** was confirmed by the measurements of NOE as shown in Fig. 2.

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6) **2c**: IR ν_{max}^{KBr} cm^{-1}: no OH, 1619, 1599 (aromatic); ^1H NMR (δ in $CDCl_3$): 0.83 (3H, s, $C\underline{H}_3$–C(–OH)), 1.08 (3H, d, *J*=6 Hz, $C\underline{H}_3$–CH), 1.27, 1.55 (each 3H, s, –O–C(CH_3)$_2$–O–), 1.77 (1H, m, –CH), 2.10 (center) (2H, m, Ar–$C\underline{H}_2$–), 3.62, 3.78, 3.93, 3.95 (each 3H, s, 4×OCH_3), 4.57 (1H, s, $C_{(6)}$-H), 5.99 (2H, s, OCH_2O), 6.50 (1H, s, $C_{(11)}$–H), 7.07 (1H, s, $C_{(4)}$-H).

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Chemische Untersuchungen der Inhaltsstoffe von *Pteris plumbaea* CHRIST.[1]

Aus den oberirdischen Teilen von *Pteris plumbaea* CHRIST. wurden neben den bereits bekannten ent-Kauran-derivaten (Creticosid A (VI) und ent-2α,14α,15β,16*S*,17-Pentahydroxy-kauran (V)) fünf neue isoliert und als ent-2α, 14α,15β-Trihydroxy-kaur-16-en (I), ent-2α,13,14α,15β-Tetrahydroxy-kaur-16-en (II), ent-2α,6α,14α,15β-Tetrahydroxy-kaur-16-en (III) und ent-2α,14α,15β,19-Tetrahydroxy-kaur-16-en (IV) sowie ent-2α,14α,15β-Trihydroxy-kaur-16-en-2-O-β-D-Glukosid (VII) identifiziert.

Keywords——*Pteris plumbaea*; Pteridaceae; ent-kaur-16-enes; glucosides; structures; spectroscopic methods; chemotaxonomy

Pteris plumbaea CHRIST. (Syn. *P. megalocretica* TAGAWA, *P. scabripes* WALL., *P. cretica* L. var. *laeta*)[2] ist eine im tropischen Asien verbreitete grosse Farnpflanze, derer schmalen Sporenblätter bis zu zwei meter Länge erreichen. Sie ist mit *P. cretica* L. nahe verwandt und von vergrösserter Form derselben Pflanze. In Fortsetzung unserer chemischen und chemotaxonomischen Untersuchungen der Gattung *Pteris* und der verwandten Gattungen wurden die oberirdischen Teile von *P. plumbaea* CHRIST. (Fundort: Bad Lu-shan, Taiwan, China; Sammelzeit: Dezember, 1976) auf die Inhaltsstoffe untersucht. Es wurde mit MeOH heiss extra-

1) Chemische und chemotaxonomische Untersuchungen der Gattung *Pteris* und der verwandten Gattungen (Pteridaceae), XXI. Mitteil., XX. Mitteil., T. Satake, T. Murakami, Y. Saiki, und C. -M. Chen, *Chem. Pharm. Bull.* (Tokyo), **26**, 2600 (1978).

2) Ein Herbarexemplar (im Besitz vom Botanischen Institut der Kyoto Universität) der im Gebirge von Taiwan gefundenen Farnpflanze wurde von Tagawa als *P. megalocretica* TAGAWA bezeichnet (nicht publiziert), während eine Sippe tailändischer Herkunft, die zweifellos mit derjenigen identisch ist, als *P. plumbaea* CHRIST. oder *P. scabripes* WALL. beschrieben ist. Diese Nomenklaturen könnten als Synonyme von *P. megalocretica* TAGAWA angesehen werden. Wir danken Herrn Prof. K. Iwatsuki für das Genehmigen uns die Exemplaren genau zu prüfen.