

(6H, s, $2 \times \text{OCH}_3$), 3.83 (6H, s, $2 \times \text{OCH}_3$), 6.47 (2H, d, $J=2$ Hz, $2 \times \text{arom.-H}$), 6.57 (2H, d, $J=2$ Hz, $2 \times \text{arom.-H}$). On the basis of the above spectral data and the result of Gibbs test, I was suggested to be 1,4-bis(3-hydroxy-4,5-dimethoxyphenyl)-2,3-dimethylbutane. In order to confirm the structure, I was thus prepared from *meso*-dihydroguaiaretic acid (III) by the procedure shown in Chart 1.^{4,6)} The product (I), $\text{C}_{22}\text{H}_{30}\text{O}_6$, mp 129—131°, was identified with pre-gomisin by the direct comparison (IR, mixed mp, PMR and TLC). On the other hand, the circular dichroism (CD) spectrum of pre-gomisin (I) shows no Cotton effect in the region 300—200 nm, indicating that I possesses 2-*R* and 3-*S* configurations (*meso*-form). Consequently, the structure of pre-gomisin is now characterized to be (2*R*, 3*S*)-1,4-bis(3-hydroxy-4,5-dimethoxyphenyl)-2,3-dimethylbutane.

Gomisin J (II): $\text{C}_{22}\text{H}_{28}\text{O}_6$ (M^+ , m/e , 388),²⁾ mp 149—150°, $[\alpha]_D^{25} -43.9^\circ$ ($c=1.00$),³⁾ UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 214 (4.70), 248 (4.15), 276 (3.53); IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3545, 3450 (OH), 1610, 1583 (aromatic); PMR (δ in CDCl_3): 0.75 (3H, d, $J=7$ Hz, $\text{C}_{(8)}-\text{CH}_3$), 0.99 (3H, d, $J=7$ Hz, $\text{C}_{(7)}-\text{CH}_3$), 1.5—2.4 (2H, m, $-\dot{\text{C}}\text{H}$), 2.0—2.7 (4H, m, $\text{Ar}-\text{CH}_2-$), 3.50 (6H, s, $\text{C}_{(1)(14)}-\text{OCH}_3$, shielded by the aromatic rings⁷⁾), 3.94 (6H, s, $2 \times \text{OCH}_3$), 5.91 (2H, s, $2 \times \text{OH}$, disappeared on addition of D_2O), 6.63 (2H, s, $2 \times \text{arom.-H}$). FeCl_3 in pyridine-chloroform: green.

The above spectral data suggested that gomisin J is a dibenzocyclo-octadiene lignan, having four methoxyl and two hydroxyl groups on the aromatic rings.¹⁾ Furthermore, the PMR spectrum of II shows two distinct methyl signals, suggesting that one methyl group (δ 0.75) is shielded by the aromatic ring and II has, therefore, a *cis*-dimethyl configuration.^{8b)} Methylation of II ($\text{Me}_2\text{SO}_4/\text{K}_2\text{CO}_3$ in acetone, reflux) afforded IV, colourless prisms, $\text{C}_{24}\text{H}_{32}\text{O}_6$,²⁾ mp 113.5—115° (*n*-hexane-ether), $[\alpha]_D^{25} -65.7^\circ$ ($c=1.37$),³⁾ which was identified with desoxyschizandrin (*dl*-form, CD: $[\theta]_{300-200} 0^\circ$ (MeOH), mp 109.5—110.5°⁸⁾ isolated from the same source (IR, PMR and TLC). In order to confirm the position of two hydroxyl groups in II, the intramolecular nuclear Overhauser effects (NOE) in II and its dibenzyl ether (IIa) ($\text{C}_6\text{H}_5\text{CH}_2\text{Cl}/\text{K}_2\text{CO}_3$ in acetone, reflux) were measured (in CDCl_3)¹⁾ (Chart 2). Irradiation of the methoxyl signals in II showed no enhancement in the integrated intensity of the aromatic protons, however, in IIa, irradiation of the benzylic methylene signals (δ 5.12(s), 5.15(s)) showed enhancement of the integrated intensities of the both aromatic protons, indicating that two hydroxyl groups are located at the vicinal positions of the aromatic protons. On the basis of the above results and the CD spectrum of IV ($[\theta]^{25}(\text{nm})$: -9800 (sh 278), -83000 (248), -62000 (236), +62000 (214) ($c=0.0077$, MeOH), biphenyl *S*-configuration^{1b)}), the absolute structure of gomisin J is thus elucidated as II.

6) The compound (III) was derived from guaiaretic acid by catalytic hydrogenation (Pd-C, MeOH) and its structure was confirmed as dimethyl ether.⁴⁾ Dimethyl ether of III: $\text{C}_{22}\text{H}_{34}\text{O}_4$,²⁾ colourless needles, mp 99.5—100.5° (lit. 101—102°), UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 229 (4.26), 280 (3.80), 285 (sh 3.72); PMR (δ in CCl_4): 0.82 (6H, d, $J=6$ Hz, $\text{CH}_3-\dot{\text{C}}\text{H}$), 1.72 (2H, m, $-\dot{\text{C}}\text{H}$), 2.02—2.82 (4H, m, $\text{Ar}-\text{CH}_2-$), 3.73 (12H, s, $4 \times \text{OCH}_3$), 6.38 (6H, m, *arom.-H*). IIIa: $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_8$,²⁾ mp 173—174.5°, orange prisms (acetone), $[\alpha]_D^{25} 0^\circ$ ($c=0.3$),³⁾ UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 225 (4.32), 254 (sh 3.87), 296 (3.90); IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3200 (OH), 1615 (aromatic), 1540, 1325 (NO_2); PMR (δ in d_6 -acetone): 0.88 (6H, d, $J=7$ Hz, $\text{CH}_3-\dot{\text{C}}\text{H}$), 1.85 (2H, m, $-\dot{\text{C}}\text{H}$), 2.22—3.00 (4H, m, $\text{Ar}-\text{CH}_2-$), 3.83 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 7.05, 7.15, 7.32, 7.42 (each 1H, d, $J=2$ Hz (*meta* coupling), $4 \times \text{arom.-H}$). IIIb: $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_8$,²⁾ mp 107.5—110°, $[\alpha]_D^{25} 0^\circ$ ($c=1.11$),³⁾ UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 222 (4.43), 265 (3.66), 330 (3.23); IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1610 (aromatic), 1540, 1350 (NO_2); PMR (δ in CCl_4): 0.85 (6H, d, $J=6$ Hz, $\text{CH}_3-\dot{\text{C}}\text{H}$), 1.75 (2H, m, $-\dot{\text{C}}\text{H}$), 2.05—2.95 (4H, m, $\text{Ar}-\text{CH}_2-$), 3.82 (3H, s, OCH_3), 3.88 (9H, s, $3 \times \text{OCH}_3$), 6.73, 6.80, 6.90, 6.97 (each 1H, d, $J=2$ Hz, $4 \times \text{arom.-H}$).

7) A.F.A. Wallis, *Tetrahedron Lett.*, **1968**, 5287.

8) a) N.K. Kochetkov, A. Khorlin, and O.S. Chizov, *Tetrahedron Lett.*, **1962**, 361; b) E. Ghera, Y. Ben-David and D. Becker, *ibid.*, **1977**, 463; c) The conformation of cyclo-octadiene ring in desoxyschizandrin is suggested to be the same twist-boat-chair form⁹⁾ as the other lignans isolated from this plant on the basis of PMR, CMR spectral and chemical studies (the data would be published in the continued report). d) *d*-desoxyschizandrin (mp 113.5—115°, colourless prisms (*n*-hexane-ether), $[\alpha]_D^{25} +92.1^\circ$ ($c=2.73$)³⁾), has been isolated from the another source collected in the market.

9) F.A.L. Anet and I. Yavari, *Tetrahedron Lett.*, **1975**, 1567.

The occurrence of I and II in this plant is interesting, since they are assumed to be the precursors in the possible biogenetical route of the oxygenated dibenzocyclo-octadiene lignans such as gomisins A-D, F and G¹⁾ as shown in Chart 3.

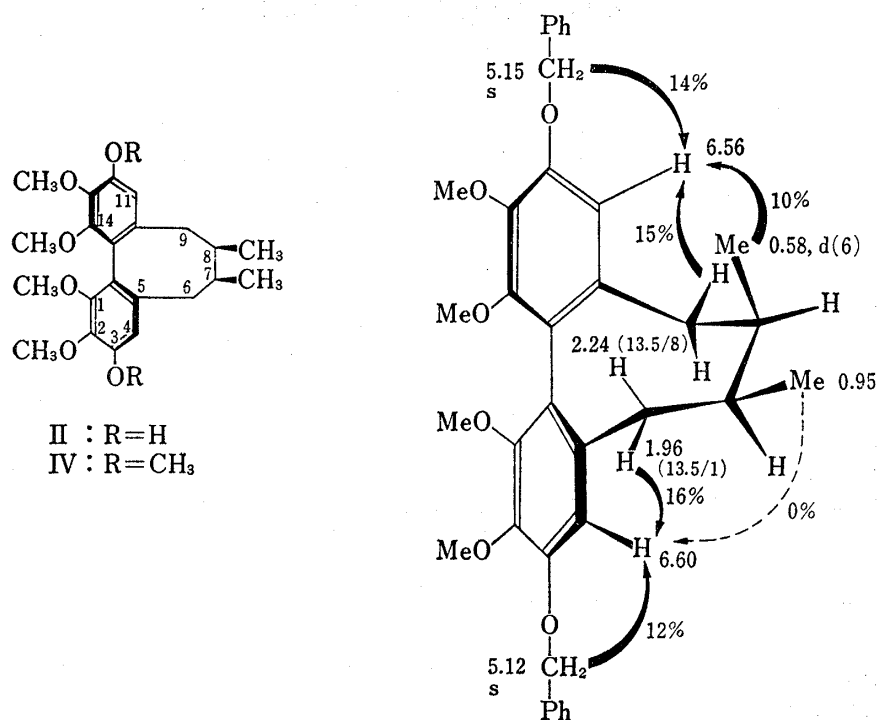


Chart 2

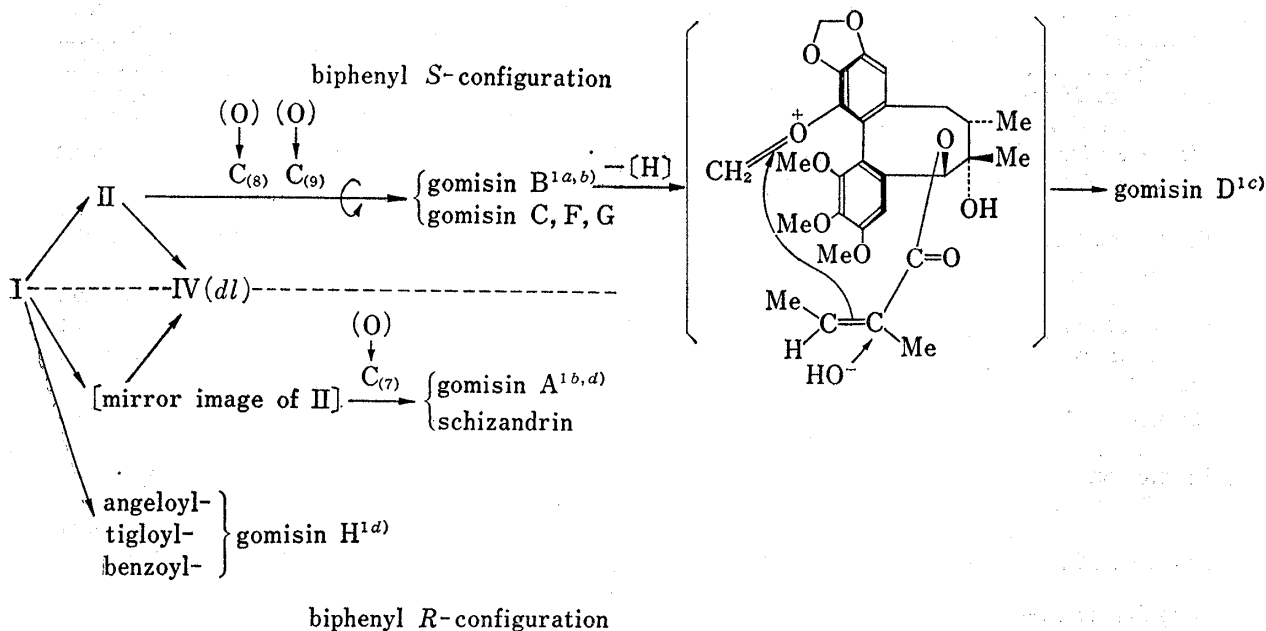


Chart 3. Possible Biogenetical Route of Gomisins

Tsumura Laboratory
1421, Izumi, Komae-shi,
Tokyo

YUKINOBU IKEYA
HEIHACHIRO TAGUCHI
ITIRO YOSIOKA

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