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Two New Bitetrahydroanthracenes from Roots of *Cassia occidentalis* L.[1]

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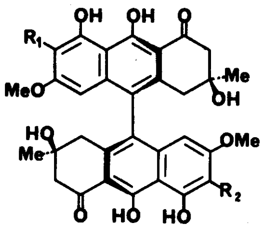
Two new bitetrahydroanthracene derivatives, occidentalol-I (2) and occidentalol-II (3), were isolated from the roots of *Cassia occidentalis* L. along with chrysophanol, emodin, pinselin, questin, germichrysone, methylgermitorosone and singueanol-I (1). The structures of 2 and 3 were established as 3,3′,4,4′-tetrahydro-3,3′,8,8′,9,9′-hexahydroxy-6,6′-dimethoxy-3,3′,7-trimethyl-1(2*H*),1′(2*H*)-10,10′-bianthracenone and 3,3′,4,4′-tetrahydro-3,3′,8,8′,9,9′-hexahydroxy-6,6′-dimethoxy-3,3′-dimethyl-1(2*H*)-,1′(2*H*)-10,10′-bianthracenone, respectively, on the basis of spectral evidence.

Keywords *Cassia occidentalis*; Leguminosae; tetrahydroanthracene; bitetrahydroanthracene; occidentalol-I; occidentalol-II

In a previous paper,[2] we reported the isolation and the structure elucidations of an anthraquinone (7-methylphyscion) and a tetrahydroanthracene (7-methyltorosachrysone) together with five anthraquinoids from the tissue culture of *Cassia occidentalis* L. In this paper, we wish to report three bitetrahydroanthracenes, singueanol-I (**1**), occidentalol-I (**2**), and occidentalol-II (**3**), along with three anthraquinones, a xanthone, and two tetrahydroanthracenes from the roots of this plant. The extraction and separation were carried out as described in Experimental.



1: $R_1 = R_2 = Me$
2: $R_1 = Me$, $R_2 = H$
3: $R_1 = R_2 = H$

Chart 1

Singueanol-I (**1**), $C_{34}H_{34}O_{10}$, mp 300 °C (dec.) was identified by direct comparison [thin layer chromatography (TLC), infrared (IR), and circular dichroism (CD)] with an authentic sample.[3]

Occidentalol-I (**2**) was obtained as yellowish brown prisms, mp 280 °C (dec.). The high resolution mass spectrum (HR-MS) of **2** gave the molecular formula $C_{33}H_{32}O_{10}$ [*m/z* 588.1994 (M^+)]. The similarity in the chromophore of **2** to that of **1** was established by comparison of their ultraviolet (UV) and IR spectra. The absorptions at 308 sh, 318, and 332 sh nm showed that **2** possessed a naphthalene ring, while a band at 1630 cm^{-1} revealed the presence of a conjugated carbonyl group. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **2** showed the presence of two aliphatic methyl, one aromatic methyl, four methylene, and two methoxy groups, as well as three aromatic protons (a singlet and two doublets for *meta*-coupled), and four doublets due to chelated hydroxyl groups (Table I). The couplings ($J = 1.0$ Hz) between the two pairs of chelated hydroxyl groups in **2** was recognized to involve a "through-space" mechanisms[4,5] as a result of an irradiation experiment so that the two pairs of hydroxy groups were shown to be located at the *peri*-positions on the naphthalene rings. A comparison of the ^{1}H-NMR chemical shifts of the corresponding protons in **1** and **2** shows that **2** has one more aromatic proton (δ 6.51) and one less aromatic methyl group (δ 2.16) than **1**.

Thus, the plane structure of **2** was shown to be 3,3′,4,4′-tetrahydro-3,3′,8,8′,9,9′-hexahydroxy-6,6′-dimethoxy-3,3′,7-trimethyl-1(2*H*),1′(2*H*)-10,10′-bianthracenone.

The CD curve of **2** exhibits strong positive first (268 nm) and negative second (236 nm) Cotton effects due to the ^1B_b transitions of the two naphthalene chromophores and this shows that the two long axes of the naphthalene nuclei in **2** are twisted in a clockwise manner, since the C_{10}–$C_{10'}$ absolute configuration is *S* (Fig. 1).[3,6,7]

Occidentalol-II (**3**) was obtained as yellowish brown prisms, mp 270 °C (dec.). HR-MS gave the molecular formula $C_{32}H_{30}O_{10}$ [*m/z* 574.1834] and major fragment ions were observed at *m/z* 556 ($M^+ - H_2O$, 538 ($M^+ - 2H_2O/2$), 270 ($M^+ - 2H_2O/2$), 269 ($M^+ - 2H_2O/2 - H$), and 241 ($M^+ - 2H_2O/2 - CO$). The UV and IR spectra of **3** showed similarity with those of **1** and **2**, so that **3** was assumed to be a bitetrahydroanthracene derivative. The ^{1}H-NMR spectrum of **3** showed the presence of two aliphatic methyl, four methylene, and two methoxy groups, as well as two pairs of *meta*-coupled aromatic protons, and two pairs of chelated hydroxyl protons. The above data indicated that **3** had two less aromatic methyl groups than **1** and one less aromatic methyl group than **2**.

Therefore, the plane structure of **3** was established as 3,3′,4,4′-tetrahydro-3,3′,8,8′,9,9′-hexahydroxy-6,6′-dime-

Table I. ^{1}H-NMR Data for Compounds **1**, **2**, and **3**[a]

	1	2	3
C_2-H	2.81, s	2.83, s	2.83, s
C_3-Me	1.27, br s	1.29, br s	1.29, br s
C_4-H	2.51, br s	2.52, br s	2.53, br s
C_5-H	6.03, s	6.02, s	6.03, d, $J = 2.4$ Hz
C_6-OMe	3.49, s	3.50, s	3.59, s
C_7-Me	2.16, s	2.16, s	
C_7-H			6.50, d, $J = 2.4$ Hz
C_8-OH	10.29, d, $J = 1.0$ Hz	10.30, d, $J = 1.0$ Hz	10.18, d, $J = 1.0$ Hz
C_9-OH	16.69, d, $J = 1.0$ Hz	16.67, d, $J = 1.0$ Hz	16.70, d, $J = 1.0$ Hz
$C_{2'}$-H		2.83, s	
$C_{3'}$-H		1.39, br s	
$C_{4'}$-H		2.52, br s	
$C_{5'}$-H		6.03, d, $J = 2.0$ Hz	
$C_{6'}$-OMe		3.57, s	
C_7-H		6.51, d, $J = 2.0$ Hz	
C_8-OH		10.18, d, $J = 1.0$ Hz	
C_9-OH		16.67, d, $J = 1.0$ Hz	

a) Measured in $CDCl_3$ at 100 MHz, with TMS as the internal standard. The following abbreviations are used: s, singlet; d, doublet; br s, broad singlet.

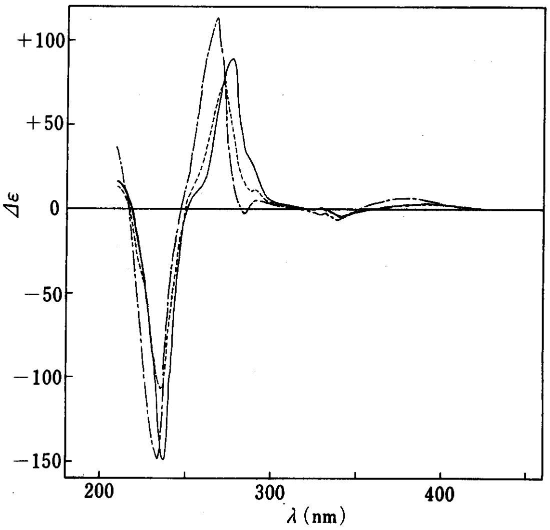


Fig. 1. CD Spectra of **1** (——), **2** (----), and **3** (—-—)

thoxy-3,3′-dimethyl-1(2*H*),1′(2*H*)-10,10′-bianthracenone.

From the CD curve, the C_{10}–$C_{10'}$ absolute configuration of **3** is proved to be *S*.

From a biogenetic consideration of hydroanthracenes in *Cassia occidentalis*, the absolute configurations at C_3 and $C_{3'}$ in singueanol-I (**1**), **2**, and **3** are presumed to be the same as those of monomeric hydroanthracenes.[3,8]

Experimental

All the melting points were taken on a Yanagimoto micro-melting-point apparatus and are uncorrected. The UV spectra were obtained on a Hitachi 200-10 spectrophotometer, and IR spectra were recorded on a JASCO IR A-2 spectrophotometer. The NMR spectra were taken on a JEOL FX-100 instrument; the chemical shifts are given in ppm relative to internal tetramethylsilane (TMS). The MS were obtained on a Hitachi RMU-7M spectrometer. Column chromatography was performed on silicic acid (SiO_2) (Mallinckrodt).

Extraction and Isolation The fresh roots (3.2 kg) of *Cassia occidentalis* L. collected at the Drug Plant Garden of the College of Science and Technology, Nihon University, were extracted with C_6H_6 (7 l × 3) at room temperature. The extract was concentrated *in vacuo* to give a brown mass (18 g). The mass was chromatographed on an SiO_2 column and eluted in succession with C_6H_6 and C_6H_6–AcOEt mixtures. Fractions 1 and 2 were eluted with C_6H_6, fractions 3 and 4 with C_6H_6–AcOEt (9 : 1), and fractions 5 and 6 with C_6H_6–AcOEt (4 : 1). Fraction 1 was rechromatographed with hexane–AcOEt (19 : 1) to give chrysophanol (15 mg). Fraction 2 was rechromatographed with C_6H_6–AcOEt (19 : 1) to afford emodin (27 mg). Fraction 4 gave pinselin (157 mg) and questin[2] (6 mg) on SiO_2 column chromatography with C_6H_6–AcOEt (17 : 3). Fraction 5 gave germichrysone[2] (57 mg) from C_6H_6 solution. Fraction 6 was rechromatographed with $CHCl_3$–AcOEt (4 : 1) to afford singueanol-I (62 mg) and fraction 6-2, then fraction 6-2 gave **2** (5 mg), methylgermitorosone[2] (1 mg) and **3** (2 mg) on preparative thin layer chromatography with C_6H_6–AcOEt (9 : 1).

Singueanol-I(1) Crude crystals were recrystallized from C_6H_6 to give yellowish brown prisms, mp 280 °C (dec.).

The ^{1}H-NMR data are shown in Table I. Compound **1** was identified as singueanol-I by direct comparison with an authentic sample.

Occidentalol-I (2) Crude crystals were recrystallized from C_6H_6 to give yellowish brown prisms: mp 280 °C (dec.). UV $\lambda_{\max}^{\text{dioxane}}$ nm (log ε): 228 (4.69), 273 (4.83), 308 sh (4.03), 318 (4.11), 332sh (3.99), 401 (4.25). CD (c = 0.0021, dioxane) $\Delta\varepsilon^{22}$: 382 (+5.2), 355 (0), 340 (−4.9), 326 (0), 290 (+11.0), 272 (+74.0), 249 (0), 236 (−106.9), 217 (0). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 2950, 1630, 1600, 1515. MS *m/z*: 558 (M^+, 100%), 570 ($M^+ - H_2O$, 36), 552 ($M^+ - 2H_2O$, 50), 284 ($M^+ - H_2O - C_{16}H_{14}O_5$, 41), 283 ($M^+ - H_2O - C_{16}H_{15}O_5$, 23), 270 ($M^+ - H_2O - C_{17}H_{16}O_5$, 73), 269 ($M^+ - H_2O - C_{17}H_{17}O_5$, 21). HR-MS: Calcd for $C_{33}H_{32}O_{10}$: 588.1993. Found: 588.1994.

The ^{1}H-NMR data are shown in Table I.

Occidentalol-II (3) Crude crystals were recrystallized from C_6H_6 to give yellowish brown prisms: mp 270 °C (dec.). UV $\lambda_{\max}^{\text{dioxane}}$ nm (log ε): 232 (4.73), 273 (4.93), 307sh (4.07), 319 (4.12), 333sh (4.00), 398 (4.38). CD (c = 0.00098, dioxane) $\Delta\varepsilon^{22}$: 380 (+7.5), 353 (0), 337 (−6.0), 328 (−3.0), 322 (0), 291 (+5.7), 287 (0), 284 (−3.3), 282 (0), 268 (+114.4), 248 (0), 234 (−149.3), 217 (0). IR $\lambda_{\max}^{\text{KBr}}$ cm^{-1}: 3400, 2950, 1625, 1590, 1510. MS *m/z*: 574 (M^+, 75%), 556 ($M^+ - H_2O$, 43), 538 ($M^+ - 2H_2O$, 56), 270 ($M^+ - 2H_2O/2 + H$, 100), 269 ($M^+ - 2H_2O/2$, 55), 255 ($M^+ - 2H_2O/2 + H - Me$, 16), 241 ($M^+ - 2H_2O/2 - CO$, 14), 267 ($M^+ - 2H_2O/2 + H - Me - CO$, 17). HR-MS: Calcd for $C_{32}H_{30}O_{10}$: 574.1836. Found: 574.1834.

The ^{1}H-NMR data are shown in Table I.

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References and Notes

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