# Traditional medicinal plants of Thailand. 10. Candenatone, a novel purple pigment from Dalbergia candenatensis

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# Candenatone, a Novel Purple Pigment from *Dalbergia candenatensis*[1]

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A labile, purple pigment was isolated from a complex mixture of closely related orange and purple pigments obtained from the heartwood of *Dalbergia candenatensis* (Leguminosae). Preliminary evidence suggested that the compound was an isoflavan with an additional $C_{15}$ unit attached. On standing in solution a mixture of tautomeric structures was produced and a pyrilium species **2** formed in acidic media. Extensive NMR studies in neutral and acidic media led to the conclusion that candenatone contains a new natural product skeleton, and crystalline candenatone was assigned structure **1a**. The absolute configuration was determined through comparison of the CD spectrum of a dihydro derivative **7** with that of (3*R*)-(−)vestitol (**9**).

The heartwood of *Dalbergia candenatensis* Prain (Leguminosae) is used in Thailand as an antibacterial and also as a red dyestuff. We have previously identified the principal compounds responsible for the antimicrobial and cytotoxic activity[4] and were naturally intrigued by the intensely red color of the plant material. A number of phytochemical investigations on several species belonging to the genus *Dalbergia*, reputed for the valuable timber and resistance to insect attacks, have been reported.[5] An extensive literature research, however, revealed no clues concerning the nature of the red pigments of *D. candenatensis*, and we therefore decided to attempt the characterization of these coloring materials.

## Results and Discussion

Preliminary TLC assays with a prepurified MeOH extract revealed a complex mixture of orange and purple pigments, all present in relatively small concentrations. Attempts to purify these compounds by column chromatography over silica gel failed, the pigments being irreversibly retained on the adsorbent despite the use of rather polar, water-containing eluents.

Therefore, a different isolation procedure was sought in an attempt to minimize the loss due to irreversible adsorption on solid stationary phases. Concerted use of liquid–liquid partitioning, followed by flash chromatography, droplet counter-current chromatography (DCCC), and gel chromatography finally led to a pure purple pigment, to which the name candenatone (**1a**) was given. The compound could be obtained as a finely crystalline material from a dilute methanolic solution; attempts to grow crystals suitable for X-ray analysis were unsuccessful.

The UV spectrum of candenatone (**1a**) showed absorption maxima at 558 and 527 nm and a shoulder at 498 nm. A bathochromic shift on addition of NaOMe suggested the presence of free phenolic groups. $AlCl_3$ caused a strong hypsochromic shift of both the 558- and 527-nm bands, and a single absorption maximum was observed at 491 nm. Identical UV spectra were obtained with addition of $AlCl_3$ and HCl or with HCl alone, indicating that the hypsochromic shift was solely caused by an acidic solution. A molecular weight of 522 daltons was deduced from the D/CI MS [$m/z$ 523 ($(M + H)^+$)], corresponding to the molecular formula $C_{32}H_{26}O_7$ as determined by high-resolution FAB MS.

During preliminary $^1H$ NMR experiments, a significant change in the aromatic region was observed within a few hours after the dissolution of the sample, resulting in an increasingly complex spectrum. These changes, however, ceased after about 24 h, suggesting that an equilibrium state had been reached. Addition of DCl to the sample stabilized and simplified the spectrum, shifting a majority of the signals in the aromatic region significantly downfield. Most of the $^1H$ NMR studies were therefore conducted in acidic media.

(1) Traditional Medicinal Plants of Thailand. 10. For Part 9, see ref 3.

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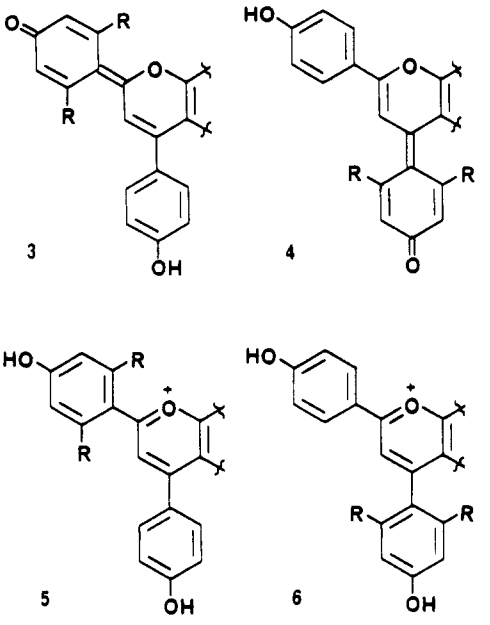
In the upfield region of the spectrum of **2** (Table I) two pairs of methylene protons were observed at δ 3.18 and 3.45 and δ 4.33 and 4.52, respectively. The homonuclear shift correlated spectrum clearly revealed a methine proton hidden under the HDO peak at δ 3.40, with diaxial couplings to the signals at δ 3.45 and 4.33, and an axial–equatorial relationship with the protons at δ 3.18 and 4.55. The methine multiplet could be directly observed in a partially relaxed spectrum, and in NOE difference experiments when irradiating the signals at δ 3.18 and 4.55. The two equatorial methylene protons exhibited a W-type coupling ($J \simeq 1$ Hz). The upfield methylene group showed further coupling to an aromatic proton observed as a slightly broadened singlet at δ 7.01. The coupling pattern of the five aliphatic protons[4,6] and the long-range coupling of the benzylic methylene group to an aromatic proton in the peri position[7] were typical for isoflavans with the dihydropyran ring in a half-chair conformation. At that point it became clear that the pigment was an isoflavan with an additional $C_{15}$ unit attached.

In the aromatic region of the spectrum, the signals for 10 protons belonging to three aromatic rings were observed. The doublets at δ 7.12 and 7.77 (2 H each) were readily assigned to a para-substituted ring (H2″, H6″ and H3″, H5″). The signals at δ 6.73, 6.77 and 8.38 (H3‴, H5‴, H6‴), and δ 6.38, 6.49, and 7.04 (H3′, H5′, H6′) belonged to two 1,2,4-trisubstituted rings. The substituents were identified as two methoxy groups (δ 3.68 and 4.02) and three hydroxyls appearing at δ 9.88, 10.77, and 11.62. In the COSY spectrum, the downfield methoxy singlet displayed a cross-peak with the signal at δ 5.77. This methoxy group was therefore attached in the 2-position of the ring. The second methoxy group exhibited NOE's to the protons at δ 6.38 and 6.49 and was placed in the 4-position on the second trisubstituted aromatic ring.

In a delayed COSY experiment emphasizing long-range coupling, the methoxy singlet at δ 3.68 displayed cross peaks with the signals at δ 6.38 and 6.49, confirming the results from the NOE experiments. The singlet at δ 8.01 exhibited cross-peaks with both singlets at δ 7.73 and 8.35, but no long-range coupling was observed between the latter two signals.

The $^1$H NMR spectrum of a freshly prepared sample of candenatone **1a** in DMSO-$d_6$ (Table I) showed some striking differences when compared with the spectra recorded in acidic solution: with the exception of H3′, H5′, H6′, and MeO-4′, all of the other aromatic protons appeared significantly upfield. Two two-proton doublets at δ 6.97 and 7.45 were readily assigned to the para-substituted aromatic ring. The signals at δ 5.77 (d, $J$ = 1.5 Hz), 6.06 (dd, $J$ = 9.8, 1.5 Hz), and 7.96 (d, $J$ = 9.8 Hz) appeared to be nonaromatic. From the coupling constants a quinone-type ring system was suggested. Furthermore, only two phenolic protons were observed instead of three for candenatone in acidic solution. These observations led to the conclusion that (i) all the aromatic protons with the exception of H3′, H5′, H6′, and MeO-4′ had to be located in the chromophore of the molecule and (ii) the quinone system observed in neutral solution became aromatic in acidic media. This conclusion was supported by the $^{13}$C NMR data of **1a** and **2**. A carbonyl carbon was observed at δ 183.08 for **1a** but was missing in the spectrum of **2**. The single carbonyl signal, the trisubstituted six-membered ring, and a carbonyl band at 1635 cm$^{-1}$ in the IR spectrum were only compatible with the partial structure of a *p*-quinone methide bearing a methoxy group in the 2-position. The combined spectral data and biogenetic considerations reduced the possible structures for the chromophore of candenatone **1a** to two, namely **3** and **4**. This chromophore would tautomerize in solution and form a pyrilium ion **5** or **6** in acidic media.




The partial structure of the chromophore was corroborated by NOE difference spectroscopy,[8] which at the same time revealed the position of attachment of the three aromatic rings in **2**. Irradiation of H3 led to a negative NOE for H6′.[9] Irradiation of H5 led to the enhancement of H2″ and H6″, establishing that the para-substituted ring was attached to C6. When irradiating H7, enhancement of H6″ was observed. The enhancement of H2″ and H6″ which was also expected, could not be clearly seen because of the close proximity to H7 in the spectrum. An NOE difference experiment performed on a freshly prepared sample of candenatone established the structure of crystalline **1a**: On irradiation of H7, an enhancement of H6″ was observed which was only compatible with tautomer **1a** (Scheme I). With the structure of **1a** established, the structure of the other tautomers present in DMSO-$d_6$ was investigated. The $^1$H NMR spectrum of an equilibrated sample revealed the presence of two major tautomers **1a** and **1b** in nearly equal concentrations, together with one or two minor tautomeric forms. Due to spectral overlapping, only partial assignments could be obtained for **1b** (Table I). No chemical shift differences were observed for the protons of the pyran ring of **1a** and **1b**. The unresolved signals corresponding to H3′, H5′, and H6′ were assigned through homonuclear shift correlation. Two two-proton doublets of a para-substituted ring were observed at δ 7.18 and 6.73. The coupling constant $J$ = 9.5–10.0 Hz indicated a quinone ring, and H6″ appeared at δ 7.32. The unre-

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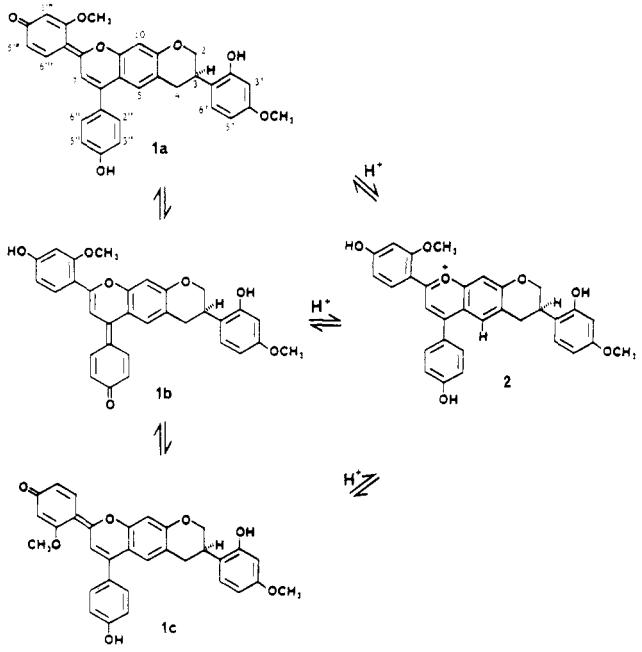
(8) Sanders, J. K. M.; Mersh, J. D. *Prog. NMR Spectrosc.* **1982**, *15*, 353.
(9) All of the NOE's observed for **1a** and **2** were negative and comparatively weak. NOE difference experiments with the simple isoflavan vestitol **8** under identical conditions showed positive enhancement. The negative sign observed for **1** and **2** may be explained by the slow tumbling rate of the molecule at room temperature due to the high viscosity of DMSO-$d_6$. NOE experiments were not performed at higher temperature, because of the eventual degradation of **2** and the faster tautomerization of **1a**.

**Table I. $^1$H NMR Assignments for 1a,[a] 1b,[a] and 2[b]**

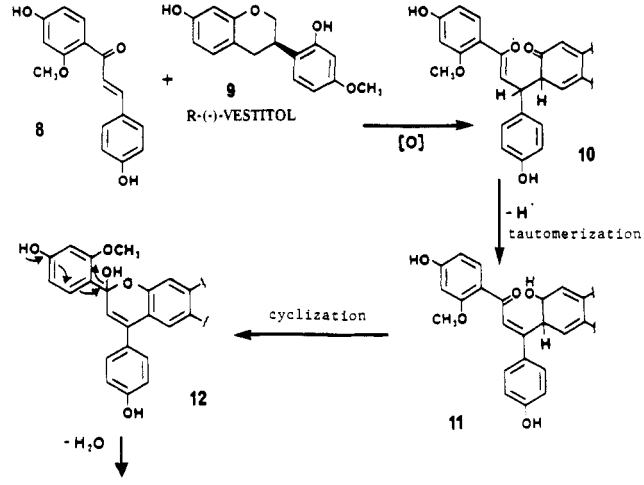
| | 1a | | | 1b[c] | | | 2 | | |
|---|---|---|---|---|---|---|---|---|---|
| proton | chem shift, ppm | mult | coupled protons, (coupling constant, Hz) | chem shift, ppm | mutl | coupled protons | chem shift, ppm | mult | coupled protons (coupling constant, Hz) |
| $2_a$ | 4.12 | dd | $2_e$ (10.5), $3_a$ (9.5) | 4.12 | | | 4.33 | dd | $2_e$ (10.3), $3_a$ (10.3) |
| $2_e$ | 4.35 | br d | $2_a$ (10.5), $3_a$ (3.5) $4_e$ (~1) | 4.35 | | | 4.52 | br dd | $2_a$ (10.3), $3_a$ (3.0) $4_e$ (~1) |
| $3_a$ | 3.40 | m | $2_a$, $2_e$, $4_a$, $4_e$ | | | | 3.45 | m | $2_a$, $2_e$, $4_a$, $4_e$ |
| $4_a$ | 3.08 | dd | $4_e$ (16.0), $3_a$ (10.5) 5 (<1) | 3.08 | | | 3.18 | dd | $4_e$ (16.2), $3_a$ (10.2) 5 (<1) |
| $4_e$ | 2.91 | br dd | $4_a$ (16.0), $3_a$ (4.0) $2_e$ (~1), 5 (<1) | 2.92 | | | 3.29 | br dd | $4_a$ (16.0), $3_a$ (4.1) $2_e$ (~1), 5 (<1) |
| 5 | 7.38 | br s | $4_a$ (<1), $4_e$ (<1) 7 (<1), 10 (<1) | | | | 8.01 | br s | $4_a$ (<1), $4_e$ (<1) 7 (<1), 10 (<1) |
| 7 | 7.74 | s | 5 (<1) | | | | 7.73 | s | 5 (<1) |
| 10 | 7.16 | s | 5 (<1) | | | | 8.35 | s | 5 (<1) |
| 3′ | 6.43 | d | 5′ (2.5) | 6.30–6.45 | unresolvd | | 6.49 | d | 5′ (2.4), 4′-$OCH_3$ (<1) |
| 5′ | 6.36 | dd | 6′ (8.2), 5′ (2.5) | | | | 6.38 | dd | 6′ (8.2), 3′ (2.4), 4′-$OCH_3$ (<1) |
| 6′ | 6.99 | d | 5′ (8.2) | 6.95 | unresolvd | | 7.04 | d | 5′ (8.2) |
| 2″ (2 H) 6″ | 7.45 | d | 3″ and 5″ (8.2) | 7.18 | d | 3″ and 5″ (10) | 7.77 | d | 3″ and 5″ (8.8) |
| 3‴ (2 H) 5″ | 6.97 | d | 2″ and 6″ (8.3) | 6.73 | d | 2″ and 6″ (~9.5) | 7.12 | d | 2″ and 6″ (8.8) |
| 3″ | 5.77 | d | 5‴ (1.5), 2‴-$OCH_3$ (<1) | | | | 6.73 | d | 5‴ (2.0), 2‴-$OCH_3$ (<1) |
| 5‴ | 6.06 | dd | 6‴ (9.8), 3‴ (1.5) | 6.30–6.45 | unresolvd | | 6.77 | dd | 6‴ (8.7), 3‴ (2.0) |
| 6‴ | 7.96 | d | 5‴ (9.8) | 7.32 | d | 5‴ (8.4) | 8.38 | d | 5‴ (8.7) |
| 2′-OH | 9.68 | br s | | 9.62[d] | br s | | 9.88 | br s | |
| 4″-OH | 10.08 | br s | | | | | 10.77[d] | br s | |
| 4‴-OH | | | | 10.10[d] | br s | | 11.62[d] | br s | |
| 4′-$OCH_3$ | 3.67 | s | | 3.67 | s | | 3.68 | s | 3′ (<1), 5′ (<1) |
| 2‴-$OCH_3$ | 3.80 | s | 3‴ (<1) | 3.76 | s | | 4.02 | s | 3‴ (<1) |

[a] Recorded in DMSO-$d_6$. [b] Recorded in DMSO-$d_6$ + DCI. [c] Data extracted from the spectra of a mixture of the tautomers. Only assignable signals are listed. [d] Assignments may be reversed.

**Scheme I. Tautomeric Forms of Candenatone 1a–c and Pyrilium Species 2**



**Scheme II. Biogenesis of Candenatone**



solved signals belonging to H5″ and H3″ at δ 6.30–6.45 were assigned with the aid of a COSY spectrum. The coupling constant $J_{5,6}$ = 8.4 Hz was typical for two ortho-coupled aromatic protons, establishing the structure of the second major tautomer as **1b**. The minor tautomers could not be identified, but we suppose at least the presence of **1c**.

Due to the limited amount and the tautomerization of **1a**, only partial $^{13}C$ NMR assignments could be obtained for **1a** and the pyrilium species **2**. In the spectrum of **1a**, the signal at δ 183.08 was readily assignable to C6‴, as well as the resonances at δ 130.29 and 115.91 to C2″, C6″ and C3″, C5″, respectively. The resonances at δ 70.00, 30.49, and 29.70 belonged to C2, C3, and C4 and were in good agreement with data obtained for simple isoflavans.[4] A partial structure of candenatone being identical with vestitol (**8**) enabled further assignments. The signals at δ 121.54, 155.91, 101.28, 158.07, 104.39, and 127.77 were attributed to C1′ through C6′. Tentative assignments were made for C4a (δ 113.58) and C10a (δ 152.93). The remaining aromatic signals could not be related to specific carbons. Their chemical shifts were, however, in the range expected for the proposed structure **1a**. The $^{13}C$ NMR spectrum of **2** exhibited eight resonances in the region δ 155–168, assignable to eight oxygen-bearing aromatic carbons. Signals for thirteen protonated and six quaternary carbons were observed in the domain δ 100–135, and the upfield region displayed signals for two methoxy groups, two aliphatic methylenes, and a methine carbon.

The absolute configuration of candenatone (**1a**) was deduced through circular dichroism studies. Assignment of the absorption bands of **1** or **2** was precluded by the complexity of the UV spectrum due to the extended chromophores and the tautomerism of **1** in solution. In an attempt to correlate the chiroptical properties of candenatone derivatives with those of simple isoflavans of known absolute configuration,[6,10] the pyrilium species **2** was subjected to catalytic hydrogenation over $PtO_2$ under acidic conditions. From the colorless reaction mixture, the dihydro derivative **7** was isolated. With the exception of the band at 346.5 nm, the UV spectrum absorption maxima were almost identical with those of the related simple isoflavan vestitol (**9**). The CD spectrum of **7** exhibited a maximum at 286 nm and a trough at 235 nm, and was virtually superimposable with the CD curve of (3*R*)-(−)-vestitol (**9**), which was previously isolated from the same plant.[4] Because of the planarity of the molecule, it was concluded that the catalytic hydrogenation was not enantioselective and had yielded a diastereomeric mixture. That the resulting CD curve was identical with that of (3*R*)-(−)vestitol (**9**) led to the conclusion that candenatone (**1a**) possesses the 3*R* configuration. Candenatone **1a** represents the first example of a new type of $C_{30}$ isoflavan. A biogenesis of the compound is outlined in Scheme II, in which a radical coupling of the chalcone **8** and the preformed isoflavan vestitol (**9**) could lead to the radical species **10**. Elimination of a H radical and tautomerization would give the intermediate **11**. Candenatone would be obtained through cyclization to **12** and subsequent elimination of water.

Isoflavonoids condensed with a chalcone unit are a rarity in Nature. The only other compounds identified so far are the orange pigments isolated from sandalwood and camwood.[11] However, their resulting fused ring system is entirely different from that of candenatone.

The structures of the other colored pigments from *D. candenatensis* have not been elucidated thus far. On the basis of chromatographic behavior and UV spectral data, we suppose that the other purple pigments must have the same chromophore as candenatone (**1**), with differences occurring in ring substitution. We have not, as yet, attempted the isolation of the minor orange pigments. A close botanical relationship of the genera *Dalbergia* and *Pterocarpus* suggests that these pigments may be similar to the coloring matters of sandalwood.

## Experimental Section

**General Procedures.** Melting points were determined on a Kofler hot plate apparatus and are uncorrected. The UV spectra were obtained with a Beckman DU-7 spectrophotometer. Shift reagents were prepared according to ref 12. IR spectra were

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(11) (a) Arnone, A.; Camarda, L.; Merlini, L.; Nasini, G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 186. (b) Arnone, A.; Camarda, L.; Merlini, L.; Nasini, G.; Taylor, D. A. H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2116. (c) Arnone, A. Camarda, L.; Merlini, L., Nasini, G.; Taylor, D. A. H. *Phytochemistry* **1981**, *20*, 799.

measured on a Nicolet MX-1 FT IR instrument. ORD curves were recorded on a Jasco J-40A automatic recording spectropolarimeter. Low-resolution EI MS were obtained with a Varian MAT-112S mass spectrometer. D/CI MS spectra were recorded with a Finnigan 4500 instrument using methane as reactant gas. High-resolution FAB MS were obtained with a MAT 731 mass spectrometer. The sample was suspended in methanol and glycerol.

TLC was performed on silica gel coated Al sheets (Merck, Darmstadt, Germany); EtOAc/MeOH/$H_2O$ (100:16:13) (system I) and $CHCl_3$/MeOH/$H_2O$ (80:20:2) (system II) were used as mobile phases. Detection was performed at daylight, UV 254 and 366 nm. The home-built DCCC instrument consisted of 300 tubes (i.d. 1.6 × 400 mm) and a Mini Pump VS (LCD/Milton Roy, Riviera Beach, FL). Partition coefficients[13] of solvent systems were estimated as follows: An aliquot (≃1 mg) of fraction B from the flash column was partitioned with 10 mL of upper and lower phase of a particular biphasic system. One milliliter of each phase was evaporated to dryness and redissolved in MeOH (10 mL), and the absorbance at 527 nm was determined. The selected solvent system $CHCl_3$/toluene/$CCl_4$/MeOH/$H_2O$ (65:30:30:70:15) showed a partition coefficient of 2 in favor of the upper phase.

$^1H$ NMR and $^{13}C$ NMR spectra were recorded with a Varian XL 300 spectrometer operating at 299.94 and 75.44 MHz, respectively. The samples were measured as approximately 0.02 M solutions in DMSO-$d_6$ with TMS as an internal standard. All spectra were recorded at 21–22 °C. For the measurement of the spectra of **2**, DCl (37% in $D_2O$) was added by suspending a droplet on a capillary tube over the sample in the 5-mm NMR tube. The capillary was removed after a few seconds and the sample mixed. This procedure was repeated until the color of the solution changed from purple to orange.

COSY 90 spectra were acquired at a sweep width of 2000 Hz (1K data points) in the F2 domain; 256 spectra (16 scans each for **1a**, 8 scans for **2**, 32 scans for mixture of tautomers) with a 1-s recycle delay were recorded. The data were transformed after zero filling to a 1K × 1K data matrix, and resolution enhancement was achieved with a pseudo-echo-shaped function to F1 and F2 prior to Fourier transformation. The parameters for recording the delayed COSY spectra of **1a** and **2** were identical, except for the additional delay Δ = 200 ms before and after the 90° observe pulse. NOE difference spectra for **1a** and **2** were acquired as 16K data sets covering a spectral width of 3000 Hz. The decoupler power was adjusted to give an approximately 70% saturation of the irradiated signal. A presaturation time of 5 s was used and 500–800 scans were accumulated for each experiment. A 1- or 2-Hz line broadening was applied to the difference FID prior to Fourier transformation.

Multiplicities for the $^{13}C$ NMR spectrum of **2** were obtained from an APT spectrum.

**Plant Material.** The dried heartwood of *D. candenatensis* Prain was purchased in 1986 in Bangkok, Thailand, in a herbal drug store. The plant material was authenticated by comparison with voucher specimens deposited in the Botany Section, Technical Division, Department of Agriculture and Cooperatives, Bangkok, Thailand.

**Extraction and Isolation.** The coarsely ground dry heartwood (2.5 kg) was exhaustively percolated at room temperature successively with light petroleum ether, $CHCl_3$, EtOAc, and MeOH. The MeOH extract (103 g) containing the pigments was washed with warm EtOAc, and the insoluble portion (32 g) was partitioned with $CHCl_3$/toluene/MeOH/$H_2O$ (13:3:7:4). The residue from the lower phase (4.8 g) was submitted to flash chromatography over silica gel. Elution with $CHCl_3$/MeOH/$H_2O$ (85:15:1.5) gave four fractions (A–D). Fraction B (1.5 g) was separated by DCCC using $CHCl_3$/toluene/$CCl_4$/MeOH/$H_2O$ (65:30:30:70:15) in the descending mode. Crude candenatone (150 mg) was purified on a Sephadex LH 20 column eluted with MeOH, to afford **1a** (15 mg) as a finely crystalline material from dilute MeOH solution.

**1a**: mp 230–233 °C; UV (MeOH) $\lambda_{max}$ (log $\epsilon$) 558 nm (4.53), 527 (4.58), 498 sh (4.39), 365 (3.95), (+NaOMe) $\lambda_{max}$ 570 nm, 545 sh, 466, 294, (+$AlCl_3$) $\lambda_{max}$ 491 nm, 432 sh, (+HCl) $\lambda_{max}$ 492 nm, 430 sh; IR (KBr) $\nu_{max}$ 3420, 2995, 1635, 1605, 1584, 1527, 1508, 1449, 1389, 1208, 1169, 990, 840 $cm^{-1}$; EI MS, $m/z$ (relative intensity) 522 (1) [$M^+$], 388 (4), 272 (4), 149 (74), 124 (75), 121 (48), 95 (40), 94 (100); D/CI MS ($CH_4$), $m/z$ 551 ([M + $C_2H_5$]$^+$), 537 ([M + $CH_3$]$^+$), 523 ([M + H]$^+$); HR FAB MS found for $MH^+$ 523.1750, calcd for $C_{32}H_{27}O_7$ 523.1757; $^{13}C$ NMR (75.44 MHz, DMSO-$d_6$) δ 183.08 (C4‴), 164.44, 159.24, 158.98, 158.07 (C4′), 155.91 (C2′), 152.93 (C8a), 149.44, 131.46, 130.29 (C2″ and C6″), 127.77 (C6′), 127.40, 126.34, 121.71, 121.54 (C1′), 118.44, 115.91 (C3″ and C5″), 113.58 (C4a), 104.39 (C5′), 103.90, 103.52, 102.95, 101.28 (C3′), 70.00 (C2), 55.26 ($CH_3O$-2‴ or $CH_3O$-4′), 54.82 ($CH_3O$-4′ or $CH_3O$-2‴), 30.49 (C3), 29.70 (C4).

**2**: $^{13}C$ NMR (75.44 MHz, DMSO-$d_6$ + DCl) δ 167.49 (s), 166.77 (s), 163.51 (s), 162.45 (s), 162.40 (s), 162.11 (s), 159.16 (s), 156.11 (s), 133.43 (d), 132.76 (d, C2″ and C6″), 129.61 (d), 127.91 (d), 127.41 (s), 124.98 (s), 117.73 (s), 116.72 (d, C3″ and C5″), 115.55 (s), 115.42 (s), 110.75 (s), 109.09 (s), 104.46 (d), 104.18 (d), 101.39 (d), 101.36 (d), 100.06 (d), 71.00 (t, C2), 56.57 (q, $CH_3O$-2‴ or $CH_3O$-4′), 54.92 (q, $CH_3O$-4′ or $CH_3O$-2‴), 30.29 (d, C3), 30.04 (t, C4).

**Synthesis of 7.** Candenatone **1a** (0.5 mg) in dilute methanolic HCl was subjected to catalytic hydrogenation over $PtO_2$ for 90 min. After filtration, the colorless solution was evaporated in vacuo and the residue chromatographed over a Si gel column (43–60 μm, 5 × 100 mm). Elution with $CHCl_3$/MeOH (98:2) yielded the dihydro derivative **7**: UV (MeOH) $\lambda_{max}$ 346.5 nm, 285, 225 sh, 216; EI MS (20 eV), $m/z$ 524 ($M^+$), 494, 425, 371, 369; CD 268 (+), 235 (–).

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**Registry No.** **1a**, 115321-26-1; **1b**, 115321-28-3; **1c**, 115321-29-4; **2**, 115321-27-2; **7**, 115321-30-7.

**Supplementary Material Available:** Figure I, COSY spectrum of **2**, Figure II, aromatic region of delayed COSY spectrum of **2**, Figure III, aromatic region of delayed COSY spectrum of **1a**, Figure IV, NOE difference spectra of pyrilium species **2** and quinone methide **1a**, Figure V, CD spectra (in MeOH) of candenatone (**1**), pyrilium **2**, dihydro derivative **7**, and (3*R*)-(–)-vestitol (**9**) (5 pages). Ordering information is given on any current masthead page.

(12) Mabry, T. J.; Markham, K. R.; Thomas, M. B. *The Systemic Identification of Flavonoids*; Springer Verlag: Berlin, 1970; p 1.

(13) The unusual chromatographic behavior of the pigments precluded the generally used solvent system selection based on TLC as described by Hostettmann, K. *Planta Med.* **1980**, *39*, 1.