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Studies on the Constituents of Orchidaceous Plants. IX.[1] Constituents of *Spiranthes sinensis* (PERS.) AMES var. *amoena* (M. BIEBERSON) HARA. (2). Structures of Spiranthesol, Spiranthoquinone, Spiranthol-C, and Spirasineol-B, New Isopentenyldihydrophenanthrenes[2]

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Four new dihydrophenanthrene derivatives, spiranthesol, spiranthoquinone, spiranthol-C, and spirasineol-B, were isolated from the roots of *Spiranthes sinensis* (PERS.) AMES var. *amoena* (M. BIEBERSON) HARA (Japanese name "nezi-bana"). The structures 1, 2, 3, and 4 were proposed for these compounds, respectively, on the basis of spectroscopic data obtained by various methods including ^{1}H-detected heteronuclear multiple-bond multiple-quantum coherence (HMBC) spectroscopy. Chemical conversions of spiranthol-A to spiranthol-C and spiranthoquinone and of spirasineol-A to spirasineol-B are also described.

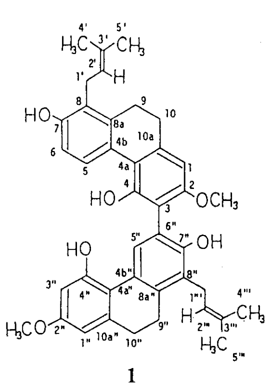
Keywords *Spiranthes sinensis* var. *amoena*; Orchidaceae; spiranthesol; dimeric dihydrophenanthrene; spiranthoquinone; spiranthol-C; spirasineol-B; dihydrophenanthrene; HMBC

In the preceding paper,[1] we reported the isolation of seven new dihydrophenanthrene derivatives (DHP-I and DHP-III to VIII) together with a known compound, orchinol (**5**, DHP-II),[3] from the roots of *Spiranthes sinensis* (PERS.) AMES var. *amoena* (M. BIEBERSON) HARA (Japanese name "nezi-bana"),[4] which is used as a crude drug in China and Taiwan.[5] Among the seven new compounds, the structures of three, spiranthol-A (**6**, DHP-III) and -B (**7**, DHP-I) and spirasineol-A (**8**, DHP-VIII), were also reported. This paper describes in detail the structure elucidation of the other four dihydrophenanthrenes named spiranthesol (**1**, DHP-IV), spiranthoquinone (**2**, DHP-V), spiranthol-C (**3**, DHP-VI), and spirasineol-B (**4**, DHP-VII). All these compounds are minor components of the roots, and their structure analyses were done with the aid of spectral methods.

Spiranthesol (**1**, DHP-IV) was obtained as an amorphous solid and showed $[\alpha]_D$ 0° (CHCl$_3$). It showed ultraviolet (UV) absorptions at 223, 273, 281, and 297sh nm (log ε: 4.59, 4.50, 4.50, and 4.39) and infrared (IR) absorptions at 3510 (OH), 1615, and 1463 cm^{-1} (benzene ring). In the negative ion fast atom bombardment mass spectrum (FAB-MS), **1** showed the quasi-molecular ion peak at m/z 617 $[M-H]^-$, although it failed to show the molecular ion peak in the electron impact mass spectrum (EI-MS). In the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra (Tables I and II), there were signals corresponding to forty-two hydrogens and forty carbons, respectively. Thus, the molecular formula of **1** was determined to be $C_{40}H_{42}O_6$.[6]

The ^{1}H-NMR spectrum of **1** showed signals due to a pair of *ortho*-coupled aromatic protons (δ 6.71 and 8.02, each d, J=8.6 Hz), a pair of *meta*-coupled aromatic protons (δ 6.31 and 6.43, each d, J=2.4 Hz), and two isolated aromatic protons (δ 6.55 and 7.78) along with signals arising from four hydroxyl protons, two methoxyls, and two isopentenyl groups (Table I). In addition, it showed signals assignable to the 9- and 10-methylene protons of dihydrophenanthrene (δ 2.76, 4H, m, and δ 2.80, 4H, br s),[7] suggesting that **1** may be a dimeric dihydrophenanthrene derivative.

In the nuclear Overhauser effect (NOE) experiments,



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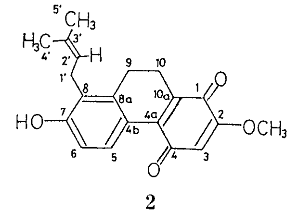

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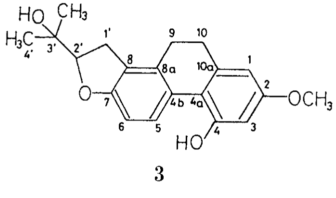

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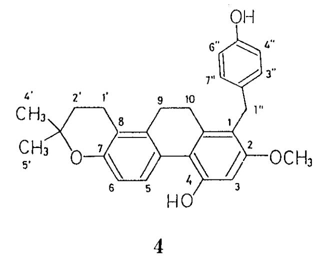

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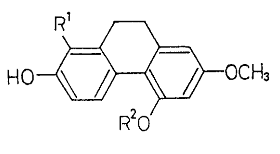
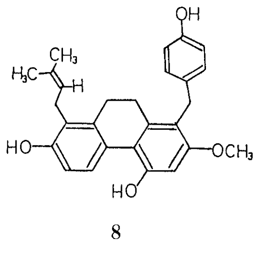


5 : R^1=H, R^2=CH$_3$
6 : R^1=isopentenyl, R^2=H
7 : R^1=isopentenyl, R^2=CH$_3$



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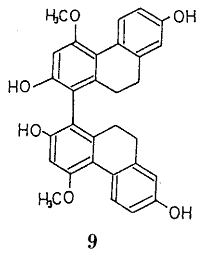

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Chart 1

TABLE I. ^{1}H-NMR Data for Dihydrophenanthrenes from *Spiranthes sinensis* var. *amoena* (*J* in Hz)

^{1}H	1$^{a)}$	2$^{a)}$	3$^{a)}$	6$^{a)}$	4$^{b)}$	8$^{a)}$
1-H	6.55 s	—	6.36 d (2.4)	6.42 d (2.4)	—	—
3-H	—	5.92 s	6.42 d (2.4)	6.36 d (2.4)	6.57 s	6.45 s
5-H	8.02 d (8.6)	7.82 d (8.9)	7.80 d (8.4)	7.75 d (8.5)	8.10 d (8.5)	7.66 d (8.2)
6-H	6.71 d (8.6)	6.76 d (8.9)	6.72 d (8.4)	6.74 d (8.5)	6.58 d (8.5)	6.75 d (8.2)
9-H_2	2.80 br s	2.76 m	2.73 m	2.73 m	2.53 m	2.60 br s
10-H_2		2.67 m	2.65 m	2.68 m	2.59 m	
2-OCH_3	3.83 s	3.85 s	3.80 s	3.79 s	3.77 s	3.79 s
1′-H_2	3.46 d (6.7)	3.42 d (6.7)	3.14 d (8.9)	3.44 d (6.7)	2.71 t (6.7)	3.42 d (7.0)
2′-H	5.17 tqq (6.7, 1.5, 1.5)	5.10 tqq (6.7, 1.2, 1.2)	4.65 t (8.9)	5.15 tqq (6.7, 1.2, 1.2)	1.83 t (6.7)	5.12 tqq (7.0, 1.5, 1.5)
4′-H_3	1.83 s	1.81 br s	1.37 s	1.82 br s	1.29 s	1.79 br s
5′-H_3	1.73 d (1.5)	1.72 d (1.2)	1.25 s	1.72 d (1.2)		1.71 d (1.5)
1″-H	6.43 d (2.4)	—	—	—	3.95 s	3.98 s
3″-H	6.31 d (2.4)	—	—	—	6.94 d (8.5)	6.98 d (8.5)
4″-H	—	—	—	—	6.68 d (8.5)	6.68 d (8.5)
5″-H	7.78 s	—	—	—	—	—
6″-H	—	—	—	—	6.68 d (8.5)	6.68 d (8.5)
7″-H	—	—	—	—	6.94 d (8.5)	6.98 d (8.5)
2″-OCH_3	3.79 s	—	—	—	—	—
9″-H_2	2.76 m	—	—	—	—	—
10″-H_2		—	—	—	—	—
1‴-H_2	3.51 dd (15.3, 6.7) 3.57 dd (15.3, 6.7)	—	—	—	—	—
2‴-H	5.20 tqq (6.7, 1.5, 1.5)	—	—	—	—	—
4‴-H_3	1.80 br s	—	—	—	—	—
5‴-H_3	1.70 d (1.5)	—	—	—	—	—
OH	5.17 br s 5.42 br s 5.43 s 5.75 s	5.45 br s	5.29 s	4.99 s 5.34 s	7.97 br s 8.28 br s	4.81 br s 5.11 s 5.50 s

a, b) Measured in $CDCl_3$ and acetone-d_6, respectively.

irradiation of the methoxy methyls at δ 3.83 (2-OCH_3) and 3.79 (2″-OCH_3) caused an NOE increase of the signals at δ 6.55 (1-H) and at δ 6.43 and 6.31 (1″-H and 3″-H), respectively. On the other hand, irradiation of the methylene protons at δ 2.80 (9- and 10-H_2) and at δ 2.76 (9″- and 10″-H_2) enhanced the signals at δ6.55 (1-H), 5.17 (2′-H), and 3.46 (1′-H_2) and at δ 6.43 (1″-H), 5.20 (2‴-H), 3.51, and 3.57 (1‴-H_2), respectively. In turn, irradiation of the methylene protons at δ 3.46 (1′-H_2) and at around δ 3.54 (1‴-H_2) enhanced the signals at δ2.80 (9- and 10-H_2) and at δ 2.76 (9″- and 10″-H_2), respectively. These observations led us to postulate the partial structures A and B to be present in **1** (Chart 2). These structures were consistent with the ^{13}C-NMR spectrum, which was analyzed by the use of ^{1}H–^{13}C shift correlation spectroscopy (^{1}H–^{13}C COSY). Most of the signals due to methyl, methylene, and methine carbons were doubled and their chemical shifts were similar to those of **6** (Table II).

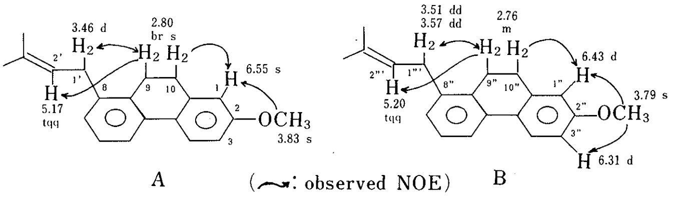

Chart 2

Next, we measured the ^{1}H-detected multiple-bond multiple-quantum coherence (HMBC) spectrum[8] to determine the total structure of **1**. As shown in Fig. 1, the quaternary carbons at δ 158.8 and 155.4 showed long-range correlation with the methoxy methyl protons at δ 3.79 (2″-OCH_3) and 3.83 (2-OCH_3), respectively. Therefore, these were assigned unequivocally to C-2″ and C-2, respectively, and the remaining four downfield carbons (δ 150.7—153.4) must be linked to hydroxyl groups. Among these, two

TABLE II. ^{13}C-NMR Data for Dihydrophenanthrenes Obtained from *S. sinensis* var. *amoena*[a]

^{13}C	**1**[b]	**2**[b]	**3**[b]	**6**[b]	**4**[c]	**8**[b]
C-1	103.0 d	181.4 s	106.7 d	106.0 d	118.1 s	118.5 s
C-2	155.4 s	158.3 s	158.6 s	158.6 s	157.8 s	157.2 s
C-3	110.3 s	107.7 d	100.8 d	100.8 d	99.5 d	98.3 d
C-4	151.3 s	187.5 s	153.3 s	153.4 s	153.3 s	151.7 s
C-4a	116.3 s	128.6 s	115.0 s	115.4 s	116.7 s	115.2 s
C-4b	125.7 s	125.1 s	125.2 s	125.6 s	126.8 s	125.9 s
C-5	126.7 d	113.7 d	106.7 d	113.3 d	128.6 d	124.1 d
C-6	113.0 d	130.0 d	125.5 d	124.6 d	115.4 d	113.4 d
C-7	152.5 s	156.2 s	157.9 s	152.5 s	156.5 s	152.6 s
C-8	124.3 s	122.6 s	125.2 s	125.3 s	118.8 s	125.3 s
C-8a	137.9 s	136.2 s	135.2 s	138.4 s	137.7 s	138.7 s
C-9	25.48[d] t	23.5[d] t	26.29[d] t	25.6 t	25.5[d] t	25.6[d] t
C-10	30.9 t	29.7 t	30.2[d] t	30.5 t	27.2[d] t	26.4[d] t
C-10a	141.0 s	139.6 s	140.6 s	140.9 s	140.4 s	139.7 s
2-OCH$_3$	55.9 q	56.2 q	55.3 q	55.3 q	56.2 q	55.7 q
C-1′	25.52[d] t	25.3[d] t	29.8[d] t	25.5 t	34.1 t	25.5 t
C-2′	122.2 d	121.4 d	89.6 d	122.1 d	21.4 t	122.0 d
C-3′	133.3 s	129.0 s	71.9 s	133.4 s	74.0 s	133.6[e] s
C-4′	18.0 q	20.1 q	24.1 q	18.0 q	27.4 q	18.0 q
C-5′	25.8 q	25.8 q	26.33 q	25.7 q	27.4 q	25.7 q
C-1″	106.1 d	—	—	—	30.9 t	30.1 t
C-2″	158.8 s	—	—	—	133.6 s	133.6[e] s
C-3″	132.0 s	—	—	—	130.1 d	129.1 d
C-4″	153.4 s	—	—	—	116.2 d	115.1 d
C-4a″	115.0 s	—	—	—	—	—
C-4b″	126.0 s	—	—	—	—	—
C-5″	126.5 d	—	—	—	154.6 s	153.4 s
C-6″	115.8 s	—	—	—	116.2 d	115.1 d
C-7″	150.7 s	—	—	—	130.1 d	129.1 s
C-8″	127.2 s	—	—	—	—	—
C-8a″	139.3 s	—	—	—	—	—
C-9″	25.6 t	—	—	—	—	—
C-10″	30.3 t	—	—	—	—	—
C-10a″	140.8 s	—	—	—	—	—
2″-OCH$_3$	55.3 q	—	—	—	—	—
C-1‴	25.8 t	—	—	—	—	—
C-2‴	122.5 d	—	—	—	—	—
C-3‴	132.0 s	—	—	—	—	—
C-4‴	18.0 q	—	—	—	—	—
C-5‴	25.8 q	—	—	—	—	—

a) ^{13}C-Signal assignments of **1**, **6**, and **8** were done by means of 2D NMR methods (see ref. 1), and those of **2**, **3**, and **4** were based on the comparisons with **6** and **8**. *b*, *c*) Measured in CDCl$_3$ and acetone-d_6 solution, respectively. *d*) Assignments may be interchanged in each column. *e*) In a higher concentration (125 mg/ml), these signals appear separately at δ 133.5 (C-3′) and 133.1 (C-2″).

hydroxyl-bearing carbons at δ 152.5 and at δ 150.7 showed long-range correlation with the methylene protons at δ 3.46 (1′-H$_2$) and at δ 3.51 and 3.57 (1‴-H$_2$), respectively, so that these carbons were considered to be C-7 and C-7″, respectively. Further, C-7 showed long-range correlation with both of the *ortho*-coupled aromatic protons (δ 6.71 and 8.02), indicating that these protons are H-6 and H-5,[9] respectively. On the other hand, both the *meta*-coupled protons at δ 6.43 and 6.31 (1″-H and 3″-H) showed long-range correlation with C-2″ (δ158.8) and with the quaternary carbon at δ 115.0, which enabled us to assign the latter carbon to C-4a″. In turn, this carbon C-4a″ showed long-range correlation with the isolated aromatic proton at δ 7.78, indicating the latter to be H-5″. Thus the location of all the aromatic protons was clarified.

Now, both the H-1 (δ 6.55) and H-5″ (δ 7.78) showed long-range correlation with the quaternary carbon at δ 110.3. Therefore, it is reasonable to assign this carbon to C-3 and also to conclude that two dihydrophenanthrene units are linked between C-3 and C-6″ and the two remaining hydroxyl groups are located at the C-4 and C-4″ positions.

On the basis of the above findings, the structure of spiranthesol was determined to be a dimeric dihydrophenanthrene as represented by the formula **1**. Recently, Majumder and Banerjee[10] have reported the isolation of flavanthrin (**9**), a new dihydrophenanthrene derivative having a symmetric structure, from an Orchidaceous plant *Eria flava*. Spiranthesol (**1**) is the first example of a natural dimeric dihydrophenanthrene with an unsymmetric structure.

Spiranthoquinone (**2**, DHP-V) was obtained as red fine needles (from CH$_2$Cl$_2$), mp 150—151 °C, and has the molecular formula C$_{20}$H$_{20}$O$_4$ (*m/z* 324) as determined by MS and high-resolution MS (HR-MS). The UV spectrum of **2** showed absorptions at 216, 238sh, 260, 311, 316, and 493 nm (log ε: 4.43, 4.25, 4.25, 3.97, 3.98, and 3.21) and the IR spectrum at 3588, 3307 (br, OH), 1642, 1631 (CO), 1600 (C=C), and 1568 cm^{-1} (benzene ring). These spectral data, coupled with the appearance of two carbonyl carbon signals (δ 181.4 and 187.5) in the ^{13}C-NMR spectrum,

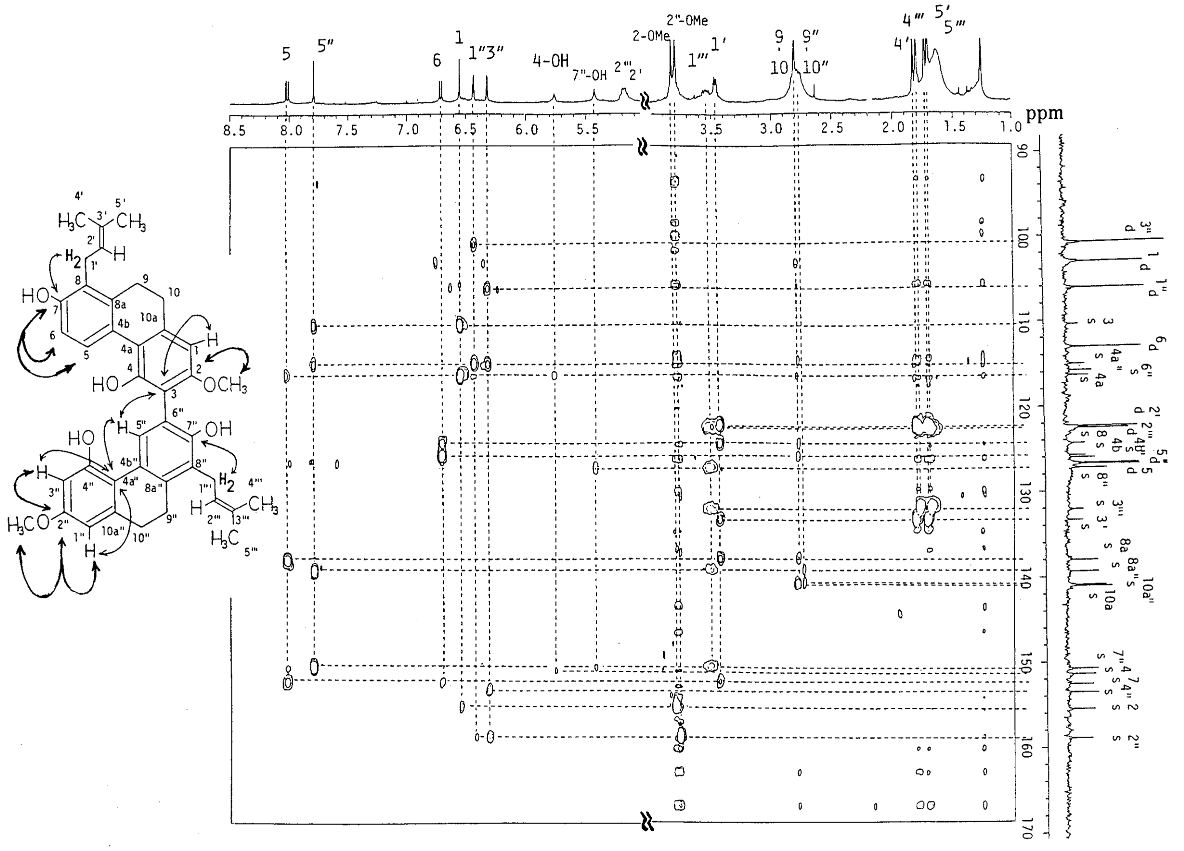

Fig. 1. HMBC Spectrum of **1** in $CDCl_3$ (Sample 4.5 mg, 36 h Run)

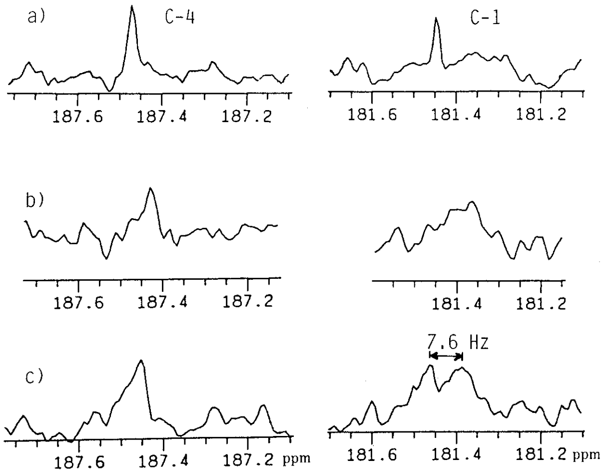

Fig. 2. LSPD Spectrum of **2** in $CDCl_3$

a) Completely decoupled spectrum. b) Nondecoupled spectrum. c) LSPD spectrum with irradiation of 10-H_2.

suggested that **2** might have a quinone grouping. Moreover, **2** is presumably a *para*-quinone in view of the chemical shift values of these two carbonyl carbons compared with those of *para*-quinone and *ortho*-quinone.[11)]

In the ^{1}H-NMR spectrum (Table I), **2** showed signals ascribable to 9- and 10-methylene protons of dihydrophenanthrene (δ2.76 and 2.67), an isolated olefinic proton (δ 5.92), and a pair of *ortho*-coupled aromatic protons (δ 6.76 and 7.82, each d, $J=8.9$ Hz) along with signals due to a methoxyl group, an isopentenyl group, and a hydroxyl proton. Thus, **2** was thought to be a quinone, possibly derived from **6**.

The location of the methoxyl, isopentenyl, and carbonyl groups was determined based on the difference NOE spectra and the ^{13}C-NMR spectra with long-range selective proton decoupling (LSPD). In the NOE experiment, irradiation of the methylene protons at δ 2.76 (9-H_2) enhanced the signals of the methylene protons at δ 3.42 (1′-H_2) and the olefinic proton at δ 5.10 (2′-H). In turn, irradiation of the methylene protons at δ 3.42 (1′-H_2) enhanced the signals of the methylene protons at δ 2.76 (9-H_2) and the methyl protons at δ 1.81 (4′-H_3). Thus, the isopentenyl group should be located at C-8. On the other hand, irradiation of the methoxy methyl protons at δ 3.85 gave an NOE increase of the isolated olefinic proton at δ 5.92 (3-H), indicating that the methoxyl group is adjacent to this olefinic proton. In the LSPD experiment irradiating the methylene protons at δ 2.67 (10-H_2), the carbonyl carbon signal at δ 181.4 was changed to a broad doublet ($J=$ 7.6 Hz), but no significant change was observed in the signal at δ 187.5 as shown in Fig. 2. Therefore, the former carbonyl carbon (δ 181.4) must be assigned to C-1. Also, this finding suggested the location of the isolated olefinic proton (δ 5.92) to be the C-2 or C-3 position, of which the C-3 position is more probable in view of the long-range ^{1}H–^{13}C coupling constant ($J=7.6$ Hz)[12)]; hence the other carbonyl group is most likely located at C-4 and the methoxyl group at C-2. This assumption was supported by comparison of the chemical shift values of two carbonyl carbons with those of 2-methoxy-6-methyl-1,4-benzoquinone.[11)]

From the above findings and the fact that the chemical shift value of one of the *ortho*-coupled aromatic protons (δ 7.82) is characteristic of 4- or 5-H,[9)] the

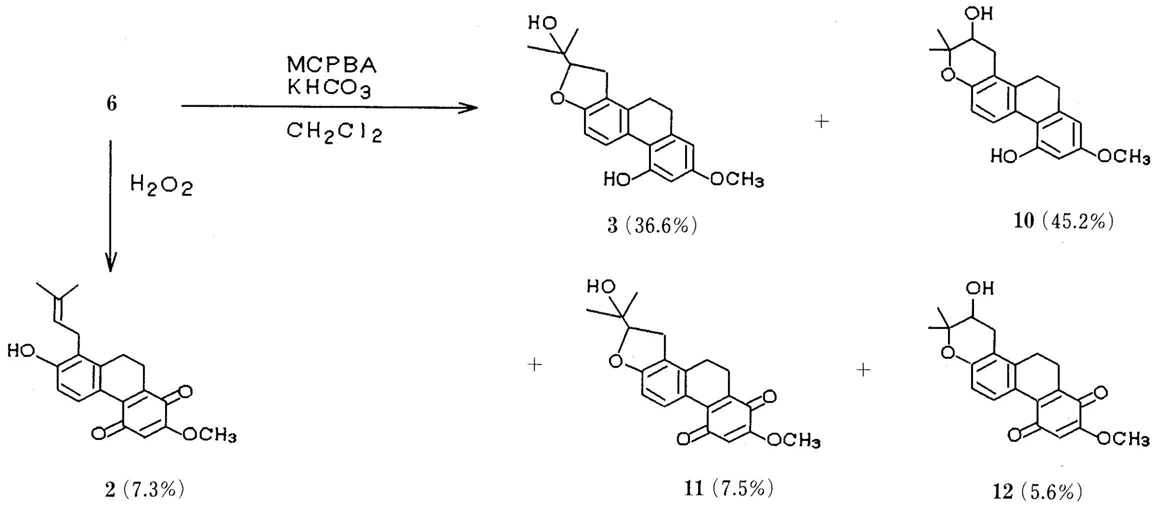

Chart 3

structure of spiranthoquinone was deduced to be 7-hydroxy-8-isopentenyl-2-methoxy-9,10-dihydrophenanthrene-1,4-quinone (**2**). This was proved by the conversion of **6** to **2** by oxidation with hydrogen peroxide (Chart 3). The product obtained was found to be identical with **2**. Spiranthoquinone (**2**) is the first example of a 9,10-dihydrophenanthrene-1,4-quinone from a natural source.[13]

Spiranthol-C (DHP-VI, **3**), $[\alpha]_D$ 0°, was obtained as a colorless amorphous solid. It showed the molecular ion peak at *m*/*z* 326 in the MS and its molecular formula $C_{20}H_{22}O_4$ was established by HR-MS measurement. The UV spectrum of **3** showed a pattern (λ_{max}: 221, 281, 296sh, and 315sh nm) similar to that of **6** and the IR spectrum showed absorptions at 3589, 3320 (br, OH), 1617, and 1467 cm^{-1} (benzene ring). The ^{1}H-NMR spectrum (Table I) exhibited signals due to *ortho*-coupled (δ 6.72 and 7.80, $J=8.4$ Hz) and *meta*-coupled aromatic protons (δ 6.36 and 6.42, $J=2.4$ Hz) and a methoxyl group (δ 3.80), which were similar to those of **6**, but it was characterized by the disappearance of signals due to the isopentenyl group. Instead, it showed new signals due to two *tert*-methyls (δ 1.25 and 1.37), a methylene (δ 3.14, d, $J=8.9$ Hz, 1′-H_2), and a methine (δ 4.65, t, $J=8.9$ Hz, 2′-H).

The above findings led us to suppose that **3** is a derivative of **6** with a new ring formed by oxidative cyclization between the isopentenyl group at C-8 and the hydroxyl group at C-7. Further, the appearance of a significant fragment ion at *m*/*z* 267 ($M^+ - C_3H_7O$) in the MS suggested that the newly formed ring is a furan ring, rather than a pyran.[14]

To validate this assumption, **6** was treated with *m*-chloroperbenzoic acid (MCPBA) in the presence of potassium hydrogen carbonate[14] to yield four products (Chart 3). Among these, one of major products was identical with **3**. Thus, the structure of spiranthol-C was determined to be **3**. The other major product (**10**) has the molecular formula $C_{20}H_{22}O_4$ (M^+: found *m*/*z* 326.1551, calcd 326.1518). The ^{1}H-NMR spectrum of **3** exhibited signals due to two *tert*-methyl groups at δ 1.34 and 1.38, a pair of methylene protons at δ 2.77 and 3.00 (each dd, $J=16.5$ and 5 Hz), and an oxymethine proton at δ 3.87 (t, $J=5$ Hz) and the MS revealed significant fragment peaks at *m*/*z* 293 ($M^+ - H_2O - CH_3$) and 254 ($M^+ - C_4H_8O$). Thus, the structure of this product was assigned as **10**.

Two minor products (**11** and **12**) were obtained as reddish-colored amorphous solids and both have the molecular formula $C_{20}H_{20}O_5$. In the ^{1}H-NMR spectra, they showed a characteristic signal at δ 5.92 (s), suggesting both have a *para*-quinone grouping. Eventually, their structures were assigned as **11** and **12** on the basis of ^{1}H-NMR and MS data.

Spirasineol-B (DHP-VII, **4**), a colorless amorphous solid, has the molecular formula $C_{27}H_{28}O_4$ as determined by HR-MS. Its UV spectrum showed a pattern (λ_{max}: 226, 274sh, 281, 301, and 315 nm) similar to that of spirasineol-A (**8**), and the IR spectrum showed hydroxyl (3390 and 3240 cm^{-1}) and aromatic absorptions (1600, 1510, 1475, and 1460 cm^{-1}). In the ^{1}H-NMR spectrum (Table I), **4** showed signals due to a pair of *ortho*-coupled aromatic protons at δ 6.58 and 8.10 ($J=8.5$ Hz), an isolated aromatic proton at δ 6.57, and a methoxyl group at δ 3.77 together with signals assignable to a *p*-hydroxybenzyl group (δ 3.95, 2H, s, 1″-H_2; 6.68 and 6.94, each 2H, d, $J=8.5$ Hz, 4″,6″-H_2 and 3″,7″-H_2, respectively). This ^{1}H-NMR pattern was similar to that of **8**, but the signals due to the isopentenyl group had disappeared and three new signals appeared at δ 1.29 (6H, s, 4′,5′-H_3), 1.83, and 2.71 (each 2H, t, $J=6.7$ Hz, 2′-H_2 and 1′-H_2, respectively).

The MS of **4** revealed the molecular ion peak at *m*/*z* 416 and a fragment ion peak at *m*/*z* 360 ($M^+ - C_4H_8$) which may be explained by retro Diels–Alder fragmentation. From these spectral data, **4** was deduced to be a derivative of **8** with a pyran ring formed by the cyclization of the 7-hydroxyl group to the 8-isopentenyl group. This was proved by the acid-catalyzed cyclization of **8**, where the major product obtained was identical with **4**. Thus, the structure of spirasineol-B was assigned as **4**.[15]

In conclusion, we have isolated orchinol (**5**), a common dihydrophenanthrene in Orchidaceous plants, and seven new dihydrophenanthrenes, having an isopentenyl substituent from *S. sinensis* var. *amoena*. Such isopentenyldihydrophenanthrenes have never previously been isolated from natural sources, and they are of interest from the viewpoint of chemotaxonomy. Also it should be noted that spiranthesol (**1**), spiranthol-A (**6**), and spirasineol-A (**8**) exhibit a weak cytotoxic activity against cancer (Balb 3

T3/H-ras) cells (*in vitro*) and a weak antibacterial activity against gram-positive bacteria.

Experimental

Melting points were determined on a Kofler-type apparatus and are uncorrected. Optical rotations were measured in CHCl$_3$ solutions on a JASCO DIP-4 automatic polarimeter at 24 °C. UV spectra were taken with a Shimadzu 202 UV spectrometer in EtOH solutions and IR spectra with a Nicolet DX5 FT-IR spectrometer in CHCl$_3$ unless otherwise specified. MS and HR-MS were obtained with a JEOL JMS D-300 spectrometer (ionization voltage, 70 eV; accelerating voltage, 3 kV) using a direct inlet system. Negative ion FAB-MS was obtained with a JEOL JMS D-300 spectrometer using triethanolamine as a matrix. ^{1}H- and ^{13}C-NMR spectra were measured with a JEOL JNM-GX400 spectrometer in CDCl$_3$ or acetone-d_6 solutions with tetramethylsilane as an internal standard, and chemical shifts are recorded in δ values. Multiplicities of carbon signals were determined by means of the distortionless polarization transfer (DEPT) method. ^{1}H–^{13}C COSY, HMBC, difference NOE, and LSPD spectra were measured by the use of the JEOL standard pulse sequences (^{1}H–^{13}C COSY: VBDCHSHF, $J=140$ Hz; HMBC: VHMBC, long-range $J_{\text{CH}}=8.3$ Hz, $^1J_{\text{CH}}=140$ Hz; NOE difference spectra: DIFNOE2, 5 s irradiation; LSPD spectrum: SGSEL) and collected data were treated by the JEOL standard software.

Isolation of Dihydrophenanthrenes Extraction and isolation of dihydrophenanthrenes from the roots (200 g) of *Spiranthes sinensis* (PERS.) AMES var. *amoena* (M. BIEBERSON) HARA were described in our previous paper[1]; *i.e.*, the ether extract (2.5 g) was separated by a combination of silica gel column chromatography and preparative thin-layer chromatography (TLC) to give spiranthesol (DHP-IV, **1**) (4 mg), spiranthoquinone (DHP-V, **2**) (10 mg), spiranthol-C (DHP-VI, **3**) (5 mg), and spirasineol-B (DHP-VII, **4**) (15 mg) in the order of increasing polarity.

Spiranthesol (DHP-IV, 1) Slightly colored amorphous solid, $[\alpha]_D$ 0°. UV $\lambda_{\max}$ nm (log ε): 223 (4.59), 273 (4.50), 281 (4.50), 297sh (4.39). IR $\nu_{\max}$ cm^{-1}: 3510 (OH), 1615, 1463 (benzene ring), 1305. ^{1}H- and ^{13}C-NMR: see Tables I and II. Negative ion FAB-MS m/z: 617 $[\text{M}-\text{H}]^-$.

Spiranthoquinone (DHP-V, 2) Red fine needles (from CH$_2$Cl$_2$), mp 150—151 °C. UV $\lambda_{\max}$ nm (log ε): 216 (4.43), 238sh (4.25), 260 (4.25), 311 (3.97), 316 (3.98), 493 (3.21). IR $\nu_{\max}$ cm^{-1}: 3588, 3307 (br, OH), 1642, 1631 (CO), 1600, 1568 (benzene ring), 1264, 1230. ^{1}H- and ^{13}C-NMR: see Tables I and II. MS m/z (%): 324 (M$^+$, 100), 322 (M$^+-$2H, 29), 269 (M$^+-$C$_4$H$_7$, 63), 268 (M$^+-$C$_3$H$_4$O and M$^+-$C$_4$H$_8$, 57), 267 (46). HR-MS: Found 324.1366, Calcd for C$_{20}$H$_{20}$O$_4$ (M$^+$) 324.1361; Found 269.0796, Calcd for C$_{16}$H$_{13}$O$_4$ (M$^+-$C$_4$H$_7$) 269.0813; Found 268.1098, Calcd for C$_{17}$H$_{16}$O$_3$ (M$^+-$C$_3$H$_4$O) 268.1099; Found 268.0743, Calcd for C$_{16}$H$_{12}$O$_4$ (M$^+-$C$_4$H$_8$) 268.0736.

Spiranthol-C (DHP-VI, 3) Colorless amorphous solid, $[\alpha]_D$ 0°. UV $\lambda_{\max}$ nm (log ε): 221 (4.10), 281 (4.10), 296sh (3.95), 315sh (3.74). IR $\nu_{\max}$ cm^{-1}: 3589, 3320 (br, OH), 1617, 1467 (benzene ring), 1163, 1149. ^{1}H- and ^{13}C-NMR: see Tables I and II. MS m/z (%): 326 (M$^+$, 100), 308 (M$^+-$H$_2$O, 52), 293 (M$^+-$H$_2$O$-$CH$_3$, 33), 267 (M$^+-$C$_3$H$_7$O, 29). HR-MS: Found 326.1518, Calcd for C$_{20}$H$_{22}$O$_4$ (M$^+$) 326.1476; Found 267.1038, Calcd for C$_{17}$H$_{15}$O$_3$ (M$^+-$C$_3$H$_7$O) 267.1022.

Spirasineol-B (DHP-VII, 4) Slightly colored amorphous solid. UV $\lambda_{\max}$ nm (log ε): 226 (4.33), 274sh (4.24), 281 (4.28), 301 (4.06), 315 (3.99). IR $\nu_{\max}$ (KBr) cm^{-1}: 3390, 3240 (OH), 1600, 1510, 1475, 1460 (benzene ring). ^{1}H- and ^{13}C-NMR: see Tables I and II. MS m/z (%): 416 (M$^+$, 100), 361 (10), 360 (M$^+-$C$_4$H$_8$, 15), 107 (hydroxytropylium cation, 6). HR-MS: Found 416.2004, Calcd for C$_{27}$H$_{28}$O$_4$ (M$^+$) 416.1988; Found 360.1386, Calcd for C$_{23}$H$_{20}$O$_4$ (M$^+-$C$_4$H$_8$) 360.1362.

Oxidation of Spiranthol-A (6) with Hydrogen Peroxide Hydrogen peroxide (30% aqueous solution, 20 μl, 0.176 mmol) was added to a CHCl$_3$–MeOH (2 : 1) solution (3 ml) of **6** (11.8 mg, 0.038 mmol), and the mixture was stirred for 23 h at room temperature. Then, the reaction mixture was poured into ice-cold saturated NaHCO$_3$ solution and extracted with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ solution was washed with saturated NaCl solution, dried over MgSO$_4$, and concentrated *in vacuo* to give a residue, which showed nine spots on TLC. Separation of this residue by preparative TLC (CHCl$_3$) gave a red colored product (*Rf ca.* 0.4) (0.9 mg, 7.3%). This was identical with **2** in ^{1}H-NMR, MS, and TLC comparisons.

Conversion of Spiranthol-A (6) to Spiranthol-C (3) A catalytic amount of KHCO$_3$ was added to a solution of **6** (12.2 mg, 0.039 mmol) and 80% MCPBA (8.5 mg, 0.039 mmol) in CHCl$_3$ (3 ml) and the mixture was stirred for 4 h at room temperature. The reaction mixture was poured into ice-water and extracted with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ solution was washed with saturated NaCl solution, dried over MgSO$_4$, and concentrated *in vacuo*. The residue was separated by preparative TLC with MeOH–CHCl$_3$ (2 : 98) to give dihydrophenanthrofuran-1,4-quinone (**11**) (1.0 mg, 7.5%), dihydrophenanthropyran-1,4-quinone (**12**) (0.8 mg, 5.6%), dihydrophenanthrofuran (**3**) (4.7 mg, 36.6%), and dihydrophenanthropyrane (**10**) (5.8 mg, 45.2%) in the order of increasing polarity. Among these products, dihydrophenanthrofuran (**3**) was identical with spiranthol-C in ^{1}H- and ^{13}C-NMR, MS, and TLC comparisons.

10: Slightly colored amorphous solid. ^{1}H-NMR: 1.34, 1.38 (each 3H, s, 4′-H$_3$ and 5′-H$_3$), 2.64, 2.72 (each 2H, m, 9-H$_2$ and 10-H$_2$), 2.77, 3.00 (each 1H, dd, $J=16.5$, 5 Hz, 1′-H$_2$), 3.80 (3H, s, 2-OC$\underline{\text{H}}_3$), 3.87 (1H, t, $J=5$ Hz, 2′-H), 6.35, 6.42 (each 1H, d, $J=2.4$ Hz, 1-H and 3-H, respectively), 6.80, 7.84 (each 1H, d, $J=8.7$ Hz, 6-H and 5-H, respectively). ^{13}C-NMR: 22.1 (q, C-4′), 24.6 (q, C-5′), 24.8 (t, C-1′), 29.8 (t, C-10), 30.1 (t, C-9), 55.3 (q, 2-O$\underline{\text{C}}$H$_3$), 70.0 (d, C-2′), 76.1 (s, C-3′), 100.8 (d, C-3), 106.2 (d, C-1), 115.0 (s, C-4a), 115.2 (d, C-5), 116.8 (s, C-8), 125.25 (d, C-6), 125.33 (s, C-4b), 138.1 (s, C-8a), 140.8 (s, C-10a), 151.3 (s, C-7), 153.4 (s, C-4), 158.7 (s, C-2). MS m/z (%): 326 (M$^+$, 100), 293 (M$^+-$H$_2$O$-$CH$_3$, 12), 255 (32), 254 (M$^+-$C$_4$H$_8$O, 30). HR-MS: Found 326.1551, Calcd for C$_{20}$H$_{22}$O$_4$ (M$^+$) 326.1518; Found 254.0919, Calcd for C$_{16}$H$_{14}$O$_3$ (M$^+-$C$_4$H$_8$O) 254.0942.

11: Red amorphous solid. UV $\lambda_{\max}$ nm (log ε): 220 (4.45), 238 (4.53), 260sh (4.29), 316 (4.35), 340sh (3.85), 392 (3.57), 485 (3.60). ^{1}H-NMR: 1.24, 1.37 (each 3H, s, 4′-H$_3$ and 5′-H$_3$), 2.69 (4H, m, 9- and 10-H$_2$), 3.13 (2H, d, $J=8.9$ Hz, 1′-H$_2$), 3.85 (3H, s, 2-OC$\underline{\text{H}}_3$), 4.70 (1H, t, $J=8.9$ Hz, 2′-H), 5.30 (1H, s, 3′-O$\underline{\text{H}}$), 5.92 (1H, s, 3-H), 6.75 (1H, d, $J=8.7$ Hz, 6-H), 7.91 (1H, d, $J=8.7$ Hz, 5-H). MS m/z (%): 342 (M$^+$+2H, 37), 340 (M$^+$, 100), 338 (M$^+-$2H, 46), 307 (15), 305 (32), 282 (39), 281 (M$^+-$C$_3$H$_7$O, 23), 280 (35). HR-MS: Found 340.1337, Calcd for C$_{20}$H$_{20}$O$_5$ (M$^+$) 340.1311; Found 281.0783, Calcd for C$_{17}$H$_{13}$O$_4$ (M$^+-$C$_3$H$_7$O), 281.0813.

12: Red amorphous solid. UV $\lambda_{\max}$ nm (log ε): 218 (4.36), 240 (4.27), 261 (4.16), 311 (4.00), 329sh (3.82), 485 (3.42). ^{1}H-NMR: 1.35, 1.37 (each 3H, s, 4′-H$_3$ and 5′-H$_3$), 2.68 (4H, br s, 9- and 10-H$_2$), 2.73 (1H, dd, $J=16.5$, 5.5 Hz, 1′-H), 2.93 (1H, dd, $J=16.5$, 5 Hz, 1′-H), 3.85 (3H, s, 2-OC$\underline{\text{H}}_3$), 3.89 (1H, dd, $J=5.5$, 5 Hz, 2′-H), 5.30 (1H, s, 2′-O$\underline{\text{H}}$), 5.92 (1H, s, 3-H), 6.81 (1H, d, $J=8.9$ Hz, 6-H), 7.89 (1H, d, $J=8.9$ Hz, 5-H). MS m/z (%): 342 (M$^+$+2H, 34), 340 (M$^+$, 100), 338 (M$^+-$2H, 27), 270 (35), 269 (47), 268 (M$^+-$C$_4$H$_8$O, 22), 267 (22). HR-MS: Found 340.1291, Calcd for C$_{20}$H$_{20}$O$_5$ (M$^+$) 340.1310.

Conversion of Spirasineol-A (8) to Spirasineol-B (4) A solution of **8** (6.9 mg) and a catalytic amount of p-TsOH in CHCl$_3$ (1.5 ml) was stirred for 36 h at room temperature. The reaction mixture was separated by preparative TLC with MeOH–CHCl$_3$ (4 : 96) to give **4** (3.7 mg, 53.6%). The identity of the product was confirmed by ^{1}H-NMR, MS, and TLC comparisons.

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