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SPIRANTHESOL, A DIMERIC DIHYDROPHENANTHRENE FROM THE ROOTS OF *SPIRANTHES SINENSIS* (PERS.) AMES VAR. *AMOENA* (M. BIEBERSON) HARA1)

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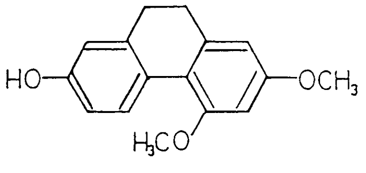
A new minor component named spiranthesol has been isolated from the roots of *Spiranthes sinensis* (Pers.) Ames var. *amoena* (M. Bieberson) Hara and its structure has been determined by means of 2D NMR spectroscopy including HMBC technique. This is the first example of dihydrophenanthrene from natural sources.

KEYWORDS Spiranthesol; dimeric dihydrophenanthrene; *Spiranthes sinensis* var. *amoena*; Orchidaceae; 2D NMR; HMBC

In a previous paper,2) we reported the isolation of seven new dihydrophenanthrene derivatives and known orchinol (**1**)3) from the roots of *Spiranthes sinensis* (Pers.) Ames var. *amoena* (M. Bieberson) Hara (Japanese name "nezi-bana"), a Orchidaceous plant. Among these, the structures of three new compounds named spiranthol-A (**2**) and -B (**3**) and spirasineol (**4**) were also reported. This communication describes the structure of another new dihydrophenanthrene, which is designated as spiranthesol (**5**).2)

Spiranthesol (**5**)4) is a minor component obtained as an amorphous solid, $[\alpha]_D$ 0° ($CHCl_3$). It showed an $[M-H]^-$ peak at m/z 617 in the negative FAB-MS, which agreed with the molecular formula $C_{40}H_{42}O_6$. It showed UV absorptions at 223 (log ε 4.50), 273 (4.50), 281 (4.50), and 297 nm (sh, 4.39) and IR absorptions at 3500 (OH), 1615, and 1463 cm^{-1} (aromatic ring). The ^{1}H-NMR spectrum of **5** showed signals due to a pair of *ortho*-coupled aromatic protons at δ6.71 and 8.02 (J=8.6 Hz), a pair of *meta*-coupled aromatic protons at δ6.31 and 6.43 (J=2.4 Hz), and two isolated aromatic protons at δ6.55 and 7.78 along with signals arising from four hydroxyl protons, two methoxyls, and two isopentenyl groups. In addition, it showed signals assignable to the 9- and 10-methylene protons of dihydrophenanthrene at δ2.76 (4H, m) and 2.80 (4H, br s), suggesting that **5** may be a dimeric dihydrophenanthrene derivative.

In the NOE experiments, irradiation of the methoxy methyls at δ3.83 (2-OCH_3) and 3.80 (2"-OCH_3) caused an NOE increase of the signals at δ6.55 (1-H) and at δ6.43 and 6.31 (1"- and 3"-H), respectively. On the other hand, irradiation of the methylene protons at δ2.80 (9- and 10-H_2) and at δ2.76 (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 δ6.43 (1"-H), 5.20 (2"'-H), 3.51,



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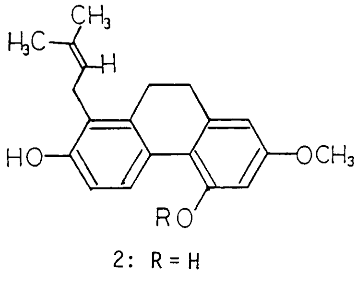
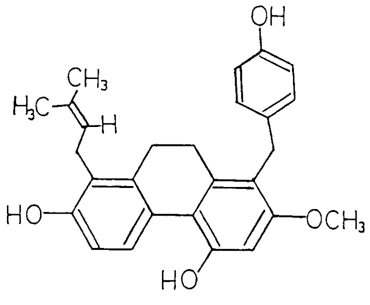


2: R = H
3: R = CH_3



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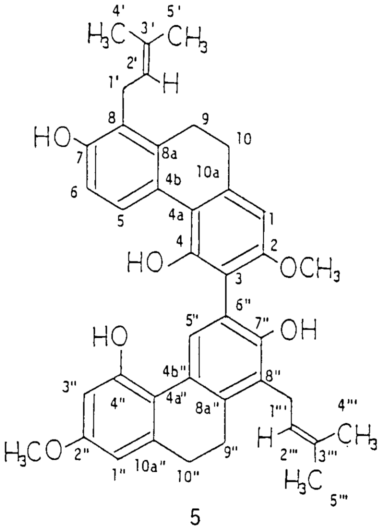
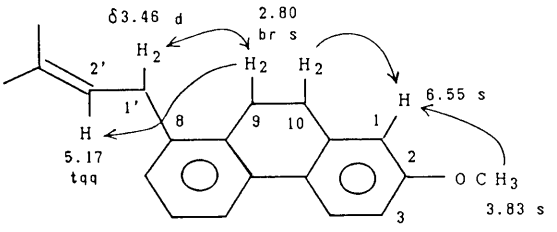
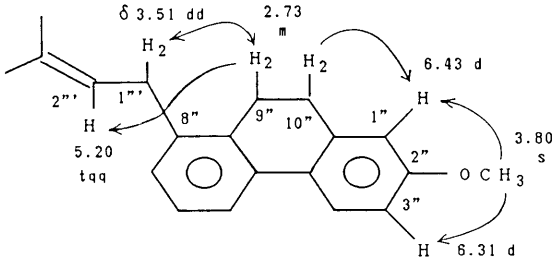


5

and 3.57 (1'''-H$_2$), respectively. In turn, irradiation of the methylenes at δ3.46 (1'-H$_2$) and at around δ3.54 (1'''-H$_2$) enhanced the signals at δ2.80 (9- and 10-H$_2$) and at δ2.76 (9"- and 10"-H$_2$), respectively. Thus the presence of partial structures A and B in 5 was deduced.



A (←: Observed NOE)



B

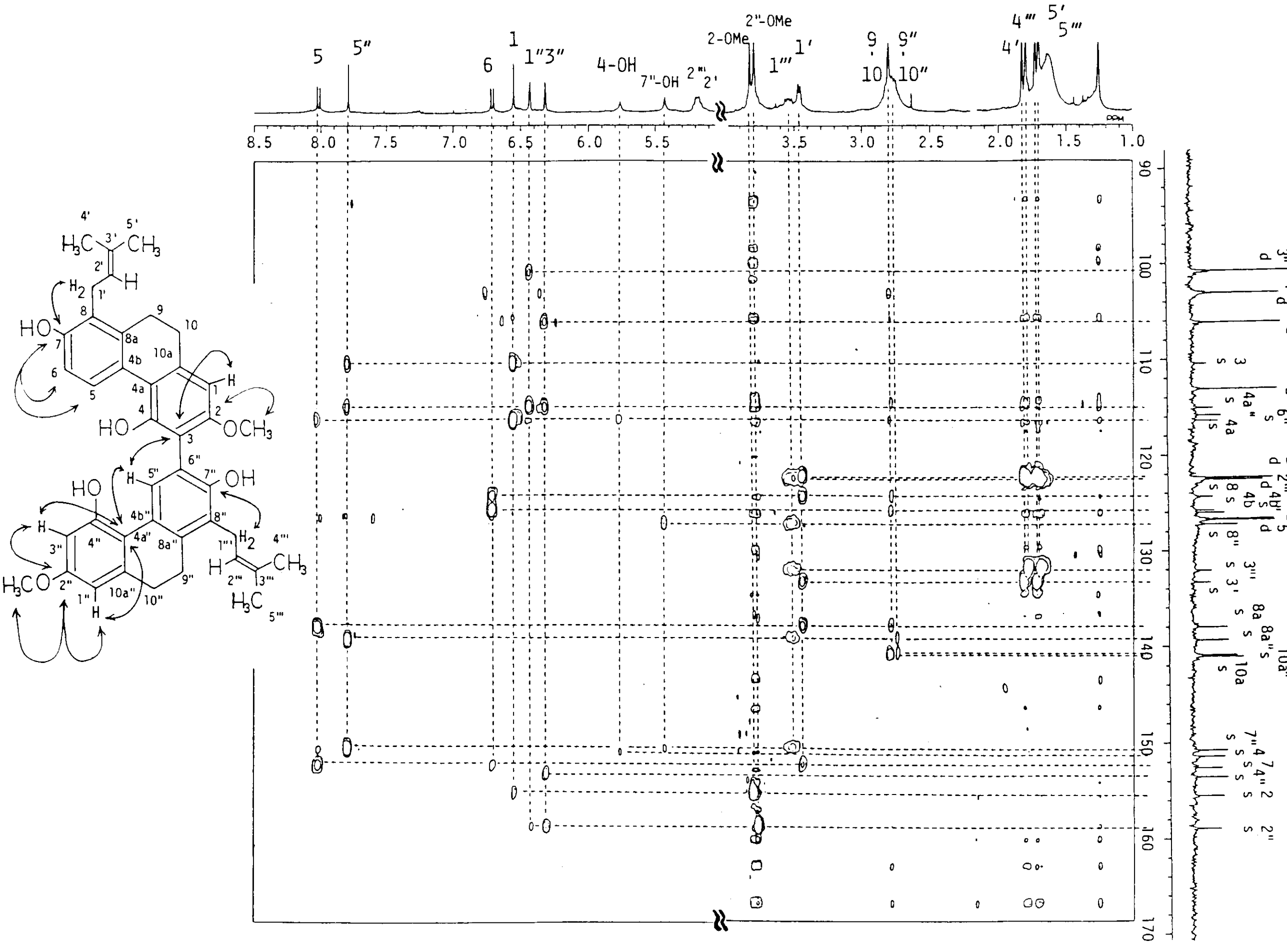


Fig. 1 HMBC Spectrum of Spiranthesol (5) in CDCl$_3$ (Sample 4.5 mg, 36 h run)

Next, we measured the HMBC spectrum[5] (Fig. 1) to determine the total structure of **5**. As shown in Fig. 1, the quaternary carbons at δ158.8 and 155.4 showed long-range correlation with the methoxy methyl protons at δ3.79 (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 down-field carbons (δ150.7-153.4) must be linked to hydroxyl groups. Two of these hydroxyl-bearing carbons (δ152.5 and 150.7) showed long-range correlation with the methylene protons at δ3.46 (1'-H$_2$) and 3.55 (1'''-H$_2$), respectively, so that these carbons were interpreted to be C-7 and C-7", respectively. Further, the C-7 showed long-range correlation with both of the *ortho*-coupled aromatic protons (δ6.71 and 8.02), indicating that these protons are H-6 and H-5,[6] respectively. On the other hand, both of the *meta*-coupled protons at δ6.43 and 6.31 (1"- and 3"-H) showed long-range correlation with C-2" (δ155.8) and with the quaternary carbon at δ115.0, 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 δ7.78, indicating the latter to be H-5". Thus the location of all the aromatic protons was clarified.

Now, both the H-1 (δ6.55) and H-5" (δ7.78) showed long-range correlation with the quaternary carbon at δ110.3. 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 two remaining hydroxyl groups are located at 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 formula **5**. This is the first example of natural dimeric dihydrophenanthrene.[7]

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4) ^{1}H- and ^{13}C-NMR signals were assigned by the use of spin-decoupling, ^{1}H-^{13}C COSY, and HMBC techniques. ^{1}H-NMR data (CDCl$_3$): δ1.70 (3H, d, J=1.5 Hz, 5"'-H$_3$), 1.73 (3H, d, J=1.5 Hz, 5'-H$_3$), 1.80 (3H, br s, 4"'-H$_3$), 1.83 (3H, br s, 4'-H$_3$), 2.76 (4H, m, 9"- and 10"-H$_2$), 2.80 (4H, br s, 9- and 10-H$_2$), 3.46 (2H, d, J=6.7 Hz, 1'-H$_2$), 3.51 and 3.57 (each 1H, dd, J=15.3 and 6.7 Hz, 1"'-H$_2$), 3.79 (3H, s, 2"-OCH$_3$), 3.83 (3H, s, 2-OCH$_3$), 4.97 (1H, s, OH), 5.17 (1H, tqq, J=6.7, 1.5, and 1.5 Hz, 2'-H), 5.20 (tqq, J=6.7, 1.5, and 1.5 Hz, 2"'-H), 5.42 (1H, br s, OH), 5.43 (1H, s, OH), and 5.75 (1H, s, OH), 6.31 (1H, d, J=2.4 Hz, 3"-H), 6.43 (1H, d, J=2.4 Hz, 1"-H), 6.55 (1H, s, 1-H), 6.71 (1H, d, J=8.6 Hz, 6-H), 7.78 (1H, s, 5"-H), and 8.02 (1H, d, J=8.6 Hz, 5-H).
^{13}C-NMR data (CDCl$_3$): δ18.0 (qx2, C-4" and -4"'), 25.48 (t, C-9), 25.52 (t, C-1"), 25.6 (t, C-9'), 25.8 (t and qx2, C-1"' and C-5" and 5"'), 30.3 (t, C-10'), 30.9 (t, C-10), 55.3 (q, 2'-OCH$_3$), 55.9 (q, 2-OCH$_3$), 100.7 (d, C-3"), 103.0 (d, C-1), 106.1 (d, C-1"), 110.3 (s, C-3), 113.0 (d, C-6), 115.0 (s, C-4a"), 115.8 (s, C-6"), 116.3 (s, C-4a), 122.2 (d, C-2'), 122.5 (d, C-2"'), 124.3 (s, C-8), 125.7 (s, C-4b), 126.0 (s, C-4b"), 126.5 (d, C-5"), 126.7 (d, C-5), 127.2 (s, C-8"), 132.0 (s, C-3"), 133.3 (s, C-3'), 137.9 (s, C-8a), 139.3 (s, C-8a"), 140.8 (s, C-10a"), 141.0 (s, C-10a), 150.7 (s, C-7"), 151.3 (s, C-4), 152.5 (s, C-7), 153.4 (s, C-4"), 155.4 (s, C-2), and 158.8 (s, C-2").

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