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NATURAL DIHYDROPHENANTHRENE DERIVATIVES FROM *TAMUS COMMUNIS*

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Several natural nitrogen-free substituted phenanthrenes and 9,10-dihydrophenanthrenes have been isolated from the Combretaceae (1) and the Dioscoreaceae (2). Some of these phenolic compounds, namely batatasins, are plant growth regulators and dormancy-inducing substances (3).

In *Tamus communis* L., a temperate species of the family Dioscoreaceae, a number of phenanthrene derivatives, including batatasin I, have been reported (2-3), but natural substituted 9,10-dihydrophenanthrenes have not been previously isolated from this species.

We now report the isolation and structural elucidation of two 9,10-dihydrophenanthrenes (**1**, **2**) from the rhizomes of *T. communis*. The co-occurrence of phenanthrenes and 9,10-dihydrophenanthrenes may be of interest. So far, only three substituted dihydrophenanthrenes, with structures different from **1** and **2**, have been described in two tropical species of the family Dioscoreaceae (4-5). Compound **1** has been synthesized by Letcher and Nhamo (6) but never reported as a naturally occurring product; compound **2** has been isolated previously from an unrelated plant of the Combretaceae family but was described only as the acetate (7).

Furthermore, in the course of our study, we have assigned unambiguously certain nmr signals of the dihydrophenanthrenes using ^{1}H- and ^{13}C-nmr spectral techniques.

EXPERIMENTAL

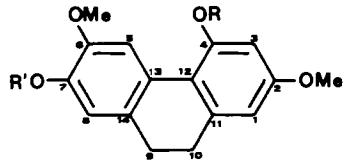
GENERAL EXPERIMENTAL PROCEDURES.—Spectral data were determined on the following instruments: ^{1}H nmr and ^{13}C nmr, Brücker MW 250 MHz Spectrospin; ei mass spectra, A.E.I. MS-30. Uv spectra were measured in $CHCl_3$.

Determination of nOe's and decoupling difference experiments were performed on Brüker MW 250 MHz Spectrospin in $CDCl_3$ with the aid of Aspect 2000 microprograms which allowed direct evaluation of spectra-difference. The samples used for nOe measures were previously degassed by bubbling Ar through the solution for 40 min.

EXTRACTION AND ISOLATION.—The rhizomes of *T. communis*, cut in small pieces, were lyophilized (350 g) and extracted in a glass Soxhlet apparatus for 24 h, successively, with light petroleum (40-70° bp) and $CHCl_3$. The $CHCl_3$ extracts were evaporated to dryness to yield 7 g of residue that was chromatographed on a silica gel column with light petroleum (40-70° bp)-EtOAc (7:3) as eluent to give main fractions, A-F.

Each fraction was rechromatographed on preparative silica gel plates in $CHCl_3$-MeOH (93:7) to afford: from fraction A, Ta I (10 mg) (2,7,8-trimethoxy-3, 4-methylenedioxyphenanthrene); from fraction B, Ta IV (15 mg) (7-hydroxy-2,8-dimethoxy-3, 4-methylenedioxyphenanthrene) and Ta V (20 mg) (8-hydroxy-2,3,4,7-tetramethoxyphenanthrene); from fraction C, the dihydrophenanthrene **1** (20 mg); from fraction D, Ta VI (7 mg) (7-hydroxy-2,4,6-trimethoxyphenanthrene); from fraction E, the dihydrophenanthrene **2** (15 mg); from fraction F, Ta VIII (27 mg) (4,7-dihydroxy-2,3-dimethoxyphenanthrene); and Ta IX (6 mg) (4,8-dihydroxy-2,3,7-trimethoxyphenanthrene).

Compounds **1** and **2** were acetylated with Ac_2O/pyridine (1:1) at room temperature. Compounds **1** and **2** and their acetates (**3**, **4**) were crystallized from EtOH.



1 R=H, R′=Me
2 R=H, R′=H
3 R=Ac, R′=Me
4 R=Ac, R′=Ac

DIHYDROPHENANTHRENE DERIVATIVES.—*Compound* **1**: Ms *m/z* 286 (M^+, base peak), 271 (M^+-CH_3), $C_{17}H_{18}O_4$; tlc Rf 0.60 ($CHCl_3$-MeOH, 93:7; mp 204-207°; uv λ max 278 nm (log ε 4.19); ^{1}H nmr, see reference 6; ^{13}C nmr, see Table 1.

Compound **3**: Ms *m/z* 328 (M^+), 286 (M^+-CH_2CO, base peak), 271, $C_{19}H_{20}O_5$; mp 140-141°; ^{1}H nmr δ 2.28 (-OAc), 2.72 (4H, broad m, H-9 and H-10), 3.81 (3H, s, -OMe at C-2), 3.88 (6H, s, -OMe at C-6 and C-7), 6.50 (1H, d, J=2.2 Hz, H-3), 6.70 (1H, d, J=2.2 Hz, H-1), 6.72 (1H, s, H-8), 7.50 (1H, s, H-5).

Compound **2**: Ms *m/z* 272 (M^+, base peak), 257 (M^+-CH_3) $C_{16}H_{16}O_4$; tlc Rf 0.42 ($CHCl_3$-MeOH, 93:7); mp 128-130°; uv λ max 277 nm (log ε 4.11); ^{1}H nmr δ 2.68 (4H, broad m, H-9 and H-10), 3.75 (3H, s, -OMe at C-2), 3.85 (3H, s, -OMe at C-6), 6.35 (1H, d, J=2.2 Hz, H-3), 6.45 (1H, d, J=2.2 Hz, H-1), 6.81 (1H, s, H-8), 7.81 (1H, s, H-5); ^{13}C nmr, see Table 1.

Compound **4**: Ms *m/z* 356 (M^+), 314 (M^+-CH_2CO), 272 (M^+-$2CH_2CO$, base peak), 257; mp 140-142°. ^{1}H nmr, see reference 7.

PHENANTHRENE DERIVATIVES.—Ta I, Ta IV, Ta V, Ta VI, Ta VIII, and Ta IX (2, 6) were identified by comparison of their experimental derived spectral data with those reported in the literature.

RESULTS AND DISCUSSION

The spectral properties of compound **1** were indicative of a 9,10-dihydrophenanthrene skeleton. Its mass spectrum established its molecular formula as $C_{17}H_{18}O_4$, its ^{1}H-nmr spectrum showed a broad multiplet at δ 2.70 characteristic of the benzylic protons of a 9,10-dihydrophenanthrene unsubstituted at C-1 and C-8. Its proton spectrum also contained signals for three methoxy groups, a singlet at δ 7.78 assigned to H-5 (the signal at lowest field in all dihydrophenanthrenes), two *meta*-coupled (J=2.2 Hz) doublets at δ6.31 (H-3) and 6.41 (H-1), and a singlet at δ 6.74 (H-8). Compound **1** formed a monoacetate **3** with Ac_2O/pyridine. On acylation, the H-5 signal was shielded appreciably (about 0.3 ppm) while the two doublets at δ 6.31 and 6.41 were deshielded, and the chemical shift of H-8; remained almost unaltered; the -OCH_3 signal at C-2 (δ 3.75) was displaced downfield whereas the signal due to the other -OCH_3 group (δ 3.88) remained unaffected. This suggested the location of the hydroxyl group at C-4.

Compound **2** formed a diacetate **4** with Ac_2O/pyridine that showed signals, in the ^{1}H-nmr spectrum, for two methoxy and two acetoxy groups and is similar to **1** except for the absence of one -OCH_3 group. A comparison of the aromatic proton chemical shifts of **1** with **2** suggested that the -OH groups are at C-4 and C-7. Additional evidence on this oxygenation pattern was obtained by nOe difference experiments in the spectrum of **4**: irradiation at δ 2.72 led to the enhancements of the H-8 (δ 6.89) and H-1 (δ 6.72) signals, indicating a relationship for these protons, while no detectable effect was observed for the H-3 resonance. In addition, when the -OCH_3 at C-2 (δ 3.78) signal was saturated, a nOe was registered for the H-1 and H-3 (δ 6.54); a nOe effect was also registered for the H-5 (δ 7.59) signal when the -OCH_3 at C-6 (δ 3.82) signal was saturated. The nOe difference experiments in the spectrum of **3** gave similar results: irradiation of δ 2.72, nOe difference for H-8 and H-1; irradiation at δ 3.81, nOe difference for H-1 and H-3; irradiation at δ 3.88, nOe difference for H-8 and H-5. The ^{13}C-nmr spectra confirmed the presence of four carbons of the dihydrophenanthrene skeleton attached to oxygen using an unsubstituted dihydrophenanthrene as a model compound and standard substitution effects (Table 1) (8). The positions of the -OCH_3 groups were elucidated by comparison of the ^{13}C-nmr spectra of **1** and **2**: carbon resonances of both compounds appear at essentially the same positions except for C-5, C-6, C-7, and C-8. On going from **2** to **1**, C-5, C-6, and C-7 signals are displaced downfield by about 1.1, 2.8, 3.6 ppm, respectively, while C-8 is shielded by 2 ppm. In addition to ordinary measurements, several selective decoupling experiments led us to confirm the ^{1}H- and ^{13}C-nmr assignments.

TABLE 1. ^{13}C-nmr Data for **1** and **2**[a]

Carbon	1	2
1	107.0	106.9
2	159.1	158.9
3	101.3	101.4
4	153.3	153.3
5	111.5	110.4
6	147.9[b]	145.1
7	147.7[b]	144.1
8	112.4	114.4
9	29.4[c]	31.0[b]
10	31.0[c]	29.2[b]
11	141.3	141.4
12	115.2	115.5
13	131.1	131.8
14	125.4	124.7
-OCH_3 at C-2	55.3	55.3
-OCH_3 at C-6	56.5[d]	56.4
-OCH_3 at C-7	56.2[d]	——

[a]Spectra were obtained at 62.9 MHz in Fourier transform mode in $CDCl_3$ solutions. Chemical shifts are expressed on the TMS scale.

[b, c, d]Assignments for these signals within a vertical column may be reversed.

The following signal correlations between the ^{1}H- and ^{13}C-nmr spectra of **2** were observed: irradiation of the proton at δ 2.68 showed, in the ^{13}C-nmr spectrum, decoupling of the signals at 31.0 and 29.2 ppm (C-9 and C-10); irradiation of the proton at δ 3.75, decoupling of -OCH_3 at C-2 (55.3 ppm); irradiation of the proton at δ 3.85, decoupling of -OCH_3 at C-6 (56.4 ppm); correlations were also observed between the proton at δ 6.35 and C-3 (101.4 ppm) signal, the proton at δ 6.45 and C-1 (106.9 ppm) signal, and the proton at δ 6.81 and C-5 (110.4 ppm) signal. Further selective decoupling experiments in the ^{13}C-nmr spectrum of **1** confirmed its ^{1}H- and ^{13}C-nmr assignments.

Thus, **1** has the structure 4-hydroxy-2, 6, 7-trimethoxy-9, 10-dihydrophenanthrene, and **2** is 4,7-dihydroxy-2,6-dimethoxy-9,10-dihydrophenanthrene.

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