Pergamon

PII: S0031-9422(96)00579-1

Phytochemistry, Vol. 44, No. 4, pp. 763–764, 1997

0031-9422/97 $17.00+0.00

A 9,10-DIHYDROPHENANTHRENE FROM *ASPARAGUS RACEMOSUS*

TOSHIKAZU SEKINE,* NOBUYAKI FUKASAWA, ISAMU MURAKOSHI and NIJSIRI RUANGRUNGSI†

Faculty of Pharmaceutical Sciences, Chiba University, Yayoi-cho 1–33, Inage-ku, Chiba 263, Japan; †Faculty of Pharmaceutical Sciences, Chulalongkorn University, Bangkok 10330, Thailand

(*Received* 24 *June* 1996)

Key Word Index—*Asparagus racemosus*; Liliaceae; roots; racemosol; 9,10-dihydrophenanthrene.

Abstract—A new 9,10-dihydrophenanthrene derivative, named racemosol, was isolated from the roots of *Asparagus racemosus*. Its structure was elucidated by spectroscopic analysis as 9,10-dihydro-1,5-dimethoxy-8-methyl-2,7-phenanthrenediol. Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

We have previously reported the isolation and characterization of a new polycyclic alkaloid, asparagamine A [1, 2], from the Thai medicinal plant, *Asparagus racemosus* [3, 4]. This alkaloid seems to be an interesting compound not only because of its unique cage-type structure but also because of its remarkable anti-oxytocic activity. In pursuit of biologically active compounds in medicinal plants, we have further investigated the chemical constituents of *A. racemosus*. We describe herein the isolation, and structural elucidation of a new dihydrophenanthrene derivative, named racemosol (**1**), from the roots of this species.

RESULTS AND DISCUSSION

Compound **1** was isolated as a minor constituent (0.013% dry wt) by repeated silica gel column chromatography from the EtOAc-soluble fraction of 75% EtOH extracts prepared from the dried roots of *A. racemosus*. It was a brown oil and the molecular formula $C_{17}H_{18}O_4$ (observed *m/z* 286.1220 $[M]^+$, calcd *m/z* 286.1205) was confirmed by a high-resolution EI-mass spectrum, indicating nine degrees of unsaturation. The IR (ν_{max} 3500, 3010, 1600, 1200 and 710 cm^{-1}) and UV (λ_{max} 280.3 nm) spectral data, in combination with the consideration of its unsaturation degrees, indicated the presence of a hydroxyl group and a biphenyl structure in the molecule.

The ^{13}C NMR combined with the DEPT spectrum ($CDCl_3$) of **1** confirmed the existence of 17 carbons, including two units of a benzene ring with one methyl (δ 11.2 (C-13)), two methoxyl (δ 55.5 (C-12) and 61.4 (C-11)) and two methylene (δ 22.1 (C-10) and 25.7 (C-9)) carbon atoms. The ^1H NMR spectrum ($CDCl_3$) showed signals for a methyl group (δ 2.16 (*s*, H-13)), two methoxyl groups (δ 3.76 (*s*, H-11) and 3.80 (*s*, H-12)), two methylene groups (δ 2.68 (*m*, H-9) and 2.74 (*m*, H-10)), three aromatic hydrogens (δ 6.39 (*s*, H-6), 6.83 (*d*, J = 9.0 Hz, H-3) and 7.85 (*d*, J = 9.0 Hz, H-4)), and two hydroxyl groups (δ 5.00 (*brs*, C_7-OH) and 5.66 (*brs*, C_2-OH)). Among them, two methylene hydrogens (δ 2.68 (H-9) and 2.74 (H-10)), both being in benzylic positions from a consideration of their chemical shifts, show a correlation peak in the HH-COSY spectrum with each other. Taking account of the degree of unsaturation, **1** was, therefore, judged to possess a 9,10-dihydrophenanthrene ring. The substitution pattern of two hydroxyls, one methyl and two methoxyl group on the ring was solved by the analysis of several 2D NMR, including a HMBC spectrum (J = 8 Hz).

A CH-COSY spectrum of **1** provided unequivocally all the one-bond ^1H–^{13}C connectivities. An aromatic hydrogen (H-3) on one of the benzene rings, *ortho*-coupling with H-4 (J = 9.0 Hz), showed two-bond correlations with C-2 (δ 146.6) bearing the hydroxyl group and C-4a (δ 126.4), and showed a three-bond correlation with C-1 (δ143.2) bearing the methoxyl group (δ 61.4, (C-11)) in the HMBC spectrum. In addition, the methylene hydrogens (H-10) correlated with C-1 and C-4a. These data place the methoxyl group and the hydroxyl group *ortho* to each other and require connection of the second benzene ring at a position *para* to the hydroxyl group.

Another aromatic hydrogen (H-6) also showed two-bond correlations in the HMBC spectrum, with C-5

* Author to whom correspondence should be addressed.

Table 1. NMR data for racemosol (1)

Position	^{13}C (DEPT)	^{1}H (*J*, Hz)	HMBC
1	143.2 (C)	—	H-3, 10, 11
2	146.6 (C)	5.66 (*brs*, OH)	H-3, 4, C_2-OH
3	112.4 (CH)	6.83 (*d*, 9.0)	C_2-OH
4	125.0 (CH)	7.85 (*d*, 9.0)	
4a	126.4 (C)	—	H-3, 10
4b	116.8 (C)	—	H-4, 6, 9
5	155.4 (C)	—	H-6, 12
6	97.9 (CH)	6.39 (*s*)	
7	152.8 (C)	5.00 (*brs*, OH)	H-6, 13
8	112.6 (C)	—	H-6, 9, 13
8a	139.3 (C)	—	H-9, 10, 13
9	25.7 (CH_2)	2.68 (2H, *m*)	H-10
10	22.1 (CH_2)	2.74 (2H, *m*)	H-9
10a	130.6 (C)	—	H-4, 9,10
11	61.4 (Me)	3.76 (3H, *s*)	
12	55.5 (Me)	3.80 (3H, *s*)	
13	11.2 (Me)	2.16 (3H, *s*)	

In $CDCl_3$, δ from TMS.

(δ 155.4) bearing the methoxyl group and C-7 (δ 152.8) bearing the hydroxyl group, and showed three-bond correlations with C-8 (δ 112.8) bearing the methyl group and C-4b (δ 116.8), which correlated with H-4 on the first benzene ring. Significant long-range correlations observed in the HMBC spectrum of **1** are summarized in Table 1 and Fig. 1. The cross-peaks between H-10 and H-11, between H-4 and H-12, and also between H-9 and H-13 observed in the NOESY and ROESY spectra (Fig. 2) further supported the validity of the structure.

Several naturally occurring phenanthrenes and 9,10-dihydrophenanthrenes have been isolated over the last three decades [5–8]. However, as far as we know, this is the first phenanthrene derivative to be isolated from this genus. Although the hydroxylation at 2-, 5- and 7-position in racemosol (**1**) is ordinary in phenanthrene derivatives, the presence of a methyl group at the 8-position seems to be interesting from the biosynthetic viewpoint.

EXPERIMENTAL

Extraction and isolation. Air-dried roots (130 g) of *A. racemosus* Willd. were ground and extracted 3 × with 75% EtOH (500 ml). The combined extract was conc to a suspension and partitioned between H_2O (400 ml) and EtOAc (400 ml × 3). The EtOAc frs were combined and evapd to dryness after drying with Na_2SO_4 to afford a residue (1.5 g). A portion (1 g) of this residue was subjected to repeated silica gel CC with EtOAc–MeOH (99 : 1) and $CHCl_3$–MeOH (99 : 1), yielding **1** (11 mg, 0.013% dry wt).

Racemosol (**1**). Brown oil. UV λ_{max} (MeOH) nm (log ε): 208.8 [4.44], 280.3 [4.10]. IR ν_{max} ($CHCl_3$) cm^{-1}: 3300–3600, 3010, 1600, 1480, 1450, 1285, 1200, 1010, 710. HR-EIMS *m/z*: 286.1220 (calcd for $C_{17}H_{18}O_4$; 286.1205). EIMS (probe) 70 eV *m/z* (rel. int.) 286 $[M]^+$ (100), 271 (9), 256 (46), 239 (21), 228 (14), 212 (11), 185 (12), 163 (11), 149 (22), 129 (19). ^1H and ^{13}C NMR ($CDCl_3$): Table 1.

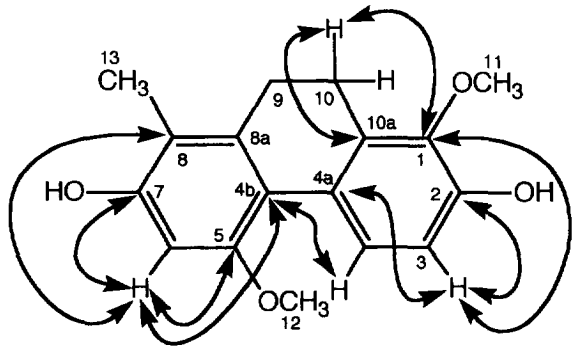

Fig. 1. Structure and significant correlations observed in HMBC spectrum of compound **1**.

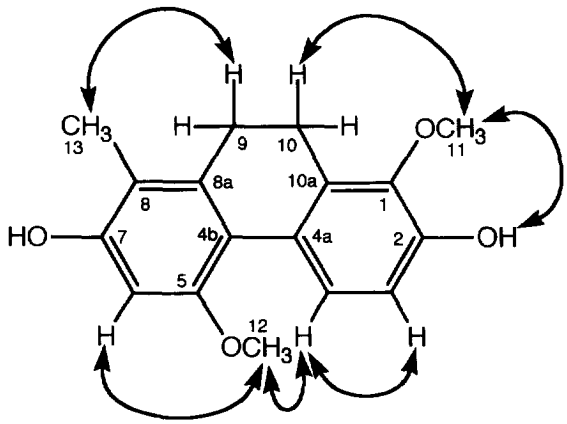

Fig. 2. NOESY and ROESY spectral data of compound **1**.

Acknowledgements—We are very grateful to the staff of the Chemical Analysis Center of Chiba University for the measurement of MS.

REFERENCES

1. Sekine, T., Ikegami, F., Fukasawa, N., Kashiwagi, Y., Aizawa, T., Fujii, Y., Ruangrungsi, N. and Murakoshi, I., *Journal of the Chemical Society, Perkin Transactions I*, 1995, 391.
2. Sekine, T., Fukasawa, N., Kashiwagi, Y., Ruangrungsi, N. and Murakoshi, I., *Chemical and Pharmaceutical Bulletin* 1994, **42**, 1360.
3. Burkill, I., *A Dictionary of the Economic Products of the Malay Peninsula*. Governments of Malaysia and Singapore, Kuala Lumpur, 1966, p. 264.
4. Pongboonrod, S., *Mai Tet Muang Thai*. Kasembunnakich Press, Bangkok, 1950 p. 612.
5. Gorham, J., *The Biochemistry of the Stilbenoids*. Chapman & Hall, London, 1995.
6. Tezuka, Y., Ueda, M. and Kikuchi, T., *Chemical and Pharmaceutical Bulletin*, 1989, **37**, 3195.
7. Tezuka, Y., Yoshida, Y., Kikuchi, T. and Xu, G., *Chemical and Pharmaceutical Bulletin*, 1993, **41**, 1346.
8. Li, W., Pan, J., Lu, M., Zang, R. and Xiao, P., *Phytochemistry*, 1995, **39**, 231.