Pergamon

PII: S0031-9422(97)00612-2

Phytochemistry, Vol. 48, No. 1, pp. 185–186, 1998
© 1998 Elsevier Science Ltd. All rights reserved
Printed in Great Britain
0031-9422/98 $19.00+0.00

AERIDIN: A PHENANTHROPYRAN FROM *AERIDES CRISPUM*

V. ANURADHA* and N. S. PRAKASA RAO

Department of Chemistry, Nagarjuna University, Nagarjuna Nagar 522 510, India

(*Received* 28 *April* 1977)

Key Word Index—*Aerides crispum*; Orchidaceae; aeridin; phenanthropyran.

Abstract—From the whole plant of *Aerides crispum*, a new phenanthropyran derivative was isolated. Its structure was elucidated as 2,7-dihydroxy-1,3-dimethoxy-9,10-dihydrophenanthropyran on the basis of spectroscopic data. This is the first report of phenanthropyran from *A. crispum*. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

In the course of our investigations on the chemical constituents of different orchids, we reported the isolation and characterization of pyrans [1–5], a pyrone [6], quinones [7], bibenzyls [8] a phenanthrene carboxylic acid [9] and a novel pyrene [10]. In this paper we report on the structural elucidation of a new phenanthropyran derivative aeridin (**1**) from *Aerides crispum* R. Br.

RESULTS AND DISCUSSIONS

Aeridin (**1**) gave positive ferric chloride reaction characteristic of a phenolic hydroxyl group ($C_{17}H_{16}O_5$; $[M]^+$, $m/z = 300$). It showed UV maxima at λ_{max}^{EtOH} 282, and 309 nm characteristic of a 9,10-dihydro-phenanthrene skeleton. A bathochromic shift of $\Delta\lambda = 11$ nm from λ_{max} 309 to 320 on addition of alkali indicated the presence of free hydroxyl groups. The IR absorption band at ν_{max}^{KBr} 3400 cm^{-1} supported the presence of phenolic hydroxyl groups.

The ^1H NMR spectrum of **1** showed two aromatic methoxyl groups at δ 3.89 and 3.95 (each *s*, 3H), two D_2O exchangeable hydroxyl groups at δ 4.99 and 5.76, and a singlet at δ 5.19 (2H) assignable to the methylene protons of a oxymethylene group indicating **1** to be a dimethoxy-dihydroxy-phenanthropyran derivative and accounting for the five oxygen atoms in **1**.

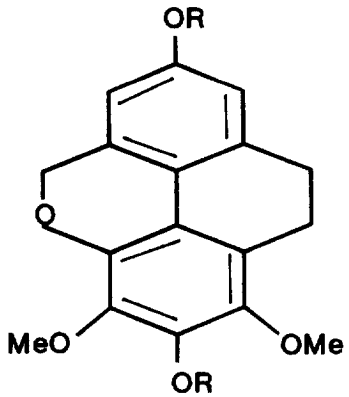
1 formed a diacetate (**2**) ($C_{21}H_{20}O_7$ $[M]^+$, $m/z = 384$) with acetic anhydride and pyridine supporting the presence of two hydroxyl groups. The two acetoxyl signals in the ^1H NMR of spectrum (**2**) at δ 2.23 (*s*, 3H) and 2.29 (*s*, 3H) further supported the presence of two hydroxyl groups.

The singlet signal at δ 2.79 (*br* s, 4H) in the ^1H NMR spectrum of **1** was assigned to the 9 and 10 methylene protons indicating it to be a 9,10-dihydrophenanthropyran derivative. The two doublets at δ 6.29 (*d*, 1H, $J = 2.5$ Hz) and 6.31 (*d*, 1H, $J = 2.5$ Hz) in **1** were shifted downfield and appeared as a singlet at δ 6.51 (*s*, 2H) in **2** indicating the two protons to be *meta* coupled to each other and *ortho* to a phenolic hydroxyl group. The small chemical shift difference in the two doublets in **1** and **2** indicated a similar chemical environment for the two protons and thus they were assigned to H-6 and H-8 with a hydroxyl group at C-7.

No considerable downfield shift of the 9,10-protons or H-5 protons was observed in **2** indicating that the hydroxyl was not in close proximity to the 9,10- protons or H-5 protons. Thus, the hydroxyl group was allocated to C-2 and the two methoxyls to C-1 and C-3. Thus **1** is 2,7-dihydroxy-1,3-dimethoxy-9,10-dihydro-phenanthropyran.

The ^{13}C NMR spectrum of **1** supported the structure. A considerable upfield shift was observed for the signals of C-2, C-4, C-4b and C-10a. The upfield shift in C-2 to δ 123.9 was expected from the combined *ortho* effect of two methoxyls at C-1 and C-3. The combined *para* and *ortho* effect of the two methoxyls at C-1 and C-3 made C-4 resonate at δ 130.9. The considerable upfield shift of C-4b to δ 102.3 was attributed to the combined effect of the three substituents at C-1, C-3 and C-7. The upfield shift of C-10a to δ 112.9 was attributed to the combined *para* effect of the C-3 methoxyl and ortho effect of the C-1 methoxyl groups. The chemical shift difference in the C-9 and C-10 carbons was atrributed to the different locations of the hydroxyls at C-2 and C-7 and the methoxyl

*Author to whom correspondence should be addressed.



(1) R = H (2) R = Ac

group at C-1, resulting in an upfield shift for C-9; resonating at δ 16.6, and a downfield shift for C-10, resonating at δ 23.4.

Thus, the structure 2,7-dihydroxy-1,3-dimethoxy-9,10-dihydrophenanthropyran was allocated to **1** and was named as aeridin. Aeridin is a new natural compound.

EXPERIMENTAL

General. Mps: uncorr.; IR: KBr; UV: EtOH; ^{1}H NMR: 270 MHz, $CDCl_3$; ^{13}C NMR: $CDCl_3$with TMS; CC and TLC: silica gel.

Plant material. The plant material of *Aeides crispum* was collected in Ooty during November 1996.

Extraction and isolation. The air dried whole plant was extracted with hexane, Me_2CO and MeOH. Each extract was impregnated with a minimum amount of silica gel and washed with hexane, Et_2O, Me_2CO and MeOH. The Et_2O wash of the three extracts were found to be similar on TLC and were mixed. The combined extract was subjected to CC using hexane, C_6H_6, CH_2Cl_2 and MeOH. The $CHCl_2$ eluate was subjected to phenolic, and non-phenolic sepn and the phenolic part was conc and rechromatographed using hexane, C_6H_6 and Me_2CO mix. The C_6H_6–Me_2CO (9:1) mixt. was subjected to PTLC using HF 254 silica gel. The fluorescent band was eluted with Me_2CO, concd and recrystallised from $CHCl_3$ to yield aeridin.

Aeridin (**1**). Mp 156°, analysed for $C_{17}H_{16}O_5$. UV λ_{max}^{EtOH} nm: 225, 284, 309, 317, 323; UV $\lambda_{max}^{EtOH+NaOH}$ nm: 225, 284, 320 and 332sh; IR ν_{max}^{KBr} cm^{-1}: 3400, 2870, 1664, 1452 and 1425; ^{1}H NMR ($CDCl_3$): δ 2.79 (4H, *s*, H-9 and H-10), 3.89 and 3.95 (each 3H, *s*, -OMe), 5.19 (2H, *s*, -O-CH_2-Ar), 4.99, 5.76 (each 1H, *s*, ArOH), 6.31 (1H, *d*, J = 2.5 Hz H-8) and 6.29 (*d*, 1H, J = 2.5 Hz H-6); ^{13}C NMR ($CDCl_3$): δ 142.9(C-1), 123.9(C-2), 133.1(C-3), 130.9(C-4), 114.3(C-4a), 102.3(C-4b), 56.2(C-5a), 129.8(C-5) 108.9(C-6) 154.9(C-7), 112.2(C-8), 136.6(C-8a), 16.6(C-9), 23.4(C-10), 112.9(C-10a), 56.3, 56.8 (OMe).

Aeridin diacetate (**2**). Mp 132°, analysed for $C_{21}H_{20}O_7$. UV λ_{max}^{EtOH}nm: 222, 269, 284, 302 and 315; IR ν_{max}^{KBr} cm^{-1}: 2940, 2845, 1756, 1450, 1410, 1275; ^{1}H NMR ($CDCl_3$): δ 2.23(3H, *s*, -OCOMe), 2.29(3H, *s*, -OCOMe), 2.80(4H, *s*, H-9, H-10), 3.79 and 3.82 (each 3H, *s*, -ArOMe), 5.17(2H, *s*, Ar-OCH_2-Ar) and 6.51(2H, *br s*, H-6 and H-8).

Ackndowledgements—The research work was supported by the grant of the Young Scientist Scheme to Dr V. Anuradha for which she is very grateful.

REFERENCES

1. Veerraju, P., Prakasa Rao, N. S., Jagan Mohan Rao, L., Jaganadha Rao, K. V. J. and Mohana Rao, P. R., *Phytochemistry*, 1989, **28**, 950.
2. Anuradha, V. and Prakasa Rao, N. S., *Phytochemistry*, 194, **35**(1) 273.
3. Anuradha, V. and Prakasa Rao, N. S., *Phytochemistry*, 1994, **37**(3) 909.
4. Anuradha, V. and Prakasa Rao, N. S., *Phytochemistry*, 1998, **48**, 181.
5. Anuradha, V. and Prakasa Rao, N. S., *Phytochemistry*, 1998, **48**, 183.
6. Udaya Bhaskar, M., Jagan Mohana Rao, L., Prakasa Rao, N. S., Jaganadha Rao, K. V. J. and Mohana Rao, P. R., *Phytochemistry*, 1989, **28**, 3545.
7. Udaya Bhaskar, M., Jagan Mohana Rao, L., Prakasa Rao, N. S., Jaganadha Rao, K. V. J. and Mohana Rao, P. R., *Journal of Natural Products*, 1991, **54**, 386.
8. Veerraju, P., Prakasa Rao, N. S., Jagan Mohan Rao, L., Jaganadha Rao, K. V. J. and Mohana Rao, P. R., *Phytochemistry*, 1989, **28**, 3031.
9. Anuradha, V., Prakasa Rao, N. S. and Udaya Bhaskar, M., *Phytochemistry*, 1994, **36**(6) 1515.
10. Anuradha, V., Prakasa Rao, N. S. and Udaya Bhaskar, M., *Phytochemistry*, 1995, **39**(6) 1429.