

PHENANTHRENE AND STILBENES FROM *PTEROLOBIUM HEXAPETALLUM*

R JAGDISH KUMAR, D. JYOTNA, G. L. DAVID KRUPADANAM and G. SRIMANNARAYANA*

Department of Chemistry, Osmania University, Hyderabad 500 007, India

(Received 26 August 1987)

Key Word Index—*Pterolobium hexapetallum*, Leguminosae, phenanthrene, tri-*O*-methyl resveratrol, methyl tri-*O*-methyl gallate, pterostilbene, resveratrol, methyl gallate.

Abstract—From the stems of *Pterolobium hexapetallum* phenanthrene, tri-*O*-methyl resveratrol, methyl tri-*O*-methyl gallate, pterostilbene, resveratrol, methyl gallate were isolated. The natural occurrence of phenanthrene has not previously been reported. The structures were determined by analytical and spectroscopic methods.

INTRODUCTION

Pterolobium hexapetallum (Roth) (sub family Caesalpinaeae) has to our knowledge, not been subjected to systematic chemical investigations. This study shows that the stems contain, phenanthrene (1), whose natural occurrence has not previously been reported, together with the known substances, tri-*O*-methylresveratrol (2), methyl tri-*O*-methyl gallate (3), pterostilbene (4), resveratrol (5) and methyl gallate (6). Tri-*O*-methyl resveratrol and methyl tri-*O*-methyl gallate were recently reported from *Virola elongata* and *Heracleus canescens* respectively for the first time [1, 2].

RESULTS AND DISCUSSION

Compound 1 is a colourless crystalline solid (M^+ 178). The UV spectrum showed only aromatic absorption and only C=C, C-C and C-H absorptions were seen in the IR spectrum. The ^1H NMR spectrum (500 MHz) showed peaks only in the aromatic region. Compound 1 was identified as phenanthrene by mp and comparison with published spectral data [3-5]. In the 500 MHz ^1H NMR spectrum of phenanthrene, now recorded, all the proton signals are clearly resolved and assigned. Whereas the 90 MHz spectrum reported earlier [5] revealed only two unresolved multiplets.

Compounds 2-6 were identified as tri-*O*-methyl resveratrol [1], methyl tri-*O*-methyl gallate [2], pterostilbene [6], resveratrol [7, 8] and methyl gallate [9] respectively, by comparison of analytical and spectral data with the reported values.

Phenanthrene may be conceived to have been derived biogenetically from the corresponding unsubstituted stilbene by ring closure [10]. It is therefore significant to note the occurrence of stilbenes 2, 4 and 5 along with phenanthrene in the same plant.

EXPERIMENTAL

The air-dried and powdered stems of *P. hexapetallum* (4 kg) obtained from the forests of Mannanoor, Andhra Pradesh, India were extracted with MeOH (12 l) and the extract concentrated under red pres to give a black gummy residue (60 g) which was

dissolved in minimum amount of MeOH (500 ml) and adsorbed onto the already extracted plant material (500 g). The adsorbed plant material was dried and re-extracted successively with petrol (bp 60-80°, 2 l), CHCl_3 (2 l) and EtOAc (2 l) in a Soxhlet extractor. The extracts were concentrated to yield the following semi-solids petrol extract (3 g), CHCl_3 extract (10 g) and EtOAc extract (16 g).

The petrol and CHCl_3 extracts were combined due to their similar behaviour on TLC. The combined extract (13 g) was then subjected to CC over silica gel (110 g, 200 mesh). Fractions of 50 ml each were collected by eluting successively with C_6H_6 - EtOAc (19:1). Fraction 1 did not yield any product. Fractions 2 and 3 afforded phenanthrene (1, 45 mg) mp 99° lit. mp 100° [3], fractions 5-8 afforded tri-*O*-methyl resveratrol (2, 60 mg) mp 57° lit. mp 56-57° [1], fractions 11-13 afforded methyl tri-*O*-methyl gallate (3, 1 g) mp 80° lit. mp 80° [2] and fractions 15-18 afforded pterostilbene (4, 100 mg) mp 88°, lit. mp 88-89° [6].

The EtOAc extract (16 g) was subjected to CC over silica gel (135 g, 200 mesh). Fractions of 50 ml each were collected by eluting with C_6H_6 - EtOAc (7:3). Fraction 1 and 2 did not yield any product. Fractions 3-5 gave a pale yellow solid which crystallized from dry Me_2CO as pale yellow needles of resveratrol (5, 120 mg) mp 248° lit. mp 248° [8] and subsequent fractions 7-20 gave methylgallate (6, 6 g) mp 202°, lit. mp 202° [3]. The spectral data (IR, UV, NMR and mass) of 1-6 are in agreement with those reported for these compounds in literature [1-9].

Phenanthrene (1) UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm 210, 220, 250, 274 (sh), 280 (sh), 293, 330 (sh), IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} 3040, 1600, 1520, 1500, 1445, 1425, 1300, 1240, 810, 730, ^1H NMR (500 MHz, CDCl_3) δ 7.63 (2H, t, J = 7.3 Hz, 7.3 Hz, H-2, H-7), 7.68 (2H, t, J = 7.6 Hz, 8.2 Hz, H-3, H-6), 7.77 (2H, s, H-9, H-10), 7.92 (2H, d, J = 7.8 Hz, H-1, H-8) and 8.72 (2H, d, J = 8.2 Hz, H-4, H-5), ^{13}C NMR (CDCl_3) δ 122.96 (d, C-4, C-5), 126.79 (d, C-2, C-3, C-6, C-7), 127.18 (d, C-9, C-10), 128.81 (d, C-1, C-8), 130.69 (s, C-9a, C-10a), 132.44 (s, C-4a, C-5a), MS 70 eV m/z (rel int) 179 (60) [M^+]⁺, 178 (100) [M^+]⁺, 177 (36), 176 (58), 152 (38), 151 (35), 150 (20), 139 (5), 126 (5), 89 (35), 76 (40).

Acknowledgements—One of the authors (RJK) thanks the CSIR, New Delhi for the award of JRF. We thank the Chief Conservator of Forests and Mr K Jaganmohan Rao (Conservator of

Forests, Government of Andhra Pradesh, Hyderabad, India) for the supply of plant material and Dr S T Ramachandra Chary (Department of Botany, Osmania University, Hyderabad) for identification of the plant material. The facilities provided by '500 MHz FT NMR facility' at Tata Institute of Fundamental Research, Bombay are gratefully acknowledged.

REFERENCES

- 1 MacRae, W D and Towers, G H N (1985) *Phytochemistry* **24**, 561
- 2 Razdan, T R, Kachroo, V, Harkar, S and Koul, G L (1982) *Phytochemistry* **21**, 923
- 3 Windholz, M (1976) *The Merck Index*, 9th Edn, pp 5937, 6992 Merck, Rahway, NJ
- 4 Silverstein, R M, Bassler, G C and Morrill, T C (1981) *Spectrometric Identification of Organic Compounds*, 4th Edn, pp 264, 327 Wiley, New York
- 5 Pouchert, C J (1983) *The Aldrich Library of NMR spectra*, Second Edition, Vol I, p 765 Aldrich USA
- 6 King, F E, Cotterill, C B, Godson, D H, Jurd, L and King, T J (1953) *J Chem Soc* 3693
- 7 Takaoka, M (1940) *J Fac Sci, Hokkaido Imperial Univ* **3**, 1
- 8 Anjaneyulu, A S R, Raghava Reddy, A V, Reddy, D S K, Ward, R S, Adhikesavulu, D and Stanley Cameron, T (1984) *Tetrahedron* **40**, 4245
- 9 Haddock, A, Gupta, R K, Al-shafi, S M and Haslam, E (1982) *J Chem Soc Perkin Trans I* 2515
- 10 Fritzemeier, K H, Kindl, H and Schloesser, E (1984) *Z Naturforsch* **39C**, 217