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Chemical Examination of the Roots of *Barleria buxifolia* LINN.[1] Structure of Barleriaquinone

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Barleriaquinone (BQ) has been isolated from the roots of *Barleria buxifolia* LINN., and its structure has been established as 1-hydroxy-7-methylanthraquinone by degradative and spectroscopic methods.

Keywords——*Barleria buxifolia*; barleriaquinone (BQ); acanthaceae; anthraquinone

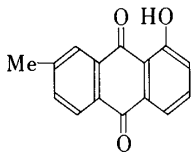
Plant belonging to the family Acanthaceae have been investigated by a number of workers[2–5] and there are records[6,7] dealing with their medicinal properties. However, so far no quinones have been reported from plant materials belonging to this family and we wish to record for the first time in the present paper the occurrence of anthraquinone pigments in the roots of *Barleria buxifolia* LINN., a plant belonging to this family. Two pigments have been isolated from this source and the chemistry of one of them, designated as "barleriaquinone" is discussed herein.

Barleriaquinone (BQ) could be isolated by benzene extraction of the roots of the plant and column chromatography of the concentrate in very low yield. The high-resolution mass spectrum indicated its molecular weight to be 238.0659, corresponding to the molecular formula, $C_{15}H_{10}O_3$. Color reactions with alcoholic ferric chloride, methanolic magnesium acetate and alkaline dithionite indicated an α-hydroxyanthraquinone structure for BQ, which was supported by the preparation of a monoacetate.

Zinc dust distillation of BQ yielded 2-methylanthracene, which could be identified by ultraviolet (UV) spectral comparison with an authentic specimen prepared by the zinc dust distillation of morindone (1,5,6-trihydroxy-2-methylanthraquinone). Since no other functional group could be detected, it was surmised that BQ is an α-hydroxy-β-methylanthraquinone.

The electronic absorption spectrum of BQ exhibited maxima at 217, 259, 285 (sh), 342 and 410 nm and its infrared (IR) spectrum exhibited absorptions at 1670 cm^{-1} (non-chelated carbonyl) and 1640 cm^{-1} (chelated carbonyl). These data are very similar to those of pachybasin[8] (1-hydroxy-3-methylanthraquinone). A literature comparison of the properties of BQ with those of all the known naturally occurring[8–10] and synthetic[11–13] α-hydroxy-β-methylanthraquinones suggested that BQ might be 1-hydroxy-7-methylanthraquinone, not so far isolated from any natural source but known[13] only as a synthetic compound. These conclusions are supported by its proton nuclear magnetic resonance (^{1}H-NMR) data where

the assignments were made by extensive decoupling experiments. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) data on BQ (both noise decoupling and off-resonance modes) were also in support of the above conclusions, though precise assignments of the ^{13}C-NMR peaks were not made. Also direct comparison (co-thin-layer chromatography (TLC), co-IR, and mixed mp) of BQ with a synthetic sample of 1-hydroxy-7-methylanthraquinone, kindly supplied by Professor R. J. Stoodley of Newcastle-upon-Tyne (U.K.) confirmed their identity.



barleriaquinone

Experimental

IR spectra were recorded with a Perkin Elmer 577 IR spectrometer in KBr wafers. UV-visible spectra were measured with a Perkin Elmer 402 UV-VIS spectrometer. ^{1}H-NMR spectra were recorded with a 100 MHz and ^{13}C-NMR spectra with a 60 MHz JEOL instrument using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal reference. Chemical shifts in both ^{1}H-NMR and ^{13}C-NMR spectra are given in parts per million (δ) downfield from TMS (abbreviations: s = singlet, d = doublet, dd = double doublet and q = quartet). For column chromatography, silica gel (60—120 mesh) from B.D.H. (India) was used and for TLC Silica gel-G of B.D.H. (India). Petroleum ether used in chromatography had a boiling range of 60—80 °C.

Extraction of BQ——Air dried roots of *Barleria buxifolia* LINN. (10 kg)[14] were extracted repeatedly with benzene (8 × 2.5 lit.) and the extract was concentrated. The crude concentrate (20 g) was chromatographed over a column of silica gel (500 g), prepared in petroleum ether, and eluted successively with (i) petroleum ether and (ii) petroleum ether–benzene mixtures with increasing amounts of benzene. Fractions of 100 ml were collected. Fractions 1—35 (eluted with petroleum ether) were combined and evaporated to give an oily wax (4.2 g). Fractions 36—110 (eluted with petroleum ether–benzene mixture, 8 : 2) were combined, evaporated and rechromatographed over another silica gel column, prepared in petroleum ether, and eluted first with the same solvent and subsequently with benzene–petroleum ether mixtures, 9 : 1, 8.5 : 1.5 and 8 : 2. Fractions of 25 ml were collected. Fractions 11—35 were combined to yield, after evaporation and recrystallization from chloroform, compound BQ as reddish-yellow needles, mp 171—172 °C, yield: 220 mg.

BQ gave a reddish-brown color with alcoholic ferric chloride and an orange-red color with methanolic magnesium acetate. With aqueous sodium hydroxide, a pink color was noticed and the color of its alcoholic solution faded on the addition of alkaline dithionite.

Craven's test and the Damm–Karrer test were negative with BQ. No quinoxaline derivative was obtainable on reaction with *o*-phenylenediamine. UV λ_{max}^{EtOH} nm (log ε): 217 (4.35), 259 (4.59), 285 sh (4.02), 342 (3.22) and 410 (3.63). IR ν_{max}^{KBr} cm^{-1}: 1670, 1640. MS: $C_{15}H_{10}O_3$ mol. wt. Calcd 238.2451; obs. 238.0659 *m/z*: 238 (M^+), 223 ($M^+ - 15$), 210 ($M^+ - 28$), 182 ($M^+ - 56$). ^{1}H-NMR: 12.16 (1H, s, C_1–OH), 7.20 (1H, dd, J = 8.0, 2.0 Hz, C_2–H), 7.64 (1H, dd, J = 8.0 Hz, C_3–H), 7.74 (1H, dd, J = 8.0, 2.0 Hz, C_4–H), 8.10 (1H, d, J = 8.0 Hz, C_5–H), 7.54 (1H, dd, J = 8.0, 2.0 Hz, C_6–H), 2.48 (3H, s, C_7–CH_3), 8.00 (1H, br s, C_8–H). ^{13}C-NMR: aliphatic carbon: 21.95 (q), aromatic carbons: 116.23 (s), 119.34 (d), 124.02 (d), 127.13 (d), 127.52 (d), 131.29 (s), 132.98 (s), 133.50 (s), 135.32 (d), 136.61 (d), 145.32 (s), 162.46 (s), C=O: 181.93 (s), 188.82 (s).

Acetylation of BQ——A mixture of BQ (50 mg), acetic anhydride (2 ml) and dry pyridine (1 ml) was refluxed on an oil bath for 2 h and the contents were poured over crushed ice. The acetate that separated was recrystallized from ethyl acetate to obtain pale yellow needles, mp 155 °C, yield 40 mg. UV λ_{max}^{EtOH} nm: 214, 232, 280 (sh), 340. ^{1}H-NMR: 2.44 (6H, s, C–OAc and C–CH_3).

Zinc Dust Distillation of BQ——A well-ground mixture of BQ (25 mg) and zinc dust (2.5 g) was packed in a long Pyrex tube which was bent at an obtuse angle, and further zinc dust (2.5 g) was added.

The latter portion was heated first and the portion containing the compound was then brought to a dull red heat. The UV spectrum of the hydrocarbon, 2-methylanthracene, that sublimed at the cooler parts of the tube, was taken. UV λ_{max}^{EtOH} nm: 251, 325, 340, 356 and 376. The spectrum was found to be identical with that of the sample obtained by the zinc dust distillation of morindone.

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References and Notes

1) Preliminary communication was presented at the Sixth Indo-Soviet Symposium on the Chemistry of Natural Products, Sec. B, 20, 1981, p. 84, National Chemical Laboratory, Pune, India. This plant was earlier erroneously identified as *Barleria cristata* LINN., and hence the pigment was named barlacristone. In view of the present corrected identification as *B. buxifolia* LINN., the name of the pigment is changed to barleriaquinone.
2) S. K. Moitra, A. N. Ganguly, N. N. Chakravarti and R. N. Adhya, *Bull. Calcutta Sch. Trop. Med.*, **18**, 7 (1970); *Chem. Abstr.*, **75**, 31350 (1971).
3) S. C. Taneja and H. P. Tiwari, *Tetrahedron Lett.*, **1975**, 1995.
4) A. N. Ganguly, S. K. Moitra, N. N. Chakravarti and R. N. Adhya, *Bull. Chalcutta Sch. Trop. Med.*, **17**, 120 (1969); *Chem. Abstr.*, **74**, 10306 (1971).
5) S. Sankarasubramanian and A. G. R. Nair, *J. Indian Chem. Soc.*, **49**, 825 (1972).
6) K. M. Nadkarni, "Indian Material Medica," Vol. I, 3rd ed., Popular Book Depot, Bombay, 1954, p. 174.
7) R. N. Chopra, S. L. Nayar and I. C. Chopra, "Glossary of Indian Medicinal Plants," C.S.I.R., New Delhi, 1956, p. 33.
8) S. Shibata and M. Takido, *Pharm. Bull.* (Tokyo), **3**, 156 (1955).
9) A. R. Burnett and R. H. Thomson, *J. Chem. Soc.*, (*C*), **1968**, 2437.
10) A. R. Burnett and R. H. Thomson, *Phytochemistry*, **7**, 1421 (1968).
11) P. C. Mitter and A. K. Sarkar, *J. Indian Chem. Soc.*, **7**, 619 (1930).
12) R. K. Boeckman, Jr., T. M. Dolak and K. O. Kulos, *J. Am. Chem. Soc.*, **100**, 7098 (1978).
13) R. C. Gupta, D. A. Jackson and R. J. Stoodley, *J. Chem. Soc., Chem. Commun.*, **1982**, 929.
14) The botanical identification of the plant as *Barleria buxifolia* was made by Prof. T. Sriganesan, Department of Botany, Madula College, Madura, India. The specimen is stored among the herbarium samples in the Department of Natural Products Chemistry, Madurai Kamaraj University, Madurai, India. The plant material used was collected during January—February, 1978.