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Note

Anthraquinone pigments of *Barleria buxifolia* Linn

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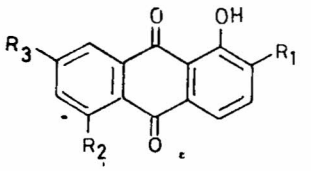

1 $R_1 = R_2 = H$; $R_3 = CH_3$
2 $R_1 = R_2 = H$; $R_3 = COOCH_3$
3 $R_1 = COOCH_3$; $R_2 = H$; $R_3 = CH_3$
4 $R_1 = H$; $R_2 = COOCH_3$; $R_3 = CH_3$

From the benzene extract of the roots of *Barleria buxifolia* Linn, three new anthraquinones have been isolated and their structures established by spectral studies as 1-hydroxy-7-carbomethoxyanthraquinone (BQ-II), 1-hydroxy-2-carbomethoxy-7-methylanthraquinone (BQ-III) and 1-hydroxy-5-carbomethoxy-7-methylanthraquinone (BQ-IV).

Barleria buxifolia (Acanthaceae), a medicinal plant, is used in indigenous system of medicine[1-6]. In an earlier communication[7], the isolation of a new anthraquinone designated as barleriaquinone was reported. In the present note, we have reported the isolation of three more new anthraquinone pigments after further investigation of the roots of the plant.

The benzene extract of the roots on column chromatography afforded four coloured pigments, viz. barleriaquinone **1**[7], BQ-II **2**, BQ-III **3** and BQ-IV **4**. Colour reactions, Shibata test[8], UV and IR spectra of these compounds revealed that these are all hydroxyanthraquinones. All the compounds gave reddish brown colour with neutral ferric chloride indicating the presence of chelated hydroxyl group and formed only monoacetate with acetic anhydride in pyridine under refluxing conditions indicating the presence of only one hydroxyl group. The structures of these compounds were established mainly by ^1H NMR studies.

BQ-II **2** was crystallised from *n*-hexane as orange red plates. The ^1H NMR spectrum of the compound showed the presence of a $-COOCH_3$ group, a chelated -OH group and six aromatic protons. The presence of $-COOCH_3$ group was confirmed by hydrolysis studies.

The analysis of the NMR peaks in the aromatic region and comparison with model compounds clearly revealed that the -OH and $-COOCH_3$ groups are present in two different rings. The -OH group was placed at C-1 position (δ 12.54). The C-2 and C-4 protons appeared as doublet of doublets at δ 7.34 and 7.87 respectively, while C-3 proton appeared as a triplet at δ 7.71.

The $-COOCH_3$ group was placed at C-7 position based on the splitting pattern of the remaining protons of that ring and also surmised that it would be derived from the C-7 methyl in barleriaquinone **1**. The C-5 proton appeared as *ortho* coupled doublet at δ 8.38. The C-8 proton appeared as *meta* coupled doublet at δ 8.96, while the C-6 proton appeared as doublet of doublet at δ 8.45. All these assignments were confirmed by decoupling studies. Based on these evidences, the structure of BQ-II **2** was established as 1-hydroxy-7-carbomethoxy-anthroquinone. The structure was further confirmed by mass spectrum which gave molecular ion $[M^+]$ peak at m/z 282 ($C_{16}H_{10}O_5$).

BQ-III **3** was crystallised from methanol as yellow spongy solid. ^1H NMR spectrum of the compound showed the presence of chelated -OH, $-COOCH_3$, a $-CH_3$ group and five aromatic protons. Examination of the NMR spectral lines in the aromatic region showed that two groups are present in one ring and the other in a different ring. The -OH was placed at C-1 position (δ 13.07) and the $-CH_3$ group was placed at C-7 position (δ 2.54) in comparison with barleriaquinone. Two of the protons appeared as clear *ortho* coupled doublets at

7.33 and 7.87 which suggested that the C-2 position should also be substituted and hence the -$COOCH_3$ group was placed at C-2 position. The splitting pattern of C-5, C-6 and C-8 protons are similar to that of BQ-II, which was further confirmed by decoupling studies. Thus the structure of BQ-III was established as 1-hydroxy-2-carbomethoxy-7-methylanthraquinone. The mass spectrum of the compound gave the base peak at m/z 268, which corresponds to (M^+–CO) peak. Further, the cleavage pattern in the mass spectrum confirmed the assignment of methyl group in one ring and -OH and -$COOCH_3$ in another ring thus confirming the structure assigned to BQ-III.

BQ-IV **4** was crystallised from methanol as reddish orange granules. ^{1}H NMR spectrum of BQ-IV also showed the presence of -OH, -$COOCH_3$ and a -CH_3 group. However, it differed from BQ-III **3** in the splitting pattern of aromatic protons. The protons of C-6 and C-8 appeared as *meta* coupled doublets, suggesting that the C-5 and C-7 positions are substituted. The -CH_3 group was placed at C-7 as in barleriaquinone and BQ-III, and –$COOCH_3$ group was placed at C-5 position. All these proposals were confirmed by extensive decoupling studies of the parent compound and its mono-acetate. The mass spectrum showed an intense base peak at m/z 268, which corresponds to (M^+–CO) peak. Further, the NMR splitting pattern confirmed the assignment of –CH_3 and –$COOCH_3$ on one ring and –OH on the other ring.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker W.H. 270 MHz spectrometer with TMS as internal reference and $CDCl_3$ as solvent (chemical shifts in δ, ppm). IR spectra were recorded in Perkin Elmer 577 IR spectrophotometer and UV in Perkin Elmer 402 spectrophotometer. MS data were obtained on Jeol-DX-300 spectrometer. Silica gel (60-120) were used for column chromatography and silica gel G for TLC. Melting points are uncorrected. The plant material was collected near Madurai Kamaraj University Campus, Madurai.

Extraction and isolation of compounds. The air-dried powdered roots (25 kg) were extracted with hot benzene. The concentrated extract (15 g) was chromatographed over silica gel and eluted with pet. ether-acetone gradient. It was separated into three fractions. Fraction 1 (500 mg) on rechromatography over silica gel and elution with petrol-benzene (8.5:1.5) gave 200 mg of 1 and 20 mg of **2**. Fraction **2** (50 mg) on further column chromatography and preparative TLC ($CHCl_3$:EtOAc; 9.6:0.4) gave 30 mg of **3** as a yellow solid. Fraction 3 afforded 18 mg of **4**.

BQ-II **2**. Orange red plates; m.p. 172°C; UV (MeOH): 220, 225, 280 (sh), 330, 412 nm; IR (KBr): 1625, 1655, 1710 cm^{-1}; ^{1}H NMR: 12.54 (1H, s, HO-1), 7.34 (1H, dd, H-2), 7.71 (1H, dd, H-4), 8.38 (1H, d, H-5), 8.45 (1H, dd, H-6), 4.02 (3H, s, $COOCH_3$-7), 8.96 (1H, d, H-8); MS (%): m/z 282 (M^+) (100), 251 (85), 223 (30), 195 (15), 167 (18), 125 (7), 113 (6), 89 (5), 75 (12).

BQ-II acetate. Yellow needles from $CHCl_3$; m.p. 162°C; ^{1}H NMR: 2.52 (3H, s, acetoxyl), 7.46 (1H, dd, H-2), 7.84 (1H, t, H-3), 8.29 (1H, s, H-4), 8.32 (1H, d, H-5), 8.42 (1H, dd, H-6), 4.0 (3H, s, carbomethoxyl), 8.88 (1H, d, H-8).

BQ-III 3. Yellow solid from MeOH; m.p. 182°C; UV (MeOH): 212, 230, 264, 290 (sh), 340 and 430 nm; IR (KBr): 1620, 1655, 1720 cm^{-1}; ^{1}H NMR: 13.07 (1H, s, OH-1), 4.02 (3H, s, $COOCH_3$-2), 7.33 (1H, d, H-3), 7.87 (1H, d, H-4), 8.16 (1H, d, H-5), 7.60 (1H, dd, H-6), 2.54 (3H, s, CH_3-7), 8.10 (1H, d, H-8); MS (%): m/z 268 (M^+–CO) (100), 250 (10), 239 (76), 225 (42), 212 (6), 197 (35), 162 (20), 151 (5), 139 (25), 115 (36), 91 (12).

BQ-III acetate. Yellow needles from $CHCl_3$; m.p. 167°C; ^{1}H NMR: 2.51 (3H, s, $OCOCH_3$), 3.98 (3H, s, $COOCH_3$), 7.33 (1H, d, H-3), 8.28 (1H, d, H-4), 8.16 (1H, d, H-5), 7.56 (1H, d, H-6), 2.52 (3H, s, CH_3), 8.01 (1H, d, H-8).

BQ-IV 4. Reddish orange crystals from methanol; m.p. 190°C; UV (MeOH): 207, 229, 262, 287 (sh), 335 and 430 nm: IR (KBr): 1620, 1655, 1720 cm^{-1}; ^{1}H NMR: 12.76 (1H, s, OH-1), 7.28 (1H, dd, H-2), 7.63 (1H, t, H-3), 7.79 (1H, dd, H-4), 4.02 (3H, s, $COOCH_3$-5), 7.63 (1H, s, H-6), 2.35 (3H, s, CH_3-2), 8.05 (1H, d, H-8); MS (%): m/z 268 (M^+–CO) (100), 253 (38), 240 (20), 239 (65), 149 (5), 121 (5), 115 (46), 93 (5), 89 (15).

BQ-IV acetate. Yellow needles from $CHCl_3$; m.p. 180°C; ^{1}H NMR: 2.50 (3H, s, $OCOCH_3$), 7.4 (1H, d, H-2), 7.75 (1H, t, H-3), 8.25 (1H, 2, H-4), 4.01 (3H, s, $COOCH_3$), 7.6 (1H, s, H-6), 2.35 (3H, s, CH_3), 8.0 (1H, s, H-8).

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