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1,4-*BIS*-(2′-HYDROXY-5′-METHYLPHENYL)-BUTAN-1,4-DIONE— A BIOGENETICALLY RARE TYPE OF PHENOLIC OF *BERBERIS CORIARIA*

PRIYALAL MAJUMDER and SUCHARITA SAHA
Department of Chemistry, University College of Science, Calcutta 700009, India

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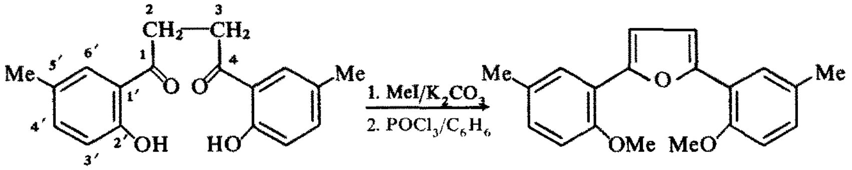
Key Word Index—*Berberis coriaria*; Berberidaceae; 1,4-*bis*-(2′-hydroxy-5′-methylphenyl)-butan-1,4-dione; phenolic.

Berberis coriaria, a native of the high altitude Himalayan region, is claimed to be synonymous with *B. aristata* [1]. Although considerable work [2] was done on the alkaloidal principles of this plant, no work has so far been reported on its non-basic constituents. Reinvestigation of the basic fraction of the chloroform and alcoholic extracts of the roots of this plant afforded berberine, berbamine, oxyacanthine and penduline, the last one being isolated for the first time from this source. Chromatographic resolution of the non-basic part gave a number of non-nitrogenous compounds in extremely poor yields. The spectral and chemical evidence leading to structure **1** for one of them, $C_{18}H_{18}O_4$ (M^+ 298), mp 185°, are summarized in the present communication [3].

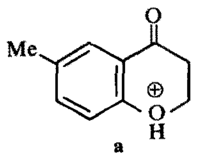
The UV spectrum of **1**, λ_{max} 257 and 340 (log ε 4.33 and 4.90) nm, is typical of an *o*-hydroxyaroyl chromophore [4]. The strong intramolecular hydrogen bonding, so characteristic of this system, is indicated by the failure of dilute alkali to induce any bathochromic shift of the UV maxima, and also by the IR spectrum of **1** showing peaks at 1645 (chelated $\rangle C{=}O$) and 3335 (bonded OH) cm^{-1}. In presence of anhydrous $AlCl_3$, however, the lower wavelength UV maximum suffered a bathochromic shift of 8 nm. The presence of two equivalent phenolic hydroxyl groups in **1** is also indicated by its PMR spectrum showing a two-proton singlet at δ 11.89, which disappears on deuterium exchange. This is confirmed by the formation of a diacetate, $C_{22}H_{22}O_6$ (M^+ 382), mp 141°, and a dimethyl ether, $C_{20}H_{22}O_4$ (M^+ 326), mp 68°. The spectral properties of these derivatives strongly attest the assigned structure. The foregoing evidence can only be accommodated in the symmetrical structure **1** for the compound. The significant peaks at *m/e* 163 (**a**), 135 (**b**) and 107 (**c**) in the MS of **1** are also in accord with this formulation. Furthermore, the natural abundance ^{13}C NMR spectrum [5] of the compound [δ_{ppm} 31.67 ($\underline{C}$-2, $\underline{C}$-3), 20.40 (Ar$\underline{C}H_3$), 118.15 ($\underline{C}$-3′), 128.06 ($\underline{C}$-5′), 129.38 ($\underline{C}$-4′), 137.43 ($\underline{C}$-6′) and 178.02 ($\rangle\underline{C}{=}O$)] clearly distinguishes all the carbon atoms of **1**.

In conformity with the 1,4-diketone structure, the dimethyl ether of **1** smoothly cyclises in presence of $POCl_3$ to a furan derivative, $C_{20}H_{20}O_3$ (M^+ 308), mp 110°, which from spectral data was shown to have the structure **2**. A compound of the same structure (**1**) was previously reported by Shamma *et al.* [6] as a double Fries rearrangement product of di-*p*-tolyl succinate but not as a natural product. The compound was resynthesized [7] and was found to be identical in all respects with the natural product.

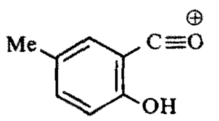
The compound **1** is the first naturally occurring *bis*-(*o*-hydroxyphenyl)-butan-1,4-dione with aromatic *C*-methyl functions. Biogenetically it may be conceived as being formed by dimerisation of two C_6-C_2 units [8] (*o*-hydroxyacetophenone or its appropriate biochemical equivalents), the extra *C*-methyls being introduced from methionine either at the monomeric or dimeric level.



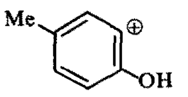
1 **2**



a



b



c

EXPERIMENTAL

Si gel (60–100 mesh) was used for column chromatography and Si gel G for TLC. All analytical samples were dried over P_2O_5 for 24 hr *in vacuo* and were tested for purity by TLC and MS. Molecular formulae are in agreement with elemental analyses. The UV spectra were recorded in 95% EtOH and the IR spectra in KBr discs. Except for the furan derivative, MS data are presented neglecting peaks of relative intensity less than 0.5%. The ^{13}C NMR spectrum was recorded in $CDCl_3$ soln using Varian CFT 20 instrument and the peaks are expressed in δ(ppm) with $\delta_{CDcl_3} = 76.9$ ppm downfield from TMS.

Isolation of **1a**. Air-dried finely ground roots (1 kg) of *Berberis coriaria* Royle ex Lindl. were successively extracted with $CHCl_3$ and EtOH in Soxhlet apparatus for 72 hr. After removal of the solvents, the residues were stirred with 5% aq. citric acid for 6 hr, filtered, and the filtrate extracted several times with $CHCl_3$, the extract washed free of acid and dried. The residue was dissolved in $CHCl_3$, the combined $CHCl_3$ solubles chromatographed using petrol and mixtures of petrol/EtOAc as eluents in order of increasing polarity. The petrol/EtOAc (20·1) eluate on evaporation gave a light brown solid which crystallized from petrol/EtOAc in light pink stout needles (**1**) (0.02 g), mp 185°. MS: *m/e* (% abundance for over 50%) 298 (M^+, 71.4), 280, 234, 219, 177, 164, 163 (98.6), 161, 145, 136, 135 (100), 117, 115, 108, 107, 106, 105, 91, 79, 78, 77 (62.9), 55, 53, 51 and 43.

Acetylation of **1**. In the usual way gave the diacetate mp 141°, λ_{max} 243 and 290 (log ε 4.77 and 3.51) nm; ν_{max} 2900, 1750, 1672, 1225 cm^{-1}; δ(ppm): 2.35 (6H, *s*; Ar–$C\underline{H}_1$), 2 42 (6H, *s*; —O—$COC\underline{H}_3$), 3.32 (4H, *s*; —CO—$C\underline{H}_2$—), 7.01 (2H, *d* *J* 9 Hz, Ar–$\underline{H}$), 7.35 (2H, *dd*; *J* 9 Hz and 2 Hz, Ar–$\underline{H}$); 7.70 (2H, *d*, *J* 2 Hz; Ar–$\underline{H}$); *m/e* (%)· 382 (M^+, < 1), 340, 323, 322, 298, 291, 290, 205, 188, 178, 177 (87.0), 164, 163 δ (98.3), 162, 161, 145, 136, 135 (100), 107, 78, 77, 45 and 43 (59.1).

Methylation of **1** with MeI/K_2CO_3 gave the dimethyl ether, mp 68°; λ_{max} 220, 250 and 320 (log ε 4.14, 4.60 and 3.07) nm; ν_{max} 2940, 2860, 1660 and 1580 cm^{-1}; δ(ppm): 2.31 (6H, *s*; Ar–$C\underline{H}_3$), 3.41 (4H, *s*; —CO—$C\underline{H}_2$—), 3.91 (6H, *s*; Ar—$OC\underline{H}_3$), 6.89 (2H, *d*, *J* 9 Hz; Ar—$\underline{H}$); 7.29 (2H, *dd*, *J* 9 Hz and 2 Hz; Ar—$\underline{H}$), 7.60 (2H, *d*, *J* 2 Hz; Ar—$\underline{H}$); *m/e* (%): 326 (M^+, 35.4), 177, 150, 149 (100), 134, 106, 105, 91 and 78.

Cyclization of the methyl ether was effected in $POCl_3$ under reflux for 6 hr. The product mp 110°; λ_{max} 295 and 330 (log ε 4.01 and 4.44) nm; ν_{max} 2935, 2860, 1607, 1502, 792 and 740 cm^{-1}; δ(ppm): 2.38 (6H, *s*; Ar–$C\underline{H}_3$), 3.89 (6H, *s*; Ar–$OC\underline{H}_3$), 6.84 (2H, *d*, *J* 8 5 Hz; Ar–$\underline{H}$), 7.01 (2H, multiplicity obscured by furan proton signals, Ar–$\underline{H}$), 7.03 (2H, multiplicity obscured by preceding signals; furan protons), 7.79 (2H, *s*; Ar–$\underline{H}$), *m/e* (%): 308 (M^+, 1.5), 307, 292, 266, 265, 249, 235, 159, 154, 149, 146, 145, 133, 125, 116, 115, 105 and 91.

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1-HYDROXY-3,7-DIMETHOXY-6-ACETOXYXANTHONE, A NEW XANTHONE FROM *LAWSONIA INERMIS*

DEVENDRA K. BHARDWAJ, RAKESH K. JAIN, BUBHASH C. JAIN and CHANDER K. MEHTA
Department of Chemistry, University of Delhi, Delhi-110007, India

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Key Word Index—*Lawsonia inermis* (syn. *L. alba*); Lythraceae; xanthones; laxanthone-III; 1-hydroxy-3,7-dimethoxy-6-acetoxyantone.

Lawsonia inermis (syn. *L. alba*), well-known as a source of an orange dye [1] and for its medicinal uses [2], has been examined extensively for its chemical components [3–12]. The present communication describes the characterisation of a new xanthone, laxanthone-III. A solvent-free ethanolic extract of the whole plant (3 kg) was chromatographed over a Si gel column using a number of solvent systems. Elutions with petrol–C_6H_6 (7:3) gave laxanthone-III (**1**) whereas other fractions yielded compounds reported earlier. Colour reactions and spectral data for **1** indicated a chelated OH. On acetylation **1** gave a monoacetate (**1a**) but remained unchanged on methylation with CH_2N_2 in ether indicating that it had only one chelated OH. Hydrolysis of **1** yielded a dihydroxydimethoxy compound (**1b**) which underwent monoethylation to yield a monoethyl ether (**1c**), and also, methylation with CH_2N_2 in ether to give a monomethyl ether identical with 1-hydroxy-3,6,7-trimethoxyxanthone (**1d**) [13] showing that **1** like laxanthone-I (**2**) and II (**3**) was also a 1,3,6,7-tetraoxygenated xanthone. The NMR spectrum of **1** showed signals for two methoxyls, one acetoxyl, a pair of *m*-coupled and two other aromatic