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Synthesis of unnatural hydroxyanthraquinones : Experiments towards total synthesis of pradimicinone

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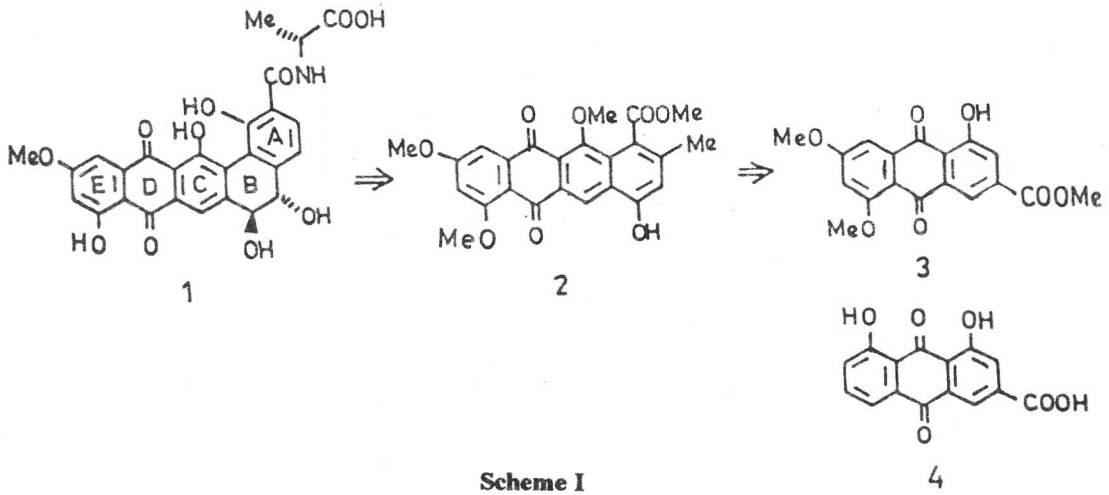
The phthalide sulfone **5** has been prepared from readily available ester **6** in four steps on multigram scales. This has been utilized in anionic [4 + 2] cycloaddition with a few cyclohexenones (**12-14**) to obtain anthraquinones (**18-26**) in good yields, compound **21** being a potential intermediate for pradimicinone **1**.

Pradimicinone **1** is the aglycon of two small groups of polyketides called pradimicins[1] and benanomycins[2], which were recently isolated from a soil sample of Fiji island. Members of these glycosidic natural products exhibit potent *in vivo* activity against a variety of fatal systemic fungal infection, and are relatively non-toxic. They are also found to have significant HIV-inhibitory activity[3].

The structural intricacy of pradimicinone **1** has, in recent years evoked considerable synthetic activity. Kelly *et al.*[4] have combined enantioselective dihydroxylation of a stilbene derivative and intramolecular palladium-catalysed biaryl coupling as key steps in building ABC ring-core of **1**. Echavarren *et al.*[5] have focussed their efforts on functionalization of commercially available anthraquinone derivatives to establish the substitution pattern of CDE ring-core. In line with the latter, we were also interested in elaboration of a suitably fabricated anthraquinone to **1**. Although the chemistry of hydroxyanthraquinones is well-established and exhaustively studied, the synthesis of a substituted anthraquinone may pose unexpected problems, as evident from the synthetic works[6] on rhein **4** and its analogs. Moreover, the anthraquinone moiety embodied in **1** represents the only example of unnatural disposition of hydroxy and methoxy groups on an anthraquinone nucleus, which is not explicable by biogenetic considerations[7]. This, a typical oxygenation pattern, prompted us to explore anionic [4 + 2] cycloaddition[8] to obtain the regiospecifically well defined anthraquinone intermediate **3** (Scheme I).

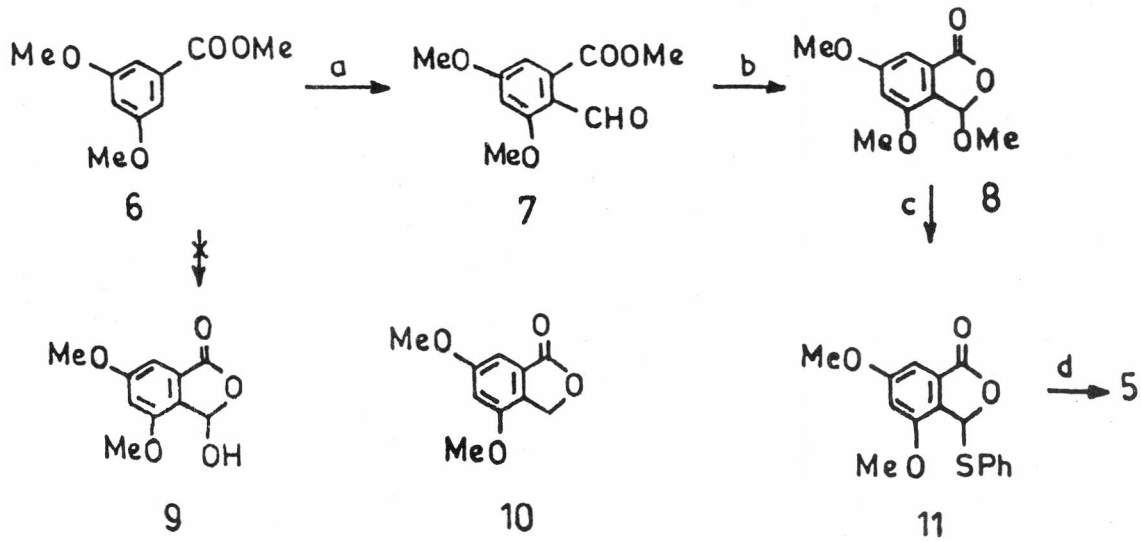
In this context, the preparation of phthalide sulfone synthon **5** was projected. But its preparation was not straightforward. Phthalide sulfones are usually prepared from phthalaldehydic acids through phenylsulfenylation and subsequent oxi-



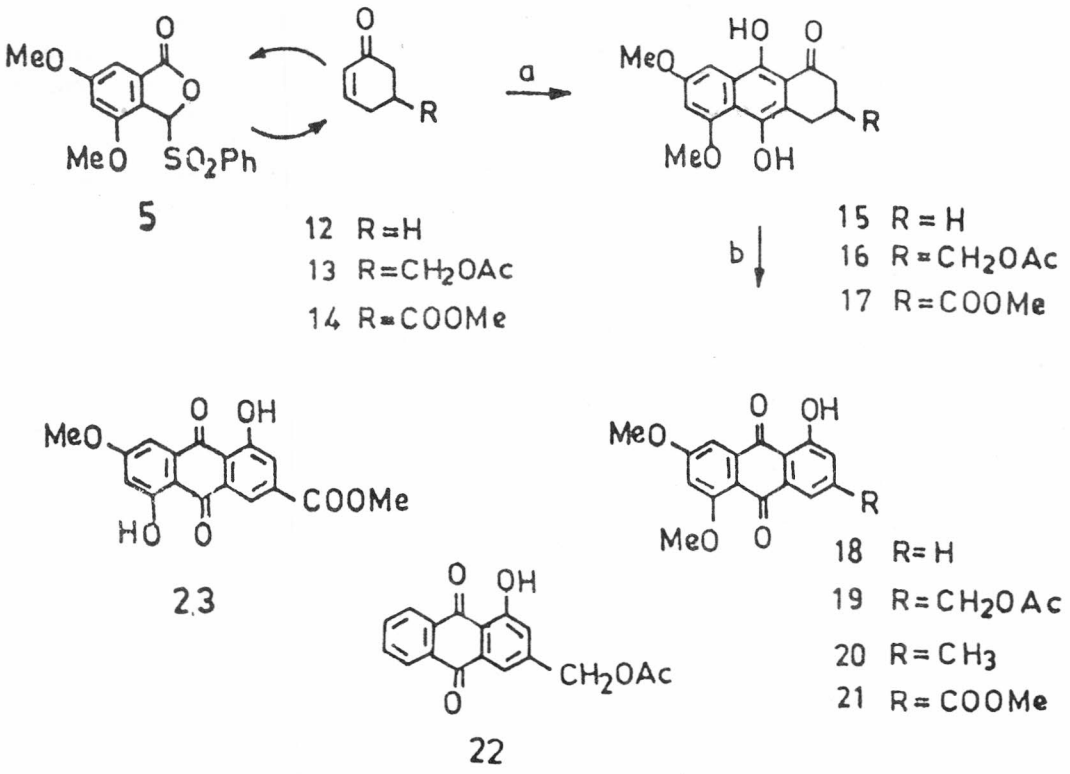
Scheme I

dation of the sulfide functionality[9]. Accordingly, our initial attempts were focussed on the conversion of **6** to **9**. Unfortunately, Gatternam formylation ($Zn(CN)_2$, $AlCl_3$, HCl) of **6** was totally unsuccessful. Attempted formylation of the corresponding acid using $CH(OEt)_3$ and $AlCl_3$ also failed. Preparation of **9** from the respective phthalide[10] **10** via benzylic bromination-hydrolysis was then planned. But, NBS bromination of phthalide **10** resulted in a complex mixture of compounds, which seemingly included a few nuclear brominated products. Finally, dimethoxy ester **6** was formylated to give **7** in accordance with the procedure of Hassal *et al.*[11] While attempting purification by recrystallization in methanol, the compound **7** cleanly transformed to trimethoxyphthalide **8** to the extent of 70%. Complete conversion of **7** to **8** was effected by refluxing it in methanol containing a few drops of conc. sulfuric acid. Condensation of methoxyphthalide **8** with thiophenol in the presence of PTSA afforded phenylthiophthalide **11** (85%) (Scheme II), which was also obtained directly from the aldehyde **7** under similar conditions, but in a poor yield (~ 30%). Attempted oxidation of the sulfide **11** under standard peroxide conditions (H_2O_2, CH_3COOH, 100°C), yielded a complex mixture of products, from which the desired sulfone **5** was isolated only in 30-40% yield. Such problems are, however, not uncommon in the oxidation of methoxy substituted phthalide sulfides[12]. Extensive experimentation on the oxidation step **11** → **5** revealed that the oxidation could be secured in 88% yield under an optimized condition (H_2O_2, AcOH, 50°C, 10 min.).

With the key building block **5** in hand, we next investigated its annulation with various cyclohexenone derivatives. Under typical annulation conditions (^{t}BuOLi, THF, −60°C → r.t), the sulfone **5** was reacted with cyclohexenone **12** to furnish, after usual work-up, a gummy material. Aerial oxidation of this crude product in DMF provided anthraquinone **18** in 23% yield (Scheme III). A similar reaction between **5** and substituted cyclohexenone **13** (ref. 13) produced three products, viz. quinol **16** (24%), quinone **19** (5%) and **26** (2%). Oxidation (O_2, DMF) of the quinol **16** gave the quinone **19** in 71% yield. Attempts to improve upon the yield of the annulation by changing the nature of base used and the proportion of reactants, proved to be futile, the overall yield remained below 30%. However, the formation of methyl derivative **20** led us to examine the reactivity of ester substituted cyclohexenone **14**. In fact, treatment of **5** with **14** in the presence of ^{t}BuOLi at −60°C yielded quinol **17** (70%) (Scheme III). Unfortunately, the yield of the reaction could not be reproduced. The reaction was repeated eleven times. In four runs, the yields were more than 50% and in rest of the runs, they were between 10-50%. The exact reasons for this anomalous behaviour of the reaction could not be traced, despite our austere attempts. On the other hand, simplest phthalide sulfone[6] could be annulated with **13** to give quinone **22** in consistently excellent yields (~80%). Oxidation of the quinol **17** proceeded smoothly to provide quinone **21** (78%). Since the target molecule **1** contains a free hydroxy group at C-5, we briefly examined selective demethylation[14] of **21**. Compound **21** on



Scheme II – Reagents and conditions: a, Cl_2CHOMe, $TiCl_4$; b, MeOH, HCl(Cat.), heat, c, PhSH, PTSA(Cat.), reflux; d, H_2O_2.AcOH, 50°C



Scheme III – Reagents and Conditions: a, ^tBuOLi, $-60°C \rightarrow$ r.t; b, O_2, DMF, heat.

treatment with $AlCl_3$ in dichloromethane produced **23** in 65% yield. Compound **21** was allylated with methallyl chloride in DMF in the presence of K_2CO_3 and KI to give an allyl ether **24** as bright needles in 88% yield. The allyl ether **24** was then subjected to reductive Claisen rearrangement[15] ($Na_2S_2O_4$, DMF-H_2O, 100°C) to furnish the product **25** (90%) (Scheme IV); the structure of which was ascertained by appearance of a phenolic peak at 12.85 ppm in its ^1H NMR spectrum. In order to get the intermediate **2** (Scheme 1), we also intended to introduce an ester function at the benzylic position of **25** via carbanion chemistry. But, all the attempts to deprotonate the benzylic carbon by LDA were unsuccessful. Similarly, an attempted deprotonation of *O*-methyl derivative **26**, prepared by conventional methylation (Me_2SO_4, K_2CO_3) of **25**, was unsuccessful.

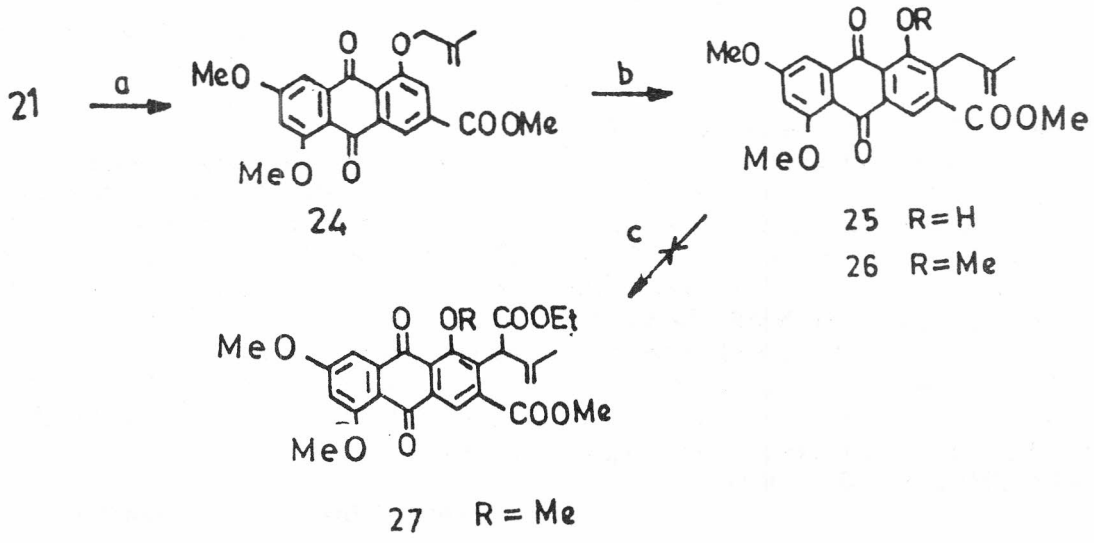
In conclusion, the potential pradimicinone intermediates and rhein analogs could be prepared through application of the phthalide sulfone annulation strategy. Further work is in progress to accomplish the total synthesis of pradimicinone.

Experimental Section

Melting points determined are uncorrected. IR spectra (ν_{max}, cm^{-1}) were recorded on a Perkin-Elmer 883 using KBr pellets and ^1H NMR spectra (chemical shifts in δ, ppm) on a 90 MHz (Varian), a 100 MHz (Jeol) or a 200 MHz (Bruker) in $CDCl_3$ solution (unless otherwise mentioned) using TMS as internal standard. Mass spectral data were collected from RSIC, Madras.

4, 6-Dimethoxy-3-(phenylsulfonyl)phthalide (5). To a warm solution of 4, 6-dimethoxy-3-(phenylthio)phthalide **11** (2.0 g, 6.6 mmoles) in gl. acetic acid (30 mL) was added dropwise hydrogen peroxide (5 mL, 30%, w/v). The resulting mixture was heated to 50°C for only 10 min. and then stirred overnight at ambient temperature. The white solid obtained by filtration was recrystallized from acetone-water mixture to furnish phthalide sulfone **5** as white crystals (1.95g, 88%), m.p. 153°C (Found: C, 58.0; H, 4.2 Calcd for $C_{16}H_{14}O_6S$: C, 57.5; H, 4.2%) IR: 3083, 1799, 1613, 1324, 1149, 1097 cm^{-1}; ^1H NMR: δ8.0-7.5(m, 5H, $SO_2C_6H_5$), 6.94(d, 1H, J=2Hz, H-7), 6.85(d, 1H, J=2Hz, H-5), 6.2(s, 1H, H-3), 3.98(s, 3H, OCH_3), 3.88(s, 3H, OCH_3); MS: m/z, 385, 218, 293, 172, 158, 141, 109, 77, 51.

3, 4, 6-Trimethoxyphthalide (8). A solution of methyl 2-formyl-3, 5-dimethoxybenzoate **7** (10g, 45 mmoles) in methanol (250 mL) containing few drops of conc. HCl was heated at reflux for 5 hr.



Scheme IV—Reagents and conditions; a, methallyl chloride, KI, K_2CO_3; b, $Na_2S_2O_4$. DMF-water, heat; c, LDA, ClCOOEt.

The solid, crystallized on cooling the reaction flask, was filtered. Concentration of the mother liquor provided a further lot of solid. The combined solid was recrystallized from methanol to give **8** as white needles (9.6 g, 96%), m.p. 152-54°C (Found: C, 58.50; H, 5.3. Calcd for $C_{11}H_{12}O_5$:C, 58.9; H, 5.3%); IR: 3069, 2958, 1778, 1630, 1345, 1156, 1039, 860 cm^{-1}; ^1H NMR: δ6.95(d, 1H, J=2Hz, H-7), 6.75(d, 1H, J=2Hz, H-5), 6.5(s, 1H, H-3), 3.92(s, 3H, OCH_3), 3.90(s, 3H, OCH_3), 3.63(s, 3H, 3—OCH_3).

4,6-Dimethoxy-3-(phenylthio)phthalide (11). A mixture of 3, 4, 6-trimethoxyphthalide **8** (5g, 22 mmoles), thiophenol (4.1 mL, 4.0 mmoles) and a catalytic amount of *p*-toluenesulfonic acid (20 mg) in dry benzene (200 mL) in a round bottomed flask (500 mL) was heated at reflux with continuous removal of water with the help of a Dean Stark apparatus. The residue obtained after removal of benzene, was dissolved in ethyl acetate (40 mL), and the resulting organic phase was successively washed with aqueous sodium bicarbonate (30 mL) and water (20 mL). It was then dried (Na_2SO_4), filtered and evaporated to give a light yellow residue which was recrystallized from ethyl acetate-hexane mixture to give **11** as white crystals (5.72g, 85%), m.p. 99-100°C; IR: 3070, 1764, 1608, 1486, 1330, 944 cm^{-1}; ^1H NMR: δ 7.62-7.2(m, 5H, SC_6H_5), 6.88(d, 1H, J=2Hz, 7-H), 6.72(d, 1H, J=2Hz, 5-H), 6.62(s, 1H, 3-H), 3.95(s, 3H, OCH_3), 3.82(s, 3H, OCH_3).

Annulation of phthalide sulfone 5 with cyclohexanones (12-14): General procedure To a stirred solution of lithium *tert*-butoxide (4.5 mmoles) in THF (15 mL) at −65°C ($CHCl_3$/liquid N_2 bath) under an argon atmosphere was added a solution of **5** (1.5 mmoles) in THF (15 mL). The resulting yellow solution was stirred at this temperature for 15-20 min., after which a Michael acceptor (1.2-1.5 equiv.) dissolved in THF (6 mL) was introduced into the reaction flask. The cooling bath was removed after 1 hr of stirring and then reaction mixture was stirred at room temperature till the sulfone reacted completely. The reaction was quenched with 10% HCl (2-3 mL). The resulting biphasic mixture was concentrated under vacuum and the residue extracted with ethyl acetate (2 × 30 mL). The combined extracts were washed with water (20 mL), dried and concentrated to afford a gummy dark residue which was subjected to column chromatography to furnish the corresponding annulated product. Occasionally, crude products were directly oxidised to anthrquinones. For the quinols **15-17**, no attempts were made to obtain analytical samples.

Aerial oxidation of quinols (15-17) to quinones (18-21): General procedure. Air was bubbled through a hot solution of pure or crude quinols (**15-17**) in DMF (20 mL) for 3-16 hr. The mixture was then cooled, poured into water (200 mL) and extracted with ethyl acetate (2 × 50 mL). The combined extracts were thoroughly washed with water (2 × 30 mL), dried (Na_2SO_4), and con-

centrated to give a crude product which was purified by preparative TLC to furnish pure quinones **18-21**.

3-(Acetoxymethyl)-9, 10-dihydroxy-5, 7-dimethoxy-1, 2, 3, 4-tetrahydroanthracen-1-one (16). It was prepared from sulfone **5** and enone **13** according to the general annulation procedure described above; brownish orange, m.p. 148-50°C; yield 25%; IR: 3390, 2928, 1734, 1629, 1586, 1463, 1249, 924 cm^{-1}; ^1H NMR: δ8.9(s, 1H, 5−OH), 7.32(d, 1H, J=1.5 Hz, 8-H), 6.66(d, 1H, J=1.5 Hz, 6-H), 4.15-4.13 (m, 2H, CH_2OAc), 4.04(s, 3H, OCH_3), 3.93(s, 3H, OCH_3), 3.32-3.28(m, 1H, 3-H), 2.90-2.75(m, 1H, ring-H), 2.70-2.44(m, 3H), 2.10(s, 3H, $COCH_3$).

Methyl 9,10-dihydroxy-5, 7-dimethoxy-1, 2, 3,4-tetrahydroanthracen- 1-one-one-3-carboxylate (17). It was prepared from sulfone **5** and enone **14** according to the general annulation procedure. orange; m.p. 165°C; yield 10-80%; IR: 3451, 2957, 1732, 1636, 1430, 1380, 1214, 1053 and 763 cm^{-1}; ^1H NMR: δ 13.22 (s, 1H, 9-OH), 8.85(s, 1H, 10-OH), 7.26(d, 1H, J=2Hz, 8-H), 6.6(d, 1H, J=2Hz, 6-H), 4.01(s, 3H, OCH_3), 3.91(s, 3H, OCH_3), 3.73(s, 3H, $COOCH_3$), 3.42(dd, 1H, J=13, 2 Hz, 3-H), 3.20-3.10(m, 1H, ring-H), 3.08-2.91(m, 3H, ring-H); ^{13}C NMR: δ203.17, 173.86, 157.4, 156.37, 153.60, 141.92, 126.27, 114.96, 113.83, 111.42, 102.13, 95.88, 56.39, 55.57, 52.1, 40.44, 39.31, 25.27.

5-Hydroxy-1, 3-dimethoxy-9, 10-anthraquinone (18). It was obtained from **5** and **12** through the general annulation procedure followed by oxidation, orange-red; m.p. 197-98°C; yield 23%; IR: 3413, 2937, 1655, 1596, 1458, 1267, 1215 and 765 cm^{-1}; ^1H NMR: δ12.41(s, 1H, 5-OH), 7.78(dd, 1H, J=7.5, 1Hz, 8-H), 7.65(t, 1H, J=8.2Hz, 7-H), 7.48(d, 1H, J=2.5 Hz, 4-H), 7.21(dd, 1H, J=7.5, 1Hz, 6-H), 6.8(d, 1H, J=2.3 Hz, 2-H), 4.01(s, 3H, OCH_3), 3.99(s, 3H, OCH_3).

3-(Acetoxymethyl)-1-hydroxy-5, 7-dimethoxy-9, 10-anthraquinone (19). Oxidation of quinol **16** according to the general procedure reported above provided **19**, yellow; m.p. 166-68°C; yield 71% (Found: C, 64.0, H, 4.5. Calcd for $C_{19}H_{16}O_7$: C, 64.1, H, 4.5%); IR: 3541, 2943, 1736, 1655, 1597, 1451, 1230 and 934 cm^{-1}, ^1H NMR: δ12.37(s, 1H, 1-OH), 7.71(s, 1H, 4-H), 7.46(d, 1H, J=1Hz, 8-H), 7.17(s, 1H, 2-H), 6.79(d, 1H, J=1Hz, 6-H), 5.18(s, 2H, $-CH_2-O$), 4.01(s, 3H, OCH_3), 3.99(s, 3H, OCH_3), 2.18(s, 3H, $COCH_3$); MS: m/z 356, 339, 314, 297, 285, 268, 255, 239, 225, 211, 197, 181, 139, 91.

1-Hydroxy-5, 7-Dimethoxy-3-methyl-9, 10-anthraquinone (20). This was obtained as a minor co-product from the annulation between **5** and **13**, orange; m.p. 214-15°C; yield 2-5%; IR: 3441, 2927, 1594, 1453, 1265 and 997 cm^{-1}; ^1H NMR: δ12.38 (s, 1H, OH), 7.58(d, 1H, J=1Hz, Ar-H), 7.46(d, 1H, J=2Hz, Ar-H), 7.02(d, 1H, J=1Hz, Ar-H), 6.78(d, 1H, J=2Hz, Ar-H), 4.01(s, 3H, OCH_3), 3.98(s, 3H, OCH_3), 2.45(s, 3H, CH_3).

Methyl 1-hydroxy-5, 7-dimethoxy-9, 10-anthraquinone-3-carboxylate (21). It was prepared from **17** according to the general procedure for oxidation of quinols, golden yellow; m.p. 252°); yield 78%. (Found: C, 63.0; H, 4.0. Calcd for $C_{18}H_{14}O_7$: C, 63.28; H, 4.19%); IR: 3423, 2932, 1723, 1651, 1592, 1425, 1307, 1243, 1017 and 716 cm^{-1}; ^1H NMR: δ12.31(s, 1H, 1-OH), 8.38(d, 1H, J=1.5Hz, 4-H), 7.87(d, 1H, J=1.6Hz, 2-H), 7.48(d, 1H, J=2.2Hz, 8-H), 6.83(d, 1H, J=2.2Hz, 6-H), 4.02(s, 3H, OCH_3), 4.00(s, 3H, OCH_3), 3.98(s, 3H, $COOCH_3$), MS: m/z 342, 327, 311, 297, 283, 253, 238, 225, 210, 197, 169, 155, 139, 126, 111, 91.

***O*-Acetyl derivative of 21.** It was prepared by acetylation of **18** using acetic anhydride and pyridine, light yellow; m.p. 221°C; yield 89% (Found: C, 62.0; H, 4.1. Calcd for $C_{20}H_{16}O_8$: C, 62.5; H, 4.1%); IR: 2928, 1758, 1721, 1671, 1595, 1466, 1248, 1017 and 760 cm^{-1}; ^1H NMR: δ8.82(d, 1H, J=1.2Hz, Ar-H), 7.9(d, 1H, J=1.2Hz, Ar-H), 7.35(d, 1H, J=2Hz, Ar-H), 6.78(d, 1H, J=2Hz, Ar-H), 4.02(s, 3H, OCH_3), 4.00(s, 3H, OCH_3), 3.98(s, 3H, OCH_3), 2.5(s, 3H, $COCH_3$); ^{13}C NMR : δ182.2, 179.37, 168.5, 165, 164.7, 162, 149.3, 138.34, 137.2, 136.1, 128, 127.3, 126.42, 115.7, 104.2, 103.2, 56.5, 56, 52.3, 21.6; MS: m/z 384, 342, 327, 283, 253, 197, 133, 105, 91, 73.

Methyl 1, 5-dihydroxy-7-methoxy-9, 10-anthraquinone-3-carboxylate (23). $AlCl_3$ (30 mg) was added to the ester **21** (20 mg) dissolved in dry dichloromethane (30 mL) at room temperature under nitrogen and the mixture was stirred for 5 hr. The mixture was then poured into aqueous sodium bicarbonate solution (15 mL). The organic phase thus separated was dried (Na_2SO_4)

and concentrated to give a reddish mass, which was purified by preparative TLC to furnish **23** as an orange solid (12 mg, 63%), m.p. 228-30°C; IR: 3445, 1729, 1612, 1457, 1383, 1292, 1244, 815 cm^{-1}; ^1H NMR: δ12.84(s, 1H, OH), 12.47(s, 1H, OH), 8.41(d, 1H, J=1.5Hz, Ar-H), 7.91(d, 1H, J=1.7Hz, Ar-H), 7.39(d, 1H, J=2.6Hz, Ar-H), 4.74(d, 1H, J=2.4Hz, Ar-H), 3.99(s, 3H, OCH_3), 3.95(s, 3H, $COOCH_3$).

3-(Acetoxymethyl)-1-hydroxy-9, 10-anthraquinone 22. It was prepared from the parent sulfone[6] and enone **13** by annulation followed by aerial oxidation, deep yellow; m.p. 138-40°C; yield 80%; ^1H NMR: δ12.63(s, 1H, OH), 8.28(m, 2H, Ar—H), 7.80(m, 3H, Ar—H), 7.26(s, 1H, Ar-H), 5.19(s, 2H, $-CH_2-$), 2.18(s, 3H, $COCH_3$).

Methyl 5, 7-dimethoxy-1-O-(2-methyl-2-propenyl)-9, 10-anthraquinone-3-carboxylate (24). To a stirred solution of hydroxyanthraquinone **21** (0.2 g, 0.58 mmole) in dry DMF (8 mL) was added potassium carbonate (80 mg, 0.58 mmole), potassium iodide (20 mg) and methallyl chloride (0.3 g, 3.3 mmoles) at room temperature and the mixture heated at 70°C for 12 hr, cooled and poured into ice-chilled water (80 mL). The solid thus precipitated was filtered and purified by PLC to give allyl ether **24** (200 mg, 88%) as a yellow crystalline substance, m.p. 225°C, IR: 3091, 1724, 1663, 1599, 1456, 1245, 1049, 757 cm^{-1}; ^1H NMR: δ 8.51(d, 1H, J=1.5Hz, Ar-H), 7.85(d, 1H, J=1.5Hz, Ar-H), 7.4(d, 1H, J=2.2Hz, Ar-H), 6.74(d, 1H, J=2.2Hz, Ar-H), 5.39(s, 1H, $=CH_2$), 5.11(s, 1H, $=CH_2$), 4.67(s, 2H, OCH_2), 4.00(s, 3H, OCH_3), 3.98(s, 3H, OCH_3), 3.96(s, 3H, $COOCH_3$), 1.94(s, 3H, CH_3); ^{13}C NMR: δ180.31, 165.6, 165.05, 162.16, 158.74, 139.51, 139.15, 137.77, 135.52, 123.61, 120.57, 117.86, 115.42, 113.45, 104.14, 103.29, 72.94, 56.49, 53.94, 52.7, 19.37; MS: m/z 395, 380, 364, 350, 336, 324, 309, 297, 281, 265, 237, 225, 209, 197, 181, 169, 149, 135, 91, 84.

Methyl 1-hydroxy-5, 7-dimethoxy-2-(2′-methyl-2′-propenyl)-9, 10-anthraquinone-3-carboxylate 25. A solution of allyl ether **24** (100 mg, 0.25 mmole) and sodium dithionite (100 mg, 0.58 mmole) in a mixture of DMF (6 mL) and water (2 mL) under argon atmosphere was heated on a steam-bath for 2 hr. The resulting solution was cooled to room temperature and poured into water (60 mL). It was then extracted with ethyl acetate (2×30 mL). The combined extract was washed with water (2×20 mL), dried (Na_2SO_4) and concentrated to give an orange residue. It was purified by column chromatography to yield **25** (90 mg, 79%) as yellow crystals, m.p. 183-84°C; IR: 3443, 1721, 1652, 1592, 1258, 1024 cm^{-1}; ^1H NMR: δ12.85(s, 1H, OH), 8.10(s, 1H, Ar-H), 7.42(d, 1H, J=2Hz, Ar-H), 6.77(d, 1H, J=2Hz, Ar-H), 4.75(brs, 1H, $=CH_2$), 4.38(brs, 1H, $=CH_2$), 4.03(s, 3H, OCH_3), 4.00(s, 3H, OCH_3), 3.96(s, 3H, $COOCH_3$), 3.82(s, 2H, $-CH_2-$), 1.95(s, 3H, $C-CH_3$); ^{13}C NMR: δ188.57, 179.44, 166.94, 164.85, 162.78, 160.66, 143.75, 138.49, 136.95, 134.89, 132.76, 119.72, 116.08, 116.03, 110.46, 105.32, 103.39, 56.54, 55.96, 52.46, 33.16, 23.22; MS: m/z 396, 381, 365, 349, 337, 322, 307, 293, 279, 233, 211, 198, 182, 165, 135, 115, 84.

Methyl 2-(2′-methyl-2-propenyl)-1, 5, 7-trimethoxy-9, 10-anthraquinone-3-carboxylate (26). It was prepared from **25** by conventional methylation using dimethyl sulfate and potassium carbonate in acetone, bright yellow; m.p. 173-74°C; yield 96%. (Found: C, 67.10; H, 5.35. Calcd for $C_{23}H_{22}O_7$: C, 67.3; H, 5.4%); IR: 2942, 1720, 1665, 1596, 1453, 1254, 1044, 729 cm^{-1}; ^1H NMR: δ8.44 (s, 1H, Ar-H), 7.38(d, 1H, J=2.4Hz, Ar-H), 6.75(d, 1H, J=2.4Hz, Ar-H), 4.74(bs, 1H, $=CH_2$), 4.23(bs, 1H, $=CH_2$), 4.00(s, 3H, OCH_3), 3.97(s, 3H, OCH_3), 3.90(s, 6H, $2\times OCH_3$), 3.83(s, 2H, $ArCH_2-$), 1.84(s, 3H, $C-CH_3$); MS: m/z 410, 395, 379, 363, 351, 336, 305, 291, 235, 218, 191, 165, 145, 84.

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