Synthetic studies towards complex diterpenoids. Part 20.[1] Total synthesis of the linear abietane *o*-quinone umbrosone

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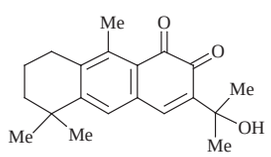
A simple total synthesis of the rearranged linear abietane diterpenoid *o*-quinone, umbrosone **1**, has been accomplished through *trans*-1,2,3,4,9,9a-hexahydro-1,1-dimethyl-6-methoxyanthracen-10(4a*H*)-one **12t**.

The unusual rearranged linear abietane diterpenoid *o*-quinone, umbrosone **1**,†[2] isolated from *Hyptis umbrosa* Slazm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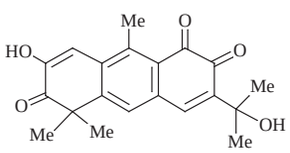
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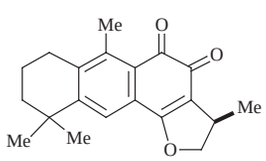
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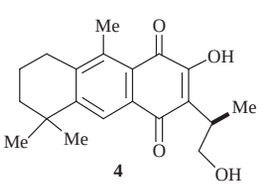
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(Lamiaceae), exhibited[2] significant activity against Gram-positive bacteria. A few other structurally related quinones, pygmaeocine E **2**,[3] aegyptinone A **3**[4] and aegyptinone B **4**[4] have been isolated from a number of traditional medicinal plants, some of which are linear homologous structures[4] related to the cytotoxic tanshinones.[5] The potential bioactivity of these new diterpenoid anthraquinones makes them attractive synthetic targets. In parallel to our communication[6] on the first total synthesis of umbrosone, the synthesis of aegyptinones A and B were reported.[7] We present in this paper a detailed account of the synthesis of **1**, employing a simple, flexible and convergent route,[1] suitable for the preparation of the other members of this group and their analogues.

Results and discussion

The *gem*-dimethylcyclohexane **7** (Scheme 1), obtained in excellent yield from Hagemann's ester **5**, *via* the known[8] cyclohexenone **6,** was transformed to the alkene **8** by a Wittig reaction. Hydroboration of the alkene **8**, followed by oxidation[1,9] with alkaline hydrogen peroxide gave an epimeric mixture of the alcohol **9**. Further oxidation of **9** with Jones' reagent[1,10] afforded an epimeric mixture of acids **11** as the major product. From the neutral fraction a crystalline γ-lactone **10** was isolated in a moderate yield, the structure of which is based upon spectral data and elemental analyses. The attempted hydrogenolysis of **10** under various conditions[11] failed to give the acids **11**. Cyclization of **11** with polyphosphoric acid gave a mixture of the epimeric ketones **12t** and **12c** in a ratio of *ca.* 80:20. As expected from earlier results[12] on related systems, the epimerisation of this mixture with sodium methoxide in methanol gave the stable *trans*-ketone **12t**, mp 118 °C as the only isolable product in a good yield. The assigned stereochemistry of **12t** has been recently confirmed[13] through its transformation to the known *trans*-1,2,3,4,4a,9,9a,10-octahydro-1,1-dimethyl-6-methoxyanthracene. The condensation of the ketone **12t** with methylmagnesium iodide followed by dehydration of the resulting alcohol gave the olefin **13**. This underwent smooth dehydrogenation leading to the tetrahydroanthracene ether **14**. Friedel–Crafts acylation of **14** gave the oxoether **15** in excellent yield, which on condensation with MeMgI afforded the alcohol **16**. Attempted deprotection of the *O*-methyl ether **16** with NaH–EtSH in boiling DMF[1,14] failed to give the desired phenolic alcohols. Demethylation of **15** with $AlCl_3$–EtSH[15] proceeded smoothly to afford the oxophenol **17**. This on condensation with an excess of MeMgI gave the relatively unstable phenolic alcohol **18**, which on oxidation with freshly prepared Fremy's salt[16] afforded umbrosone **1** in good yield.

In conclusion, the first synthesis of the rearranged diterpenoid umbrosone, has been realised through a simple convergent route.

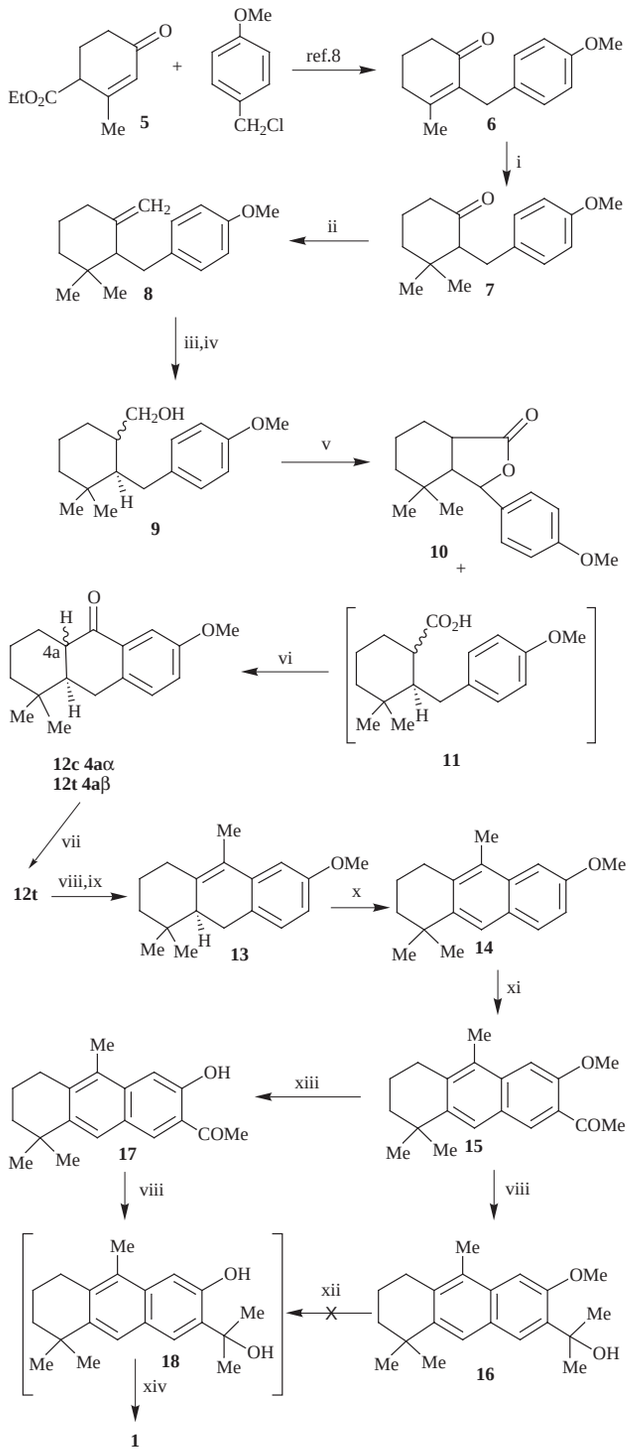
Experimental

Compounds described are all racemates. Unless otherwise stated, IR spectra of solids (KBr), and liquid (film) were recorded on a Perkin-Elmer model PE 298. UV spectra were recorded on a Beckman DU instrument; absorption coefficients, ε, were measured in $dm^3\ mol^{-1}\ cm^{-1}$. The ^1H NMR spectra were taken at 60 MHz on a Varian EM-360L and at 200 MHz on a Varian Gemini-200 with $SiMe_4$ as internal standard and *J* values given in Hz. Column chromatography was performed on neutral alumina [Brockmann Grade 1, of BDH (India)] or silica gel [Glaxo Laboratories (India) Ltd.]. Light petroleum refers to the fraction of bp 60–80 °C. Ether refers to diethyl ether.

2-(*p*-Methoxybenzyl)-3,3-dimethylcyclohexanone 7

This compound was prepared using a procedure described earlier.[1] To a stirred suspension of CuI (8.2 g, 43.15 mmol) in dry ether (30 cm^3) under N_2 at −25 °C, was added MeLi in dry ether (1.5 mol dm^{-3}, 58 cm^3, 78 mmol). The resulting yellow suspension was cooled to −50 °C and $BF_3{\cdot}Et_2O$ (6.1 g, 43.26 mmol) was added to it. After 5 min, the enone **6** (3.2 g, 14.33

† IUPAC name: 1,2,3,4,5,6-hexahydro-7-(2-hydroxy-2-propyl)-1,1,10-trimethylanthracene-5,6-dione.



Scheme 1 *Reagents and conditions*: i, $LiMe_2Cu$–BF_3, Et_2O (−50 °C, 1 h); ii, $Ph_3P^+Me^-$ + $tC_5H_{11}ONa$–toluene (60–65 °C, 3 h); iii, B_2H_6–THF; iv, NaOH–H_2O_2; v, Jones' reagent–CH_3COCH_3 (0 °C, 1 h); vi, PPA (85 °C, 2 h); vii, NaOMe–MeOH (rt, 3.5 h); viii, MeMgI–Et_2O; ix, $KHSO_4$ (140 °C, 30 min); x, Pd/C (10%)–xylene (reflux, 7 h); xi, CH_3COCl (1.5 eq.)–$AlCl_3$ (1.6 eq.)–CH_2Cl_2 (0 °C, 1 h, rt, overnight); xii, NaH–EtSH–DMF (heat 4 h); xiii, $AlCl_3$ (1.2 eq.)–EtSH (2.5 eq.)–CH_2Cl_2 (0 °C, 1 h, rt, overnight); xiv, Fremy's salt (2 eq.)–KH_2PO_4 (2 eq.)–MeOH (0 °C, 1 h, rt, overnight).

mmol) in dry ether (5 cm^3) was added dropwise during 15 min and the resulting suspension was stirred at −30 °C for 15 min. Additional BF_3·Et_2O (6.1 g, 43.26 mmol) was added and the mixture was stirred at −30 °C for 1 h. The reaction mixture was allowed to warm slowly to 0 °C and then quenched with saturated aqueous NH_4Cl. It was extracted with ether, washed with aqueous $Na_2S_2O_3$, water and dried (Na_2SO_4). Evaporation of solvent *in vacuo* afforded a thick yellow liquid which was chromatographed on neutral alumina (25 g). Elution with light petroleum afforded the ketone **7** as a light yellow liquid (2.88 g, 82%) (Found: C, 77.9; H, 8.9. $C_{16}H_{22}O_2$ requires C, 78.0; H, 9.0%), ν_{max}/cm^{-1} 1710 (CO); δ_H (60 MHz, CCl_4) 0.84 (3H, s, Me), 1.20 (3H, s, Me), 1.46–2.54 (7H, m, methylenes and methine), 2.75–3.25 (2H, m, $ArCH_2$), 3.81 (3H, s, ArOMe) and 6.83 (4H, AB_q, *J* 9, ArH).

2-(*p*-Methoxybenzyl)-3,3-dimethyl-1-methylenecyclohexane 8

A procedure described[1] earlier was adopted. A suspension of methyl(triphenyl)phosphonium iodide (4.5 g, 11.6 mmol) in toluene (3 cm^3) and a toluene solution of freshly prepared sodium 2,2-dimethylpropoxide (1.5 mol dm^{-3} solution, 7 cm^3) was stirred at room temperature (*ca*. 25 °C) for 20 min. The ketone **7** (1.2 g, 4.8 mmol) in toluene (4 cm^3) was added dropwise to the mixture after which it was refluxed for 3 h and then quenched with saturated aqueous NH_4Cl and extracted with ether. The extract was washed with aqueous NH_4Cl and water, dried (Na_2SO_4) and evaporated to yield an oil which was dissolved in light petroleum (100 cm^3) and immediately filtered through a short column of silica gel (10 g). MeI (3 cm^3) was added to the filtrate and left for 1 h at room temperature. The precipitated salt was filtered off and the filtrate was evaporated *in vacuo* to give the pure alkene **8** (950 mg, 80%). The analytical sample was prepared by evaporative distillation (bp 160–165 °C at 0.2 mm Hg) (Found: C, 83.3; H, 9.8. $C_{17}H_{24}O$ requires C, 83.6; H, 9.9%); ν_{max}/cm^{-1} 1635 (C=C); δ_H (60 MHz, CCl_4), 0.98 (6H, s, CMe_2), 0.98–2.75 (9H, m), 3.69 (3H, s, ArOMe), 4.22 (1H, br d, *J* 4, C=CH_2), 4.54 (1H, br d, *J* 4, C=CH_2) and 6.88 (4H, AB_q, *J* 9, ArH).

2-(*p*-Methoxybenzyl)-3,3-dimethyl-1-hydroxymethylcyclohexane 9

The procedure described earlier[1,9] was adopted. Diborane gas [prepared from $NaBH_4$ (3 g, 78.9 mmol), BF_3·Et_2O (9.9 cm^3, 80.7 mmol) in diglyme (15 cm^3)] was passed through a cold (0 °C) solution of the alkene **8** (3.25 g, 13.33 mmol) in dry THF (15 cm^3) for 22 h under a continuous slow stream of N_2. The mixture was kept in refrigeration overnight and then carefully decomposed with ice and transferred into aqueous NaOH (3 mol dm^{-3}; 60 cm^3). To a well stirred cooled mixture (*ca*. 0–10 °C) was added H_2O_2 (30% v/v; 50 cm^3) dropwise. Stirring was continued for an additional 30 min after which further H_2O_2 (25 cm^3) was added to the mixture and then set aside overnight. It was extracted with ether and the extract washed with water and evaporated to afford the epimeric mixture of the alcohol **9** (3.11 g, 89%) which was directly used for Jones' oxidation. The analytical sample was prepared by evaporative distillation, bp 180–185 °C (0.2 mmHg) (Found: C, 77.7; H, 9.8. $C_{17}H_{26}O_2$ requires C, 77.8; H, 10.0%); ν_{max}/cm^{-1} 3440 (br, OH); δ_H (60 MHz, CCl_4), 0.84 (3H, br s, Me), 1.01 (3H, br s, Me), 1.15–2.75 (11H, m), 3.28–3.65 (2H, m, –C*H*$_2$OH), 3.68 (3H, s, OMe) and 6.60–7.22 (m, 4H, ArH).

trans-1,2,3,4,9,9a-Hexahydro-1,1-dimethyl-6-methoxyanthracen-10(4a*H*)-one 12t

The procedure described[1] earlier was adopted. The cooled (5–10 °C) alcohol **9** (3.56 g, 13.7 mmol) in acetone (30 cm^3) was stirred with an excess of Jones' reagent[10] (5.5 cm^3, 15 mmol) for 1 h. After dilution with water, the mixture was extracted with ether. The ether extract was washed with aqueous KOH (0.36 mol dm^{-3}, 60 cm^3), water, dried (Na_2SO_4) and evaporated to give a thick yellow gum, which on chromatography over neutral alumina (25 g) and elution with ether–light petroleum (1:19) afforded 2-(1-hydroxy-*p*-methoxybenzyl-3,3-dimethylcyclohexane-1-carboxylic acid lactone **10** (780 mg, 21%), mp 84 °C (ether–light petroleum) (Found: C, 74.3; H, 7.9. $C_{17}H_{22}O_3$ requires C, 74.4; H, 8.1%); ν_{max}/cm^{-1}

1780 (γ-lactone); δ_H (60 MHz, CCl_4) 0.74 (3H, s, Me), 1.01 (3H, s, Me), 1.14–2.64 (8H, m, methylenes and methine), 3.74 (3H, s, ArOMe), 5.21 (1H, d, *J* 6, C*H*Ar) and 6.92 (4H, AB_q, *J* 9, ArH). The solution was acidified with HCl (6 mol dm^{-3}) and work-up afforded the acid **11** (2.82 g) as a thick light yellow glass [ν_{max}/cm^{-1} 1710 (CO_2H)], which was directly subjected to cyclization. To a well stirred homogeneous solution of PPA, prepared from P_2O_5 (40 g) and H_3PO_4 (20 cm^3), was added the acid **11** (2.82 g) and the mixture was heated at 80–85 °C for 2 h. The dark red mixture was cooled, decomposed with ice and extracted with ether. The ether extract was washed with aqueous NaOH (0.5 mol dm^{-3}, 20 cm^3), water, dried (Na_2SO_4) and then evaporated to dryness to afford a stereoisomeric mixture of ketones **12t** and **12c** in a ratio of *ca.* 8:2 (^{1}H NMR) δ_H (60 MHz, CCl_4) 0.99 and 1.08 (each CMe_2 for major isomer), 0.99 and 1.05 (each s, CMe_2 for the minor isomer). The stereoisomeric mixture of the ketones was treated with methanolic MeONa (0.1 mol dm^{-3}, 15 cm^3) at room temperature under N_2 for 3.5 h, diluted with water acidified with HCl (6 mol dm^{-3}) and worked up to give a solid which on chromatography over silica gel (25 g) using ether–light petroleum (1:19) afforded the *trans* ketone **12t** (1.8 g, 50%), mp 118 °C (Found: C, 78.9; H, 8.5. $C_{17}H_{22}O_2$ requires C, 79.0; H, 8.6%); ν_{max}/cm^{-1} 1685 (CO); δ_H (60 MHz, CCl_4) 0.99 (3H, s, Me), 1.08 (3H, s, Me), 1.2–2.8 (10H, m), 3.82 (3H, s, OMe) and 6.74–7.4 (3H, m, ArH).

6-Methoxy-1,1,10-trimethyl-1,2,3,4,9,9a-hexahydroanthracene 13

To an ice-cooled stirred solution of MeMgI, prepared from Mg (240 mg, 10 mg atom) in ether (30 cm^3), a solution of ketone **12t** (1.82 g, 7.05 mmol) in ether (20 cm^3) was added dropwise. After the addition was completed stirring was continued for 1 h at room temperature and finally refluxed for 1 h. The chilled reaction mixture was decomposed with aqueous NH_4Cl and extracted with ether. Work-up of the extract afforded the respective crude alcohol which was directly subjected to dehydration by heating with fused $KHSO_4$ (2.1 g, 15.27 mmol) at 140–160 °C for 45 min in a short-path distillation flask. The resulting mixture on evaporative distillation gave the olefin **13** as a colourless oil (1.12 g, 62%) bp 135–138 °C (0.12 mmHg) (Found: C, 84.2; H, 9.4. $C_{18}H_{24}O$ requires C, 84.3; H, 9.4%); ν_{max}/cm^{-1} 1635 (C=C); δ_H (60 MHz, CCl_4) 0.62 (3H, s, Me), 1.01 (3H, s, Me), 1.41–1.92 (7H, m), 2.01 (3H, s, C=C–Me), 2.62–3.12 (2H, m, $ArCH_2$), 3.72 (3H, s, ArOMe) and 6.4–7.01 (3H, m, ArH).

6-Methoxy-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracene 14

A solution of the olefin **13** (820 mg, 3.2 mmol) in dry xylene (20 cm^3) was refluxed for 7 h with Pd/C (110 mg, 10%). The catalyst was filtered off from the cooled reaction mixture and washed with ether. The combined filtrate and washings were evaporated and the residual light yellow solid on chromatography over alumina (30 g) using ether–light petroleum as eluent afforded the tetrahydroanthracene ether **14** as a colourless solid (1.08 g, 60%) mp 110 °C (ether–light petroleum) (Found: 84.9; H, 8.6. $C_{18}H_{22}O$ requires C, 85.0; H, 8.7%); ν_{max}/cm^{-1} 1645, 1610; δ_H (200 MHz, $CDCl_3$) 1.38 (6H, s, CMe_2), 1.5–1.92 (4H, m, CH_2), 2.52 (3H, s, ArMe), 2.58–2.92 (2H, m, $ArCH_2$), 3.91 (3H, s, ArOMe), 7.04 (1H, dd, *J* 8, 2-ArH), 7.31 (1H, d, *J* 2, ArH) and 7.62–7.68 (2H, m, ArH).

7-Acetyl-6-methoxy-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracene 15

Anhydrous $AlCl_3$ (360 mg, 2.69 mmol) was added to a stirred solution of the ether **14** (400 mg, 1.57 mmol) in dry CH_2Cl_2 (5 cm^3) and CH_3COCl (0.4 cm^3), with cooling in an ice-bath. The mixture was stirred for an additional 1 h and left overnight at room temperature. It was then poured into HCl (6 mol dm^{-3}) and extracted with ether. Work-up of the extracts afforded the crude product which was purified by chromatography over alumina (20 g) and eluted with ether–light petroleum (1:10) to give the oxoether **15** as light yellow needles (390 mg, 83%) mp 91 °C (ether–light petroleum) (Found: C, 80.9; H, 8.0. $C_{20}H_{24}O_2$ requires C, 81.0; H, 8.6%); ν_{max}/cm^{-1} 1680 (CO); δ_H (200 MHz, $CDCl_3$) 1.34 (6H, s, CMe_2), 1.62–2.34 (4H, m, CH_2), 2.48 (3H, s, ArMe), 2.70 (3H, s, COMe), 2.84–3.24 (3H, m, $ArCH_2$), 3.99 (2H, s, ArOMe), 7.20 (1H, s, ArH), 7.72 (1H, s, ArH) and 8.14 (1H, s, ArH).

1,2,3,4-Tetrahydro-7-(1-hydroxy-1-methylethyl)-6-methoxy-1,1,10-trimethylanthracene 16

To an ice-cold stirred solution of MeMgI, prepared from Mg (36 mg, 1.5 g atom) in ether (15 cm^3), a solution of the oxoether **15** (207 mg, 0.7 mmol) in ether (10 cm^3) was added dropwise. The stirring was continued for an additional 1 h and refluxed for 30 min. The chilled reaction mixture was decomposed with aqueous NH_4Cl and extracted with ether. Work-up followed by filtration through a short column of silica gel using ether–light petroleum (1:10) as the eluent afforded the alcohol **16** as a thick colourless liquid (180 mg, 82%) (Found: C, 80.6; H, 9.0. $C_{21}H_{28}O_2$ requires C, 80.7; H, 9.0%); ν_{max}/cm^{-1} 3300 (br OH); δ_H (60 MHz, CCl_4) 1.26 (6H, s, CMe_2), 1.31 (6H, s, C(*Me*$_2$)OH), 1.0–3.1 (6H, m), 2.48 (3H, s, ArMe), 3.99 (3H, s, ArOMe), 7.14 (1H, br s, ArH) and 7.52–7.64 (2H, m, ArH).

7-Acetyl-6-hydroxy-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracene 17

The procedure[1] described earlier was adopted. Anhydrous $AlCl_3$ (160 mg, 1.2 mmol) was added to a stirred solution of the oxoether **15** (300 mg, 1 mmol) and EtSH (1.4 cm^3) in CH_2Cl_2 (12 cm^3) with cooling in an ice-bath. The mixture was stirred at 0 °C for an additional 1 h and then left overnight. It was then poured into aqueous HCl (6 mol dm^{-3}) and extracted with ether. Work-up of the extract afforded the crude oxophenol **17**. The residue was chromatographed on silica gel (15 g) and eluted with ether–light petroleum (1:5 to 1:3) to afford the pure oxophenol **17** (205 mg, 68%) as a light yellow crystalline solid, mp 210 °C (ether–light petroleum) (Found: C, 80.6; H, 7.7. $C_{19}H_{22}O$ requires C, 80.8; H, 7.9%); ν_{max}/cm^{-1} 3150 (phenolic OH), 1660 (CO) and 1600; δ_H (200 MHz, $CDCl_3$) 1.35 (6H, s, CMe_2), 1.45–1.82 (4H, m, CH_2), 2.45 (3H, s, ArMe), 2.77 (3H, s, COMe), 2.81–2.89 (2H, m, $ArCH_2$), 7.39 (1H, s, ArH), 7.70 (1H, s, ArH), 8.28 (1H, s, ArH) and 11.46 (1H, s, OH).

Umbrosone 1

To an ice-cold stirred solution of MeMgI, prepared from Mg (100 mg, 4.16 mg atom) in ether (15 cm^3), a solution of the oxophenol **17** (105 mg, 0.35 mmol) in ether (10 cm^3) was added dropwise. The resulting white suspension was refluxed for 2 h. The chilled reaction mixture was decomposed with aqueous NH_4Cl and extracted with ether. Work-up of the extract gave the crude phenolic alcohol (110 mg), [ν_{max}/cm^{-1} 3300 (phenolic OH), 3150 (OH) and 1600] which was dissolved in anhydrous MeOH (16 cm^3) and cooled in an ice-bath. To the cooled stirred solution, a freshly prepared solution of Fremy's salt (240 mg, 0.85 mmol) and $KHPO_4$ (60 mg, 0.44 mmol) in H_2O (16 cm^3) was added dropwise. The resulting violet solution was stirred at room temperature for 14 h. The reaction mixture was diluted with water and extracted with ether. Work-up of the extract afforded a brown solid which was carefully chromatographed on silica gel (10 g) and eluted as follows: (i) ether–light petroleum (1–1.5 : 8.5–9, 30 cm^3) gave the unchanged **18** (15 mg); (ii) ether–light petroleum 2:3, 60 cm^3) afforded umbrosone **1** as a dark red solid (75 mg, 67%) mp 160–162 °C. Recrystallization from ether–light petroleum gave **1** as a shining dark red needles, mp 163 °C (lit.[2] mp 163–165 °C) (Found: C, 76.8; H, 7.7.

$C_{20}H_{24}O_3$ requires C, 76.9; H, 7.7%); ν_{max} ($CHCl_3$)/cm^{-1} 3510, 1680, 1650 and 1580 [lit.[2] ν_{max} ($CHCl_3$)/cm^{-1} 3520, 1680, 1650 and 1580]; λ_{max} (EtOH)/nm 431 (log ε 3.48), 364 (log ε 3.56) and 270 (log ε 4.47) [lit.[2] λ_{max} (MeOH)/nm 430 (log ε 3.38), 366 (log ε 3.58) and 268 (log ε 4.45); δ_H (200 MHz, $CDCl_3$) 1.31 (6H, s, CMe_2), 1.54 (6H, s, CMe_2), 1.64 (2H, m, CH_2), 1.84 (2H, m, CH_2), 2.57 (3H, s, ArMe), 2.68 (2H, t, *J* 6, CH_2), 3.20 (1H, br s, OH), 7.17 (1H, s, ArH) and 7.39 (1H, s, ArH) [lit.[2] δ_H (100.6 MHz, $CDCl_3$), 1.32 (6H, s, CMe_2), 1.55 (6H, s, CMe_2), 1.65 (2H, m, CH_2), 1.85 (2H, m, CH_2), 2.58 (3H, s, ArMe), 2.70 (2H, t, *J* 6, CH_2), 3.20 (1H, br s, OH), 7.18 (1H, s, ArH and 7.41 (1H, s, ArH).

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