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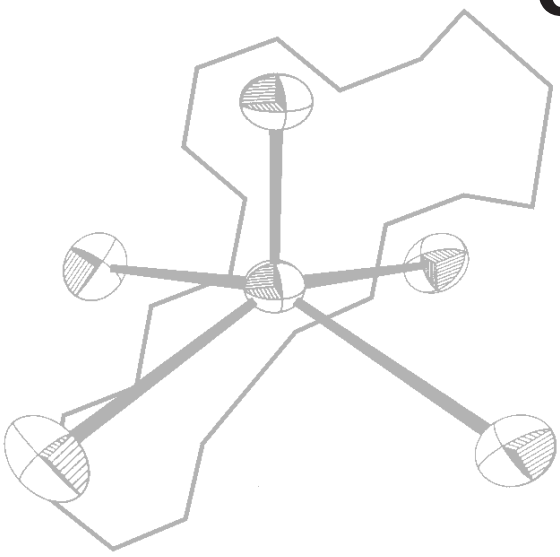

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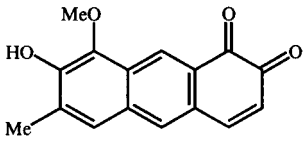
Synthesis of Hallachrome

Donald W. Cameron,[A,B] *D. Ross Coller*[A] *and Clinton A. McDonald*[A]

[A] School of Chemistry, The University of Melbourne, Parkville, Vic. 3052.
[B] Author to whom correspondence should be addressed.

Hallachrome (1), the only known example of a naturally occurring 1,2-anthraquinone, has been synthesized by successive cycloadditions involving the dienophile (8) with the dienes (7) and (12). Synthetic intermediates (18) and (6) are known derivatives of natural hallachrome.

Hallachrome (1), the only known example of a naturally occurring 1,2-anthraquinone, has been isolated from the seaworms *Halla parthenopeia*[1,2] and *Lumbriconereis impatiens.*[2,3] It poses several synthetic challenges. The specific substitution patterns of the respective outer rings have to be assembled regioselectively, despite being separated by an unsubstituted central ring. Furthermore, any precursor based on a parent 1,2,7,8-tetraoxy anthracene skeleton, such as (2), requires not only that selective *O*-methylation should involve an α rather than a β position but that it should proceed regioselectively so as to affect only the ring containing the *C*-methyl group.



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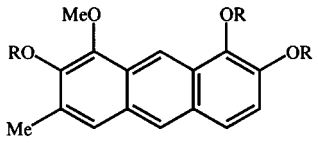
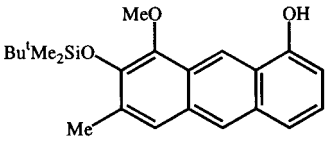


(2) R = H
(3) R = Ac



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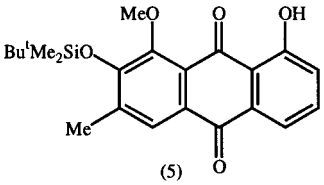

(5)

In 1985, Comber and Sargent[4] published the first synthesis of a hallachrome derivative, the leucotriacetate (3). This involved formation of the tricyclic skeleton by intramolecular Friedel–Crafts acylation of an appropriate benzylbenzoic acid derivative, and reduction of an intermediate anthrone. In 1993 Krohn and Khanbabaee synthesized hallachrome (1) itself, for the first time.[5] Their approach involved molybdenum-catalysed oxygenation of the anthracene (4), generated by reduction of the anthraquinone (5). The latter system was obtained by cycloaddition chemistry.

This paper describes alternative access to (1) via the corresponding anthraquinone (6), in which all of the substituents of the two outer rings are correctly positioned. It was hoped that (6) could be deoxygenated to (2), thereby giving the corresponding quinone (1) on final oxidation.

Cycloaddition of the 1,1,2-trioxy butadiene (7)[6] to trichloro benzoquinone (8) followed by aromatization of the crude cycloadduct with sodium acetate in methanol gave the naphthoquinone (9) efficiently. As has been observed here previously,[7] the quinone (8) undergoes addition exclusively to its monochloro side, generating a dichloro naphthoquinonoid dienophile for subsequent reaction. The ^{1}H n.m.r. spectrum of (9) showed β- and α-hydroxy resonances at δ 6.33 and 11.78 respectively, and a new aromatic singlet at δ 7.63. Selective protection of the β-hydroxy group then resulted from heating in acetic anhydride, readily giving the monoacetate (10). A new acetate resonance (δ 2.41) replaced the β-hydroxy signal of (9) and an α-hydroxy resonance was retained, at δ 11.72. The acetate (10) was then methylated in high yield, with methyl iodide/silver(I) oxide. The ^{1}H n.m.r. spectrum of the product (11) showed appropriate *C*-methyl, acetate and methoxy resonances at δ 2.32, 2.41 and 3.89 respectively.

While the position of the α-methoxy group of (11) has obvious structural parallel with the methoxy group of hallachrome (1), it also was hoped to exert a controlling electronic influence, in the desired regiochemical sense, on attachment of the third ring. Thus reaction between (11) and the neat diene (12)[8] proceeded largely through the cycloadduct (13) which, on being aromatized with nucleophilic attack of sodium acetate, gave largely the desired anthraquinone (14) (52%). Formation of the latter involved the expected acetyl-group migration from an α- to a β-oxy group, giving a chelated α-hydroxy substituent in the product.[7] The ^{1}H n.m.r. spectrum of the product, however, showed two α-hydroxy signals at δ 13.02 and 12.65 in an intensity ratio of 9 : 1. This suggested that the desired product (14) was contaminated with its regioisomer (15), consistent with which the hydroxy proton of the major isomer (14) was the more deshielded, being *peri* to a methoxy carbonyl system.[9]

While the overall yield of this mixture was satisfactory, the two isomers (14) and (15) proved chromatographically inseparable. However, repeated recrystallization of a sample enabled isolation of pure (14). The aromatic region of its ^{1}H n.m.r. spectrum was consistent with the assigned structure,

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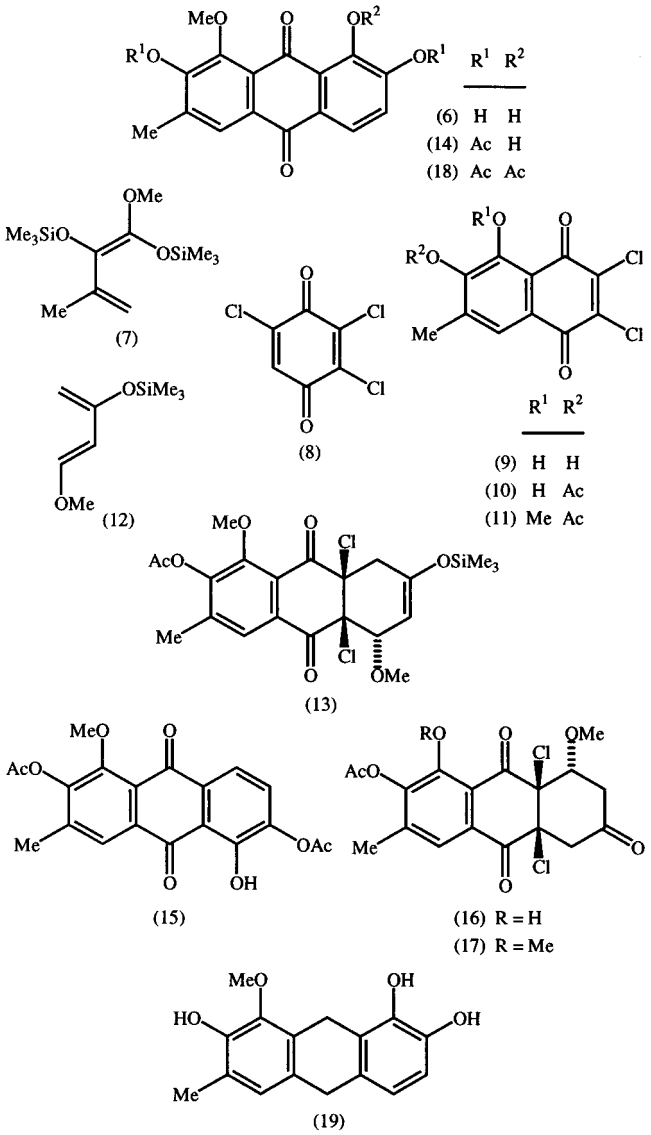
showing two *ortho*-coupled aromatic doublets (δ 7.43, 7.81, *J* 8.3 Hz) and a singlet (δ 8.04).

Confirmation that the cycloaddition to (11) had indeed involved major control by the α-methoxy group, without significant perturbation from its two adjoining β-substituents, was provided by parallel chemistry involving its α-hydroxy parent (10). This was expected to afford regiocontrol in the opposite sense. Reaction between (10) and the diene (12) gave a single hydrolysed adduct (16) (65%). This was *O*-methylated with methyl iodide/silver(I) oxide and the product (17), without purification, was then treated with sodium acetate in acetic acid. The resulting anthraquinone (15) was thereby obtained efficiently as the only regioisomeric outcome, within the limits of spectroscopic detection. The aromatic region of its ^{1}H n.m.r. spectrum showed two *ortho*-coupled doublets (δ 7.45, 7.80, *J* 8.2 Hz) and a singlet (δ 8.04), indistinguishable from the spectrum of the minor isomer obtained from cycloaddition of (11).

With confirmation thereby obtained, of the desired anthraquinone (14) being the major isomer from the latter cycloaddition, its mixture with (15) was acetylated with acetic anhydride/pyridine. Pleasingly, the regioisomeric mixture of acetates obtained was chromatographically separable, allowing isolation of the major component (18) (85%). This triacetate is a reported transformation product of natural hallachrome (1).[2] Physical data for synthesized (18) were in good agreement with those cited for the naturally derived material. Treatment of (18) with methanolic sodium methoxide gave the triol (6), whose data also agreed with those for hallachrome-derived material.[2]



Conversion of (6) into hallachrome (1) itself required reduction to at least the anthracene level and reoxidation to give the 1,2-quinone. Controlled reduction of (6) proved difficult. A conventional approach via the corresponding anthrone was envisaged but no stable anthrone could be obtained from (6) under several standard reducing conditions. The most effective involved hydrogenating (6) in ethanol over Adams catalyst, such as has been used previously to form an anthrone from the natural anthraquinone catenarin.[10] While this gave no coherent outcome from (6), addition of hydrochloric acid to the hydrogenating mixture was found to afford far more extensive reduction than for analogous treatment of catenarin. The result was a nearly colourless solution possessing very little chromophoric character and showing only a broad electronic absorption band at 260 nm. Attempts to isolate a major reduction product from this mixture were unsuccessful, owing to considerable associated darkening. However, deliberate exposure of a chloroform solution of the material to air resulted in formation of a red colouring matter, whose spectroscopic characteristics pleasingly proved to be indistinguishable from those for hallachrome (1).[2,3] It was thereby obtained from (6) in a limited but acceptable yield of 34%.

While the hydrogenation product could not be characterized as such, owing to the onset of oxidation, its lack of chromophoric character seems compatible with over-reduction of (6) having proceeded, possibly as far as the 9,10-dihydroanthracene (19), which then oxidized to (1) in air. Carrying out the reduction under milder conditions, with a view to defining the process more effectively and reducing the extent of side-reaction, gave only mixtures of products, none of which could be made to serve as a basis for conversion into hallachrome.

Experimental

General

Melting points were determined on a Kofler hot stage and are uncorrected. Microanalyses were carried out by National Analytical Laboratories, Melbourne, or by Chemical and Microanalytical Services, Geelong. Electronic spectra were recorded in methanol containing 1% formic acid unless otherwise stated; a Perkin–Elmer Lambda 2 spectrophotometer was used. Infrared spectra were recorded as potassium bromide disks, a Perkin–Elmer 983G grating spectrophotometer being used. Proton nuclear magnetic resonance (^{1}H n.m.r.) spectra were recorded on a Varian Unity 300 spectrometer. The solvent was (D)chloroform unless otherwise stated. High- and low-resolution mass spectra were recorded with either a V.G. Micromass 7070F or a JEOL AX-505H instrument at 70 eV. The mass of each ion is given followed by its relative intensity. In general, only peaks greater than 20% are quoted. Flash chromatography was carried out by using Merck silica No. 9385 containing 2% oxalic acid. Thin-layer chromatography

(t.l.c.) was carried out on glass plates coated with Merck silica gel containing 2% oxalic acid. The separated compounds were recovered by using ethyl acetate or dichloromethane, washing the extract twice with water and then drying it before evaporation. All solvents used were of analytical reagent (A.R.) grade or were redistilled prior to use. Dried solvents were used for all cycloaddition reactions and manipulations of cycloadducts. Petrol refers to the fraction boiling in the range 60–80°. Organic extracts were generally dried over magnesium sulfate before evaporation at reduced pressure.

2,3-Dichloro-5,6-dihydroxy-7-methyl-1,4-naphthoquinone (9)

Diene (7)[6] (6.00 g) was added to a stirred solution of quinone (8) (3.90 g) in dichloromethane (15 cm^3). After 1 h, acetic acid (5 cm^3) was added followed 5 min later by sodium acetate (500 mg) and methanol (50 cm^3). The solution was stirred for 1 h, then acidified with aqueous hydrochloric acid (1 M, 250 cm^3). The suspension was extracted with ethyl acetate (2×250 cm^3), and the combined extracts were washed well with water, dried and evaported. Flash chromatography eluting with dichloromethane afforded a major red band consisting of the *naphthoquinone* (9) (4.56 g, 91%). Recrystallization from ethyl acetate/petrol gave (9) as red needles, m.p. 205–206° (Found: C, 48.2; H, 2.5. $C_{11}H_6Cl_2O_4$ requires C, 48.4; H, 2.2%). λ_{max} (log ε) ($CHCl_3$) 279, 303, 453 nm (4.23, 4.23, 3.83). ν_{max} 3418, 1633, 1564 cm^{-1}. δ 2.36, s, Me; 6.33, s, 6-OH; 7.63, s, H 8; 11.78, s, 5-OH. *m/z* 276 (M[$^{37}Cl_2$], 10%), 274 (M[$^{37}Cl^{35}Cl$], 63), 272 (M[$^{35}Cl_2$], 96), 239 (35), 237 (100), 209 (30), 89 (21), 18 (71).

6-Acetoxy-2,3-dichloro-5-hydroxy-7-methyl-1,4-naphthoquinone (10)

Quinone (9) (150 mg) was dissolved in acetic anhydride (10 cm^3) and heated to 100° for 20 h. The solvent was removed and the residue was subjected to flash chromatography eluting with dichloromethane. The major orange band afforded the *naphthoquinone* (10) (170 mg, 98%) as an orange solid, which was recrystallized from ethanol as orange needles, m.p. 168–170° (Found: C, 49.5; H, 2.5%; $M^{+\bullet}$ 313.9749. $C_{13}H_8Cl_2O_5$ requires C, 49.6; H, 2.6%; $M^{+\bullet}$ 313.9749). λ_{max} (log ε) ($CHCl_3$) 253, 297, 438 nm (4.20, 4.32, 4.13). ν_{max} 1772, 1680, 1642, 1577 cm^{-1}. δ 2.33, s, Me; 2.41, s, OAc; 7.65, s, H 8; 11.72, s, OH. *m/z* 316 (M[$^{37}Cl^{35}Cl$], 0.7%), 314 (M[$^{35}Cl_2$], 1.1), 274 (66), 272 (100), 237 (43), 43 (67).

6-Acetoxy-2,3-dichloro-5-methoxy-7-methyl-1,4-naphthoquinone (11)

Silver(I) oxide (200 mg) and methyl iodide (3 cm^3) were added to a solution of quinone (10) (100 mg) in dichloromethane (30 cm^3) and the suspension was stirred away from light for 24 h. The mixture was then filtered and the solvent was removed from the filtrate to give the *naphthoquinone* (11) (102 mg, 98%) as a yellow solid. Recrystallization from ethanol gave (11) as yellow needles, m.p. 160–162° (Found: C, 51.2; H, 3.1%; $M^{+\bullet}$ 327.9905. $C_{14}H_{10}Cl_2O_5$ requires C, 51.1; H, 3.1%; $M^{+\bullet}$ 327.9905). λ_{max} (log ε) ($CHCl_3$) 253, 261, 279sh, 290, 370 nm (4.53, 4.54, 4.53, 4.63, 4.11). ν_{max} 1760, 1684, 1580 cm^{-1}. δ 2.32, s, Me; 2.41, s, OAc; 3.89, s, OMe; 7.91, s, H 8. *m/z* 330 (M[$^{37}Cl^{35}Cl$], 1.3%), 328 (M[$^{35}Cl_2$], 1.4), 288 (66), 286 (100), 270 (34), 268 (51), 240 (26).

2,7-Diacetoxy-8-hydroxy-1-methoxy-3-methyl-9,10-anthraquinone (14)

A solution of quinone (11) (50 mg) in diene (12) (2 cm^3) was stirred at room temperature for 2 days. The bulk of the residual diene was removed under high vacuum and to the residue was added sodium acetate (200 mg) in acetic acid (50 cm^3). The solution was heated at 100° for 2 h, then the solvent was evaporated. Flash chromatography eluting with dichloromethane gave a yellow solid (30 mg, 52%) consisting of two isomers (9 : 1). δ (major isomer) (14) 2.35, s, Me; 2.40, 2.42, s, s, 2×OAc; 3.93, s, OMe; 7.43, d, *J* 8.3 Hz, H 6; 7.81, d, *J* 8.3 Hz, H 5; 8.04, s, H 4; 13.02, s, OH. δ (minor isomer) (15) 2.35, s, Me; 2.40, 2.42, s, s, 2×OAc; 3.93, s, OMe; 7.45, d, *J* 8.3 Hz, H 7; 7.80, d, *J* 8.3 Hz, H 8; 8.04, s, H 4; 12.65, s, OH. Repeated recrystallization of a small sample of this mixture from ethyl acetate/petrol gave the *2,7-diacetoxy-9,10-anthraquinone* (14), m.p. 196–198° (Found: C, 62.2; H, 3.8. $C_{20}H_{16}O_8$ requires C, 62.5; H, 4.2%). λ_{max} (log ε) 261, 284, 390 nm (4.56, 4.05, 3.88). ν_{max} 1765, 1752, 1666, 1636 cm^{-1}. *m/z* 384 (M, 1.4%), 342 (55), 300 (100), 282 (93).

(4α,4aβ,9aβ)-6-Acetoxy-4a,9a-dichloro-5-hydroxy-4-methoxy-7-methyl-3,4,4a,9a-tetrahydroanthracene-2,9,10(1H)-trione (16)

Diene (12) (320 mg) was added to a solution of quinone (10) (100 mg) in benzene (5 cm^3) and the solution was heated at reflux for 2 days. The solvent was evaporated and the oily residue was subjected to preparative t.l.c. in toluene/ethyl acetate (9 : 1). The major pale yellow band (R_F 0.4; purple staining to ammonia) was isolated to yield the *anthracenetrione* (16) (86 mg, 65%), which was recrystallized from ethyl acetate/petrol as colourless needles, m.p. dec. >209° (Found: C, 52.4; H, 3.6. $C_{18}H_{16}Cl_2O_7$ requires C, 52.1; H, 3.9%). λ_{max} (log ε) ($CHCl_3$) 251, 292, 358 nm (4.30, 3.83, 3.76). ν_{max} 1766, 1733, 1648 cm^{-1}. δ 2.33, s, Me; 2.40, s, OAc; 2.79, ddd, *J* 16.1, 2.7, 2.0 Hz, H 3α; 2.97, s, OMe; 3.07, d, *J* 15.1 Hz, H 1β; 3.14, dd, *J* 16.1, 3.2 Hz, H 3β; 3.72, dd, *J* 15.1, 2.0 Hz, H 1α; 4.17, dd, *J* 3.2, 2.7 Hz, H 4; 7.51, s, H 8; 11.80, s, OH. *m/z* 418 (M[$^{37}Cl_2$], 0.2%), 416 (M[$^{37}Cl^{35}Cl$], 0.9), 414 (M[$^{35}Cl_2$], 1.3), 372 (29), 279 (48), 270 (27), 119 (35), 85 (100).

2,6-Diacetoxy-5-hydroxy-1-methoxy-3-methyl-9,10-anthraquinone (15)

Trione (16) (20 mg) in dichloromethane was stirred with methyl iodide (5 cm^3) and silver(I) oxide (100 mg) for 24 h. The suspension was filtered and the filtrate was evaporated. The residue was treated with sodium acetate (50 mg) in acetic acid (10 cm^3) at 100° for 1 h, and then the solvent was evaporated. The crude solid was subjected to preparative t.l.c. eluting with toluene/ethyl acetate (9 : 1). Isolation of the major yellow band (R_F 0.6) gave the *2,6-diacetoxy-9,10-anthraquinone* (15) as a yellow solid. Recrystallization from ethyl acetate/petrol afforded (15) as yellow needles, m.p. 211–214° (Found: C, 62.4; H, 4.2. $C_{20}H_{16}O_8$ requires C, 62.5; H, 4.2%). λ_{max} (log ε) 259, 286sh, 390 nm (4.64. 4.13, 3.96). ν_{max} 1760, 1669, 1636 cm^{-1}. δ 2.35, s, Me; 2.40, 2.42, s, s, 2×OAc; 3.93, s, OMe; 7.45, d, *J* 8.2 Hz, H 7; 7.80, d, *J* 8.2 Hz, H 8; 8.04, s, H 4; 12.65, s, OH. *m/z* 384 (M, 3%), 341 (31), 299 (74), 298 (24), 282 (25), 281 (100), 254 (33), 115 (32).

2,7,8-Triacetoxy-1-methoxy-3-methyl-9,10-anthraquinone (18)

The crude mixture of quinones (14)/(15) (9 : 1, 30 mg), acetic anhydride (10 cm^3) and pyridine (2 cm^3) were heated together at 80° for 4 h. The solution was poured into dilute hydrochloric acid (1 M, 250 cm^3) and extracted with ethyl acetate (2×100 cm^3). The combined extracts were washed with dilute hydrochloric acid (3×100 cm^3) and with water (2×100 cm^3), dried and evaporated. Preparative t.l.c. of the crude residue using toluene/ethyl acetate (9 : 1) gave a major pale yellow band (R_F 0.5) which afforded the triacetoxy quinone (18) (28 mg, 85%). Recrystallization from ethyl acetate/petrol gave (18) as yellow laths, m.p. 203–205° (Found: C, 61.9; H, 4.2. Calc. for $C_{22}H_{18}O_9$: C, 62.0; H, 4.3%). λ_{max} (log ε) 261, 340 nm (4.56, 3.75). ν_{max} 1766, 1672 cm^{-1}. δ 2.33, s, Me; 2.36, 2.40, 2.46, s, s, s, 3×OAc; 3.87, s, OMe; 7.57, d, *J* 8.4, Hz, H 6; 7.97, s, H 4; 8.22, d, *J* 8.4 Hz, H 5. *m/z* 426 (M, 0.5%), 383 (21), 342 (35), 300 (100), 71 (24), 69 (30), 56 (41), 53 (30).

Reported[2] for (18) derived from natural hallachrome, m.p. 206–208°. δ 2.29, s, Me; 2.33, 2.37, 2.42, s, s, s, 3×OAc; 3.88, s, OMe; 7.55, d, *J* 8.6 Hz, H 6; 7.96, s, H 4; 8.22, d, *J* 8.6 Hz, H 5.

2,7,8-Trihydroxy-1-methoxy-3-methyl-9,10-anthraquinone (6)

Quinone (18) (50 mg) was dissolved in methanol (25 cm^3) and treated with sodium methoxide (200 mg) for 15 min. The solution was acidified with dilute hydrochloric acid, poured into water and extracted with ethyl acetate (2×100 cm^3). The combined extracts were washed with water, dried and evaporated to give the trihydroxy quinone (6) (32 mg, 97%) as an orange solid. Sublimation (180°/1×10^{-4} Torr) gave (6) as orange microneedles, m.p. 259–261° (Found: $M^{+\bullet}$ 300.0626. Calc. for $C_{16}H_{12}O_6$: $M^{+\bullet}$ 300.0634). λ_{max} (log ε) 278, 358sh, 421 nm (4.49, 3.68, 3.81). ν_{max} 3378, 1630 cm^{-1}. δ [$(CD_3)_2CO$] 2.37, s, Me; 2.81, br s, 3×OH; 3.94, s, OMe; 7.23, d, *J* 8.2 Hz, H 6; 7.68, d, *J* 8.2 Hz, H 5; 7.89, s, H 4. *m/z* 300 (M, 100%), 283 (20), 282 (92), 257 (23), 254 (51).

Reported[2] for (6) derived from natural hallachrome, m.p. 256–258°. *m/z* 300 (M, 100%), 283 (28), 282 (98), 271 (13), 257 (30), 254 (66), 229 (15).

7-Hydroxy-8-methoxy-6-methyl-1,2-anthraquinone (Hallachrome) (1)

Quinone (6) (10 mg) was dissolved in ethanol (5 cm^3), and Adams catalyst (10 mg) and concentrated hydrochloric acid (10 drops) were added. The suspension was stirred under an atmosphere of hydrogen for 3 h. It was then filtered, the filtrate evaporated, and the residue dissolved in chloroform. The clear solution was stirred in air for 24 h and then evaporated. Preparative t.l.c. eluting with toluene/ethyl acetate (7 : 3) gave a major red band (R_F 0.5) which afforded hallachrome (1) (3 mg, 34%) as a red solid. Recrystallization from chloroform/petrol gave (1) as red microneedles, m.p. 221–223° (Found: $M^{+\bullet}$ 268.0733. Calc. for $C_{16}H_{12}O_4$: $M^{+\bullet}$ 268.0735). λ_{max} (log ε) (MeOH) 249, 312, 497 nm (4.61, 4.47, 4.30). ν_{max} 3404, 1695, 1650, 1612, 1581 cm^{-1}. δ 2.47, s, Me; 4.01, s, OMe; 6.16, br s, 7-OH; 6.47, d, *J* 10.0 Hz, H 3; 7.46, s, H 5; 7.55, d, *J* 10.0 Hz, H 4; 7.64, s, H 10; 8.74, s, H 9. *m/z* 268 (M, 16%), 240 (48), 225 (60), 197 (27), 111 (21), 97 (35), 95 (27), 85 (30), 83 (43), 81 (30), 71 (54), 69 (59), 67 (24), 56 (100).

Reported[2] for natural hallachrome, m.p. 224–226° (dec.). λ_{max} (log ε) (MeOH) 250, 312, 500 nm (4.51, 4.52, 3.75). ν_{max} 3300, 1695, 1652, 1610, 1580 cm^{-1}.

Reported[3] for natural hallachrome, δ ($CDCl_3$) 2.47, s, Me; 4.01, s, OMe; 6.19, br s, 7-OH; 6.47, d, *J* 10.0 Hz, H 3; 7.46, s, H 5; 7.55, d, *J* 10.0 Hz, H 4; 7.64, s, H 10; 8.73, s, H 9.

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