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Periodate Oxidation of Phenols. XV.* Oxidation of 3,5-Dimethyl- and 2,5-Dimethyl-4-hydroxybenzyl Alcohols

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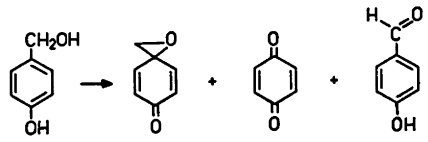
Oxidation of 4-hydroxy-3,5-dimethylbenzyl alcohol (*5*) in aqueous acetic acid with periodate gave 2,6-dimethyl-1,4-benzoquinone (*6*), 4-hydroxy-3,5-dimethylbenzaldehyde (*7*), and 6-acetoxy-4-hydroxymethyl-2,6-dimethyl-2,4-cyclohexadienone (*8*), whereas only *6* and *7* were obtained when bismuthate was used as oxidant. Preferential *para* oxidation by the latter reagent was also observed when mesitol was used as substrate.

When *5* was oxidized with periodate in H_2O/EtOH (60:5), a Diels-Alder adduct (*20*) of *o*-quinol *21* with simultaneously formed *p*-quinone *6* was obtained, in addition to *o*-quinol dimer *22* and aldehyde *7*. Under similar conditions, 4-hydroxy-2,5-dimethylbenzyl alcohol (*25*) yielded the corresponding *p*-benzoquinone *26* and aldehyde *27*, as well as the dimeric *o*-quinol *29* which in the solid state had the structure of a cyclic hemiketal (*29a*).

In a preceding paper,[1] oxidation of 4-hydroxybenzyl alcohol (*1*) with sodium periodate in 80 % aqueous acetic acid was reported to give



1 *2* *3* *4*

p-benzoquinone (*3*) and 4-hydroxybenzaldehyde (*4*), as well as considerable amounts of polymeric material. If sodium bismuthate was used as oxidant, the spiro(oxirane-2,5-cyclohexadienone) *2* was formed in addition to *3* and *4*.

In the present study the behaviour of 4-hydroxy-3,5-dimethylbenzyl alcohol (*5*) towards the two oxidants has been examined using aqueous acetic acid as solvent. Unlike the unsubstituted 4-hydroxybenzyl alcohol, *5* failed to give a spiro compound on treatment with bismuthate, but certain differences in the ratio of *ortho* and *para* oxidation products formed by periodate and bismuthate, respectively, were observed. For comparison, the oxidation of 2,4,6-trimethylphenol (*15*) in the same solvent has been investigated. Furthermore, the oxidation of the 3,5- and 2,5-dimethyl derivatives of *1* with aqueous periodate, in the absence of acetic acid, has been studied.

Oxidation in aqueous acetic acid

4-Hydroxy-3,5-dimethylbenzyl alcohol (5) (Chart 1). Both periodate and bismuthate produced 2,6-dimethylbenzoquinone (*6*) and 4-hydroxy-3,5-dimethylbenzaldehyde (*7*), *i.e.*, the dimethyl homologues of the products (*3*, *4*) formed on similar oxidation of unsubstituted 4-hydroxybenzyl alcohol.[1] With periodate as oxidant a third product, *viz.* the *o*-quinol acetate *8*, was obtained. The total yields of identified products formed after a reaction time of 30 min, which was sufficient for the starting material (*5*) to be completely consumed, were considerably higher than those obtained from *1*, since in the latter case large amounts of amorphous material were formed.[1]

The spiro compound *11* could not be detected in the bismuthate reaction mixture, although

* Part XIV, see Ref. 1.

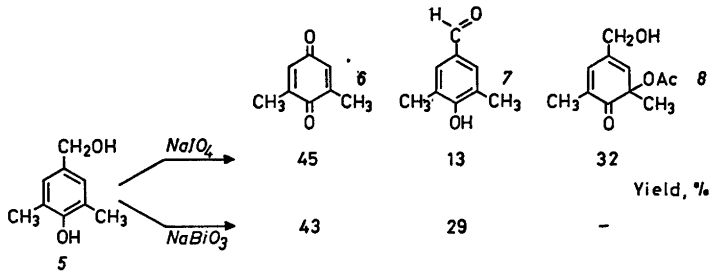


Chart 1.

its formation in the bismuthate system had been expected, since the parent compound *2* had been obtained from *1* in the same system.[1] The failure of the phenol alcohol *5* to give *11* may possibly be understood as shown in Chart 2.

Assuming that the initially formed aryl bismuthate *9* decomposes by two-electron transfer to give the phenoxonium ion *10*, the latter could undergo ring closure to provide the spiro-oxirane *11*. The same result would be obtained if *9* undergoes concerted ring closure and loss of a trivalent bismuth species (dashed line arrow). The unsubstituted analogue *2* of the spiro compound *11* has been found to be slowly hydrolyzed by 80 % aqueous acetic acid, the reaction being complete after about 24 h at room temperature.[1] In the present case, however, the two allylic methyl groups may stabilize the cation *10*, thus favouring reaction *11*→*10* and increasing the rate of hydrolysis. The resulting *p*-quinol *12* would lose formaldehyde to give 2,6-dimethylhydroquinone (*13*) which would be oxidized to the quinone *6* (*cf.* Ref. 1).

The second reaction product (*7*) can be assumed to arise by loss of a proton from the carbinol C-atom of *10* or by a corresponding concerted reaction of *9* (dotted line arrow) followed by rearrangement of the resulting enol *14*.

The fact that *o*-quinol acetate (*8*) is formed in the periodate system but not in the bismuthate system and, furthermore, the comparatively high yield of aldehyde *7* obtained with bismuthate (Chart 1) seemed to indicate that bismuthate preferentially acts as a *para*-oxidizing agent. With the aim of obtaining further support for this view, the following experiments with 2,4,6-trimethylphenol (mesitol) were carried out.

2,4,6-Trimethylphenol (15) (Chart 3). When treated in 80 % aqueous acetic acid with

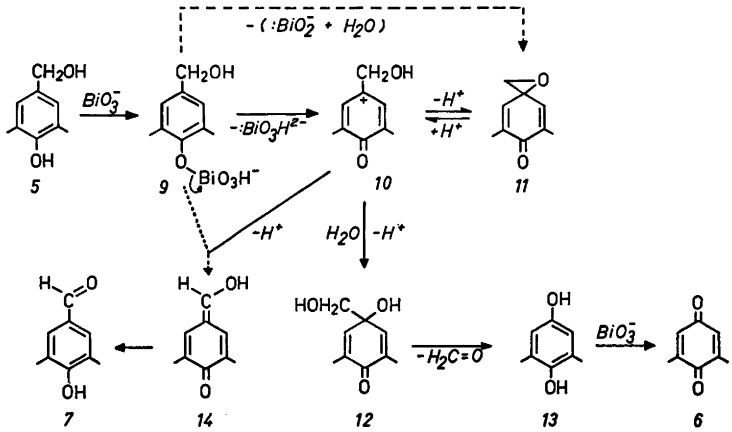


Chart 2.

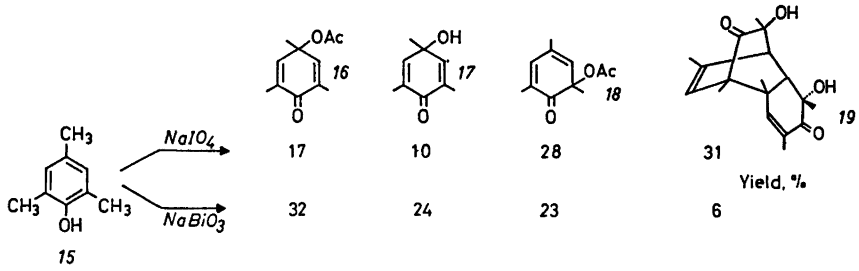


Chart 3.

periodate or bismuthate for 30 min, products *16* – *19* were obtained in either case. However, with periodate as oxidant, the ratio of *ortho*/*para* oxidation products was 59/27, whereas almost the inverse ratio (29/56) was found for the bismuthate system.

Oxidation in aqueous ethanol

In earlier work on the periodate oxidation of 2-methyl- and 2-hydroxymethyl-substituted phenols the reaction had been carried out in aqueous [2-4] or aqueous ethanolic [5] solution and therefore it was of interest to examine the behaviour of the 4-hydroxybenzyl alcohols *5* and *25* under similar conditions. The solvent mixture used in this study contained a small amount of ethanol which was sufficient to keep the starting material, as well as the reaction products, in solution.

4-Hydroxy-3,5-dimethylbenzyl alcohol (5) (Chart 4). Treatment of *5* with periodate gave, in addition to *p*-quinone *6* and aldehyde *7*, which also had been obtained when aqueous acetic acid was used as solvent, two compounds, $C_{17}H_{20}O_5$ and $C_{18}H_{24}O_6$, melting at 129 – 130 °C and 179 – 180 °C, respectively.

The lower-melting yellow compound, $C_{17}H_{20}O_5$, was assigned the structure of a Diels-Alder adduct (*20*) between *o*-quinol *21* and *p*-quinone *6*. This structure is based on the following spectral and chemical evidence.

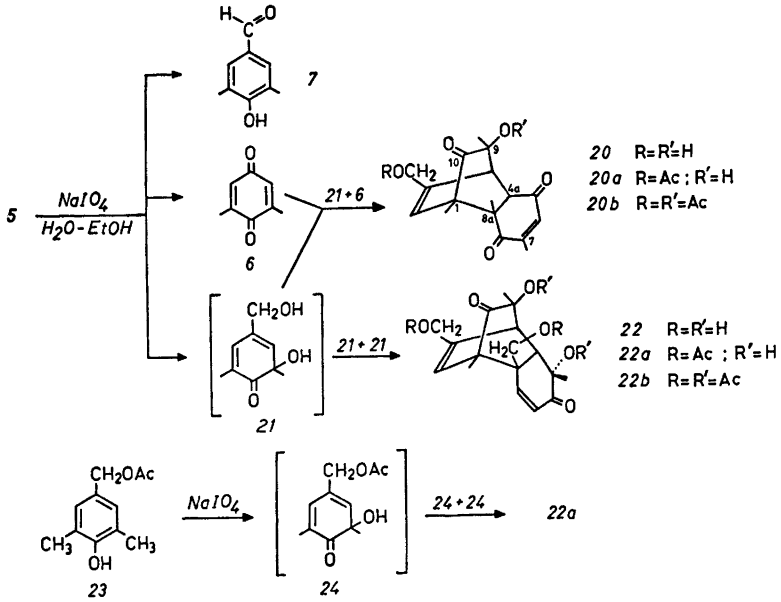


Chart 4. (*Note added in proof*: Formula *22* – *22b* should carry a CH_3 group in position 7.)

The ethanolic solution of *20* showed strong UV absorption with maxima at 215 and 234 nm, as well as low-intensity absorption at 305 nm (sh) and 375 nm. The absorption band at 215 nm can be attributed to transannular charge transfer between the 2,3-ethylenic bond and the C-10 keto group; strong absorption at a similar wavelength has previously been found to be characteristic of the β,γ-conjugated carbonyl system present in dimeric *o*-quinols.[5,6] The maxima at 234, 305, and 375 nm can be ascribed to the enedione system present in the dienophile moiety of the molecule; similar absorption has been reported to be typical of enediones.[7-9] In the IR spectrum of *20* the conjugated CO groups are reflected by an absorption band at 1660 cm^{-1}, whereas the isolated CO group gives rise to a peak at 1723 cm^{-1}.

The NMR spectrum of the compound was in full agreement with structure *20* (see Experimental).

Treatment of *20* with Ac_2O/pyridine, which does not acetylate tertiary hydroxyl groups, gave the monoacetate *20a*, whereas the diacetate *20b* was obtained with $Ac_2O/HClO_4$.[10]

The product $C_{18}H_{24}O_6$, m.p. 179–180 °C, was colourless and had the spectral properties expected for an *o*-quinol dimer of structure *22*. A diacetate (*22a*) was formed with Ac_2O/pyridine and a tetraacetate (*22b*) was obtained from either *22* or *22a* with $Ac_2O/HClO_4$, which is in accord with this structural assignment. Diacetate *22a* was also formed, *via* the intermediary *o*-quinol *24*, on periodate oxidation of 4-hydroxy-3,5-dimethylbenzyl acetate (*23*).

The dimeric *o*-quinol *22* was obtained in a yield of 14 % and the *o*-quinol-*p*-quinone adduct *20* in a yield of 33 %. The formation of these compounds at room temperature illustrates the high diene reactivity of *o*-quinols.

4-Hydroxy-2,5-dimethylbenzyl alcohol (*25*) (Chart 5). Periodate was consumed at a considerably lower rate by *25* than by its isomer *5*, which is in analogy with the exceptionally sluggish reaction of 2,5-dimethylphenol as compared with other phenols, such as 2,6-dimethylphenol.[4] Expectedly, *25* gave the *p*-benzoquinone *26* and the aldehyde *27*. In addition, a colourless compound of m.p. 203–204 °C was isolated. Its composition, $C_{18}H_{24}O_6$, seemed to indicate the compound to be a Diels-Alder dimer (*29*) of the intermediary *o*-quinol *28*. The IR spectrum of the substance (in KBr) revealed the presence of the conjugated keto group at C-6, but, surprisingly, the expected peak due to the keto group at C-10, which in dimeric *o*-quinols is found within the range of 1710–1725 cm^{-1}, was missing. It was supposed, therefore, that the latter keto group was masked by the formation of a hemiketal with the hy-

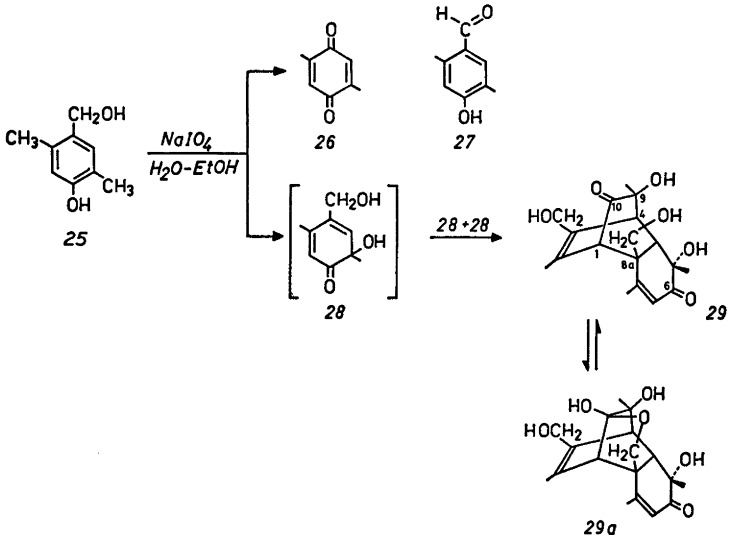


Chart 5.

droxyl group of the substituent at C-8a. In fact, the IR spectrum of the compound dissolved in DMSO, ethanol or dioxan showed peaks due to both the conjugated and the isolated keto groups. Structure *29a* is therefore ascribed to the compound in the solid state and the structure of a dimeric *o*-quinol (*29*) to the substance dissolved in a polar solvent ("ring-chain tautomerism").

No *o*-quinol-*p*-quinone adduct of type *20* was detected in the reaction mixture obtained from phenol *25*.

Structural and stereochemical orientation in dimers *22* and *29* and in adduct *20*

The structural and stereochemical specificity characteristic of the Diels-Alder dimerisation of 2,4-cyclohexadienones [4,6,11] is illustrated again by the fact that only a single *o*-quinol dimer (*22* and *29*, respectively) has been detected in the oxidation of each of the phenols *5* and *25*. Similarly, the Diels-Alder reaction *21*+*6* gives a single adduct (*20*).

The assignment of the structural orientation given in formulae *20* and *22* is based on the NMR spectra of these compounds. They showed the patterns required for coupling between the vicinal protons at C-4 and C-4a as well as between the protons at C-4 and C-2 (for *20*: $J_{4,4a}=2.2$ Hz, $J_{4,2}=2.0$ Hz; for *22*: $J_{4,4a}=2.1$ Hz, $J_{4,2}=2.0$ Hz. See also Experimental).

The dimers *22* and *29*, as well as adduct *20*, were stable towards periodate, in spite of the presence of the 9,10-hydroxyketone grouping. As discussed in Part XII,[6] this can be interpreted to be due to the steric orientation of the 9-OH group as shown in the formulae, in combination with the presence of the CH_2OH or the CH_3 substituent, respectively, at C-8a. Although there is no direct evidence for the configuration at C-5 to be that given in formulae *22* and *29*, its correctness is highly probable since it is favoured if steric approach control is operative in the dimerization and since it actually has been established for other dimeric *o*-quinols.[6,11]

The formation of hemiketal *29a* constitutes proof of the *endo* configuration of this dimer. *Endo* configuration has also been assumed above for dimer *22*, as well as for adduct *20*. This seems justified because the dimerization of *o*-quinols has been shown earlier to follow the *endo* addition rule.[4,11,12]

EXPERIMENTAL

UV spectra were recorded on a Cary Model 14 spectrophotometer; IR and NMR spectra were obtained using Beckman 9 A and Varian A-60 instruments, respectively. Chemical shifts are given in δ (ppm units, TMS being used as internal standard).

4-Hydroxy-3,5-dimethylbenzyl alcohol (*5*), the corresponding benzyl acetate (*23*), and 4-hydroxy-2,5-dimethylbenzyl alcohol (*25*) were prepared according to Refs. 13, 14, and 15, respectively.

Oxidation with periodate in aqueous acetic acid. A solution of phenols *5* or *15* (0.03 mol) in acetic acid (320 ml) was mixed with a solution of $NaIO_4$ (0.06 mol) in a mixture of acetic acid (80 ml) and water (100 ml). After 30 min (room temperature) ethylene glycol (5 ml) was added to remove excess periodate and the mixture was extracted with three 150 ml portions of dichloromethane. The combined extracts were washed with aqueous bicarbonate, dried over Na_2SO_4 and brought to dryness. The resulting residue was chromatographed on a silica gel column (4 × 60 cm) using benzene/ethyl acetate (4:1) as eluent.

Periodate oxidation products obtained from 4-hydroxy-3,5-dimethylbenzyl alcohol (5). The eluate fractions gave:

(a) 2,6-Dimethyl-1,4-benzoquinone (6), $R_F=0.43$; yield, 45 %. M.p., after sublimation, 69–71 °C (Lit.[16] 72–73 °C). The IR spectrum of the compound was in accord with that reported for *6*.[17]

(b) 6-Acetoxy-4-hydroxymethyl-2,6-dimethyl-2,4-cyclohexadienone (8). $R_F=0.38$, yellow oil. Yield, 32 %. (Found: *M*, by mass spectrometry, 210.0902. Calc. for $C_{11}H_{14}O_4$: *M* 210.0892.) IR (KBr): ν_{max}, cm^{-1} 1668 (conj. CO), 1740 (ester CO), 3460 (OH). NMR ($CDCl_3$): δ 1.36 (s, 3 H, CH_3), 1.95 (broad s, 3 H, olefinic CH_3), 2.07 (s, 3 H, CH_3COO), 4.20 (d, 2 H, CH_2), 5.33 (1 H, OH), 6.06 and 6.83 (multiplets, 1 H each, 2 olefinic H).

(c) 4-Hydroxy-3,5-dimethylbenzaldehyde (7), $R_F=0.29$; yield, 13 %. M.p., after recrystallization from benzene, 113–114 °C (Lit.[18] 114–115 °C). The IR spectrum of the compound was in accord with that reported for *7*.[19]

Periodate oxidation products obtained from mesitol (15). The eluate fractions gave:

(a) 6-Acetoxy-2,4,6-trimethyl-2,4-cyclohexadienone (18), $R_F=0.47$; yield, 28 %. Yellow crystals, m.p. 80–82 °C (Lit.[20] 82–84 °C)

(b) 4-Acetoxy-2,4,6-trimethyl-2,5-cyclohexadienone (16), $R_F=0.43$. Pale yellow oil;[20] yield, 17 %. NMR ($CDCl_3$): δ 1.51 (s, 3 H, CH_3-4),

1.89 (s, 6 H, CH_3-2 and CH_3-6), 2.00 (s, 3 H, CH_3COO), 6.69 (s, 2 H, H-3 and H-5).

(*c*) *4-Hydroxy-2,4,6-trimethyl-2,5-cyclohexadienone (17)*, $R_F = 0.14$; yield, 10 %. M.p. 45–46 °C (Lit.[21] 45.5–46 °C). The IR and NMR spectra of the compound were in agreement with those expected for structure *17*.

(*d*) *1,4a,5,8a-Tetrahydro-5,9-dihydroxy-1,3,5,7,8a,9-hexamethyl-1,4-ethanonaphthalene-6,10 (4H)-dione (19)*, $R_F = 0.09$, yield, 31 %. Identical by m.p. and mixed m.p. with an authentic sample.[5]

Oxidation with bismuthate in aqueous acetic acid. Sodium bismuthate ($NaBiO_3$, 0.06 mol) was added to a stirred solution of phenol *5* or *15* (0.03 mol) in 300 ml of acetic acid/water (4:1). After 30 min the mixture was filtered and the filtrate worked up as described for the periodate procedure.

Phenol *5* gave *2,6-dimethyl-1,4-benzoquinone (6)* in a yield of 43 % and *4-hydroxy-3,5-dimethylbenzaldehyde (7)* in a yield of 29 %.

Mesitol (*15*) gave o-*quinol acetate* 18 (23 %); p-*quinol acetate* 16 (32 %), p-*quinol* 17 (24 %) and *dimeric* o-*quinol* 19 (6 %).

Periodate oxidation of 4-hydroxy-3,5-dimethylbenzyl alcohol (5) in aqueous ethanol. A solution of $NaIO_4$ (3.84 g, 18 mmol) in water (150 ml) was added to a solution of *5* (1.80 g, 12 mmol) in 500 ml of ethanol-water (1:10). After 16 h (room temp.) the mixture was extracted with 3 × 200 ml of hexane. The combined extracts gave *2,6-dimethyl-1,4-benzoquinone (6)*; yield, 21 %.

The aqueous phase was extracted with 5 × 400 ml of ethyl acetate. The combined extracts were dried over Na_2SO_4 and evaporated, and the residue obtained was chromatographed on a silica gel column using acetone/hexane (2:1) as eluent. The eluate fractions gave:

(*a*) *4-Hydroxy-3,5-dimethylbenzaldehyde (7)*, $R_F = 0.60$; yield, 6 %.

(*b*) *1,4,4a,8a-Tetrahydro-9-hydroxy-3-hydroxymethyl-1,7,8a,9-tetramethyl-1,4-ethanonaphthalene-5,8,10-trione (20)*, $R_F = 0.53$; yield, 33 %. Yellow crystals, m.p. 129–130 °C (ethyl acetate/hexane). (Found: C 66.7; H 6.5. Calc. for $C_{17}H_{20}O_5$: C 67.1; H 6.6). UV (ethanol): λ_{max}, nm (log ε) 215 (4.05), 234 (4.05), 305 sh (2.70), 375 (2.12). IR (KBr): ν_{max}, cm^{-1} 1635 (C=C), 1660 (conj. CO), 1723 (CO), 3330, 3460 and 3540 (OH). NMR ($CDCl_3$): δ 1.37, 1.40 and 1.42 (singlets, 3 H each, 3 CH_3), 2.10 (d, 3 H, CH_3-7), 2.60 (broad, 2 H, 2 OH, exchangeable with D_2O), 3.31 (t, 1 H, H-4), 3.62 (d, 1 H, H-4a), 4.20 (d, 2 H, CH_2), 5.79 (m, 1 H, H-2), 6.71 (quartet, 1 H, H-6).

(*c*) *1,4a,5,8a-Tetrahydro-5,9-dihydroxy-3,8a-bis(hydroxymethyl)-1,5,7,9-tetramethyl-1,4-ethanonaphthalene-6,10(4H)-dione (22)*, $R_F = 0.42$; yield, 14 %. Colourless crystals, m.p. 179–180 °C (benzene). (Found: C 64.25; H 7.16. Calc. for $C_{18}H_{24}O_6$: C 64.28; H 7.19). UV (ethanol): λ_{max}, nm (log ε) 210 (3.94), 240 sh (3.78), 310 sh (2.48). IR (KBr): ν_{max}, cm^{-1} 1650 (C=C), 1690 (α,β-conj. CO), 1718 (CO), 3400 (broad, OH). NMR (DMSO-d_6): δ 1.09, 1.12 and 1.25 (singlets, 3 H each, 3 CH_3), 1.70 (s, 3 H, CH_3-7), 2.81 (d, 1 H, H-4a), 2.93 (t, 1 H, H-4), 3.50 and 3.83 (broad signals, 2 H each, 2 CH_2), 4.67 and 5.25 (broad signals, 1 H each, 2 prim. OH), 4.82 and 5.41 (singlets, 1 H each, 2 tert. OH), 5.02 (m, 1 H, H-2), 6.19 (broadened s, 1 H, H-8).

Monoacetate 20a. From *20* by treatment with Ac_2O/pyridine. The crude solid obtained was treated with a small amount of diethyl ether and the yellow crystalline product collected. M.p. 106–107 °C (ethyl acetate/hexane). (Found: C 65.67; H 6.53. Calc. for $C_{19}H_{22}O_6$: C 65.88; H 6.40). IR (KBr): ν_{max}, cm^{-1} 1644 (C=C), 1670 (conj. CO), 1722 (CO), 1740 (ester CO), 3450 (OH).

Diacetate 20b. From *20* by treatment with $Ac_2O/HClO_4$.[10] Yellow crystals of m.p. 115–116 °C (ethanol). (Found: C 64.97; H 6.08. Calc. for $C_{21}H_{24}O_7$: C 64.93; H 6.22). IR (KBr): ν_{max}, cm^{-1} 1626 (C=C), 1661 (conj. CO), 1722 (CO), 1740 (ester CO).

Diacetate 22a. (*a*) From *22* by treatment with Ac_2O/pyridine, m.p. 168–169 °C (methanol). (Found: C 62.98, H 6.83. Calc. for $C_{22}H_{28}O_8$: C 62.89; H 6.71). IR (KBr): ν_{max}, cm^{-1} 1638 (C=C), 1673 (α,β-conj. CO), 1728 (CO), 1746 (broad, ester CO), 3470 and 3530 (*tert.* OH).

(*b*) A solution of 4-hydroxy-3,5-dimethylbenzyl acetate (*23*) (2.91 g, 15 mmol) in a mixture of acetic acid (100 ml) and water (300 ml) was mixed with a solution of $NaIO_4$ (4.91 g, 23 mmol) in water (100 ml). After 90 min the solution was extracted with 5 × 75 ml of dichloromethane. The residue obtained from the combined extracts was treated with a few milliliters of ether. The crystalline product formed (yield, 34 %) was identical by m.p. and mixed m.p. with *22a* prepared according to (*a*).

Tetraacetate 22b. From *22* or *22a* by treatment with $Ac_2O/HClO_4$,[10] m.p. 166–167 °C (methanol). (Found: C 61.8; H 6.5. Calc. for $C_{26}H_{32}O_{10}$ C 61.9; H 6.4). IR (KBr): ν_{max}, cm^{-1} 1708 (α,β-conj. CO), 1732 (CO), 1748 (broad, ester CO).

Periodate oxidation of 4-hydroxy-2,5-dimethylbenzyl alcohol (25) in aqueous ethanol. A solution of $NaIO_4$ (10.3 g, 48 mmol) in water (300 ml) was added to a solution of *25* (1.80 g, 12 mmol) in a mixture of ethanol (400 ml) and water (1300 ml). After 72 h (room temp.) the solution was extracted with 3 × 300 ml of hexane. The combined hexane phases gave *2,5-dimethyl-1,4-benzoquinone (26)* in a yield of 22 %. After sublimation (0.05 mmHg, 30 °C) the compound melted at 121–122 °C (Lit.[16] 124–124.5 °C). The IR spectrum of the compound was in accord with that reported for *26*.[17]

The aqueous phase was further extracted with 5 × 400 ml of ethyl acetate. The combined extracts were dried over Na_2SO_4 and evaporated, leaving a dark-coloured oil which was dissolved

in a few milliliters of acetone. A crystalline product deposited, which was recrystallized from acetone to give the *hemiketal* 29a of *1,4a,5,8a-tetrahydro-5,9-dihydroxy-3,8a-bis(hydroxymethyl)-2,5,8,9-tetramethyl-1,4-ethanonaphthalene-6,10(4H)-dione (29)*, m.p. 203–204 °C. Yield, 14 %. (Found: C 64.34; H 7.20. Calc. for $C_{18}H_{24}O_6$: C 64.28; H 7.19). UV (ethanol): λ_{max}, nm (log ε) 210 (3.73), 236 (3.70), 312 sh (2.22). IR (KBr): ν_{max}, cm^{-1} 1630 (C=C); 1680 (α,β-conj. CO), 3400 (broad, OH). IR (DMSO-d_6): ν_{max}, cm^{-1} 1630 (C=C), 1684 (α,β-conj. CO), 1722 (CO). NMR (DMSO-d_6): δ 1.11, 1.40 and 1.43 (singlets, 3 H each, 3 CH_3), 1.96 (broadened s, 3 H, CH_3-8), 2.75 (s, 1 H, H-1), 2.91 and 3.21 (doublets, 1 H each, H-4 and H-4a), 3.62 and 3.74 (broad signals, 2 H each, 2 CH_2), 4.68 and 5.12 (broad signals, 1 H each, 2 prim. OH), 4.83 and 5.48 (singlets, 1 H each, 2 *tert.* OH), 5.84 (s, 1 H, H-7). $J_{4,4a}$ = 2.0 Hz.

The acetone filtrate was chromatographed on a silica gel column using benzene/ethyl acetate (4:1) as eluent. *4-Hydroxy-2,5-dimethylbenzaldehyde (27)*, R_F = 0.31, was isolated in a yield of 5 %. After recrystallization from benzene, m.p. 129–130 °C (Lit.[22] 132–133 °C).

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