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QUINONES AND QUINONE METHIDES—IV

DIMERIZATION REACTIONS OF 2-PHENYLMETHYL-5-METHOXY-1,4-BENZOQUINONES

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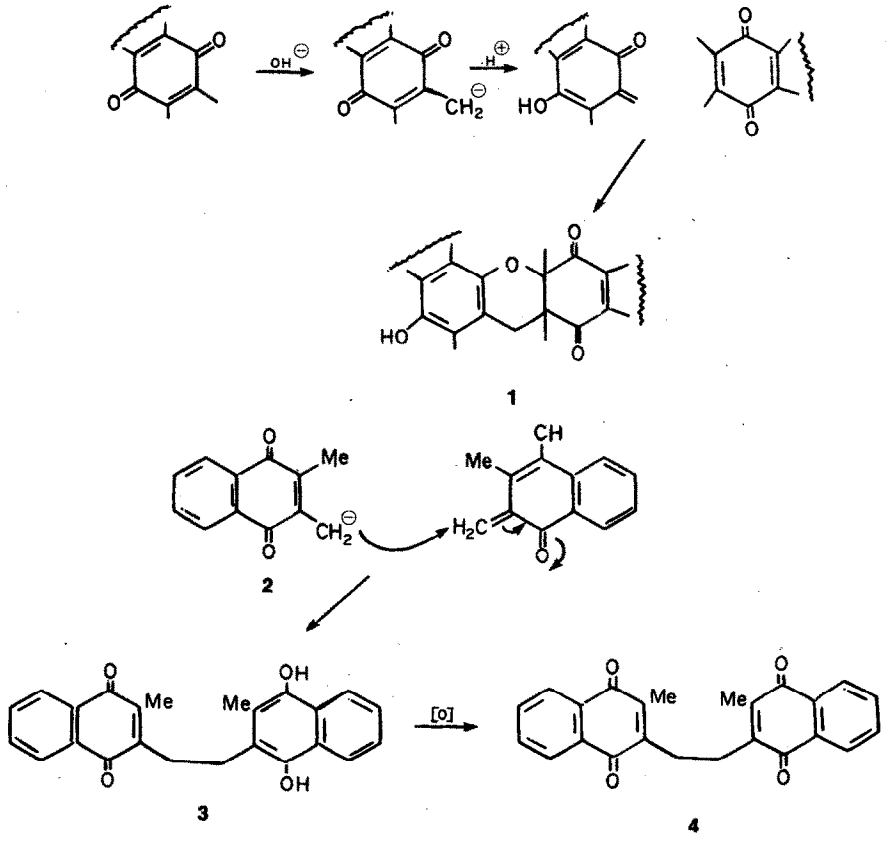
Abstract—Base catalyzed dimerization of 2-(4-methoxyphenylmethyl)-5-methoxy-1,4-benzoquinone **6** yields as the chief product an unusual tetrahydroxanthen derivative **7a**. The structure of **7a** suggests that it is formed by combination of two molecules of the *ortho*-quinone methide tautomer of **6**. Rearrangement of **7a** yields the dihydro-oxepin derivative **15** and the indanspirocyclohexene derivatives **17** and **18a**, all of which are formed as minor products in the dimerization of **6**. In contrast to **6** related 2-(1-phenylethyl)-1,4-benzoquinones do not dimerize in basic media.

Unstable quinone methides have been implicated as intermediates in many chemical and biochemical reactions of quinones.[1] More recently it has been proposed that the toxicological[2] and antineoplastic properties of some drugs, including substituted 1,4-benzoquinones,[3,4] may be due to their *in vivo* conversion to active *ortho*-quinone methide alkylating agents. Substantial evidence for the formation of tautomeric quinone methide intermediates from methyl-1,4-benzoquinones and naphthoquinones has been obtained by structural identification of products resulting from their base catalyzed dimerization, their reactions with secondary amines[5,6] and enolate anions,[7] and from reactions of the quinonylmethyl carbanion **2** with various quinones.[8] In these earlier studies it was recognized that dimerization of methylquinones may yield products of two different structural types. Thus, in alcoholic sodium hydroxide tetramethyl-1,4-benzoquinone (duroquinone)[9] and 2,3-dimethylnaphthoquinone[10] yield xanthen derivatives of type **1** by a suggested[10] reaction sequence involving cycloaddition of an intermediate quinone methide to the quinone ethylenic double bond.

In methanolic sodium acetate, however, the carbanion **2** of 2,3-dimethylnaphthoquinone, generated from its diazomethane adduct, reacts[6,11] with the *ortho*-quinone methide to yield the highly colored quinhydrone **3**, which is easily oxidized to the ethylenediquinone **4**.

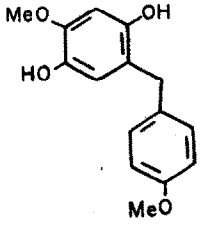
The participation of anions of the quinone methide



type in these reactions has been further confirmed by more recent work on the incorporation of tritium[12] and photochemical decomposition[13] of duroquinone.

The recent observation[14] that certain benzylphenols are highly effective insect sterilants and growth inhibitors prompted our interest in the chemistry of quinone methides which may be derived from benzyl compounds and possibly account for their sterilizing activity. The earlier studies on the participation of quinone methides in the dimerization of C-methylquinones, therefore, have now been extended to 2 - phenylmethyl - 5 - methoxy - 1,4 - benzoquinones and 2 - (1 - phenylethyl) - 5 - methoxy - 1,4 - benzoquinones.

4-Methoxybenzyl alcohol condenses readily with 2-methoxyhydroquinone in aqueous citric acid solution to give high yields of the quinol **5**, which is oxidized by silver oxide to the 1,4-benzoquinone **6**.



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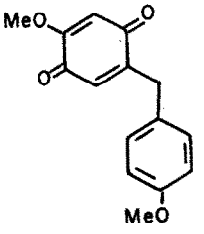

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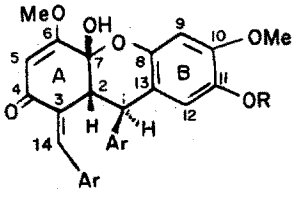
On warming solutions of the quinone **6** in pyridine or methanolic sodium hydroxide it forms a dimer A, $C_{30}H_{28}O_8$ (m.p. 220–222°; 50–60% yields) and minor amounts of three other dimeric products, viz. B, $C_{30}H_{26}O_8$ (m.p. 214–216°), C, $C_{30}H_{26}O_8$ (m.p. 244°), and D, $C_{30}H_{28}O_8$ (m.p. 166–168°). With the exception of monoacylation, the reactions of dimer A with acids and bases, and with oxidizing and reducing agents lead in all cases to molecular rearrangements; e.g. in methanolic sodium acetate dimer A rearranges to yield the crystalline dimers B, C and D. Although these rearrangements considerably complicated the structural identification of the various products, we have determined from X-ray crystallographic and spectral data that dimers A, B and C are the entirely unexpected xanthen, oxepin and indan derivatives **7a**, **15** and **17**, respectively. Dimer D is the hydroquinone precursor **18a** of dimer C.

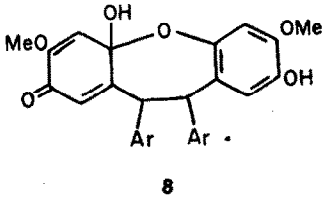
Dimer A is an almost colorless compound which contains both OH and unsaturated CO groups (ν_{max} 3340, 1645 (weak) 1620 (strong), cm^{-1}). Although it can be reductively acetylated and reduced with sodium borohydride,† it does not form an oxime and is not reduced by sodium dithionite or hydrogen and a palladium catalyst, indicating that it is not a quinone, unlike previously described dimers of types **1** and **3**. Two OH groups are present, only one of which is easily acylated. Thus, with acetic anhydride or benzoyl chloride in pyridine at room temperature it yields colorless monoacetyl and monobenzoyl derivatives. On heating with these reagents it forms yellow di-O-acetyl and di-O-benzoyl derivatives. These diacyl derivatives, however, are not formed by acylation of the second OH group, but rather as a result of opening of a heterocyclic ring.

The PMR spectrum of dimer A (in d_5-pyridine) shows the presence of a methine proton as a doublet (J = 11 Hz) at δ4.45, coupled to a methine proton at δ4.25, which is in turn allylically coupled to a downfield olefinic proton at δ7.94. These signals may be assigned to protons at positions 1, 2 and 14 of **7a** respectively. The olefinic proton at C5 appears as a singlet at δ5.89 and the two OH protons as a broad 2H singlet at δ10.38. The signals of the two aromatic protons (positions 9 and 12) overlap those of the eight aromatic protons of the *p*-methoxyphenyl rings giving rise to two 5H multiplets at δ6.50–6.72 and δ6.84–7.06. The ^{13}C NMR spectrum of the dimer indicates the presence of a single CO group (at 186.7). Although these data are in accord with the xan-

†These reactions of dimer A are described in the following paper of this series.



7a: R = H
b: R = $COCH_3$



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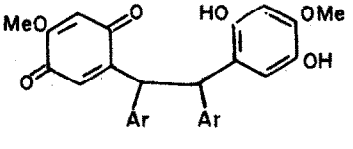

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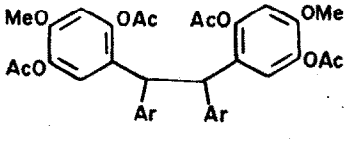

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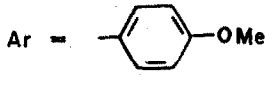


then structure **7a**, they could be accounted for by an alternative dihydro-oxepin structure **8**, which could be formed by cyclization of an intermediate quinhydrone **9**. Furthermore, support for the oxepin structure **8** was provided by the observation that reductive acetylation of the dimer yields an ethylenediquinol tetra-acetate **10**. While the formation of **10** from **8** would be expected, its formation from **7a** by reductive acetylation would require an unusual rearrangement of the carbon nucleus.

The structure of dimer A therefore, was unequivocally established as **7a** by X-ray crystallographic analysis. The molecular structure, atomic thermal motion and numbering system are illustrated in the Ortep drawing,[15] Fig. 1 and the crystal data are summarized in Table 1. The molecule consists of a 6-membered heterocyclic ring fused on one side to a benzene ring and on the other to a cyclohexene ring. In addition, a *p*-methoxyphenyl group is attached to the cyclohexene ring through a C=C double bond and another *p*-methoxyphenyl group is attached to the heterocyclic ring. The two *p*-methoxyphenyl groups lie toward the convex face of the molecule. The best least-squares planes of the two *p*-methoxyphenyl groups are nearly parallel to each other with their OMe groups pointing in opposite directions, an orientation minimizing intramolecular steric hindrance between the adjacent units in the molecule. The heterocyclic and cyclohexene rings assume flattened chair conformations with the H atom on C(2) *trans* to the H atoms on C(1) and C(14) but *cis* to O(28). The heterocyclic ring is almost co-planar with its adjacent phenyl ring, but the adjacent cyclohexene ring is twisted upward because of the *cis* fused ring configuration. All atoms in the phenyl rings [C(8)–C(13) and C(21)–C(26)] lie within ±0.02 Å of their least squares planes.

Structure refinement indicated a molecular disorder in the crystal; atoms in one of the *p*-methoxyphenyl groups [C(15)–C(20)] have unusually high thermal vibrational parameters. Atoms C(18), C(19), C(20), O(31) and C(36),

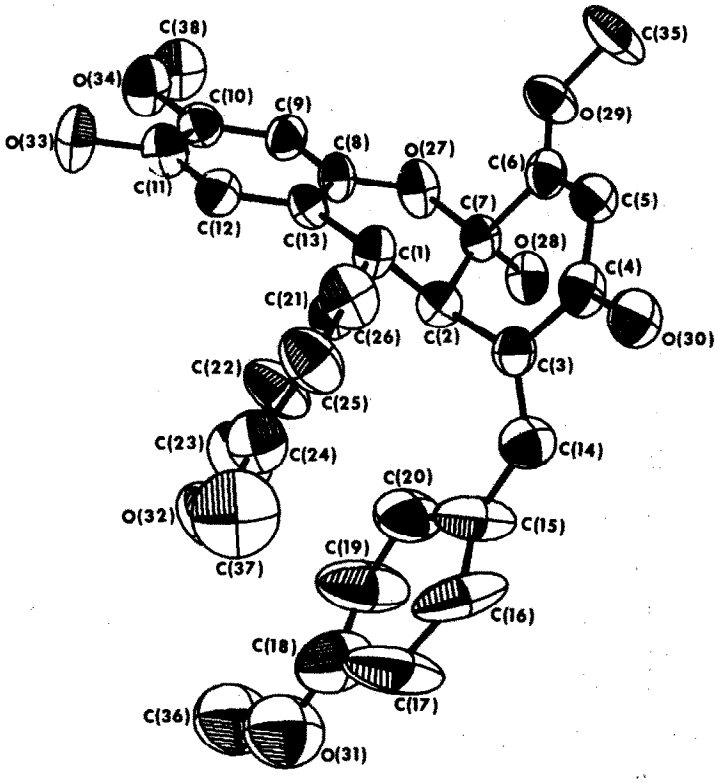


Fig. 1. Ortep drawing of Dimer A with 50% probability thermal ellipsoids.

Table 1. Crystal data

	7a	15
	monoclinic	monoclinic
Space Group	$P2_1/C$	$P2_1/C$
Molecules/unit cell	4	4
a	6.595 (4) Å	10.045 (5) Å
b	8.614 (4)	8.911 (4)
c	45.713 (8)	29.650 (8)
$\angle\beta$	98.43 (1)°	106.18 (1)°

Table 2. Dihedral angle (deg.) between planes*

Planes	7a	15
1-2	71.4	70.7
1-3	58.5	58.6
1-4		-22.6
2-3	24.0	19.0
2-4		88.6
3-4		-81.0

* Definition of Planes:

Plane 1 - C(8) - C(13)

2 - C(21) - C(26)

3 - C(15) - C(20)

4 - C(2) - C (7) [for 15 only]

each tend to occupy two separate crystallographic positions in the unit cell. The dihedral angle between the best least-squares planes formed by the two positions of the disordered phenyl rings is 54.7°. Dihedral angles between the best least-squares planes of the other phenyl rings are listed in Table 2. The appreciable degree of delocalization between O(29), C(6), C(5), C(4), C(3), C(14) and C(15) is apparent from the carbon single bonds (mean = 1.46 Å) slightly shorter and the carbon double bonds (mean = 1.35 Å) slightly longer than for a non-resonating single and double bond system. The molecules in the crystal structure are held together by intermolecular H bonds formed by O(28)[O(28)–O(30) = 2.67 Å, O(28)–O(33) = 2.87 Å].

Having shown the structure of dimer A to be **7a** the chemical shifts in its ^{13}C NMR spectrum can be assigned† as shown in Table 3. These assignments are based upon the multiplicities shown in the "gated" proton ^{13}C coupled spectrum, and by comparison with predicted shifts from reported values for the additive effects of methoxyl, hydroxyl, and alkyl substituents on aromatic and olefinic C atoms.[16,17] Significant signals include a carbonyl C at 186.7 (C4) and an oxygen-substituted quaternary C at 95.3 (C7), two aliphatic CH carbons at 46.7, 48.0 (C1, C2), and the phenyl substituted olefinic carbon at 134.7 (C14). Comparison with the spectrum reported[18] for the model compound, O-ethyldimedone **11**, supports assignment of the signal at 173.3 to the olefinic C6 of the cyclohexenone ring, and one of a pair of doublets at 102.6 and 100.6 to C5, the second doublet being due to the aromatic carbon C9.

The PMR and ^{13}C NMR spectra of the colorless dimer A monacetate, (and other monoacyl derivatives), formed by acylation in cold pyridine, are similar to those of the dimer itself, and its IR spectrum shows, in addition to acetyl CO (1755 cm^{-1}), the characteristic dimer CO bands at 1620 cm^{-1} (strong), 1650 cm^{-1} (weak). The monoacetate, therefore, is considered to be **7b**.

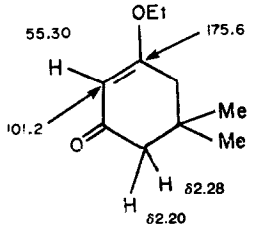
†To facilitate description of PMR and ^{13}C NMR spectra an arbitrary numbering system for the carbon nucleus of dimer A and its derivatives is used in the text. Dimers B, C and D are numbered to indicate their derivation from Dimer A.

Table 3. ^{13}C chemical shifts of dimer derivatives[a]

Carbon	7a	7b	12b	13	15	17	18b
1	46.7[b]	47.0[b]	49.8[b]	48.3[b]	45.8	60.6[b]	59.7[c]
2	48.0[b]	47.7[b]	54.5[b]	53.6[b]	145.7[b]	147.3[c]	128.8[b]
3	134.0	133.1	132.0	130.7	146.1[b]	145.7[c]	126.9[b]
4	186.7	188.0	193.2	192.4	186.6	184.1	152.2
5	102.6	103.4	112.3	112.9	107.5	107.8	106.5
6	173.3	172.5	161.7	161.1	158.2	159.4	144.7
7	95.3	96.2	187.5	187.5	181.8	179.2	138.2
8	147.4	151.1	146.4	186.1	142.7[c]	196.6	197.2
9	100.6	101.3	107.1	107.6	108.3	112.7	112.9
10	145.1	150.6	150.6	158.1	142.0[c]	159.3	161.1
11	140.7	134.6	137.5	181.7	141.3[c]	191.3	192.2
12	114.7	123.0	123.5	132.2	114.9	47.3	46.8
13	115.4	116.3	123.8	146.9	128.5	63.9	65.6
14	134.7	137.8	137.3	138.4	78.1	52.2[b]	52.2[c]

[a] Chemical shifts in $CDCl_3$ (except for 7a in DMSO) in ppm downfield from TMS. All assignments supported by proton coupled ^{13}C spectra and by comparison with predicted values from reported substituent effects. Signals due to methoxyl, acetyl and the p-methoxyphenyl ring carbon atoms are omitted.

[b] and [c]: assignments of these signals may be reversed.



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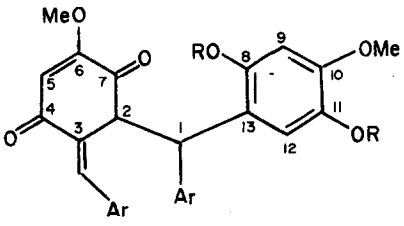
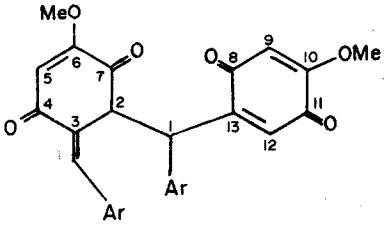


12A: R = H
b: R = $COCH_3$



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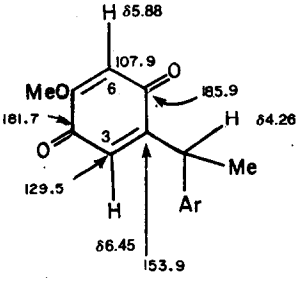

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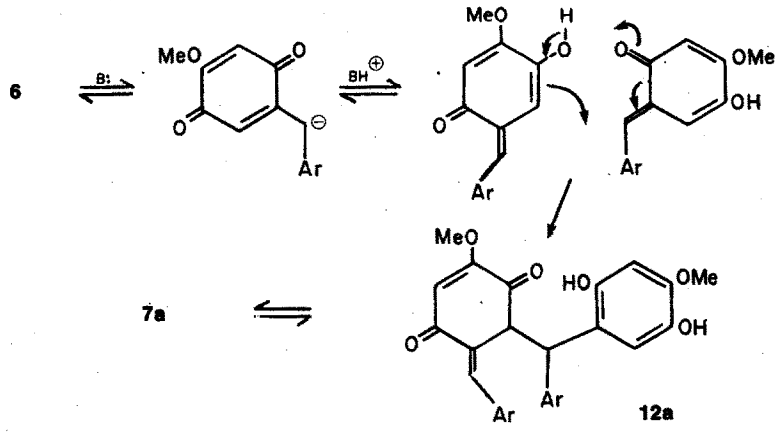
The spectral properties of the slightly yellow diacetyl derivative, formed by acetylation of dimer A in hot pyridine, differ markedly from those of the monoacyl derivatives. In the PMR spectrum of the monoacetate **7b** the coupled methine protons at C1 and C2 appear at δ4.00 and δ3.79; the olefinic protons at C5 and C14 appear at δ5.58 and δ7.52 respectively. In the diacetate, however, the two methine protons and the C5 olefinic proton shift downfield to δ4.42, δ4.98 and δ5.96, respectively. The chemical shift (δ7.52) of the olefinic proton at C14 in the monoacetate is unchanged in the diacetate (δ7.52), indicating that the *p*-methoxyphenyl-methylidene group is still present in the diacetate. In addition to an acetyl CO band (1770 cm^{-1}) the IR spectrum of the diacetate has two strong CO absorption bands at 1715 and 1655 cm^{-1}. On the basis of these data the dimer A diacetate is considered to be **12b**, and to be formed by base-catalyzed fission of the heterocyclic ring during the acylation reaction. This assignment was further confirmed by comparison of the ^{13}C NMR spectrum of the diacetate with that of the monoacetate **7b**. In the spectrum of **7b** signals of the A ring CO (C4) and quaternary C (C7) occur at 188 and 96.2, respectively. In the diacetate the quarternary C signal is absent and two A ring CO signals appear at 193.2 (C4) and 187.5 (C7). A signal at 137.8 in **7b**, assigned to C14, occurs in the diacetate (137.3), confirming the presence of the *p*-methoxyphenylmethylidene group. Since acetylation of a phenolic OH results in a downfield shift (4–12 ppm) of the signal of a C *ortho*- to the acetoxyl-substituted C,[19] the downfield shifts of C9, C10, C12, C13 in the diacetate (Table 3) relative to the corresponding signals in the dimer are in accord with location of both acetoxyl groups on the B ring.

Oxidation of dimer A with silver oxide yields quantitatively a yellow compound, $C_{30}H_{26}O_8$, which is reduced by sodium dithionite to the original dimer. In accord with the quinone structure **13** the PMR spectrum of the oxidation product shows the methine protons at positions 1 and 2 as doublets (J = 10 Hz) at δ4.52 and 4.91, and the olefinic protons at positions 12 and 14 as singlets (slightly broadened due to allylic coupling with the methine protons) at δ6.66 and 7.42, respectively. The quinoidal proton at position 9 and the olefinic proton at position 5 appear as singlets (unassigned) at δ5.77, 6.12. The presence of cyclohexen-1,4-dione and quinone rings in the oxidation product was established by comparison of its IR and ^{13}C NMR spectra with those of the dimer diacetate **12b** and the model quinone **14**. In the IR spectra of **12b** the two en-dione CO's absorb at 1655, 1715 cm^{-1}, and in **14** the two quinone CO's at 1645, 1670 cm^{-1}. In the oxidation product four CO absorption bands appear at 1650, 1662, 1670 and 1700 cm^{-1}. Similarly, in the ^{13}C NMR spectrum of **14** CO carbon signals occur at 181.7 and 185.9, while in the diacetate **12b** the CO carbon signals of the cyclohexen-1,4-dione ring appear at 187.5 and 193.2. The oxidation product shows four CO carbon signals at 181.7, 186.1, 187.5 and 192.4. Finally, the dimer oxidation product shows four olefinic CH signals at 107.6, 132.2, 112.9, 138.4, which correspond to the olefinic CH signals of **14** (107.9, 129.5) and of C5 (112.3) and C14 (137.3) of **12b**.

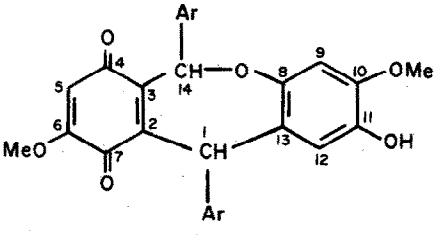
The structure of dimer A indicates that it is formed in an unexpected way by combination of two molecules of the *ortho*-quinone methide tautomer of the quinone **6**, in which the quinone-methide functions as both nucleophile and electrophile.

The quinol intermediate **12a** is the precursor of the dimer oxidation product **13** and of the dimers B, C and D.

Dimer B. As previously indicated this product is formed in trace amounts in the reaction of **6** in pyridine, and along with products C and D by the reaction of dimer A in methanolic sodium acetate. Dimer B is also formed quantitatively by brief warming of the dimer A oxidation product **13** in pyridine. It has IR absorption bands at



3495 cm^{-1} (OH) and 1630, 1645, 1785 cm^{-1} (CO), forms a monoacetate, and is readily reduced by sodium dithionite or sodium borohydride to a trihydroxy compound, $C_{30}H_{28}O_8$. Dimer B, therefore, is a monophenolic quinone, and it has now been identified by X-ray crystallographic analysis as the dihydro-oxepin derivative **15**.



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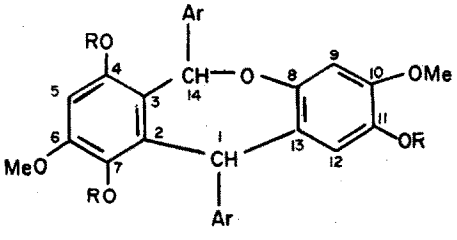
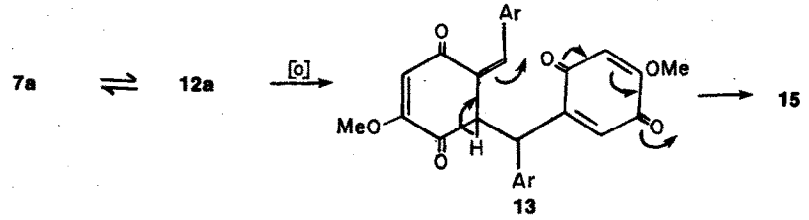


16a: R = H
b: R = $COCH_3$

The conformation of the molecule, atomic thermal motion and numbering system are shown in Fig. 2; crystal data are summarized in Table 1. The molecule consists of a 7-membered heterocyclic puckered ring fused on one side with a phenyl ring and on the other with a quinone ring. In addition there are a pair of *p*-methoxyphenyl groups attached to the opposite sides of the heterocyclic ring (*trans*). The best least-squares planes of the two *p*-methoxyphenyl groups are almost parallel to each other with their OMe groups pointing in opposite directions. The phenyl rings of both *p*-methoxyphenyl groups are approximately perpendicular to the plane of the quinone ring, permitting a compact molecular packing in the crystal. All three phenyl rings in the molecule are planar and the atoms in the quinone ring lie within ±0.07 Å of their least-squares plane. Dihedral angles between the best least-squares planes of the ring units in the molecule are listed in Table 2. The H atoms on the two asymmetric C atoms of the heterocyclic ring are *trans*. Due to the conjugation effect in the quinone ring, its single bonds are slightly shorter and double bonds are slightly longer than the normal expected values of 1.54 Å and 1.34 Å, respectively. The rest of the bond lengths and angles in the molecule are quite normal and there are no intermolecular H-bonds in the crystal structure.

The PMR spectrum of dimer B shows an OH singlet at δ 5.31, and five 1H singlets at δ5.43, 5.76, 5.82, 6.52 and 6.84, which can be assigned to the protons at positions 1, 5 (or 14), 14 (or 5), 9 and 12 of **15**, respectively. Assignment of chemical shifts in the ^{13}C NMR spectrum of **15** is unambiguous except for signals at 141.3, 142.0, 142.7, 145.7 and 146.1 which arise from the five quarternary olefinic carbons C2, C3, C8, C10 and C11. However, an alkyl substituent on a quinone nucleus produces[17] and upfield shift of the adjacent olefinic C signal of about 8 ppm. For the model quinone **14** the chemical shift of the alkyl substituted C2 is 153.9. Substitution of a second, similar alkyl group at C3 of **14** would be expected, therefore, to result in chemical shifts of about 145 for both C2 and C3. From these considerations the signals at 145.7 and 146.1 in the spectrum of **15** are tentatively assigned to the quinone ring carbons C2 and C3. The PMR spectrum (Experimental) of the triacetate of the trihydroxy compound formed by reduction of **15** confirms that this phenol is the corresponding hydroquinone **16a**.

The formation of dimer B from dimer A can be accounted for by the observation that the dimer A oxidation product **13** rapidly isomerizes to **15** in base. In **13** the allylic H atom at position 2, adjacent to a CO, is acidic. Removal of this proton results in direct cyclization to the dihydro-oxepin **15**:



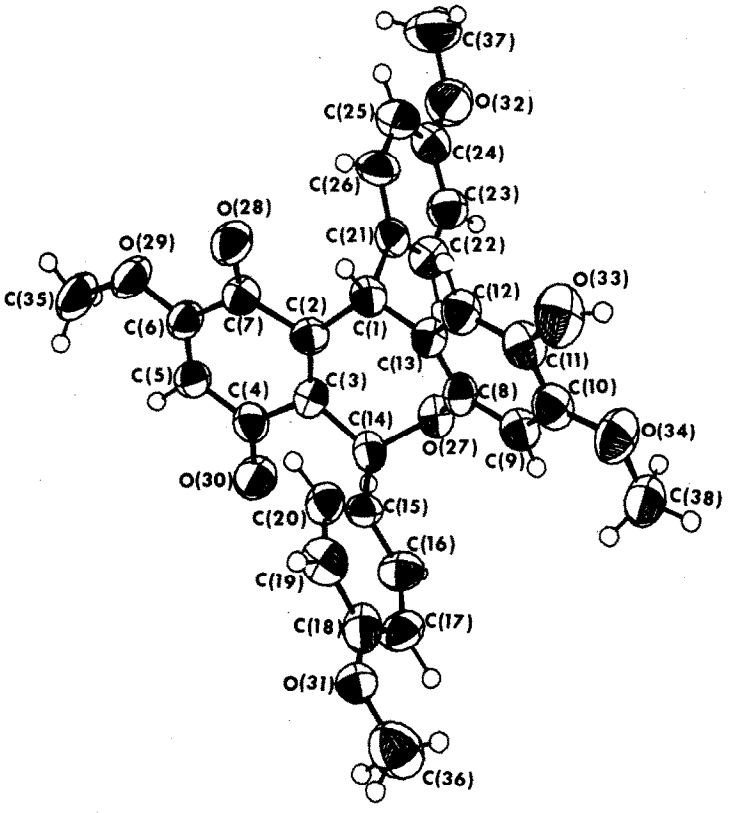
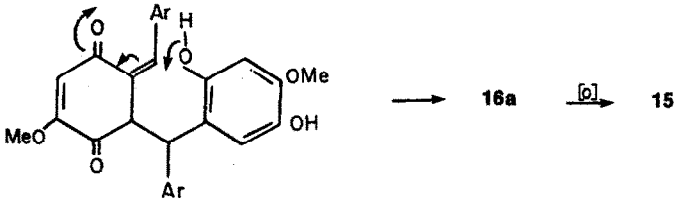


Fig. 2. Ortep drawing of Dimer B with 50% probability thermal ellipsoids. For hydrogen atoms an arbitrary temperature parameter of 1.0 Å^2 was used.

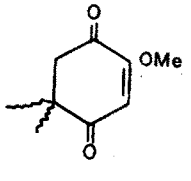


12a

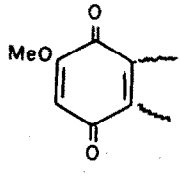
It is also possible that dimer B can be formed directly from **7a** by an alternative ring closure of the quinol **12a**.

We consider this second mechanism less likely, however, since the quinol **16a** has not been detected in either the pyridine reaction of **6** or in the methanolic sodium acetate reaction of **7a**.

Dimer C does not form an acetate, but is reduced by sodium dithionite (indicating a quinone nucleus) to a quinol identical with *dimer D*. Neither C nor D become colored in HCl fumes, unlike dimer A and its oxidation product **13** which develop a characteristic, intensely red color under these conditions. The absence of OH groups and the presence of multiple CO groups in dimer C was indicated by its IR spectrum which showed strong absorption bands at 1650, 1667, 1675, 1687, 1707 cm^{-1}. In addition to the protons of two *p*-methoxyphenyl groups, the PMR spectrum of dimer C shows the presence of a non-aromatic OMe group (δ3.50), an isolated methylene group adjacent to CO as a pair of doublets (J = 16 Hz) at δ2.26 and δ2.60, and an olefinic proton as a singlet at δ5.43. These shifts can be accomodated by the partial structure I and agree well with the corresponding proton shifts in the model O-ethyldimedone **11**. The remaining signals in the PMR spectrum are those of a OMe group, an olefinic proton (singlet at δ5.77) and two coupled methine protons (doublets, J = 2 Hz, at δ4.33 and δ5.50). In the model quinone **14** the olefinic proton *ortho*- to the OMe appears at δ5.88, the second olefinic proton appearing downfield as an allylically coupled doublet at δ6.45. The olefinic proton signal at δ5.77 in dimer C, therefore, indicates the presence of a quinone nucleus substituted as shown in II. Combination of the partial structures I and II with the remaining two coupled methine groups leads to the indan-spirocyclohexendione



I



II

structure **17** for dimer C. This structural assignment is fully supported by the ^{13}C NMR spectrum of dimer C which shows *inter al.* signals of two quinone CO's at 179.2 (C7) and 184.1 (C4), two en-dione CO's at 191.3 (C11) and 196.6 (C8), and a methylene triplet at 47.3 (C12). In addition signals for two CH groups appear at 52.2, 60.6 (C1, C14) and two olefinic CH groups at 107.8 (C5; cf. 107.5 for C5 in **15**, 107.9 for C6 in **14**) and at 112.7 (C9; cf. 112.9 for C5 in **13**). A signal at 63.9 (C13) of a quaternary carbon, unattached to oxygen, confirms the indan-spirocyclohexene ring junction. The signals of two olefinic carbons at 145.7, 147.3 may be assigned to two alkyl-substituted olefinic carbons (C2, C3) of the quinone ring (cf. 145.7, 146.1 for C2, C3 of **15**).

Dimer D forms crystalline diacetyl and di-O-Me derivatives, rapidly reduces ammoniacal silver nitrate, and is oxidized by silver oxide to dimer C. Dimer D, therefore, is the hydroquinone precursor **18a** of dimer C. In accord with this structure its IR spectrum has two CO bands at 1635, 1715 cm^{-1}, and its PMR spectrum is similar to that of **17**, except that the quinoidal proton signal at δ5.77 in **17** is replaced by an aromatic proton singlet at δ6.37 in the spectrum of dimer D. Assignments of signals in the ^{13}C NMR spectrum of the diacetate **18b** of dimer D are shown in Table 3. Signals of two quarternary aromatic carbons at 126.9, 129.8 are noteworthy. These chemical shifts agree well with the shifts of aromatic carbons *ortho*- to C-acetoxyl groups[19] and may be assigned to C2, C3 of the indan ring system.

Additional chemical evidence for the spirocyclohexen-1, 4-dione ring system of **17** and **18a** was provided by oximation and reduction experiments. Thus, whereas the CO group at position 11 of **18a** would be expected to react normally with "carbonyl" reagents, that at position 8, being the vinylog of an ester, should be unreactive. This proved to be the case. The dimethyl derivative **18c** formed a monoxime with excess of hydroxylamine in pyridine, and with sodium borohydride was reduced to two, easily separable, stereoisomeric alcohols **19c** and **20c**. Similarly, sodium borohydride reduction of **18a** gave a mixture of the phenolic alcohols **19a** and **20a**, separated as their crystalline triacetates **19b** and **20b** respectively. Silver oxide oxidation of the alcohols **19a** and **20a** yielded the crystalline alcoholic quinones **21** and **22**.

The stereochemistry of the asymmetric centers of dimers C and D and their alcoholic reduction products can be assigned with reasonable certainty on the basis of the relevant PMR data shown in Table 4. The rigidity of the indan system requires near eclipsing of substituents on C14 and C1; the very low vicinal coupling J_{1-14} observed for all ten compounds indicates that the protons H1 and H14 are *trans* to one another. Furthermore the alternative *cis* configuration would place two bulky aryl groups in very close proximity, a very unfavorable steric arrangement. The stereochemical disposition of the fused spiro ring is not so easily determined, but careful consideration of the data obtained from the compounds in which the C11 keto group has been reduced suggests

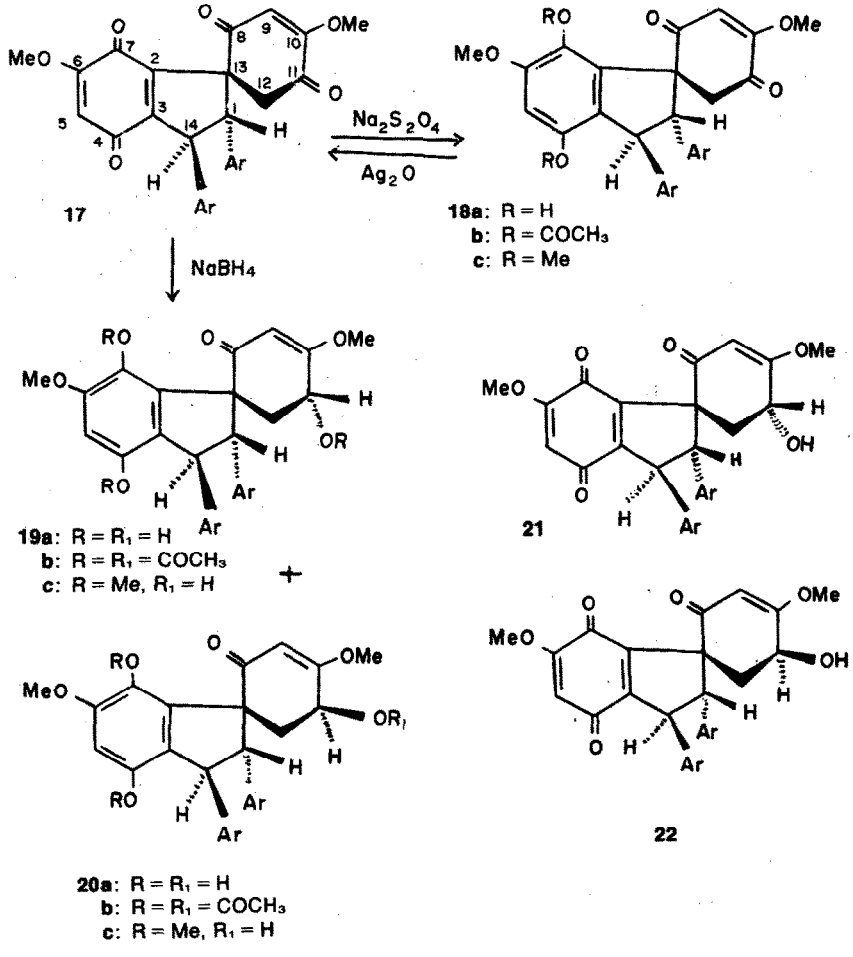
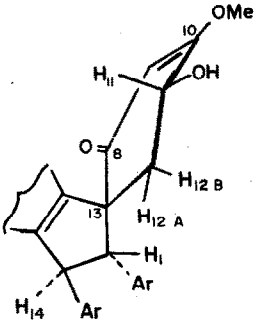


Table 4. Selected chemical shifts and coupling constants of spiroindan compounds[a]

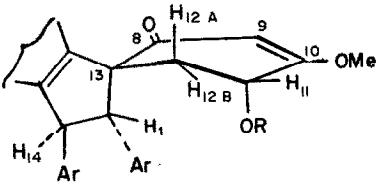
Compounds	m.p.	H_5	H_9	H_{14}	H_1	H_{12A}	H_{12B}	H_{11}	J_{1-14}	J_{11-12A}	J_{11-12B}	$J_{12A-12B}$
17		5.77	5.43	5.50	4.33	2.26	2.60	---	2.0			
18a		6.37	5.50	5.47	4.48	2.40	2.64	---	< 1			
18b		6.65	5.51	5.48	4.38	2.44	2.74	---	< 1			
18c		6.37	5.51	5.61	4.37	2.28	2.70	---	< 1			
19b	212-214°	6.60	5.16	5.65	4.94	1.74	2.05	5.55	< 1	6	2	16
20b	174-175°	6.60	5.04	5.47	4.58	1.55	2.08	6.11	< 1	10	6	14
19c	186-187°	6.38	5.03	5.62	5.33	1.53	2.07	4.19	< 1	6	3	15
20c	158-159°	6.38	5.01	5.62	4.55	1.32	2.12	4.85	< 1	10.5	6	12.5
21	260-262°	5.82	5.02	5.64	5.29	1.50	2.06	4.30	1.5	6	2.5	15
22	201-202°	5.80	4.98	5.55	4.54	1.36	2.08	4.83	1.5	11	6	13.5

[a] Chemical shifts are given in ppm downfield from TMS; coupling constants are in Hz and reported as absolute values.

that C8 and C9 lie on the same side of the plane defined by the indan ring as H14, while C11 and C12 lie on the same side as H1. The reasons for this are as follows: reduction at C11 produces a pair of epimeric compounds which can be separated from each other. Examination of the chemical shift of H1 for each epimeric pair (i.e. **19b** and **20b**, **19c** and **20c**, **21** and **22**) shows a large shift difference (0.4–0.8 ppm) caused by epimerization. The effect on H1 can be caused only by spatial proximity of the C11 oxygen which can occur only if C11 and C12 lie on the same side of the indan plane as H1 as shown in III.

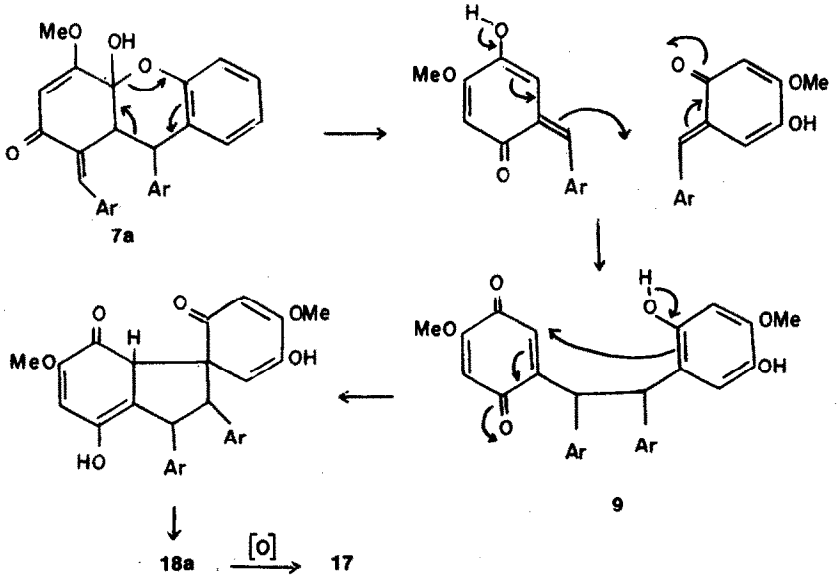


111B



111A

From Dreiding models it can be seen that C8, C9, C10, C11 and C13 lie in or very nearly in a plane, and the array of substituents on C11 and C12 is the same as for cyclohexane rings in the chair form. Of the two likely conformations, IIIA and IIIB, contributions from the latter are considered to be minor, since C11 is too far removed for either epimer to affect H1. For confor-



mation IIIA however, an axial oxygen is only *ca.* 2.1 Å removed from H1. This assumption is further supported by the coupling constants J_{11-12}, which are on the order of 6 and 2.5 Hz for one epimer of each pair and 10.5 and 6 Hz for the other epimer. The isomer having H11 in the axial position, i.e. **22**, **20b** and **20c** gives rise to one large coupling constant due to *trans* diaxial coupling with $H12_A$ and one small coupling constant due to gauche coupling with $H12_B$. Furthermore, assuming reduction by sodium borohydride proceeds predominantly by attack on the C11 CO (of **17**, **18a**, **18c**) from the least hindered side, one would predict that the major epimer formed would have H11 in the equatorial configuration: in fact epimers **21**, **19b** and **19c** predominate by a factor of about 2:1 over **22**, **20b** and **20c**.

The rearrangement of dimer A into the indan dimers C and D can be rationalized by initial dissociation of dimer A into the orthoquinone methide (*cf.* the recent report by Dean and Matkin[20] on the dissociation of xanthen derivatives to *ortho*-quinone methides), recombination to give the intermediate quinhydrone **9**, and cyclization of **9** to give dimer D **10a**.

It is interesting to note that another reasonable mechanism can be written which does not involve dissociation of dimer A, but the formation of an intermediate cyclopropane derivative **23** from **12a**.

The formation of the cyclopropane **23** is similar to the mechanism proposed by Schmidt *et al.*[21] to account for the formation of isomeric dihydrobenzofurans in acid-catalyzed cyclizations of *ortho*-allylphenols.

The methyl **24** and methylenedioxy **25** analogs of **6** also dimerize in pyridine. On the basis of their PMR spectra the chief products formed in these reactions are the xanthens **26a** and **26b** respectively. Oxidation of **26b** yields the quinone **27**.

In contrast to **6**, related α-alkylbenzyl-1,4-benzoquinones do *not* dimerize in basic media. As previously reported[22] for 5 - methoxy - 2 - [1 - (4 - methoxyphenyl)propyl] - 1,4 - benzoquinone, **14** does not react in pyridine and in ethanolic KOH it merely undergoes alkoxy interchange to give the ethoxy analog **28**. The inability to dimerize **14** may be due to both steric and inductive effects of the Me group, which decreases the electrophilicity of the olefinic carbon of the intermediate quinone methide **29**.

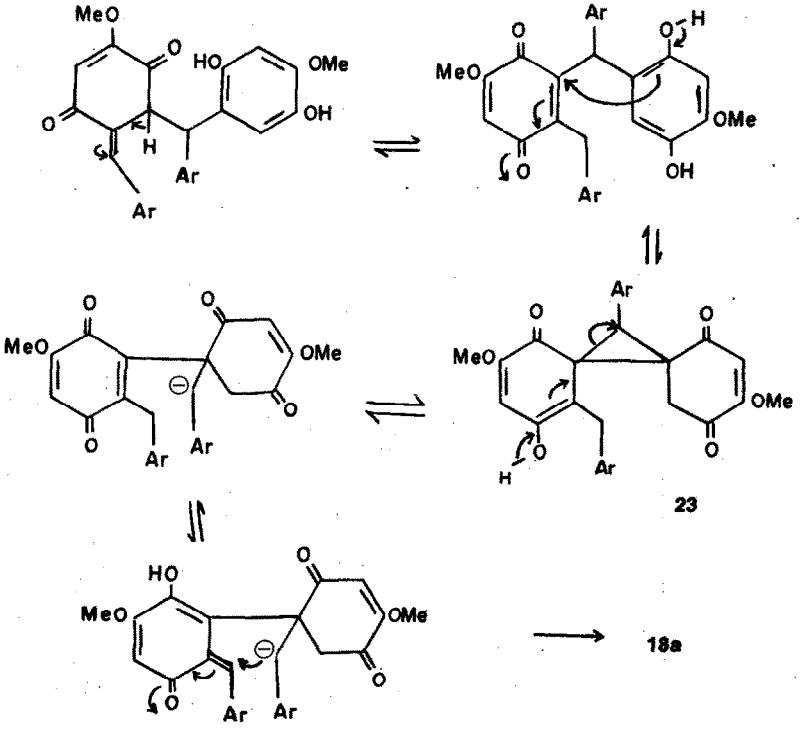
In this connection it is noteworthy that secondary amines react with **14** at the α-Me carbon, indicating[23] the ability of **14** and **29** to isomerize in basic solutions to the ethylene quinol **30**.

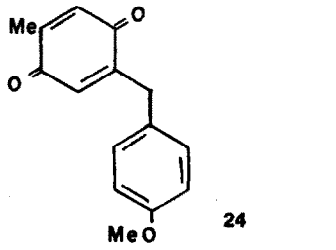
EXPERIMENTAL

All m.ps are uncorrected. PMR spectra, unless stated otherwise, were determined in $CDCl_3$ with TMS as internal standard on a modified Varian HA-100 instrument. IR data were obtained in mineral oil on a Perkin–Elmer model 237 B grating IR spectrophotometer. ^{13}C NMR spectra were measured on a PFT-100 spectrometer in $CDCl_3$ with TMS as internal reference.

5 - *Methoxy* - 2 - (4 - *methoxyphenylmethyl*) *hydroquinone* **5**. A suspension of methoxyhydroquinone (28 g) and 4-methoxybenzyl alcohol (28 g) in 2% aqueous citric acid (500 ml) containing ascorbic acid (5 g) was heated to boiling under reflux for 4 hr. The solid product obtained on cooling was recrystallized from benzene to give **5** as colorless needles, m.p. 114° (49.4 g). (Found: C, 69.3; H, 6.22. $C_{15}H_{16}O_4$ requires: C, 69.2; H, 6.20%). PMR spectrum: δ3.76, 6H, s; δ3.82, 2H, s; δ4.57, 1H(OH), s; δ5.22, 1H(OH), s; δ6.38, 1H, s; δ6.64, 1H, s; δ6.80, 2H, d, J = 8.5 Hz; δ7.11, 2H, d, J = 8.5 Hz.

Warmed with Ac_2O and a drop of pyridine **5** formed a *diacetate*, colorless, glistening plates from MeOH, m.p. 83–84°. (Found: C, 66.4; H, 5.91. $C_{19}H_{20}O_6$ requires: C, 66.3; H, 5.85%). PMR spectrum: δ2.21, 3H, s; δ2.25, 3H, s; δ3.75, 2H, s; δ3.80, 6H, s; δ6.68, 1H, s; δ6.76, 1H, s; δ6.80, 2H, d, J = 9 Hz; δ7.05, 2H, d, J = 9 Hz. Treated with benzoyl chloride and pyridine **5** formed a *dibenzoate*, colorless needles from Me_2CO–MeOH, m.p. 136°. (Found: C, 74.6; H, 5.29. $C_{29}H_{24}O_6$ requires: C, 74.3; H, 5.16%). PMR spectrum: δ3.74, 3H, s; δ3.79, 3H, s; δ3.84, 2H, s; δ6.75, 2H, d, J = 8.5 Hz; δ6.87, 1H, s; δ6.95, 1H, s; δ7.07, 2H, d, J = 8.5 Hz; δ7.38–7.64, 6H, m; δ8.06–8.22, 4H, m.





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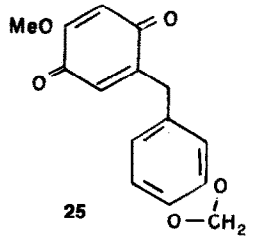

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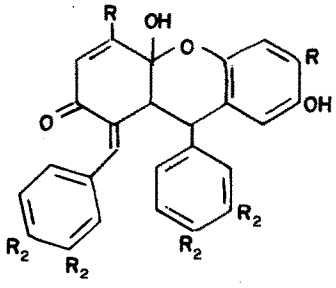
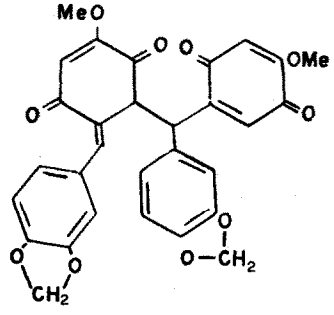
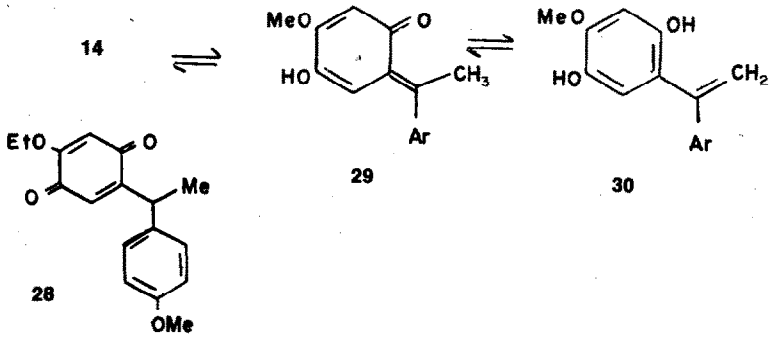


26a: R = Me, R_1 = OMe, R_2 = H
b: R = OMe, R_1R_2 = OCH_2O



27



14 29 30 28

5 - Methoxy - 2 - (4 - methoxyphenylmethyl) - 1,4 - benzoquinone **6**. A soln of **5** (20 g) in acetone (200 ml) was warmed with Ag_2O (30 g) for 15 min. Yellow crystals rapidly separated from the filtered soln. Recrystallized from Me_2CO–MeOH the quinone **6** separated as glistening, golden yellow plates, m.p. 132–133° (16.5 g). (Found: C, 69.8; H, 5.49. $C_{15}H_{14}O_4$ requires: C, 69.7; H, 5.46%); PMR spectrum: δ3.70, 2H, d, J = 2 Hz; δ3.80, 3H, s; δ3.82, 3H, s; δ5.93, 1H, s; δ6.28, 1H, d, J = 2 Hz; δ6.84, 2H, d, J = 9 Hz; δ7.11, 2H, d, J = 9 Hz.

Formation of dimers A, B, C and D

(a) A soln of **6** (40 g) in pyridine (200 ml) was heated on a steam-bath for 1 hr and diluted with water (1.5 l). The solid which separated on standing was collected and heated to boiling with MeOH (250 ml), leaving dimer A as an undissolved, cream-colored solid (26 g). The MeOH filtrate was concentrated and cooled, where upon dimer C separated as yellow needles (2.5 g). Tlc of the MeOH filtrate from C showed the presence of two dimers with color reactions and R_f values in a number of solvent systems identical to dimers B and D, prepared as described in (b).

(b) A soln of dimer A (**7a**; 20 g) in 50% THF–MeOH (1 l) was refluxed with anhyd NaOAc (20 g) for 2.5 hr, concentrated to small volume and diluted with water. The solid product was dissolved in MeOH, concentrated, and cooled. The crystalline product which separated (4.9 g) was recrystallized from acetone–methanol to give dimer D as golden bronze needles. On standing for several days the MeOH filtrate from dimer D deposited dimer C. Recrystallized from Me_2CO–MeOH dimer C was obtained as yellow prisms, m.p. 241–242° (2.35 g). The MeOH filtrate from dimer C was evaporated and chromatographed on a short silicic acid column (80 g) with benzene–THF (9:1) to remove polymeric material. The crude eluate was evaporated to a solid which crystallized from Me_2CO–MeOH to give dimer B as orange needles (2.9 g).

Dimer C was also obtained by oxidation of dimer D (100 mg) in acetone (10 ml) by refluxing with Ag_2O (200 mg) for 2 hr. The residue obtained on evaporation of the filtered soln crystallized from Me_2CO–MeOH to give dimer C (80 mg).

Dimer A (1,4a,9,9a - tetrahydro - 4a,7 - dihydroxy - 4,6 - dimethoxy - 9 - [4 - methoxyphenyl] - 1 - [4 - methoxyphenylmethylene] - xanthen - 2 - one) **7a**

Recrystallized from Me_2CO–MeOH dimer A (**7a**) separated as glistening, cream-colored needles, which become orange colored at about 210–212° and melt with dec. at 220–222°. On silicic acid tlc **7a** characteristically appears as a bright red spot on exposure to HCl gas; it slowly (10–20 min) reduces ammoniacal $AgNO_3$. (Found: C, 69.8; H, 5.46; MW 516 (MS). $C_{30}H_{28}O_8$ requires: C, 69.7; H, 5.46%; MW, 516).

Mono-acylation of dimer A

A soln of **7a** (0.30 g) in pyridine (1 ml) at 30° was treated with Ac_2O (1 ml). After 3 min water was added and the solid product was crystallized from MeOH. Recrystallized from Me_2CO–MeOH **7b** separated as brittle, colorless prisms m.p. 195° (0.27 g). (Found: C, 68.7; H, 5.51. $C_{32}H_{30}O_9$ requires: C, 68.8; H, 5.41%); PMR spectrum: δ2.16, 3H, s; δ3.70, 3H, s; δ3.74, 6H, s; δ3.78, 3H, s; δ3.79, 1H, d, J = 10.5 Hz; δ4.00, 1H, d, J = 10 Hz; δ4.81, 1H(OH), s; δ5.58, 1H, s; δ6.30, 1H, s; δ6.42–6.94, 9H, m; δ7.52,

1H, s. **7a** *monopropionate*, formed similarly with propionic anhydride and pyridine, crystallized from MeOH as cream colored needles, m.p. 190–191°. (Found: C, 69.2; H, 5.60. $C_{33}H_{32}O_9$ requires: C, 69.2; H, 5.63%); PMR spectrum: δ1.16, 3H, t, J = 8 Hz; δ2.46, 2H, q, J = 8 Hz; δ3.71, 3H, s; δ3.74, 6H, s; δ3.78, 3H, s; δ3.80, 1H, d, J = 10.5 Hz; δ4.00, 1H, d, J = 10.5 Hz; δ4.60, 1H(OH), s; δ5.58, 1H, s; δ6.30, 1H, s; δ6.40–6.90, 9H, m; δ7.52, 1H, s.

7a *Monobenzoate* was prepared by reacting dimer A with benzoyl chloride and pyridine at room temp., separated from Me_2CO–MeOH as slightly yellow prisms, m.p. 215° (Found: C, 71.8; H. 5.25. $C_{37}H_{32}O_9$ requires: C, 71.6; H, 5.20%); PMR spectrum: δ3.70, 3H, s; δ3.76, 3H, s; δ3.78, 6H, s; δ3.83, 1H, d, J = 10.5 Hz; δ4.02, 1H, d, J = 10.5 Hz; δ4.42, 1H(OH), s; δ5.62, 1H, s; δ6.40–6.90, 10H, m; δ7.38–7.60, 3H, m; δ7.53, 1H, s; δ7.98–8.17, 2H, m.

Di-acylation of dimer A

A mixture of dimer A (0.5 g), Ac_2O (1.0 ml) and pyridine (0.5 ml) was heated to boiling for 2 min and then heated on a steam bath for 10 min. Addition of water gave a gummy product which was dissolved in warm MeOH. The product which slowly crystallized on cooling was recrystallized from Me_2CO–MeOH to give the *diacetate* **12b** as yellow needles, m.p. 198° (0.21 g). On silicic acid tlc this diacetate has distinctly higher R_f values than the above dimer monoacetate. (Found: C, 68.0; H, 5.35. $C_{34}H_{32}O_{10}$ requires: C, 68.0; H, 5.37%); PMR spectrum: δ2.19, 3H, s; δ2.27, 3H, s; δ3.67, 3H, s; δ3.74, 6H, s; δ3.82, 3H, s; δ4.42, 1H, d, J = 7 Hz; δ4.98, 1H, d, J = 7 Hz; δ5.96, 1H, s; δ6.61, 1H, s; δ6.69, 2H, d, J = 9 Hz; δ6.75, 2H, d, J = 9 Hz; δ6.92, 1H, s; δ7.04, 2H, d, J = 9 Hz; δ7.09, 2H, d, J = 9 Hz; δ7.52, 1H, s.

Oxidation of dimer A

A soln of **7a** (4.0 g) in warm THF (200 ml) was stirred with Ag_2O (12 g) until tlc showed complete conversion to the quinone (50 min). The filtered soln was concentrated, diluted with EtOAc, and reconcentrated until yellow crystals began to separate (3.8 g). Recrystallized from THF–EtOAc, **13** separated as glistening, yellow prisms, which melt at 188–190°, resolidify, and melt again with decomp at 232–233°. On silicic acid chromatograms **13** becomes intensely red in HCl fumes. (Found: C, 70.2; H, 5.12. $C_{30}H_{26}O_8$ requires: C, 70.0; H, 5.09%); PMR spectrum: δ3.72, 3H, s; δ3.76, 3H, s; δ3.80, 3H, s; δ3.86, 3H, s; δ4.52, 1H, d, J = 10.5 Hz; δ4.91, 1H, d, J = 10.5 Hz; δ5.77, 1H, s; δ6.12, 1H, s; δ6.54, 2H, d, J = 9 Hz; δ6.66, 1H, s; δ6.79, 2H, d, J = 9 Hz; δ6.83, 2H, d, J = 9 Hz; δ7.02, 2H, d, J = 9 Hz; δ7.42, 1H, s.

A soln of the dimer oxidation product **13** (0.5 g) in warm THF (20 ml) and MeOH (10 ml) was slowly diluted with 5% aqueous sodium dithionite soln (25 ml). The soln was heated for 5 min and diluted with excess water. The recrystallized product (0.4 g) was identical (tlc, m.p. and m.m.p.) with dimer A.

A soln of the dimer oxidation product **13** (1.0 g) in pyridine (12 ml) was warmed for 4 min on the steam-bath and diluted immediately with water (100 ml). The ppt was collected, washed with dil. HCl, and recrystallized from MeOH–Me_2CO giving orange needles of dimer B, m.p. 214–216° (0.7 g).

Dimer B (5,11 - *dihydro* - 9 - *hydroxy* - 2,8 - *dimethoxy* - 5,11 - *di* - [4 - *methoxyphenyl*] - *dibenzo*[b,e]*oxepin* - 1,4 - *dione* **15**

Prepared either by treatment of **7a** with methanolic NaOAc or by pyridine on the oxidation product **13**, dimer B crystallized from MeOH–Me_2CO as orange needles m.p. 214–216°. When sprayed with 0.5% ethyl cyanoacetate in 5% ethanolic KOH, spots of dimer B on tlc plates turn dark blue in contrast to the turquoise green spots produced by dimers C and D and the violet spot of dimer A. (Found: C, 69.9; H, 5.12. $C_{30}H_{26}O_8$ requires: C, 70.0; H, 5.09%); PMR spectrum δ3.45, 3H, s; δ3.73, 6H, s; δ3.76, 3H, s; δ5.31, 1H, s, (OH); δ5.43, 1H, s; δ5.76, 1H, s; δ5.82, 1H, s; δ6.52, 1H, s; δ6.68, 2H, d, J = 8 Hz; δ6.75, 2H, d, J = 8 Hz; δ6.84, 1H, s; δ6.95, 2H, d, J = 8 Hz; δ7.38, 2H, d, J = 8 Hz.

Acetylation of dimer B

A mixture of **15** (120 mg), Ac_2O (2 ml), and pyridine (3 drops) was warmed for 10 min on the steam bath, diluted with water (25 ml) and allowed to stand for 1 hr. The ppt was recrystallized from MeOH–Me_2CO to give yellow needles of **15** *monoacetate* m.p. 171–173° (80 mg). (Found: C, 68.8; H, 5.06; MW, 556 (MS); $C_{32}H_{28}O_9$ requires: C, 69.1; H, 5.07%; MW, 556); PMR spectrum: δ2.25, 3H, s; δ3.39, 3H, s; δ3.72, 6H, s; δ3.76, 3H, s; δ5.46, 1H, br. s; δ5.82, 2H, s; δ6.54, 1H, s; δ6.69, 2H, d, J = 9 Hz; δ6.77, 2H, d, J = 9 Hz; δ6.94, 2H, d, J = 9 Hz; δ6.98, 1H, s; δ7.36, 2H, d, J = 9 Hz.

Reductive acetylation of dimer B

A mixture of **15** (1.5 g), anhyd NaOAc (3.0 g), Zn dust (3.0 g), and Ac_2O (15 ml) was boiled for 2 min, heated on the steam bath for 10 min, filtered, and diluted with water (200 ml). The solid which formed was crystallized as nearly colorless needles from Me_2CO–MeOH (1.5 g). Recrystallization from Me_2CO–MeOH gave colorless needles of **16b** m.p. 191–192° (1.3 g). (Found: C, 67.3; H, 5.41; MW 642 (ms); $C_{36}H_{34}O_{11}$ requires: C, 67.3; H, 5.33%; MW 642); PMR spectrum: δ1.73, 3H, s; δ2.20, 3H, s; δ2.27, 3H, s; δ3.39, 3H, s; δ3.71, 6H, s; δ3.80, 3H, s; δ5.33, 1H, br. s; δ5.76, 1H, s; δ6.52, 1H, s; δ6.60–6.90, 7H, m; δ7.02, 1H, s; δ7.03, 2H, d, J = 8.5 Hz.

Reduction of dimer B

A soln of **15** (200 mg) in ether–THF (100 ml) was shaken briefly with 5% aqueous sodium dithionite (100 ml). The organic layer was washed with water, dried over Na_2SO_4, and evaporated to dryness. Crystallization of the residue from MeOH gave slightly orange crystals (140 mg). Recrystallization from MeOH gave nearly colorless needles of **16a** m.p. 246–247° (60 mg). (Found: C, 69.6; H, 5.60. $C_{30}H_{28}O_8$ requires: C, 69.7; H, 5.46%); IR spectrum (KBr); 3375, 1610 cm^{-1}; PMR spectrum, d_6-acetone: δ3.41, 3H, s; δ3.69, 6H, s; δ3.76, 2H, s (OH); δ3.79, 3H, s; δ5.69, 1H, br. s; δ5.73, 1H, s; δ6.48, 1H, s; δ6.55, 1H, s; δ6.65, 2H, d, J = 9 Hz; δ6.69, 2H, d, J = 9 Hz; δ6.86, 2H, d, J = 9 Hz; δ6.88, 2H, s; δ7.14, 2H, d, J = 9 Hz. Acetylation of **16a** gave a triacetate, m.p. 190–191°, identical (mmp and PMR spectrum) with the reductive triacetate **16b** of dimer B.

Dimer D (1,2 - *dihydro* - 4,7 - *dihydroxy* - 4',6 - *dimethoxy* - 2,3 - *di* - (4 - *methoxyphenyl*) - 3H - *inden* - 1 - *spiro* - 1' - *cyclohex* - 3' - *en* - 2',5' - *dione* **18a**

Recrystallized from MeOH–Me_2CO, dimer D separated as golden needles, m.p. 166–168°, containing one MeOH of crystallization not removed by drying. (Found: C, 67.6; H, 5.86; MW 516 (MS). $C_{30}H_{28}O_8 \cdot CH_3OH$ requires: C, 67.9; H, 5.88%; $C_{30}H_{28}O_8$ requires: MW, 516); PMR spectrum: δ1.26, 1H, broad s ($CH_3\underline{O}H$): δ2.40, 1H, d, J = 16 Hz; δ2.64, 1H, d, J = 16 Hz; δ3.47, 3H, s ($\underline{CH_3}OH$); δ3.53, 3H, s; δ3.76, 3H, s; δ3.78, 3H, s; δ3.83, 3H, s; δ4.48, 2H, br. s, (1-CH, 1-OH); δ5.10, 1H, s (OH); δ5.47, 1H, s; δ5.50, 1H, s; δ6.37, 1H, s; δ6.75, 2H, d, J = 9 Hz; δ6.81, 2H, d, J = 9 Hz; δ6.90, 2H, d, J = 9 Hz; δ7.04, 2H, d, J = 9 Hz.

Acetylation of dimer D

A mixture of dimer D (200 mg), Ac_2O (4 ml) and pyridine (4 drops) was warmed for 5 min on the steam bath, diluted with water (50 ml), and allowed to stand. The solid product was recrystallized twice from MeOH–Me_2CO to give **18b** as pale yellow glistening plates, m.p. 226–227° (170 mg). (Found: C, 68.0; H, 5.40; MW, 600 (MS). $C_{34}H_{32}O_{10}$ requires: C, 68.0; H, 5.37%; MW 600); PMR spectrum: δ1.70, 3H, s; δ1.76, 3H, s; δ2.44, 1H, d, J = 16 Hz; δ2.74, 1H, d, J = 16 Hz; δ3.57, 3H, s; δ3.78, 3H, s; δ3.80, 3H, s; δ3.81, 3H, s; δ4.38, 1H, s; δ5.48, 1H, s; δ5.51, 1H, s; δ6.65, 1H, s; δ6.76, 4H, s; δ6.84–7.14, 4H, m.

Oxidation of dimer D

A soln of dimer D (100 mg) in Me_2CO (10 ml) was refluxed with Ag_2o (500 mg) for 1 hr. Evaporation of the filtered soln to dryness followed by crystallization of the residue twice from MeOH–Me_2CO gave fine yellow needles of dimer C, m.p. 244–245° (70 mg).

Reduction of dimer D

To a suspension of dimer D (500 mg) in MeOH (8 ml) and THF (2 ml) was added $NaBH_4$ (60 mg), and the mixture was warmed for 10 sec on the steam bath to initiate the reaction. After 8 min a

second portion of $NaBH_4$ was added and the mixture was swirled until all of the solids had dissolved. Addition of AcOH (0.5 ml) and water (100 ml) precipitated a colorless solid. Because tlc (benzene–EtOH, 9:1) revealed two products and attempts at recrystallization failed, the entire crude product was warmed on the steam bath with Ac_2O (4 ml) and pyridine (10 drops) for 5 min. After dilution with water the solid was collected and dissolved in wet MeOH (20 ml). After several days the soln had deposited two distinctly different types of crystals; samples of each were obtained by mechanical separation and tlc (benzene–THF 9:1) showed them to be different and essentially pure.

The remaining crystals and soln were dissolved in MeOH–Me_2CO (8 ml) after removal of solvents and seeded with the higher R_f crystals. The fine needles which separated were collected and recrystallized three times to give pure **19b** m.p. 212–214° (130 mg). (Found: C, 67.0; H, 5.73; MW 644 (MS). $C_{36}H_{36}O_{11}$ requires: C, 67.1; H, 5.63%; MW 644); IR spectrum: 1770, 1750, 1655, 1630, 1610 cm^{-1}; PMR spectrum δ1.54, 3H, s; δ1.74, 1H, dd, J = 6, 16 Hz; δ1.96, 3H, s; δ2.05, 1H, dd, J = 2, 16 Hz; δ2.25, 3H, s; δ3.62, 3H, s; δ3.75, 3H, s; δ3.77, 3H, s; δ3.79, 3H, s; δ4.94, 1H, s; δ5.16, 1H, s; δ5.55, 1H, dd, J = 2, 6 Hz; δ5.65, 1H, s; δ6.60, 1H, s; δ6.74, 2H, d, J = 8 Hz; δ6.78, 2H, d, J = 8 Hz; δ6.88, 2H, d, J = 8 Hz; δ7.06, 2H, d, J = 8 Hz. The first filtrate from **19b** was concentrated and seeded with the lower R_f crystals. After standing for several days the dense prisms were collected and recrystallized from MeOH–Me_2CO providing pure isomeric **20b**, m.p. 174–175° (100 mg). (Found: C, 66.8; H, 5.67; MW 644 (MS). $C_{36}H_{36}O_{11}$ requires: C, 67.1; H, 5.63%; MW 644); IR spectrum: 1770, 1750, 1650, 1610 cm^{-1}; PMR spectrum: δ1.55, 1H, dd, J = 10, 14 Hz; δ1.63, 3H, s; δ1.80, 3H, s; δ2.04, 3H, s; δ2.08, 1H, dd, J = 6, 14 Hz; δ3.50, 3H, s; δ3.74, 3H, s; δ3.77, 6H, s; δ4.58, 1H, s; δ5.04, 1H, s; δ5.47, 1H, s; δ6.11, 1H, dd, J = 6, 10 Hz; δ6.60, 1H, s; δ6.69, 2H, d, J = 8 Hz; δ6.78, 4H, d, J = 8 Hz; δ6.86, 2H, d, J = 8 Hz.

Reduction-reoxidation of dimer D

A suspension of dimer D (1.0 g) in MeOH (16 ml) and THF (4 ml) was reduced with $NaBH_4$ (*vide supra*); the crude product was collected, dried and refluxed in Me_2CO (30 ml) for 15 min with Ag_2O (1.5 g). The filtered soln was diluted with MeOH and concentrated on the steam bath. The crystals which formed were recrystallized from MeOH–Me_2CO to give golden-bronze needles of **21**, m.p. 260–262°. (Found: C, 69.5; H, 5.45. $C_{30}H_{28}O_8$ requires: C, 69.7; H, 5.46%); IR spectrum: 3375, 1685, 1675, 1650, 1630, 1612 cm^{-1}; PMR spectrum: δ1.50, 1H, dd, J = 6, 15 Hz; δ2.06, 1H, dd, J = 2.5, 15 Hz; δ2.70, 1H, d, J = 3 Hz (OH); δ3.62, 3H, s; δ3.76, 3H, s; δ3.78, 6H, s; δ4.30, 1H, ddd, J = 2.5, 3, 6 Hz; δ5.02, 1H, s; δ5.29, 1H, d, J = 2.5 Hz; δ5.64, 1H, d, J = 2.5 Hz; δ5.82, 1H, s; δ6.74, 2H, d, J = 8 Hz; δ6.80, 2H, d, J = 8 Hz; δ6.97, 2H, d, J = 8 Hz; δ7.02, 2H, d, J = 8 Hz. Warmed with Ac_2O containing a trace of **21** formed a monoacetate m.p. 218–219°. (Found: C, 68.6; H, 5.35. $C_{32}H_{30}O_9$ requires: C, 68.8; H, 5.41%); PMR spectrum: δ1.53, 1H, dd, J = 6, 15 Hz; δ1.97, 1H, dd, J = 2, 15 Hz; δ2.24, 3H, s; δ3.60, 3H, s; δ3.76, 6H, s; δ3.79, 3H, s; δ5.01, 1H, d, J = 2 Hz; δ5.14, 1H, s; δ5.50, 1H, dd, J = 2, 6 Hz; δ5.73, 1H, d, J = 2 Hz; δ5.80, 1H, s; δ6.75, 4H, d, J = 8 Hz; δ6.91, 2H, d, J = 8 Hz; δ7.00, 2H, d, J = 8 Hz.

Treated with pyridinium chlorochromate and anhyd NaOAc in CH_2Cl_2, **21** gave a good yield of yellow needles, m.p. 238–239°, identical (tlc, PMR) to dimer C.

The mother liquor from **21** contained a second isomer (tlc, benzene THF 9:1), and after removal of solvents the residue was chromatographed on silicic acid employing benzene–THF as eluant. In addition to more **21** (135 mg) a second more polar **22** was isolated (226 mg). Recrystallized from cyclohexane–EtOAc (1:1, 5 ml) **22** separated as dense orange prisms, m.p. 201–202°. (Found: C, 69.7; H, 5.62. $C_{30}H_{28}O_8$ requires: C, 69.7; H, 5.46%); IR spectrum; 3490, 1675, 1663, 1650, 1612 cm^{-1}; PMR spectrum; δ1.36, 1H, dd, J = 11, 13.5 Hz; δ2.08, 1H, dd, J = 6, 13.5 Hz; δ2.52, 1H, br. s (OH); δ3.56, 3H, s; δ3.76, 3H, s; δ3.77, 3H, s; δ3.78, 3H, s; δ4.54, 1H, d, J = 2.5 Hz; δ4.83, 1H, dd, J = 6, 11 Hz; δ4.98, 1H, s; δ5.55, 1H, d, J = 2.5 Hz; δ5.80, 1H, s; δ6.72, 2H, d, J = 8 Hz; δ6.78, 2H, d, J = 8 Hz; δ6.90, 2H, d, J = 8 Hz; δ6.95, 2H, d, J = 8 Hz.

Methylation of dimer D

A mixture of dimer D (700 mg) Me_2SO_4 (2.0 ml), anhyd K_2CO_3 (5.0 g), and Me_2CO (20 ml) was refluxed for 1 hr, concentrated and diluted with water. The solid product was recrystallized from MeOH–Me_2CO to give **18c** as glistening slightly yellow needles, m.p. 182–183° (500 mg). (Found: C, 70.6; H, 5.95. $C_{32}H_{32}O_8$ requires: C, 70.6; H, 5.92%); IR spectrum: 1703, 1663, 1607 cm^{-1}; PMR spectrum: δ2.28, 1H, d, J = 16 Hz; δ2.70, 1H, d, J = 16 Hz; δ3.40, 3H, s; δ3.51, 3H, s; δ3.58, 3H, s; δ3.69, 3H, s; δ3.72, 3H, s; δ3.81, 3H, s; δ4.37, 1H, s; δ5.51, 1H, s; δ5.61, 1H, s; δ6.37, 1H, s; δ6.69, 4H, s; δ6.73, 2H, d, J = 8 Hz; δ7.03, 2H, d, J = 8 Hz.

Reduction of dimer D dimethyl ether

A soln of **18c** (200 mg) in MeOH (3 ml) and THF (3 ml) was stirred with $NaBH_4$ (30 mg) for 10 min. Another portion of $NaBH_4$ was added and stirring continued for 10 min; AcOH (3 drops) and water (100 ml) were added and the solid ppt was collected and dried. Because tlc (benzene–THF, 9:1) revealed a mixture of two major compounds and crystallization separated them with low efficiency, the crude mixture was eluted from a silicic acid column with benzene–THF (19:1) to give two isomeric products. Recrystallized from wet MeOH the less polar isomer **19c** separated as colorless needles, m.p. 186–187° (65 mg). (Found: C, 70.2; H, 6.26. $C_{32}H_{34}O_8$ requires: C, 70.3; H, 6.27%); IR spectrum (KBr): 3525, 1665, 1620 cm^{-1}; PMR spectrum: δ1.53, 1H, dd, J = 6, 15 Hz; δ2.07, 1H, dd, J = 3, 15 Hz; δ3.20, 1H, d, J = 3 Hz (OH); δ3.37, 3H, s; δ3.50, 3H, s; δ3.57, 3H, s; δ3.67, 3H, s; δ3.70, 3H, s; δ3.80, 3H, s; δ4.19, 1H, m; δ5.03, 1H, s; δ5.33, 1H, s; δ5.62, 1H, s; δ6.38, 1H, s; δ6.62, 2H, d, J = 8 Hz; δ6.70, 2H, d, J = 8 Hz; δ6.85, 2H, d, J = 8 Hz; δ7.05, 2H, d, J = 8 Hz. The more polar isomer **20c** was recrystallized from wet MeOH to give colorless needles, m.p. 158–159° (56 mg). (Found: C, 69.2; H, 6.44. $C_{32}H_{34}O_8 \cdot 1/2H_2O$ requires: C, 69.2; H, 6.35%). IR spectrum (KBr): 3425, 1630, 1610 cm^{-1}; PMR spectrum: δ1.32, 1H, dd, J = 11, 13 Hz; δ1.96, 1H, s (1/2H_2O); δ2.12, 1H, dd, J = 6, 13 Hz; δ2.91, 1H, d, J = 3 Hz (OH); δ3.36, 3H, s; δ3.49, 3H, s; δ3.52, 3H, s; δ3.68, 6H, s; δ3.76, 3H, s; δ4.55, 1H, s; δ4.85, 1H, m; δ5.01, 1H, s; δ5.62, 1H, s; δ6.38, 1H, s; δ6.68, 4H, s; δ6.70, 2H, d, J = 9 Hz; δ7.01, 2H, d, J = 9 Hz.

Oximation of dimer D dimethyl ether

A soln of **18c** (200 mg) and excess hydroxylamine hydrochloride in pyridine was warmed for 10 min on the steam bath and diluted with water. The ppt was recrystallized from MeOH to give colorless crystals of mono-oxime, m.p. 210° (140 mg). (Found: C, 68.5; H, 5.93; N, 2.56. $C_{32}H_{33}O_8N$ requires: C, 68.7; H, 5.94; N, 2.50%); PMR spectrum: δ1.83, 1H, d, J = 16 Hz; δ3.34, 1H, d, J = 16 Hz; δ3.38, 3H, s; δ3.50, 3H, s; δ3.62, 3H, s; δ3.68, 3H, s; δ3.72, 3H, s; δ3.80, 3H, s; δ4.28, 1H, s; δ5.23, 1H, s; δ5.74, 1H, s; δ6.38, 1H, s; δ6.68, 4H, s; δ6.73, 2H, d, J = 9 Hz; δ7.11, 2H, d, J = 9 Hz.

Dimer C (1,2 - dihydro - 4',6 - dimethoxy - 2,3 - di(4 - methoxyphenyl) - 3H - inden - 1 - spiro - 1' - cyclohex - 3' - en - 2'4,5'7 - tetrone **17**

Prepared by Ag_2O oxidation of dimer D (*vide supra*) or by the reaction of **6** in pyridine dimer C separated from MeOH–Me_2CO as fine yellow needles, m.p. 244–245°. (Found: C, 69.6; H, 5.08. $C_{30}H_{26}O_8$ requires: C, 70.0; H, 5.09%); PMR spectrum: δ2.26, 1H, d, J = 16 Hz; δ2.60, 1H, d, J = 16 Hz; δ3.50, 3H, s; δ3.70, 3H, s; δ3.73, 3H, s; δ3.74, 3H, s; δ4.33, 1H, d, J = 2 Hz; δ5.43, 1H, s; δ5.50, 1H, d, J = 2 Hz; δ5.77, 1H, s; δ6.60–7.00, 8H, m.

Reduction of dimer C (sodium borohydride)

Reduction of **17** with $NaBH_4$ followed by acetylation or oxidation with Ag_2O gave products identical to those prepared by like treatments of dimer D.

Reduction of dimer C (sodium dithionite)

A soln of **17** (200 mg) in ether–THF was shaken for several minutes with 5% aqueous sodium dithionite. The ether layer was evaporated and the residue acetylated (Ac_2O–pyridine) to give a diacetate, m.p. 223–224°, identical (tlc, PMR) with dimer D diacetate **18b**.

5 - *Methoxy* - 2 - (3,4 - *methylenedioxyphenylmethyl*) *hydroquinone*. A soln of 2-methoxyhydroquinone (14 g), piperonyl alcohol (15.2 g) and ascorbic acid (5 g) in 2% aqueous citric acid (250 ml) was heated under reflux for 2 hr and cooled. The crystalline product was recrystallized from aqueous MeOH to yield 5-*methoxy*-2-(3,4-*methylendioxyphenylmethyl*) *hydroquinone*, as colorless needles, m.p. 151–152° (26.2 g). (Found: C, 65.7; H, 5.15. $C_{15}H_{14}O_5$ requires: C, 65.7; H, 5.15%); PMR spectrum: δ3.80, 2H, s; δ3.83, 3H, s; δ4.31, 1H, s; δ5.12, 1H, s; δ5.90, 2H, s; δ6.41, 1H, s; δ6.74, 4H, s.

With Ac_2O and pyridine the product formed the *di*-O-*acetyl derivative*, colorless needles from MeOH, m.p. 90–91°. (Found: C, 63.8; H, 5.09. $C_{19}H_{18}O_7$ requires: C, 63.7; H, 5.06%); PMR spectrum: δ2.23, 3H, s; δ2.26, 3H, s; δ3.72, 2H, s; δ3.78, 3H, s; δ5.90, 2H, s; δ6.54–6.78, 5H, m.

5 - *Methoxy* - 2 - (3,4 - *methylenedioxyphenylmethyl*) - 1,4 - *benzoquinone* **25**. A soln of the above hydroquinone (5 g) in Me_2CO (50 ml) was warmed with Ag_2O (10 g) for 20 min. The filtered soln was concentrated, diluted with MeOH, and reconcentrated until yellow crystals separated. Recrystallized from Me_2CO–MeOH the **25** separated as golden yellow needles, m.p. 169–170° (4.2 g). (Found: C, 65.9; H, 4.42. $C_{15}H_{12}O_5$ requires: C, 66.2; H, 4.44%); PMR spectrum: δ3.69, 2H, d, J = 1 Hz; δ3.82, 3H, s; δ5.94, 3H, s; δ6.31, 1H, d, J = 1 Hz; δ6.58–6.80, 3H, m.

A soln of **25** (5.0 g) in pyridine (20 ml) was heated on a steam-bath for 1 hr and diluted with water. The crude product was digested with 50% Me_2CO–MeOH (100 ml). The undissolved solid was recrystallized from THF–MeOH to give **26b** as colorless, glistening prisms, m.p. 242–243° (2.60 g). (Found: C, 66.1; H, 4.46. $C_{30}H_{24}O_{10}$ requires: C, 66.2; H, 4.44%); IR spectrum: 3350, 1645, 1615 cm^{-1}. PMR spectrum (d_5 pyridine): δ3.53, 3H, s; δ3.72, 3H, s; δ4.23, 1H, d, J = 10 Hz; δ4.48, 1H, d, J = 10 Hz; δ5.92, 4H, s; δ5.95, 1H, s; δ6.56–6.80, 7H, m; δ7.00, 1H, s; δ7.99, 1H, s; δ10.40, 2H (OH), s. **26b** slowly reduces ammoniacal $AgNO_3$ and it becomes intensely red on silicic acid chromatograms with HCl fumes.

A soln of **26b** (0.5 g) in warm THF (200 ml) was stirred with Ag_2O (2.5 g) for 6 hr. The filtered soln was concentrated, diluted with EtOAc and reconcentrated until the product crystallized. Recrystallized from THF–EtOAc **27b** was obtained as yellow-orange needles, m.p. 249–250° d. (0.23 g). (Found: C, 66.6; H, 4.21. $C_{30}H_{22}O_{10}$ requires: C, 66.4; H, 4.09%); IR spectrum: 1695, 1670, 1645 cm^{-1}; PMR spectrum: δ3.78, 3H, s; δ3.84, 3H, s; δ4.43, 1H, d, J = 11 Hz; δ4.83, 1H, d, J = 11 Hz; δ5.82, 1H, s; δ5.86, 2H, s; δ6.05, 2H, s; δ6.16–6.82, 8H, m; δ7.37, 1H, s.

5 - *Methyl* - 2 - (4 - *methoxyphenylmethyl*)*hydroquinone*. A mixture of *p*-toluhydroquinone (24.8 g), 4-methoxybenzyl alcohol (27.6 g), and ascorbic acid (5 g) was heated under reflux in 2% aqueous citric acid (500 ml) for 5 hr and cooled. The solid product was crystallized from benzene to give 5 - *methyl* - 2 - *methoxyphenylmethyl*)*hydroquinone* as colorless needles, m.p. 127° (21.0 g). (Found: C, 73.6; H, 6.62. $C_{15}H_{16}O_3$ requires: C, 73.7; H, 6.60%); PMR spectrum: δ2.18, 3H, s; δ3.78, 3H, s; δ3.85, 2H, s; δ4.38, 2H (OH), s; δ6.51, 1H, s; δ6.58, 1H, s; δ6.84, 2H, d, J = 9 Hz; δ7.15, 2H, d, J = 9 Hz. The dibenzoate of the product crystallized from Me_2CO–MeOH as colorless needles, m.p. 119°. (Found: C, 77.1; H, 5.35. $C_{29}H_{24}O_5$ requires: C, 77.0; H, 5.35%); PMR spectrum: δ2.23, 3H, s; δ3.76, 3H, s; δ3.89, 2H, s; δ6.76, 2H, d, J = 8 Hz; δ6.97, 1H, s; δ7.07, 2H, d, J = 8 Hz; δ7.12, 1H, s; δ7.38–7.72, 6H, m; δ8.04–8.30, 4H, m.

5 - *Methyl* - 2 - (4 - *methoxyphenylmethyl*) - 1,4 - *benzoquinone* **24**. A soln of the above hydroquinone (10 g) in Me_2CO (100 ml) was stirred with Ag_2O (15 g) for 1 hr. The filtered soln was concentrated, diluted with MeOH and cooled. The crystalline product (9.1 g) was recrystallized from Me_2CO–MeOH to give **24** as large, glistening yellow needles, m.p. 78–79°. (Found: C, 74.8; H, 5.82. $C_{15}H_{14}O_3$ requires: C, 74.4; H, 5.83%); PMR spectrum: δ2.02, 3H, d, J = 1 Hz; δ3.67, 2H, d, J = 1 Hz; δ3.78, 3H, s; δ6.35, 1H, d, J = 1 Hz; δ6.59, 1H, d, J = 1 Hz; δ6.84, 2H, d, J = 9 Hz; δ7.11, 2H, d, J = 9 Hz.

A soln of **24** (4.0 g) in pyridine (8 ml) was heated on a steam-bath for 1 hr. The gummy product obtained on adding water was dissolved in warm MeOH. On cooling slightly yellow crystals slowly separated (0.70 g). Recrystallized from Me_2CO–MeOH, the dimer **26a** separated as cream-colored needles, m.p. 222–223°. (Found: C, 74.5; H, 5.86. $C_{30}H_{28}O_6$ requires: C, 74.4; H, 5.83%); IR spectrum: 3300, 1650 cm^{-1}; PMR spectrum (d_5 pyridine): δ2.16, 3H, d, J = 1.5 Hz; δ2.42, 3H, s; δ3.57, 3H, s; δ3.60, 3H, s; δ4.13, 1H, dd, J = 9, 0.5 Hz; δ4.41, 1H, d, J = 9 Hz; δ6.38, 1H, d, J = 1.5 Hz; δ6.48–6.68, 5H, m; δ6.78–7.00, 4H, m; δ7.08, 1H, s; δ7.83, 1H, d, J = 0.5 Hz. Reaction of **26a** with Ac_2O and pyridine at room temp. gave **26a** *monoacetate*, slightly yellow needles from MeOH, m.p. 177–178°. (Found: C, 72.9; H, 5.78. $C_{32}H_{30}O_7$ requires: C, 73.0; H, 5.74%); IR spectrum: 3210, 1760, 1650, 1615, 1605 cm^{-1}; PMR spectrum: δ2.03, 3H, d, J = 0.5 Hz; δ2.10, 3H, s; δ2.17, 3H, s; δ3.70, 3H, s; δ3.74, 3H, s; δ3.82, 1H, d, J = 10 Hz; δ3.84, 1H (OH), s; δ3.96, 1H, d, J = 10 Hz; δ6.15, 1H, d, J = 0.5 Hz; δ6.31, 1H, s; δ6.46–6.82, 9H, m; δ7.49, 1H, s.

5 - *Ethoxy* - 2 - [1 - (4 - *methoxyphenyl*)*ethyl*] - 1,4 - *benzoquinone* **28**. A soln of **28**[23] (1.0 g) in EtOH (25 ml) containing one drop of 15% KOH aq was heated to boiling for 10 min and allowed to stand at room temp. for 24 hr. The crystalline product (0.9 g) was recrystallized from Me_2CO–EtOH to give **29** as yellow needles, m.p. 96°. (Found: C, 71.3; H, 6.35. $C_{17}H_{18}O_4$ requires: C, 71.3; H, 6.34%); PMR spectrum: δ1.38–1.56, 6H, m; δ3.79, 3H, s; δ3.99, 2H, q, J = 7 Hz; δ4.28, 1H, d, q, J = 7, 1 Hz; δ5.87, 1H, s; δ6.46, 1H, d, J = 1 Hz; δ6.84, 2H, d, J = 9 Hz; δ7.15, 2H, d, J = 9 Hz.

Heated with pyridine or methanolic KOH for 1 hr **28** was recovered unchanged (m.p. and m.m.p. 165–166°).

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