mg, 1.8 mmol) were reacted and then poured into 0.3 M hydrochloric acid by following the procedure described above. After this aqueous layer was washed twice with methylene chloride, it was transferred to a round-bottom flask bearing a glass tube leading into a solution of 2,4-dinitrophenylhydrazine (182 mg, 0.92 mmol) in 10 mL of methanol and concentrated hydrochloric acid (10 drops). Some of the aqueous solution was transferred to the 2,4-dinitrophenylhydrazine solution by distillation, leading to the formation of a yellow precipitate. Filtration yielded 77 mg (41%) of the 2,4-dinitrophenylhydrazone of formaldehyde of mp 165–167 °C.

Two control reactions were run. In one control, the usual procedure was followed but 1 was omitted and no 2,4-DNP was formed. In the other control, the reaction product was simulated by a mixture of TEMPO, 1-hydroxy-2,2,6,6-tetramethylpiperidine, 3, and formaldehyde in methylene chloride. Extraction with dilute hydrochloric acid and distillation led to production of the anticipated amount of the 2,4-DNP of formaldehyde.

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Registry No. 1, 26864-01-7; 2, 121-69-7; 3, 100-61-8; 6, 91-66-7; TEMPO, 2564-83-2; BMA, 3416-49-7; B_2MA, 614-30-2; $PhNH_2$, 62-53-3; $PhN(CH_2CH_3)CH_3$, 613-97-8; $H_3CC(=NPh)CH_3$, 1124-52-3; $PhNHC(CH_3)_3$, 937-33-7; $PhN(CH_3)C(CH_3)_3$, 70974-88-8; $PhN(CH_3)CH(CH_3)_3$, 10545-45-6; $PhNHCH_2Ph$, 103-32-2; $PhNHCH(CH_3)_2$, 768-52-5; $PhNH(CH_2)_3CH_3$, 1126-78-9; $PhNHCH_2CH_3$, 103-69-5; $PhN(CH_2CH_3)CHO$, 5461-49-4; $PhN((CH_2)_3CH_3)CHO$, 35082-00-9; $PhN(CH(CH_3)_2)CHO$, 52008-97-6; $H_3CN(Ph)CHO$, 93-61-8; 1-hydroxy-2,2,6,6-tetramethylpiperidine, 7031-93-8.

Oxidations of Vitamin E (α-Tocopherol) and Its Model Compound 2,2,5,7,8-Pentamethyl-6-hydroxychroman. A New Dimer

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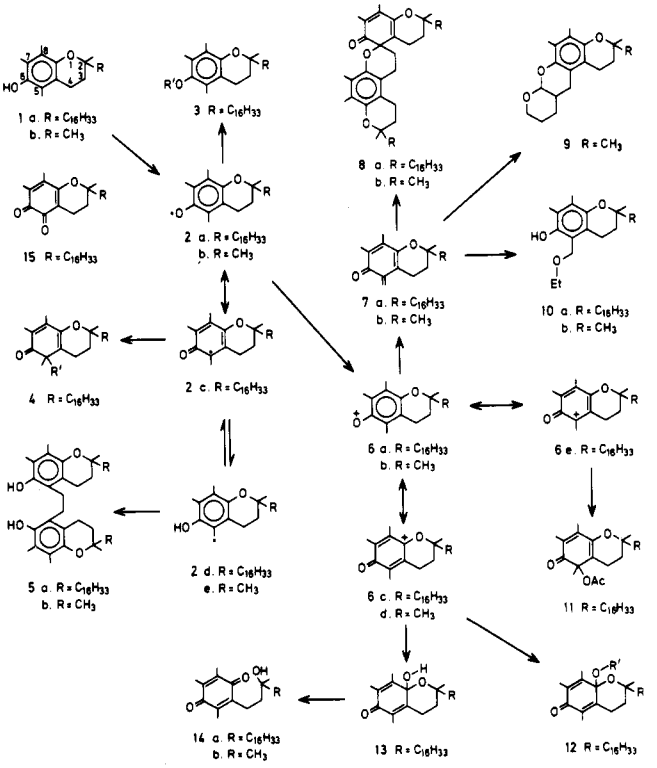
Oxidation of α-tocopherol (**1a**) with *tert*-butyl hydroperoxide in reagent-grade chloroform gave a new dimeric product which appeared to be both aromatic and quinonoid. Repetition of the reaction with the tocopherol model compound 2,2,5,7,8-pentamethyl-6-hydroxychroman (**1b**) gave the corresponding dimer in high yield (30%). This product was shown by two-dimensional, long-range proton–carbon correlation NMR spectra and subsequently by X-ray diffraction to be 2,3-dihydro-3,3,5,6,9,10,11a(*R*)-heptamethyl-7a(*S*)-(3-hydroxy-3-methylbutyl)-1*H*-pyrano[2,3-*a*]xanthene-8(7a*H*),11(11a*H*)-dione (**16b**). It appeared to be formed by Diels–Alder addition of the intermediate quinone methide **7b** to 2-(3-hydroxy-3-methylbutyl)-3,5,6-trimethylbenzo-1,4-quinone (**14b**), a known product of oxidation.

Since the major role of α-tocopherol (**1a**) appears to be that of a cellular antioxidant,[1] much interest has been shown in the products of its reactions, and those of its model compound 2,2,5,7,8-pentamethyl-6-hydroxychroman (**1b**), with many organic and inorganic oxidants.[2,3]

Oxidation of **1a** and **1b** is believed to occur in two single-electron steps leading firstly to the tocopheroxyl (**2a**) and chromanoxyl (**2b**) radicals, respectively (Scheme I).[4-6] **2a** and **2b** are capable of reacting with alkyl radicals to form derivatives at both the 6-phenoxyl (**3**) and also the 5-position (**4**)[7] and also of dimerization to produce stable dihydroxy dimers (**5a**, **5b**).[8]

Loss of a second electron from the initial radicals leads to the phenoxylium (**6a**, **6b**) and subsequently quinone methide (**7a**, **7b**) species both of which are unstable and react further. **6a** and **6b** have not been isolated but such species are known to exist[9,10] and their presence in oxidations of **1a** is inferred from products which include the 8a-hydroxy- (**13**), 8a-alkoxy- (**12**), 8a-acetoxy-, and 5-acetoxy-5-methyltocopherones (**11**)[11-13] and the 1,4-

Scheme I



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benzoquinones **14a**, **14b**.[14] **7a** and **7b** also have not been isolated as such but have been trapped as Diels–Alder adducts with dihydropyran (**9**), tetracyanoethylene, and styrene.[15,16] Products of **7a** and **7b** include the spiro dimers (**8a**, **8b**)[17] and spirotrimers[8] and the recently observed 5-ethoxymethyl derivatives (**10a**, **10b**).[3] The 5-formyl derivatives[18] may be considered to be derived from the Michael addition of water to **7a** and **7b** to form the 5-hydroxymethyl compound, followed by further oxidation. Both phenoxylium and quinone methide species are believed to be involved in C-demethylation of *o*-methylphenols which leads to the formation of orthoquinones such as **15**.[19,20]

It was demonstrated recently that when **1a** and **1b** were oxidized by *tert*-butyl hydroperoxide in purified chloroform, to which a small amount of ethanol had been added, **10a** and **10b** were formed in amounts that increased with the concentration of ethanol.[3]

In the present work **1a** was oxidized by *tert*-butyl hydroperoxide in reagent-grade chloroform which contained ethanol (2%) as stabilizer. No additional ethanol was added. In this reaction a much higher level of **10a** (58%) was formed than before and a new, polar compound isolated whose EI mass spectrum gave a strong molecular ion at 874, indicating a dimer (**16a**). The UV (λ_{max} 250, 297 nm) and IR spectra (3450 (OH), 1670 (C=O), and 1100 (C—O—C) cm^{-1}) of this compound suggested that it was both aromatic and quinonoid. The complexity of its ^1H NMR spectrum in the range δ 1–2 indicated that the compound was probably a mixture of stereoisomers. There was no trace of the monomeric benzoquinone (**14a**) which had been observed when the reactions were carried out in purified chloroform.[3]

In order to simplify the structural analysis, the oxidation was repeated using **1b** and a yellow crystalline product obtained in good yield (31%).

The ^1H NMR spectrum of the oxidation product is dominated by eight intense resonances, which were assigned to methyl groups. The only other readily assigned feature in the spectrum is a doublet at δ 2.70, which was shown to be coupled to the resonance at δ 2.38 by a coupling constant of 16.8 Hz, a value characteristic of coupled geminal protons. The remainder of the spectrum is extensively overlapped and could not be assigned by conventional one-dimensional NMR techniques; the entire spectrum covers less than 1.6 ppm.

The ^{13}C NMR spectrum is considerably more useful and provides the key to the analysis of the ^1H NMR spectrum and the determination of the structure of the oxidation product. The broad band decoupled ^{13}C NMR spectrum consists of 28 resonances with intensities consistent with a single carbon contributing to each resonance. A two-dimensional heteronuclear *J*-resolved NMR spectrum was recorded to determine the multiplicity of the carbon resonances.[21]

Table I. Observed Chemical Shifts of ^{13}C and Directly Bound Protons

carbon index[a]	type[d]	chemical shift (ppm)[b]	chemical shifts of directly bound protons (ppm)[c]
18	s	37.02	1.78, 1.20
7	s	33.85	2.70, 2.38
11	s	32.47	1.70
17	s	29.97	2.07, 1.71
20	p	29.56	1.18
21	p	28.90	1.18
25	p	27.32	1.26
26	p	26.24	1.24
10	s	19.81	2.43, 2.29
24	p	16.43	1.30
23	p	13.06	2.01
22	p	12.91	1.99
28	p	11.78	2.18
27	p	11.68	2.08

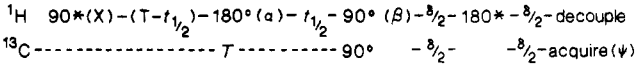
[a] Carbon index is taken from Figure 1. [b] Relative to $^{13}CDCl_3$ at 77.0 ppm. [c] Relative to $CHCl_3$ at 7.26 ppm. [d] Chemical shifts (index numbers) of quaternary carbons are 201.27 (5), 198.00 (2), 145.58 (13), 142.77 (16), 142.31 (3), 142.21 (4), 124.12 (15), 123.05 (14), 115.03 (9), 112.58 (8), 85.04 (1), 72.42 (12), 70.33 (19), and 51.33 (6).

Table II. Phase Cycle for Long-Range Carbon-Proton Coupling Sequence

X	X	X
X	-X	-X
X	Y	Y
X	-Y	-Y
-X	X	X
-X	-X	-X
-X	Y	Y
-X	-Y	-Y

The analysis of the ^1H NMR spectrum was completed by means of a two-dimensional carbon–proton correlation spectrum, which associates each carbon resonance with the resonances of the protons directly bonded to the carbon. The assignments of the ^{13}C and the ^1H NMR spectra are summarized in Table I.

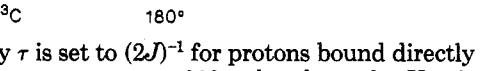
Two-dimensional, long-range proton–carbon correlation using the pulse sequence of Bauer et al.[22] provided sufficient information to determine the structure of the oxidation product. The pulse sequence is given in a diagrammatic form below:



(1)

The pulse phases, denoted α and β, and the receiver phase, ψ, are cycled according to the scheme presented in Table II. Sequence 1 is simply an INEPT pulse sequence[23] with modifications designed to suppress signals from $^1J_{CH}$ coupling by taking advantage of the much greater magnitude of $^1J_{CH}$ as compared to $^2J_{CH}$ or $^3J_{CH}$.

90*(X) denotes a TANGO pulse sequence:[24]



where the delay τ is set to $(2J)^{-1}$ for protons bound directly to ^{13}C. This sequence acts as a 90° pulse about the *X* axis for protons remote from carbon-13, but as a 180° pulse for

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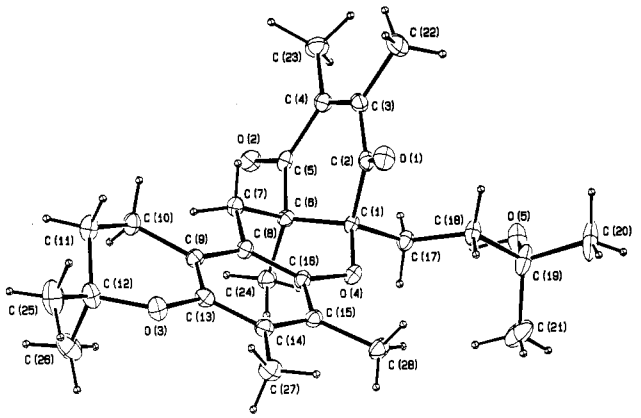
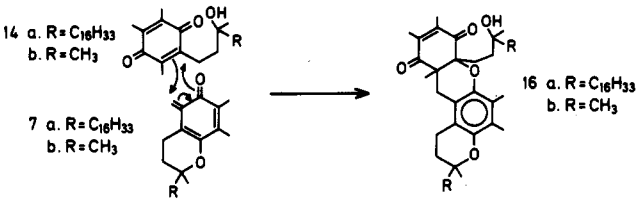


Figure 1.

Scheme II



directly bound protons. The 180* denotes the related BIRD pulse sequence:[25]

$$^{1}H \quad 90°(X)-\tau-180°(Y)-\tau-90°(X)$$
$$^{13}C \qquad\qquad 180°$$

which inverts all protons coupled to carbon-13 by long-range (small J) interactions but acts as an identity operator on directly bound protons. The TANGO and BIRD pulses serve to attenuate signals from protons bonded directly to carbon-13. The choice of the fixed delay, T, between the initial TANGO pulse and the 90° pulses transfering magnetization from the protons to the carbon-13, has a dramatic effect on the observed spectrum. This is also true of the choice of the time δ. We used a T of 286 ms and a δ of 56 ms, with these settings long-range coupling to methyl group protons tended to be emphasized. The pulse sequence does not distinguish between two-bond couplings, $^{2}J_{CH}$, and three-bond couplings, $^{3}J_{CH}$, which may have similar magnitudes. Table III summarizes the observed long-range couplings. Structure **16b** was consistent with these observed couplings and was subsequently confirmed by X-ray diffraction (Figure 1). The inability to distinguish between coupling due to $^{2}J_{CH}$ from that due to $^{3}J_{CH}$, using sequence (1), makes the assignment of pairs of atoms 3 and 4, 14 and 15, and 1 and 6 ambiguous. However these atom labels may be swapped in Figure 1 without significantly altering the conclusions concerning the structure of the compound. In addition to the expected $^{2}J_{CH}$ and $^{3}J_{CH}$ couplings, a small number of $^{4}J_{CH}$ couplings are listed in Table III based on the structure presented in Figure 1. The signals attributed to four-bond couplings are weak in all cases.

16b appeared to be a Diels–Alder adduct of the quinone methide (**7b**) and the benzoquinone (**14b**) (Scheme II). Such compounds have not been reported in oxidations of **1b** or **1a** but have been formed in reactions of methyl benzoquinone and methyl naphthoquinone carbanions with benzoquinones.[26-28] Previous attempts to form such an adduct from the quinone methide and benzoquinone failed.[15] The reasons for previous failures as opposed to the apparent ease of formation under the present conditions are not known but are under investigation.

Table III. Observed Long-Range Carbon–Proton Couplings

carbon atom index[a]	coupled protons[b]	carbon atom index[a]	coupled protons[b]
5	H24 ($^{3}J_{CH}$), H23 ($^{3}J_{CH}$)	18	H20 ($^{3}J_{CH}$), H21 ($^{3}J_{CH}$)
2	H22 ($^{3}J_{CH}$)	7	H24 ($^{3}J_{CH}$)
13	H27 ($^{3}J_{CH}$)	11	H25 ($^{3}J_{CH}$), H26 ($^{3}J_{CH}$)
16	H7 ($^{3}J_{CH}$), H28 ($^{3}J_{CH}$), H27 ($^{4}J_{CH}$)	17	H20[c] ($^{4}J_{CH}$), H21[c] ($^{4}J_{CH}$)
3	H22 ($^{2}J_{CH}$), H23 ($^{3}J_{CH}$)	20	H21 ($^{3}J_{CH}$)
4	H23 ($^{2}J_{CH}$)	21	H20 ($^{3}J_{CH}$)
15	H28 ($^{2}J_{CH}$), H27 ($^{3}J_{CH}$)	25	H26 ($^{3}J_{CH}$)
14	H28 ($^{3}J_{CH}$), H27 ($^{2}J_{CH}$)	26	H25 ($^{3}J_{CH}$)
9	H7 ($^{3}J_{CH}$), H11 ($^{3}J_{CH}$) H10 ($^{2}J_{CH}$)	10	H11 ($^{2}J_{CH}$)
8	H7 ($^{2}J_{CH}$)	24	H7 ($^{3}J_{CH}$)
1	H24 ($^{3}J_{CH}$)	22	
12	H25 ($^{2}J_{CH}$), H26 ($^{2}J_{CH}$)	23	
19	H20 ($^{2}J_{CH}$), H21 ($^{2}J_{CH}$)	28	
6	H24 ($^{2}J_{CH}$)	27	

[a] Carbon index is taken from Figure 1. [b] The type of coupling constant ($^{2}J_{CH}$, $^{3}J_{CH}$, or $^{4}J_{CH}$) responsible for the observed signal is indicated (based on the structure in Figure 1). [c] Very weak, possibly dubious assignments.

It is interesting to note that **7b** added cis to the more heavily substituted side of **14b** and that only one isomer of **16b** has been observed so far.

It proved impossible to obtain a sample of **16b** for elemental analysis which was free of water of crystallization. The X-ray structure showed the reason for this as intermolecular hydrogen bonding occurs between the hydroxyl oxygen O(5) and O(2) (O···O, 2.92 Å) and between O(5) and two water molecules (O···O, 2.85 and 2.93 Å). Atomic coordinates of the non-hydrogen atoms are available as supplementary material (see paragraph at the end of paper).

It seems likely that **16a** has the same structure as that of **16b**. The UV and IR spectra of the two compounds are almost identical and the ^{1}H NMR resonances of the aromatic and quinonoid methyl groups and the low field ring methylene protons are also identical. However the low field ring methylene resonances of **16a** are broader than those in **16b** and indicate the overlap of at least three protons, suggesting that at least three isomers are present. The region between δ 1–2 is also very complex, indicating that isomers are present and has not yet been assigned.

Materials and Methods

IR spectra were determined on a Perkin-Elmer 580B spectrometer, UV spectra on a Perkin-Elmer 124 double beam spectrophotometer, ^{1}H and ^{13}C NMR spectra on a Bruker CXP 300 spectrometer and a Bruker AM 500 spectrometer, and electron-impact mass spectra on an A.E.I MS 12 mass spectrometer. NMR spectra were taken in $CDCl_3$ and are reported in parts per million downfield from tetramethylsilane as internal standard. Reflection data for crystallography were measured with an Enraf-Nonius CAD-4 diffractometer in the $\theta/2\theta$ scan mode using nickel-filtered copper radiation (λ 1.540 56 Å). The crystal of **16b** was somewhat unstable under radiation, becoming cloudy, and the standard reflection oscillated in intensity, but with an overall upward drift of 20%. Data were corrected for absorption. Reflections with $I > 3\sigma(I)$ were considered observed. The structures

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were solved by using direct phasing and Fourier methods. Hydrogen atoms were poorly resolved and were positioned by a combination of difference Fouriers and calculation. They were assigned thermal parameters equal to those of the atom to which bonded. Positional and anisotropic thermal parameters were refined for the non-hydrogen atoms. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\sum w\Delta^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors and anomolous dispersion parameters were from International Tables for X-ray Crystallography.[29] Structure solution was by MULTAN 80,[30] and refinement used BLOCKLS, a local version of ORFLS.[31] ORTEP II[32] was used for the preparation of the structural diagram. A Cyber 172 computer was used for all calculations (see paragraph at the end of paper about supplementary material).

1a (Roche Products, Sydney, Australia) was used without further treatment.

Distilled, reagent-grade chloroform (Ajax Chemicals, Sydney, Australia) was used as a solvent for the oxidation reactions.

Chloroform for elution of TLC plates was purified by washing with 18 M sulfuric acid and distilled water until the washings were neutral, drying (Na_2SO_4), and distilling immediately before use.

tert-Butyl hydroperoxide (70% EGA CHEMIE, Steinheim, West Germany) was purified by the sodium salt method.[33] Purity (iodometrically) was 95%.

1b together with its spirodimer **8b** and spirotrimer, **14b**, 5-formyl-2,2,7,8-tetramethyl-6-hydroxychroman, **10b**, the spiro dimer and spiro trimer of **1a**, **14a** and 8a-ethoxy-α-tocopherone were prepared as reference compounds by known methods.[3,8,11,14,18,34]

Oxidation of 1a by *tert*-Butyl Hydroperoxide. A typical reaction was as follows: To **1a** (1011 mg, 2.25 mmol) in reagent-grade chloroform (150 mL) was added *tert*-butyl hydroperoxide (223 mg, 2.48 mmol), and the solution was refluxed for 3 h. The solution was then washed with 5% ferrous sulfate solution (6 × 30 mL) and distilled water (7 × 30 mL) and dried (Na_2SO_4), and the solvent was removed in vacuo. The residue was chromatographed on thin layers of silica gel GF_{254} (solvent, light petroleum ether (bp 60–80 °C)/ethyl acetate (9:1)), the products were located under UV light and eluted with purified chloroform, and the solvent was removed under a stream of nitrogen and weighed. The following products were identified by comparison of their UV and ^1H NMR spectra with those of the prepared reference compounds: 5-formyl-7,8-dimethyltocol R_f 0.61; **10a** R_f 0.53 (582 mg, 58%); **1a** R_f 0.42. Products of unknown composition were isolated with R_fs 0.87, 0.75, 0.69, 0.24, 0.17, 0.12, and 0.0.

The overlapping bands with R_f 0.12 (pink) and R_f 0.0 (yellow) were combined, rechromatographed on silica gel GF_{254} (solvent, light petroleum ether (bp 60–80 °C)/chloroform (2:8)) and resolved into three bands with R_fs 0.21 (pale yellow, 11 mg, 1.1%), 0.34 (pink-orange, 24 mg, 2.4%), and 0.56. The compounds with R_fs 0.21 and 0.34 are under investigation.

The dimer quinone **16a** (R_f 0.56), a yellow oil (71 mg, 7.1%), was identified by IR (KBr) 3450 (OH), 2930, 2850, 1670 (CH=CH—C=O), 1630, 1450, 1370, 1250, 1220, 1160, 1120, 1100 (C—O—C) cm^{-1}; UV (hexane) 250 nm (log ϵ, 4.09), 297 (3.58); ^1H NMR ($CDCl_3$) δ 0.85 (m, 24 H), 1.25 (br m, 57 H), 1.99 (s, 3 H, vinylic CH_3), 2.01 (s, 3 H, vinylic CH_3), 2.08 (s, 3 H, $ArCH_3$), 2.19 (s, 3 H, $ArCH_3$), 2.4 (br m, 3 H), 2.69 (d, 1 H, J = 16.8 Hz); MS (EI), m/e (relative intensity) 874 (M^+) (97), 856 (42), 446 (16), 430 (100), 428 (51).

Formation of 2,3-Dihydro-3,3,5,6,9,10,11a(*R*)-heptamethyl-7a(*S*)-(3-hydroxy-3-methylbutyl)-1*H*-pyrano[2,3-*a*]xanthene-8(7a*H*),11(11a*H*)-dione (16b). To **1b** (1009 mg, 4.59 mmol) in reagent-grade chloroform (150 mL) was added *tert*-butyl hydroperoxide (426 mg, 4.74 mmol), and the solution was refluxed for 3 h. The solution was then washed with 5% ferrous sulfate solution (6 × 30 mL), distilled water (10 × 30 mL), and dried (Na_2SO_4), and the solvent was removed in vacuo. The residue was chromatographed on thin layers of silica gel GF_{254} (solvent, light petroleum ether (bp 60–80 °C)/ethyl acetate (9:1)), the products were located under UV light and eluted with purified chloroform, and the solvent was removed under a stream of nitrogen and weighed. The following products were identified by comparison of their UV and ^1H NMR spectra with those of the prepared reference compounds: mixture of **8b** and spirotrimer of **1b**, R_f 0.57 (9 mg, 0.9%; separated by further chromatography); 5-formyl-2,2,7,8-tetramethyl-6-hydroxychroman, R_f 0.46 (109 mg, 10.8%); **10b**, R_f 0.41 (447 mg, 44.3%); **1b**, R_f 0.29 (41 mg, 4.1%). Products of unknown composition were isolated with R_f 0.54 (16 mg, 1.6%), R_f 0.08 (19 mg, 1.9%), and R_f 0.05 (33 mg, 3.3%).

The dimer quinone **16b**, R_f 0.02 (309 mg, 30.6%), was rechromatographed on silica gel GF_{254} (solvent, light petroleum ether (bp 60–80 °C)/ethyl acetate/benzene (7.2:1.8:1)) and crystallized from light petroleum ether as a yellow solid, mp 174–175 °C. It was identified by the following: IR (KBr) 3430 (OH), 2970, 2930 (CH_3), 1680 (CH=CH—C=O), 1620, 1450, 1378, 1258, 1225, 1166, 1125, 1100 (C—O—C) cm^{-1}; UV (hexane) 250 nm (log ϵ, 4.11), 297 (3.59); ^1H NMR ($CDCl_3$) δ 1.18 (s, 6 H, 2 × CH_3), 1.20 (m, 1 H, CH_2), 1.24 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 1.7 (m, 4 H, CH_2), 1.99 (s, 4 H, CH_3 + CH_2), 2.01 (s, 3 H, CH_3), 2.08 (s, 3 H, $ArCH_3$), 2.18 (s, 3 H, $ArCH_3$), 2.29 (m, 1 H), 2.38 (d, 1 H, J = 16.7 Hz), 2.43 (m, 1 H), 2.70 (d, 1 H, J = 16.9 Hz); MS (EI), m/e (relative intensity) 454 (M^+) (100), 436 (7), 352 (7), 244 (12), 219 (37), 218 (58). Anal. Calcd for $C_{28}H_{38}O_5 \cdot {}^1/_3H_2O$; C, 73.04; H, 8.41. Found: C, 72.87; H, 8.57.

Crystal data for **16b** ($C_{28}H_{38}O_5 \cdot H_2O$) M_r 472.6, monoclinic, space group $P2_1/c$, a = 10.380 (1), b = 19.253 (5), and c = 13.772 (2) Å, β = 104.03 (1)°, V = 2670.2 (8) Å^3, D_c = 1.27 g cm^{-3}, Z = 4, μ_{Cu} = 6.20 cm^{-1}. Crystal size 0.11 by 0.11 by 0.46 mm, $2\theta_{max}$ = 120°, number of reflections was 2013 considered observed out of 3963 measured. Final residuals R, R_w were 0.064, 0.083.

Supplementary Material Available: Atomic coordinates of the non-hydrogen atoms together with all positional and thermal parameters, bond distances, bond angles, and torsional angles (9 pages). Ordering information is given on any current masthead page.

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