X-Ray Crystal and Molecular Structure of a Trimeric *o*-Quinone Methide Derived from 2,6-Dibromomethyl-4-methylphenyl

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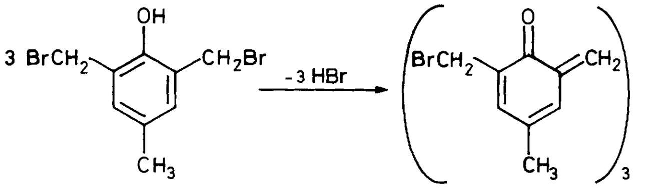
The crystal and molecular structure of 3′-bromomethyl-5′,8-bis(methoxymethyl)-4a′,6,7′-trimethyl-2′-oxo-1′,2′,4a′,9a′-tetrahydrospiro[chroman-2,1′-xanthene], the trimerisation product obtained from 2-bromomethyl-4-methyl-6-methylenecyclohexa-2,4-dienone, an *o*-quinone methide formed by elimination of hydrogen bromide from 2,6-dibromomethyl-4-methylphenol, was determined by *X*-ray diffraction. Crystals grown from methanol were triclinic, a = 10.761(2), b = 12.090(1), c = 10.404(2) Å, α = 101.51(1), β = 97.49(1), γ = 87.28(1)°, space group $P\bar{1}$. The molecular structure shows that the trimerisation takes place by a twofold Diels–Alder cycloaddition in which two molecules of the original *o*-quinone methide, acting as heterodienes, add to a third molecule. Of the three remaining bromomethyl groups the two which are attached to an aromatic ring are converted into methoxymethyl groups during recrystallization from methanol.

Quinone methides (methylenecyclohexadienones)[1] are often discussed as reactive intermediates in the synthesis of phenolic oligomers.[2] Indeed, they are easily obtained by the elimination of hydrogen chloride or hydrogen bromide from *ortho-* or *para-*chloro- or -bromo-methylated phenols with weak bases such as tertiary amines.[3–6] In the absence of further reactants in dilute solutions these monomeric quinone methides are often sufficiently stable to yield the usual addition product when a suitable nucleophile is added.[7] In the case of *o*-quinone methides their existence may be shown also by trapping *via* cycloaddition with a suitable dienophile.[1,8]

The isolation of pure, monomeric quinone methides has been observed in special cases.[9–11] Compounds with an unsubstituted methylene group, however, undergo further reactions in the absence of trapping reagents, leading to dimers or trimers or similar oligomers. With *p*-quinone methides, 1,6-addition steps as well as further redox reactions (disproportionation) are involved,[3,4] while in the case of *o*-quinone methides the dimerisation and trimerisation proceeds as a Diels–Alder cycloaddtion.[5,12–15]

Several *X*-ray structures have been reported either for special substituted monomeric quinone methides[10,11] or for their dimerization products.[16–18] To our knowledge, however, no structures have been determined for trimers or of quinone methides derived from halomethylated phenols, although their trimeric nature has been known or suspected for some time.[1] In this paper we describe the structure of such a trimer which is also the first example derived from a bisbromomethylated phenol.

During our studies on the synthesis of special substituted calixarenes,[19] bridged calixarenes[20] or double calixarenes[21] we treated 2,6-bisbromomethylphenols with other phenols or phenolic oligomers in boiling dioxane in the presence of $TiCl_4$. From such experiments (see the Experimental section) we isolated, by flash chromatography, a pure compound (overall yield 2–3%) which was identified by mass spectrometry and shown to be the trimer of the quinone methide; this could have been formed by elimination of hydrogen bromide from 2,6-bisbromomethyl-4-methylphenol. This was easily deduced from the molecular ion (M^+ = 636/638/640/642 for ^{79}Br/^{81}Br) and from further peaks which can be understood by the loss of bromine and hydrogen bromide (M^+ − Br = 557/559/561, M^+ − Br − HBr = 477/479, M^+ − Br − 2HBr = 397). The bromomethylated *p*-cresol had obviously reacted with itself according to the following reaction scheme:



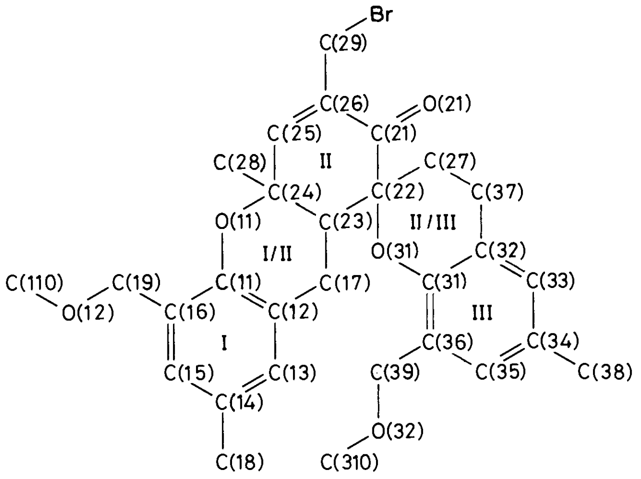
The compound was recrystallized from methanol to give single crystals suitable for *X*-ray analysis. This analysis showed, however, that two bromine atoms had been replaced by methoxy groups, a result which was also confirmed by mass spectroscopy and by ^{1}H n.m.r. spectroscopy. We attributed this finding to methanolysis during the recrystallization from methanol.

Experimental

Synthesis.—A solution of 2,6-bisbromomethyl-4-methylphenol (4.4 g, 15 mmol), the bis(*p*-hydroxybenzoate) of diethylene glycol (2.6 g, 7.5 mmol) (which most probably is not involved in the formation of the quinone methide), and $TiCl_4$ (7.6 g, 40 mmol) was heated at 100 °C in dioxane (500 cm^3) for 100 h. During this time two additional portions of 2,6-bisbromomethyl-4-methylphenol (2.2 g, 7.5 mmol) were added, one after 25 h and the other after 50 h. Solvent was evaporated under reduced pressure, the dark red residue was dissolved in $CHCl_3$, silica gel (50 g) was added, and the solvent was evaporated once more. The silica gel was extracted in a Soxhlet apparatus using CH_2Cl_2 over 24 h. This procedure was then repeated. After evaporation of the solvent a crude mixture resulted (5 g) which was separated by flash chromatography (silica gel, $CHCl_3$). Further purification of the first fraction by

Table 1. Atomic co-ordinates, given in units of the lattice constants, with e.s.d.s in parentheses.

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Br	1.437 74(7)	0.144 78(6)	0.381 2(1)	C(25)	1.347 9(4)	0.428 4(4)	0.287 9(5)
C(11)	1.230 9(5)	0.676 6(4)	0.191 0(5)	C(26)	1.335 3(4)	0.324 4(4)	0.263 7(5)
C(12)	1.107 2(5)	0.644 5(4)	0.163 6(5)	C(27)	1.165 0(4)	0.394 8(4)	0.493 2(5)
C(13)	1.014 9(5)	0.724 9(4)	0.138 9(5)	C(28)	1.346 5(5)	0.605 7(5)	0.449 8(5)
C(14)	1.047 1(6)	0.835 4(5)	0.140 3(5)	C(29)	1.419 3(5)	0.223 7(5)	0.233 3(7)
C(15)	1.170 2(6)	0.862 7(5)	0.163 5(6)	O(21)	1.152 2(3)	0.215 8(3)	0.201 1(4)
C(16)	1.266 4(5)	0.785 7(4)	0.190 2(5)	C(31)	0.945 8(4)	0.291 8(4)	0.351 2(4)
C(17)	1.084 5(4)	0.526 1(4)	0.175 7(5)	C(32)	1.002 0(4)	0.245 5(4)	0.456 5(5)
C(18)	0.944 6(8)	0.923 1(6)	0.119 3(8)	C(33)	0.940 6(4)	0.159 2(4)	0.491 6(5)
C(19)	1.402 1(6)	0.817 2(6)	0.220 3(7)	C(34)	0.829 0(4)	0.117 4(4)	0.423 4(5)
C(110)	1.597(1)	0.797(1)	0.140(1)	C(35)	0.776 5(4)	0.165 1(4)	0.317 2(5)
C(110′)	1.543(7)	0.900(5)	0.110(6)	C(36)	0.831 6(4)	0.253 5(4)	0.280 3(4)
O(11)	1.320 5(3)	0.595 1(3)	0.216 1(3)	C(37)	1.127 9(4)	0.284 8(4)	0.526 7(5)
O(12)	1.469 0(5)	0.777 2(6)	0.113 0(6)	C(38)	0.765 8(6)	0.022 9(5)	0.463 4(7)
O(12′)	1.435(2)	0.866(2)	0.106(2)	C(39)	0.771 7(4)	0.306 2(4)	0.169 2(5)
C(21)	1.199 8(4)	0.301 9(4)	0.261 8(5)	C(310)	0.662 5(7)	0.469 7(7)	0.122 0(8)
C(22)	1.129 4(4)	0.395 9(4)	0.345 2(4)	O(31)	0.997 2(3)	0.380 3(3)	0.310 9(3)
C(23)	1.154 1(4)	0.510 9(4)	0.311 3(5)	O(32)	0.705 3(3)	0.406 5(3)	0.220 5(3)
C(24)	1.296 3(4)	0.533 0(4)	0.318 6(5)				



Scheme. Numbering scheme of the molecule. The first number of each atom and the roman numbers of the rings refer to the three monomeric quinone methide molecules from which the trimer is formed by cycloaddition.

flash chromatography ($CHCl_3$–CCl_4, 5:1; $CHCl_3$–CCl_4, 1:1) finally gave a slightly yellow oil (152 mg; $R_F = 0.9$, $CHCl_3$), which crystallized on the addition of methanol. These crystals showed a molecular peak, corresponding to the formula $C_{27}H_{27}Br_3O_3$. Further recrystallization from methanol gave single crystals, which were used for the *X*-ray analysis, m.p. 98–99.5 °C. The mass spectrum of these was also consistent with the formula $C_{29}H_{33}BrO_5$.

X-*Ray Structure Analysis*.—A colourless crystal of dimensions *ca.* 0.2 × 0.3 × 0.5 mm was used. The lattice parameters were obtained from least-squares analysis of 25 reflections with $11.33 < \theta < 45.11°$ from graphite monochromated Cu-K_α radiation on an Enraf-Nonius CAD-4 diffractometer.

Intensity data of 10 323 reflections were collected at room temperature by $\omega - 2\theta$ scan technique with θ between 1 and 73° and $-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 14$, $-12 \leqslant l \leqslant 12$. Intensity and orientation standards were measured again every 60 min and 200 reflections respectively; no significant decomposition or movement of the crystal was observed.

After averaging ($R_{int} = 0.04$), 5 252 unique observed reflections remained with $I > 3\sigma(I)$. Corrections were made for Lorentz and polarization but not for absorption effects.

The structure was solved by direct methods using normalized structure factors with $E_{min} = 1.4$. Some atoms came out from one of the *E* maps with the highest figure of merit and the remaining non-hydrogen atoms were revealed after successive *E* maps. Full-matrix least-squares refinements on *F* were performed for positional parameters and isotropic, then anisotropic, temperature factors.

Difference electron density maps revealed disorder on O(12) and C(110) which have another position noted O(12′) and C(110′) with fractional site occupation factors of *ca.* 80 and 20%. Most of the hydrogen atoms appeared on difference electron density maps after further refinements. The missing hydrogen atoms and those insufficiently well located were placed in calculated positions. Refinement of co-ordinates for all atoms (with C–H bond distances restrained) with isotropic temperature factors for hydrogen atoms led to fractional site occupation factors of 0.82(2) and 0.18(2). The final *R* value is 0.081 for the unique observed reflections and 0.075 for 4 553 reflections, after suppression of those for which absorption effects had led to bad agreement [by an $F < 2.5\sigma(F)$ test]. A unit weighting scheme was used.

Calculations were performed with the SHELX-76 System[22] on the Micro VACS-II of the Centre de Diffractometrie-Lyon 1. Geometric calculations were carried out with the SDP package.[23]

Full lists of atomic co-ordinates and tables of thermal parameters and least-squares planes have been deposited at the Cambridge Crystallographic Data centre.*

Results and Discussion

Crystal Data.—$C_{29}H_{33}BrO_5$, $M = 541.5$, triclinic, $a = 10.761(2)$, $b = 12.090(1)$, $c = 10.404(2)$ Å, $\alpha = 101.51(1)$, $\beta = 97.49(1)$, $\gamma = 87.28(1)°$, $V = 1\,314.7$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.368$ g cm^{-3}, $\mu = 24.2$ cm^{-1}.

Fractional atomic co-ordinates of non hydrogen atoms are listed in Table 1. Bond distances, bond angles and relevant torsion angles are given in Table 2. Atoms are numbered as indicated in the Scheme, referring to the three monomeric

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* For details of the CCDC deposition scheme, see 'Instructions for Authors (1989),' *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

Table 2. Bond distances, bond angles, and selected torsion angles.

Bond distances/Å

C(11)–C(12)	1.381(7)	C(19)–O(12)	1.400(9)	C(22)–C(27)	1.540(6)	C(31)–O(31)	1.386(6)
C(11)–C(16)	1.392(8)	C(19)–O(12′)	1.51(3)	C(22)–O(31)	1.433(5)	C(32)–C(33)	1.392(7)
C(11)–O(11)	1.384(6)	C(110)–O(12)	1.39(1)	C(23)–C(24)	1.555(6)	C(32)–C(37)	1.503(6)
C(12)–C(13)	1.393(7)	C(110′)–O(12′)	1.25(7)	C(24)–C(25)	1.492(6)	C(33)–C(34)	1.376(6)
C(12)–C(17)	1.496(7)	Br–C(29)	1.951(7)	C(24)–C(28)	1.517(6)	C(34)–C(35)	1.391(7)
C(13)–C(14)	1.393(8)	O(11)–C(24)	1.476(6)	C(25)–C(26)	1.312(7)	C(34)–C(38)	1.510(9)
C(14)–C(15)	1.359(9)	C(21)–C(22)	1.522(6)	C(26)–C(29)	1.489(7)	C(35)–C(36)	1.387(7)
C(14)–C(18)	1.519(9)	C(21)–C(26)	1.493(6)	C(27)–C(37)	1.523(8)	C(36)–C(39)	1.489(7)
C(15)–C(16)	1.398(8)	C(21)–O(21)	1.204(5)	C(31)–C(32)	1.386(7)	C(39)–O(32)	1.424(6)
C(16)–C(19)	1.503(9)	C(22)–C(23)	1.545(7)	C(31)–C(26)	1.396(5)	C(310)–O(32)	1.415(9)
C(17)–C(23)	1.548(7)						

Bond angles/°

C(12)–C(11)–C(16)	122.1(5)	C(16)–C(19)–O(12′)	107.3(9)	O(11)–C(24)–C(23)	111.2(4)	C(31)–C(32)–C(33)	118.1(4)
C(12)–C(11)–O(11)	117.6(4)	C(11)–O(11)–C(24)	115.1(4)	O(11)–C(24)–C(25)	102.2(3)	C(31)–C(32)–C(37)	120.5(4)
C(16)–C(11)–O(11)	120.3(4)	C(19)–O(12)–C(110)	113.9(8)	O(11)–C(24)–C(28)	105.9(4)	C(33)–C(32)–C(37)	121.4(4)
C(11)–C(12)–C(13)	118.9(5)	C(19)–O(12′)–C(110′)	119.(3)	C(23)–C(24)–C(25)	114.0(4)	C(32)–C(33)–C(34)	122.2(5)
C(11)–C(12)–C(17)	115.2(4)	C(22)–C(21)–C(26)	114.0(4)	C(23)–C(24)–C(28)	111.7(4)	C(33)–C(34)–C(35)	117.9(5)
C(13)–C(12)–C(17)	125.6(5)	C(22)–C(21)–O(21)	123.6(4)	C(25)–C(24)–C(28)	111.1(4)	C(33)–C(34)–C(38)	120.7(5)
C(12)–C(13)–C(14)	120.4(5)	C(26)–C(21)–O(21)	122.3(4)	C(24)–C(25)–C(26)	126.0(4)	C(35)–C(34)–C(38)	121.3(4)
C(13)–C(14)–C(15)	118.9(5)	C(21)–C(22)–C(23)	110.2(4)	C(21)–C(26)–C(25)	120.5(5)	C(34)–C(35)–C(36)	122.3(4)
C(13)–C(14)–C(18)	119.6(6)	C(21)–C(22)–C(27)	110.3(4)	C(21)–C(26)–C(29)	116.4(4)	C(31)–C(36)–C(35)	117.6(4)
C(15)–C(14)–C(18)	121.4(5)	C(21)–C(22)–O(31)	109.4(3)	C(25)–C(26)–C(29)	123.1(5)	C(31)–C(36)–C(39)	120.9(4)
C(14)–C(15)–C(16)	123.0(5)	C(23)–C(22)–C(27)	112.2(3)	C(22)–C(27)–C(37)	111.2(4)	C(35)–C(36)–C(39)	121.5(4)
C(11)–C(16)–C(15)	116.7(5)	C(23)–C(22)–O(31)	105.2(3)	Br–C(29)–C(26)	109.0(4)	C(27)–C(37)–C(32)	112.5(4)
C(11)–C(16)–C(19)	120.5(5)	C(27)–C(22)–O(31)	109.5(4)	C(32)–C(31)–C(26)	121.8(4)	C(36)–C(39)–O(32)	109.5(4)
C(15)–C(16)–C(19)	122.8(5)	C(17)–C(23)–C(22)	112.7(4)	C(32)–C(31)–O(31)	122.6(4)	C(22)–O(31)–C(31)	117.2(3)
C(12)–C(17)–C(23)	106.2(4)	C(17)–C(23)–C(24)	110.4(4)	C(36)–C(31)–O(31)	115.6(4)	C(39)–O(32)–C(310)	112.1(4)
C(16)–C(19)–O(12)	112.2(5)	C(22)–C(23)–C(24)	112.6(3)				

Torsion angles/°

O(11)–C(11)–C(12)–C(17)	4.9(0.6)	C(26)–C(21)–C(22)–O(31)	165.4(0.4)	C(17)–C(23)–C(24)–O(11)	17.5(0.5)
C(12)–C(11)–O(11)–C(24)	−52.2(0.5)	O(21)–C(21)–C(22)–C(23)	−131.0(0.5)	C(22)–C(23)–C(24)–C(25)	29.6(0.5)
C(11)–C(12)–C(17)–C(23)	49.2(0.5)	C(22)–C(21)–C(26)–C(25)	−25.7(0.6)	C(23)–C(24)–C(25)–C(26)	−3.8(0.7)
C(12)–C(17)–C(23)–C(24)	−58.7(0.5)	O(21)–C(21)–C(26)–C(25)	155.5(0.5)	C(24)–C(25)–C(26)–C(21)	1.5(0.8)
C(16)–C(19)–O(12)–C(110)	−175.2(0.9)	C(21)–C(22)–C(23)–C(24)	−52.1(0.5)	C(22)–C(27)–C(37)–C(32)	−40.6(0.5)
C(16)–C(19)–O(12′)–C(110′)	179.2(3.6)	C(27)–C(22)–C(23)–C(24)	71.2(0.4)	O(31)–C(31)–C(32)–C(37)	−4.3(0.7)
C(11)–O(11)–C(24)–C(23)	37.4(0.5)	O(31)–C(22)–C(23)–C(24)	−169.9(0.3)	C(32)–C(31)–O(31)–C(22)	23.0(0.6)
C(26)–C(21)–C(22)–C(23)	50.2(0.5)	O(31)–C(22)–C(27)–C(37)	58.0(0.5)	C(31)–C(32)–C(37)–C(27)	14.5(0.6)
C(26)–C(21)–C(22)–C(27)	−74.2(0.5)	C(27)–C(22)–O(31)–C(31)	−49.0(0.5)	C(36)–C(39)–O(32)–C(310)	170.9(0.4)

quinone methide subunits. Figures 1 and 2 show stereoscopic views of the molecule seen from different directions.

The molecule consists of five six-membered rings, three (I, II, and III) deriving from the original aromatic rings and two (I/II and II/III) formed by cycloaddition.

Rings I and III are benzenoid with C–C bond distances between 1.36 and 1.40 Å and bond angles between 116 and 123°. The methoxymethyl group attached to ring I is disordered. Two positions [O(12)–C(110)] and [O(12′)–C(110′)] were found with site occupation factors of 0.82(2) and 0.18(1), respectively. An analysis of the torsional angles shows that for each group the four atoms C–C–O–C are nearly coplanar. The angles between the mean planes of I and III and the least-square planes obtained from those four atoms have the following values:

76.7(6)° between I and C(16)–C(19)–O(12)–C(110)

56.0(1)° between I and C(16)–C(19)–O(12′)–C(110′)

97.0(2)° between III and C(36)–C(39)–O(32)–C(310)

Ring II contains the structural elements of an α, β unsaturated ketone with a C–C double bond (1.31 Å) between C(25) and C(26). This system, however, is not planar [torsion angle C(25)–C(26)–C(21)–O(21) = 155.5(5)°]. The single bond between C(21) and C(26) is also only slightly shorter (1.49 Å) than the other single bonds in this ring (1.49–1.56 Å). The bonding is trigonal around carbon atoms C(21), C(25), and C(26) and tetrahedral around C(22), C(23), and C(24). Analysis of the torsion angles shows that carbon atoms C(21), C(23), C(24), C(25), and C(26) are roughly coplanar. The distances between their mean plane (plane II) and atoms C(22) and O(21) are −0.621(4) and +0.401(4) Å, respectively.

The plane of the bromomethyl group [C(26)–C(29)–Br] is inclined by 71.0(3)° relative to plane II. Around the C(23)–C(24) bond a *cis*-configuration is observed for the substituents C(17) and O(11); all four atoms are close to a plane [torsion angle O(11)–C(24)–C(23)–C(17) = 17.5(5)°]. On the tetrahedral carbon C(22) the substituent O(31) is in a pseudo-equatorial position [*cis*-relative to C(17) and O(11)] and C(27) is in a pseudo-axial postion with respect to ring II.

Ring I/II is 'folded' along the axis O(11)···C(17). Both atoms are situated (nearly) in the aromatic plane of ring I, which forms an angle of 53.7(2)° with the best plane through O(11)–C(24)–C(23)–C(17), which on the other hand forms an angle of 72.2(2)° with the above defined plane II.

Ring II/III has a twisted shape with C(31), C(32), O(31), and C(37) located close to the least-squares plane II/III obtained from the six atoms of the ring [distances: −0.033(4), +0.046(5), −0.149(3), and 0.106(5) Å]. Carbon atoms C(22) and C(27) are +0.309(4) and −0.281(5) Å from this plane. The angle

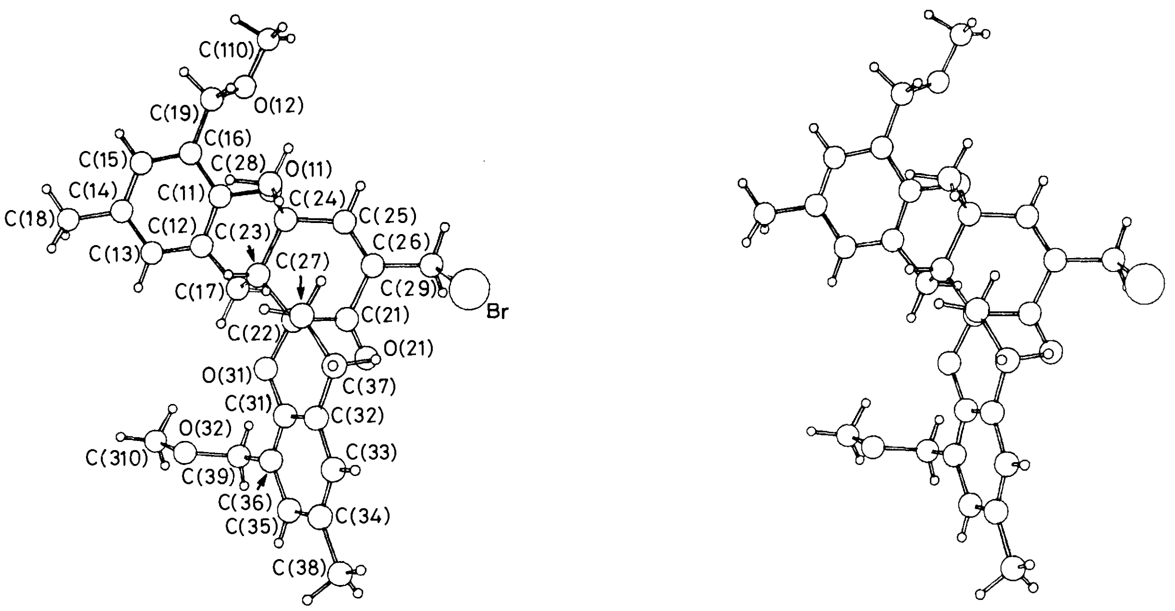

Figure 1. Stereoscopic view of the molecule perpendicular to plane II.

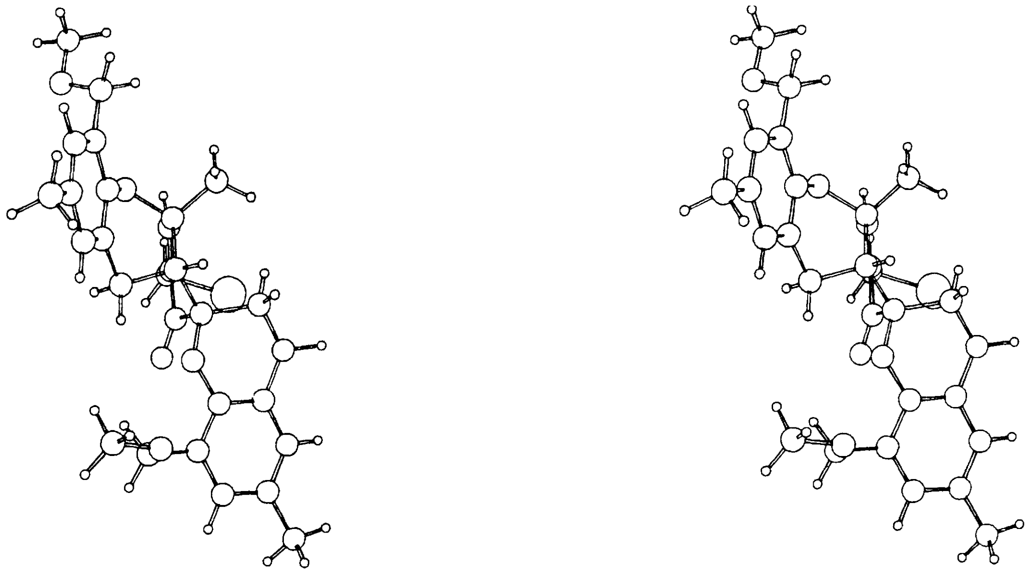

Figure 2. Stereoscopic view of the molecule parallel to plane II.

between plane III and plane II/III is 4(2)°; it is thus possible to state that the mean plane of ring II/III is approximately the plane of the phenolic ring III. With the above-defined plane II it forms an angle of 64.2(1)°.

In conclusion, the compound is obviously formed by elimination of hydrogen bromide from the bisbromomethylated phenol followed by cycloaddition. Here two molecules of the intermediate *o*-quinone methide* acts as hetero dienes which are added to a third molecule which act twice as a dienophile. Two aromatic systems (I and III) are thereby generated, and consequently the bromomethyl groups attached to these rings are most reactive, thus being substituted in an S_N1 reaction by methanol during recrystallization.

The structure of the trimer,† is exactly analogous to that observed in similar cases, as shown by n.m.r. spectroscopy and chemical evidence,[5,12–15] although isomeric trimers were also found.[5] Whether this represents the only mode of trimerization (or oligomerization) cannot be deduced from our experiments. It should be possible, however, to obtain higher yields of oligomerization products by treatment of 2,6-bisbromomethyl-4-methylphenol with a tertiary amine.

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* *Systematic name:* 2-bromomethyl-4-methyl-6-methylene-2,4-cyclohexadienone.

† *Systematic name:* 3′-bromomethyl-5′,8-bis(methoxymethyl)-4a′,6,7′-trimethyl-2′-oxo-1′,2′,4a′,9a′-tetrahydrospiro[chroman-2,1′-xanthene].

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