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Novel Manganese(III) Oxidation Chemistry: X-ray Crystal Structure of 5,7,8-Trimethoxy-1-(2,4,5-trimethoxyphenyl)-1,2-dihydronaphthalene

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Abstract. $C_{22}H_{26}O_6$, $M_r = 386.4$, monoclinic, $P2_1/c$, $a = 13.021$ (4), $b = 11.044$ (2), $c = 14.036$ (9) Å, $\beta = 102.53$ (4)°, $V = 1970.4$ Å³, $Z = 4$, $D_x = 1.30$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.56$ cm⁻¹, $F(000) = 824$, $T = 293$ K, final $R = 0.054$ for 1576 observed [$F_o \geq 5\sigma(F_o)$] reflections. There is no crystallographically imposed symmetry. The title compound is prepared by manganese(III) acetate oxidative dimerization of two molecules of 2,4,5-trimethoxystyrene.

Introduction. During the course of our investigations on manganese(III) acetate mediated ring annulative approaches to the antineoplastic podophyllotoxins (Peterson, Do, Winter & Surjasmita, 1988; Peterson, Do & Surjasmita, 1988), an unusual oxidation product was obtained when the alkene component of the annulation reaction was 2,4,5-trimethoxystyrene. The single electron transfer oxidation (SETO) of electron-rich alkenes by manganese(III) recently had been reported by one of us to provide 1,2-diacetates, 1,2-hydroxyacetates, and their oxidation products (Fristad, Peterson, Ernst & Urbi, 1986). 2,4,5-Trimethoxystyrene was found to react by an entirely different pathway, however. Only products resulting from oxidative dimerization of this substrate, 5,7,8-trimethoxy-1-(2,4,5-trimethoxyphenyl)-1,2-dihydronaphthalene and some of the corresponding naphthalene, were obtained in the presence of manganese(III) acetate. This result was particularly surprising in view of the possibility for solvolysis of radical-cation intermediates in acetic acid. We wish to describe in this paper the X-ray crystal structure determination, synthesis, and spectral characterization of the title compound.

Experimental. The title compound was prepared by reaction of a 343 K glacial acetic acid (35 mL) solution of 2,4,5-trimethoxystyrene (1.36 g, 7.0 mmol) and potassium acetate (0.69 g, 7.0 mmol) with manganese(III) acetate dihydrate (4.13 g, 2.2 mole equivalents of oxidant). The reaction was monitored for complete reduction of Mn^{III} to Mn^{II} with starch–potassium iodide test paper. Workup consisted of dilution with water, extraction with chloroform, and water washes of the combined extracts. Flash chromatography of the concentrate on silica gel using 40% ethyl acetate–hexane as eluent afforded 5,7,8-trimethoxy-1-(2,4,5-trimethoxyphenyl)-1,2-dihydronaphthalene† (544 mg) in 40% yield. Crystals (m.p. 430–431 K) suitable for X-ray analysis were obtained by recrystallization from chloroform–hexane. D_m not determined. Crystal 0.10 × 0.20 × 0.33 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$. Cell constants from setting angles of 25 reflections ($\theta > 18^\circ$). Correction for Lorentz–polarization effect. $\theta_{\max} = 50^\circ$; h 0 to 15, k 0 to 13, l –16 to 16. Standard reflections observed every 3600 s of data collection time, 400; 060; 006. Variation = ±3%. 3748 reflections measured, 1576 independent observed reflections [$F_o \geq 5\sigma(F_o)$]. Structure solved utilizing *MULTAN*

† Physical data: IR (KBr) 2980, 2945, 2915, 2825, 1620 (CH=CH), 1590 (aromatic C=C), 1500 (aromatic C=C), 1490, 1460, 1450, 1390, 1335, 1320, 1305, 1225, 1195, 1165, 1100, 1030, 805, 785 cm⁻¹; ¹H NMR (CDCl₃, 200 MHz) δ 6.82 (*dd*, $J = 9.78, 2.93$ Hz, 1H, –CH=CH–CH₂–), 6.53 (*s*, 1H, aromatic H), 6.44 (*s*, 1H aromatic H), 6.30 (*s*, 1H aromatic H), 5.75–5.60 (*m*, 1H, –CH=CH–CH₂–), 4.88 (*d*, $J = 7.68$ Hz, 1H, –CH–CH₂–), 3.91 (*s*, 3H, OCH₃), 3.87 (*s*, 6H, OCH₃), 3.85 (*s*, 3H, OCH₃), 3.57 (*s*, 3H, OCH₃), 3.39 (*s*, 3H, OCH₃), 2.77–2.55 (*m*, 1H, –CH–CH₂–), 2.42 (*dd*, $J = 17.25, 7.68$ Hz, 1H, –CH–CH₂–). Analysis: calculated for C₂₂H₂₆O₆: C, 68.38; H, 6.78%; found: C, 68.35; H, 6.82%.

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Table 1. Final fractional coordinates and equivalent isotropic thermal parameters for $C_{22}H_{26}O_6$

	x	y	z	$B_{eq}^*(\text{\AA}^2)$
O(1)	0.1458 (3)	0.5197 (3)	0.8480 (3)	3.14
O(2)	0.3082 (3)	0.6502 (3)	0.8171 (3)	3.88
O(3)	0.4814 (3)	0.5980 (3)	1.1566 (3)	3.38
O(4)	-0.0236 (3)	0.2673 (3)	0.9373 (3)	3.30
O(5)	0.2063 (3)	-0.0766 (3)	0.9248 (3)	3.55
O(6)	0.3726 (3)	0.0648 (3)	1.0102 (3)	3.92
C(1)	0.1412 (4)	0.4110 (4)	1.0297 (4)	2.36
C(2)	0.2309 (4)	0.4910 (4)	1.0146 (4)	2.25
C(3)	0.2318 (4)	0.5381 (4)	0.9248 (4)	2.48
C(4)	0.3155 (4)	0.6081 (4)	0.9104 (4)	2.79
C(5)	0.4001 (4)	0.6292 (4)	0.9862 (4)	2.87
C(6)	0.4003 (4)	0.5816 (4)	1.0758 (4)	2.70
C(7)	0.3157 (4)	0.5127 (4)	1.0939 (4)	2.42
C(8)	0.3135 (4)	0.4613 (4)	1.1896 (4)	3.00
C(9)	0.2266 (4)	0.4173 (5)	1.2100 (4)	3.29
C(10)	0.1247 (4)	0.4195 (5)	1.1346 (4)	3.22
C(11)	0.1608 (5)	0.4301 (5)	0.7808 (4)	3.96
C(12)	0.3869 (5)	0.7314 (6)	0.8000 (5)	5.28
C(13)	0.5656 (4)	0.6750 (5)	1.1452 (4)	4.10
C(14)	0.1568 (4)	0.2813 (4)	1.0018 (3)	2.24
C(15)	0.0727 (4)	0.2111 (4)	0.9551 (4)	2.43
C(16)	0.0856 (4)	0.0916 (4)	0.9282 (4)	2.69
C(17)	0.1851 (4)	0.0400 (4)	0.9483 (4)	2.58
C(18)	0.2699 (4)	0.1085 (5)	0.9956 (4)	2.70
C(19)	0.2556 (4)	0.2263 (4)	1.0213 (4)	2.55
C(20)	-0.1116 (4)	0.2084 (5)	0.8783 (4)	3.60
C(21)	0.1228 (5)	-0.1438 (5)	0.8673 (4)	3.70
C(22)	0.4022 (5)	-0.0168 (7)	1.0854 (5)	5.52

$$* B_{eq} = \frac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + abc\cos\gamma\beta_{12} + accos\beta\beta_{13} + bccos\alpha\beta_{23}).$$

Table 2. Bond distances (\AA) and angles ($^\circ$) for $C_{22}H_{26}O_6$

O(1)—C(3)	1.391 (6)	O(1)—C(11)	1.410 (6)
O(2)—C(4)	1.374 (6)	O(2)—C(12)	1.420 (7)
O(3)—C(6)	1.383 (6)	O(3)—C(13)	1.424 (6)
O(4)—C(15)	1.372 (5)	O(4)—C(20)	1.418 (6)
O(5)—C(17)	1.372 (5)	O(5)—C(21)	1.416 (6)
O(6)—C(18)	1.394 (6)	O(6)—C(22)	1.377 (7)
C(1)—C(2)	1.516 (6)	C(1)—C(10)	1.535 (6)
C(1)—C(14)	1.510 (6)	C(2)—C(3)	1.366 (6)
C(2)—C(7)	1.408 (6)	C(3)—C(4)	1.386 (7)
C(4)—C(5)	1.376 (7)	C(5)—C(6)	1.365 (7)
C(6)—C(7)	1.405 (7)	C(7)—C(8)	1.464 (6)
C(8)—C(9)	1.320 (7)	C(9)—C(10)	1.509 (7)
C(14)—C(15)	1.385 (6)	C(14)—C(19)	1.396 (6)
C(15)—C(16)	1.393 (6)	C(16)—C(17)	1.387 (6)
C(17)—C(18)	1.383 (7)	C(18)—C(19)	1.374 (6)
C(3)—O(1)—C(11)	114.6 (4)	C(4)—O(2)—C(12)	118.1 (5)
C(6)—O(3)—C(13)	117.2 (4)	C(15)—O(4)—C(20)	119.3 (4)
C(17)—O(5)—C(21)	117.3 (4)	C(18)—O(6)—C(22)	116.1 (5)
C(2)—C(1)—C(10)	111.8 (4)	C(2)—C(1)—C(14)	111.4 (4)
C(10)—C(1)—C(14)	111.2 (4)	C(1)—C(2)—C(3)	120.8 (5)
C(1)—C(2)—C(7)	119.0 (5)	C(3)—C(2)—C(7)	120.1 (5)
O(1)—C(3)—C(2)	119.5 (4)	O(1)—C(3)—C(4)	119.7 (5)
C(2)—C(3)—C(4)	120.7 (5)	O(2)—C(4)—C(3)	115.7 (5)
O(2)—C(4)—C(5)	123.9 (5)	C(3)—C(4)—C(5)	120.4 (5)
C(4)—C(5)—C(6)	119.2 (5)	O(3)—C(6)—C(5)	123.6 (5)
O(3)—C(6)—C(7)	114.4 (5)	C(5)—C(6)—C(7)	122.0 (5)
C(2)—C(7)—C(6)	117.5 (5)	C(2)—C(7)—C(8)	119.4 (5)
C(6)—C(7)—C(8)	123.1 (5)	C(7)—C(8)—C(9)	122.1 (5)
C(8)—C(9)—C(10)	120.4 (5)	C(1)—C(10)—C(9)	112.8 (4)
C(1)—C(14)—C(15)	121.1 (4)	C(1)—C(14)—C(19)	122.1 (4)
C(15)—C(14)—C(19)	116.7 (4)	O(4)—C(15)—C(14)	115.4 (4)
O(4)—C(15)—C(16)	122.6 (5)	C(14)—C(15)—C(16)	122.0 (5)
C(15)—C(16)—C(17)	119.7 (5)	O(5)—C(17)—C(16)	124.3 (5)
O(5)—C(17)—C(18)	116.6 (5)	C(16)—C(17)—C(18)	119.1 (5)
O(6)—C(18)—C(17)	121.4 (5)	O(6)—C(18)—C(19)	118.0 (5)
C(17)—C(18)—C(19)	120.3 (5)	C(14)—C(19)—C(18)	122.1 (5)

(Germain, Main & Woolfson, 1971) direct-methods program. Geometrically constrained H atoms were placed 0.95 \AA from the bonded C atom with a fixed isotropic thermal parameter $B = 5.5 \text{\AA}^2$ and allowed to ride on that atom. The methyl H atoms were located from a difference Fourier map and included with fixed contributions ($B = 5.5 \text{\AA}^2$). Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); structure refined with *SHELX76* (Sheldrick, 1976). $\sum w(|F_o| - |F_c|)^2$ minimized, weights = $[\sigma(F_o)^2 + 0.00003F_o^2]^{-1}$, 253 parameters varied. $R = 0.054$, $wR = 0.054$, $S = 1.26$. Δ/σ in final least-squares refinement cycle < 0.01 , $\Delta\rho < 0.2 \text{ e \AA}^{-3}$ in final difference map.

Discussion. Fractional coordinates and B_{eq} values are given in Table 1,* bond distances and angles in Table 2, and an *ORTEP* drawing (Johnson, 1976) in Fig. 1. The 1-aryl-1,2-dihydronaphthalene carbocyclic framework of the synthetic product is immediately obvious upon examination of the *ORTEP* diagram. The bond distance between atoms C(8) and C(9) is 1.320 (7) \AA , while that between C(1) and C(10) is 1.535 (6) \AA . Consistent with sp^2 hybridization at atoms C(8) and C(9) are the bond angles C(7)—C(8)—C(9) and C(8)—C(9)—C(10) of 122.1 (5) and 120.4 (5) $^\circ$, respectively.

The dihydronaphthalene ring atoms C(1)—C(9) define a plane to within 0.169 \AA , with the deviation from this plane greatest for atom C(9). The C(1)—C(9) plane can be further divided into two planes intersecting

* Lists of structure factors, anisotropic thermal parameters, least-squares-planes results and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51311 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

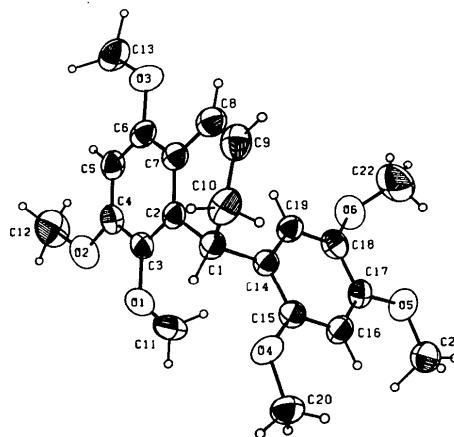


Fig. 1. Thermal-ellipsoid plot of the title compound. The atom-numbering scheme is arbitrary. H atoms have been given arbitrarily reduced radii.

at an angle of 14.2°. The first of these planes is defined by atoms C(2)–C(7) and the other by atoms C(7)–C(9). The former is planar to within 0.010 Å and the latter is planar by definition. Atom C(10) was found to lie 0.543 Å below the C(1)–C(9) plane. This slight puckering of the dihydronaphthalene ring permits a relief of steric eclipsing interactions between the H atom(s) or pendant aromatic ring substituents at positions C(1), C(9) and C(10). Finally, the pendant aromatic ring defined by atoms C(14)–C(19) is planar to within 0.003 Å and intersects the C(1)–C(9) plane at an angle of 84.8°.

The β,β' -coupling of two 2,4,5-trimethoxystyrene molecules to a 1-aryldihydronaphthalene ring system illustrates a new oxidative pathway for manganese(III) acetate. The reaction presumably proceeds by a SETO pathway with slow or rapidly reversible solvolysis of the radical-cation intermediate. Hence, the mechanism of this reaction appears to be similar to that reported for the ferric ion-mediated phenolic couplings of methyl cinnamates (Ahmed, Schreiber & Stevenson, 1976; Stevenson & Williams, 1977), and to the β,β' -dimerizations of cinnamic acids to dicinnamic acid dilactones (Surjasmita, 1987). Further work is now in progress to discover the scope and limitations of this unusual oxidation process.

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Structure of Tinosporide, a Diterpenoid Furanolactone from *Tinospora cordifolia* Miers

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Abstract. (1*S*,2*S*,3*R*,4*R*,5*R*,8*S*,10*R*,12*S*)-4-Hydroxy-2,3:15,16-diepoxycleroda-13(16),14-dieno-17,12:18,1-biscarbolactone, C₂₀H₂₂O₇, *M_r* = 374, m.p. = 509–511 K, orthorhombic, *P*2₁2₁2₁, *a* = 9.191 (2), *b* = 13.8230 (6), *c* = 26.956 (2) Å, *V* = 3424.50 Å³, *Z* = 8, *D_x* = 1.450, *D_m*(by flotation) = 1.446 g cm⁻³,

$\lambda(\text{Cu K}\alpha) = 1.5418 \text{ \AA}$, $\mu = 8.20 \text{ cm}^{-1}$, $F(000) = 1584$, $T = 295 \text{ K}$, $R = 0.0464$, $wR = 0.0579$ for 3437 observed reflections. The asymmetric unit contains two molecules. The structure resembles that of a similar compound [Swaminathan, Sinha, Bhatt & Sabata (1988). *Acta Cryst.* **C44**, 1421–1424] with atom H(15) replacing the tertiary hydroxyl group at C(8). Atoms H(4) and H(15) are α - and β -oriented respectively at

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