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 (Surjasasmita, 1987). Further work is now in progress to discover the scope and limitations of this unusual oxidation process.

The authors are greatly indebted to the American Cancer Society, Illinois Division, Inc. (JRP, grant No. 87-53), the Milheim Foundation for Cancer Research (JRP, grant No. 87-32), the Elsa U. Pardee Foundation (JRP), the Donors of the Petroleum Research Fund (JRP and RDR), administered by the American Chemical Society, and to the Northern Illinois University Graduate School and Biomedical Research Support Group (JRP) for their generous support of this research. The US National Science Foundation's Chemical Instrumentation Program provided funding to purchase the diffractometer.

References

AHMED, R., SCHREIBER, F. G. & STEVENSON, R. (1976). *Tetrahedron*, **32**, 1339–1344.

FRISTAD, W. E., PETERSON, J. R., ERNST, A. B. & URBI, G. B. (1986). *Tetrahedron*, **42**, 3429–3442.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

PETERSON, J. R., DO, H. D. & SURJASASMITA, I. B. (1988). *Synth. Commun.* **18**(16). In the press.

PETERSON, J. R., DO, H. D., WINTER, T. J. & SURJASASMITA, I. B. (1988). Poster No. 32. *21st National Medicinal Chemistry Symposium*, Minneapolis, Minnesota, USA.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination as locally modified. Univ. of Cambridge, England.

STEVENSON, R. & WILLIAMS, J. R. (1977). *Tetrahedron*, **33**, 285–288.

SURJASASMITA, I. B. (1987). *Toward the Synthesis of Podophyllotoxin*. MS Thesis, Northern Illinois Univ., DeKalb, Illinois, USA.

Acta Cryst. (1989). C**45**, 134–136

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

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(*Received* 2 *June* 1988; *accepted* 8 *August* 1988)

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, $C_{20}H_{22}O_7$, $M_r = 374$, m.p. = 509–511 K, orthorhombic, $P2_12_12_1$, $a = 9{\cdot}191$ (2), $b = 13{\cdot}8230$ (6), $c = 26{\cdot}956$ (2) Å, $V = 3424{\cdot}50$ Å^3, $Z = 8$, $D_x = 1{\cdot}450$, D_m(by flotation) = 1·446 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 8{\cdot}20$ cm^{-1}, $F(000) = 1584$, $T = 295$ K, $R = 0{\cdot}0464$, $wR = 0{\cdot}0579$ 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.* C**44**, 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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0108-2701/89/010134-03$03.00

Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
C(11)	1925 (3)	280 (2)	1020 (1)	39 (2)
C(21)	3172 (3)	847 (2)	808 (1)	52 (3)
C(31)	2876 (3)	1877 (2)	815 (1)	49 (2)
C(41)	1383 (3)	2091 (2)	1030 (1)	37 (2)
C(51)	218 (3)	1563 (1)	705 (1)	32 (2)
C(61)	−1282 (3)	1730 (2)	932 (1)	41 (2)
C(71)	−2509 (3)	1144 (2)	692 (1)	46 (2)
C(81)	−2047 (3)	137 (2)	505 (1)	37 (2)
C(91)	−666 (2)	−264 (1)	759 (1)	30 (2)
C(101)	613 (2)	453 (1)	677 (1)	27 (2)
C(111)	−349 (3)	−1244 (1)	521 (1)	34 (2)
C(121)	−170 (3)	−1212 (2)	−38 (1)	36 (2)
C(131)	−244 (3)	−2192 (2)	−284 (1)	38 (2)
C(141)	343 (3)	−2431 (2)	−756 (1)	47 (2)
C(151)	−7 (3)	−3348 (2)	−845 (1)	50 (2)
C(161)	−935 (4)	−2987 (2)	−115 (1)	60 (3)
C(171)	−2004 (3)	90 (2)	−61 (1)	45 (2)
C(181)	1413 (3)	1612 (2)	1540 (1)	41 (2)
C(191)	259 (4)	2010 (2)	184 (1)	48 (2)
C(201)	−1016 (3)	−462 (2)	1306 (1)	44 (2)
O(11)	−797 (3)	−3717 (1)	−462 (1)	68 (2)
O(21)	−1271 (3)	−620 (1)	−285 (1)	53 (2)
O(31)	−2707 (3)	624 (2)	−326 (1)	72 (2)
O(41)	1094 (2)	3082 (1)	1097 (1)	50 (2)
O(51)	1272 (3)	2000 (2)	1933 (1)	62 (2)
O(61)	1616 (2)	643 (1)	1512 (1)	45 (2)
O(71)	3941 (2)	1462 (2)	1151 (1)	63 (2)
C(12)	880 (4)	−91 (3)	−2661 (1)	71 (4)
C(22)	−310 (5)	−815 (3)	−2743 (2)	95 (5)
C(32)	−1694 (4)	−440 (3)	−2571 (2)	79 (4)
C(42)	−1535 (3)	580 (2)	−2361 (1)	44 (2)
C(52)	−455 (2)	528 (1)	−1914 (1)	32 (2)
C(62)	−198 (3)	1545 (2)	−1717 (1)	47 (2)
C(72)	945 (4)	1586 (3)	−1311 (2)	82 (4)
C(82)	2287 (3)	928 (2)	−1395 (1)	45 (2)
C(92)	2443 (2)	540 (2)	−1928 (1)	36 (2)
C(102)	998 (2)	56 (2)	−2097 (1)	33 (2)
C(112)	3691 (3)	−192 (2)	−1921 (1)	41 (2)
C(122)	3477 (3)	−1017 (2)	−1560 (1)	38 (2)
C(132)	4864 (3)	−1559 (2)	−1475 (1)	38 (2)
C(142)	5538 (4)	−2221 (2)	−1798 (1)	64 (3)
C(152)	6759 (4)	−2512 (2)	−1587 (1)	61 (3)
C(162)	5821 (3)	−1460 (2)	−1092 (1)	51 (2)
C(172)	2423 (3)	174 (2)	−984 (1)	46 (2)
C(182)	−803 (4)	1166 (3)	−2759 (1)	59 (3)
C(192)	−1139 (3)	−98 (3)	−1509 (1)	61 (3)
C(202)	2946 (3)	1380 (3)	−2258 (2)	76 (4)
O(12)	6976 (2)	−2053 (2)	−1151 (1)	61 (2)
O(22)	2987 (2)	−689 (1)	−1074 (1)	52 (2)
O(32)	2089 (3)	354 (2)	−564 (1)	77 (2)
O(42)	−2904 (2)	944 (2)	−2248 (1)	61 (2)
O(52)	−1239 (3)	1920 (2)	−2928 (1)	90 (3)
O(62)	491 (3)	812 (3)	−2899 (1)	85 (3)
O(72)	−1406 (4)	−541 (3)	−3095 (1)	135 (5)

Table 2. *Bond lengths* (Å), *important bond angles* (°) *and torsion angles* (°) *for first* ($N = 1$) *and second* ($N = 2$) *molecules with e.s.d.'s in parentheses*

	$N = 1$	$N = 2$
C(2*N*)–C(1*N*)	1·501 (4)	1·499 (6)
C(10*N*)–C(1*N*)	1·538 (3)	1·536 (4)
O(6*N*)–C(1*N*)	1·445 (3)	1·449 (5)
C(3*N*)–C(2*N*)	1·451 (4)	1·449 (6)
O(7*N*)–C(2*N*)	1·442 (4)	1·435 (6)
C(4*N*)–C(3*N*)	1·518 (4)	1·526 (5)
O(7*N*)–C(3*N*)	1·451 (4)	1·445 (6)
C(5*N*)–C(4*N*)	1·565 (3)	1·564 (3)
C(18*N*)–C(4*N*)	1·526 (3)	1·503 (4)
O(4*N*)–C(4*N*)	1·407 (3)	1·389 (3)
C(6*N*)–C(5*N*)	1·526 (3)	1·521 (3)
C(10*N*)–C(5*N*)	1·578 (3)	1·566 (3)
C(19*N*)–C(5*N*)	1·534 (3)	1·528 (4)
C(7*N*)–C(6*N*)	1·533 (4)	1·518 (5)
C(8*N*)–C(7*N*)	1·541 (4)	1·548 (5)
C(9*N*)–C(8*N*)	1·545 (3)	1·542 (4)
C(17*N*)–C(8*N*)	1·528 (4)	1·526 (4)
C(10*N*)–C(9*N*)	1·554 (3)	1·555 (3)
C(11*N*)–C(9*N*)	1·527 (3)	1·530 (3)
C(20*N*)–C(9*N*)	1·536 (3)	1·533 (5)
C(12*N*)–C(11*N*)	1·515 (3)	1·511 (3)
C(13*N*)–C(12*N*)	1·510 (3)	1·497 (3)
O(2*N*)–C(12*N*)	1·462 (3)	1·458 (3)
C(14*N*)–C(13*N*)	1·422 (4)	1·408 (4)
C(16*N*)–C(13*N*)	1·348 (4)	1·361 (4)
C(15*N*)–C(14*N*)	1·330 (4)	1·321 (5)
O(1*N*)–C(15*N*)	1·362 (4)	1·350 (4)
O(1*N*)–C(16*N*)	1·380 (4)	1·351 (4)
O(2*N*)–C(17*N*)	1·335 (3)	1·322 (3)
O(3*N*)–C(17*N*)	1·212 (4)	1·199 (3)
O(5*N*)–C(18*N*)	1·193 (3)	1·205 (5)
O(6*N*)–C(18*N*)	1·355 (3)	1·341 (4)
O(6*N*)–C(1*N*)–C(2*N*)	108·5 (2)	109·3 (3)
C(3*N*)–C(2*N*)–C(1*N*)	111·4 (2)	110·8 (3)
O(7*N*)–C(2*N*)–C(1*N*)	116·0 (3)	115·7 (3)
O(7*N*)–C(3*N*)–C(2*N*)	59·6 (2)	59·5 (3)
O(7*N*)–C(3*N*)–C(4*N*)	116·7 (2)	115·7 (3)
O(4*N*)–C(4*N*)–C(18*N*)	108·1 (2)	111·5 (2)
O(3*N*)–C(17*N*)–O(2*N*)	116·8 (2)	117·4 (3)
C(16*N*)–O(1*N*)–C(15*N*)	106·8 (2)	105·7 (2)
C(3*N*)–O(7*N*)–C(2*N*)	60·2 (2)	60·4 (3)
C(10*N*)–C(1*N*)–C(2*N*)–C(3*N*)	63·6 (3)	63·3 (4)
C(2*N*)–C(1*N*)–C(10*N*)–C(9*N*)	165·7 (2)	163·0 (3)
O(7*N*)–C(2*N*)–C(3*N*)–C(4*N*)	−109·1 (3)	−108·1 (4)
C(3*N*)–C(4*N*)–C(5*N*)–C(6*N*)	177·2 (2)	176·4 (2)
C(3*N*)–C(4*N*)–C(5*N*)–C(10*N*)	54·9 (3)	55·1 (3)
C(7*N*)–C(8*N*)–C(9*N*)–C(10*N*)	−58·0 (3)	−51·9 (3)
C(7*N*)–C(8*N*)–C(9*N*)–C(11*N*)	−178·5 (2)	−172·4 (3)
C(7*N*)–C(8*N*)–C(17*N*)–O(2*N*)	162·1 (2)	148·6 (3)
C(9*N*)–C(11*N*)–C(12*N*)–O(2*N*)	−44·1 (3)	−46·0 (3)
C(11*N*)–C(12*N*)–C(13*N*)–C(16*N*)	25·9 (4)	98·1 (3)

sites C(12) and C(8). The terpene ring *A* is locked into a boat conformation by the C(1)–C(4) lactone bridge. The hydroxyl at C(4) is involved in hydrogen bonding.

Introduction. In continuation of the research work on *Tinospora cordifolia* (Bhatt, Hanuman & Sabata, 1988; Hanuman, Bhatt & Sabata, 1986; Hanuman, Mishra & Sabata, 1986; Hanuman, Bhatt & Sabata, 1988) the structural investigation of the title compound was undertaken to determine the stereochemistry and illuminate its medicinal properties.

Experimental. *Tinospora cordifolia* was extracted with chloroform in a Soxhlet apparatus and the compound was isolated by column chromatography over silica gel using 50% ethyl acetate–petroleum ether (333–353 K). Recrystallization from methanol. A crystal of dimensions 0·30 × 0·32 × 0·40 mm was selected for data collection with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ radiation, ω–2θ scan. Unit-cell parameters, obtained by photographic method, were refined by least-squares analysis using 25 reflections, $15 < \theta < 45°$. Data were collected in the range $0 < \theta < 70°$ ($h_{max} = 11$, $k_{max} = 16$, $l_{max} = 32$, resolution $d = 0{\cdot}82$ Å). Two standard reflections, 5·3% intensity variation. 3699 unique reflections of which 149 reflections had $|F_o| < 3\sigma(|F_o|)$. Lp corrections, no absorption correction. Structure solution by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms were located from difference Fourier maps. Structure refinement by *SHELX*76 (Sheldrick, 1976) using least-squares method based on F values, with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. In the final calculation reflections with $|F_o| < 5\sigma(|F_o|)$ and those for which $F_o < F_c$ with $(F_o - F_c)/\sigma(|F_o|) > 4{\cdot}0$ were omitted. Number of parameters refined: 663, including H atoms. $(\Delta/\sigma)_{\max} = 0{\cdot}650$. $\Delta\rho$ in the final difference Fourier map $-0{\cdot}1198$ to $0{\cdot}1559$ e Å^{-3}. For 3437 reflections $R = 0{\cdot}0464$ and $wR = 0{\cdot}0579$ (Stout & Jensen, 1968) where $w = k/[\sigma^2(F_o) + g(F_o)^2]$ with $k = 1{\cdot}0000$ and $g = 0{\cdot}0012$. Structure was solved with NEC-1000 computer at National Informatics Centre, Pune, and refinement with CYBER-180 at IIT, Bombay. Atomic scattering factors those of *SHELX76*.

Discussion. Table 1 gives the positional parameters and equivalent isotropic temperature factors for non-H atoms.* Table 2 gives some important bond lengths, bond angles and torsion angles. The structural formula is given in Fig. 1. The structure for this compound was first assigned by Ahmed, Khaleque & Wahed (1978) and revised by Ahmed, Katri, Karim, Khaleque & Wahed (1978), but the stereochemistry was not determined. The present work supports the revised structure. The chirality was assigned on the basis of detailed ^{1}H NMR, proton spin-decoupling and ^{13}C NMR studies. The epoxy oxygen O(7) which is bonded to C(2) and C(3) is β-oriented [lies on the same side of ring *A* as the C(1)–C(4) lactone bridge] in the standard view, Fig. 2 (*PLUTO* drawing; Motherwell & Clegg, 1978). The bond lengths C(21)—C(31) and C(22)—C(32) are nearly equal [1·451 (4), 1·449 (6) Å]. Ring *A* is locked into a boat conformation by the C(1)–C(4) lactone bridge. The hydroxyl group at C(4) is α-oriented [lies below C(4)]. The bond lengths C(41)—O(41) and C(42)—O(42) are 1·407 (3) and 1·389 (3) Å. Atoms H(15) at C(8) and H(4) at C(12) are β- and α-oriented. Atom H(7) at C(10) and the lactone group at C(1) indicate the *trans*-diaxial relationship. The furan ring is planar with maximum deviation from planarity 0·0031 (3) and 0·0192 (2) Å in the first and the second molecules. This ring is connected equatorially to ring *C* at atom C(12). No marked difference between the two independent molecules is observed except in the rotation of the furan ring. This is clear from the torsional angles C(111)—C(121)—C(131)—C(161) = 25·9 (4) and C(112)—C(122)—C(132)—C(162) = 98·1 (3)°. The hydroxyl group at C(4) is involved in intermolecular hydrogen bonding, with bond distances O(41)···O(31) 2·955 (8) and O(42)···O(51) 3·061 Å.

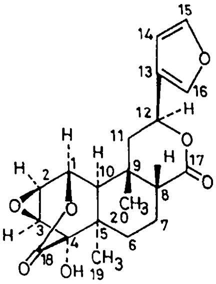

Fig. 1. Structural formula.

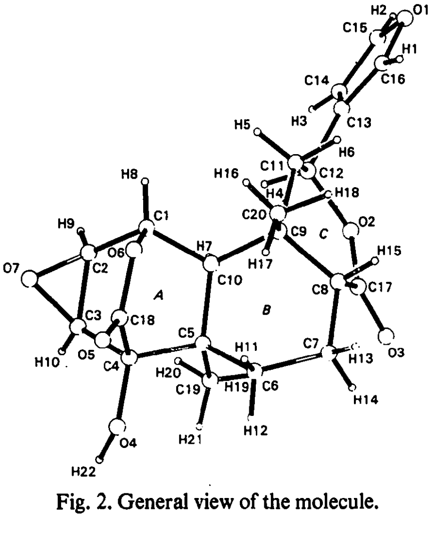

Fig. 2. General view of the molecule.

References

Ahmed, M., Katri, A. B., Karim, R., Khaleque, A. & Wahed, M. A. (1978). *J. Bangladesh Acad. Sci.* **2**(2), 25–30.

Ahmed, M., Khaleque, A. & Wahed, M. A. (1978). *Indian J. Chem.* **16B**, 317–318.

Bhatt, R. K., Hanuman, J. B. & Sabata, B. K. (1988). *Phytochemistry*, **27**, 1212–1216.

Hanuman, J. B., Bhatt, R. K. & Sabata, B. K. (1986). *Phytochemistry*, **25**, 1677–1680.

Hanuman, J. B., Bhatt, R. K. & Sabata, B. K. (1988). *J. Nat. Prod.* **51**, 197–201.

Hanuman, J. B., Mishra, A. K. & Sabata, B. K. (1986). *J. Chem. Soc. Perkin Trans.* 1, pp. 1181–1185.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO78*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Stout, G. H. & Jensen, L. H. (1968). *X-ray Structure Determination*. New York: Macmillan.

Swaminathan, K., Sinha, U. C., Bhatt, R. K. & Sabata, B. K. (1988). *Acta Cryst.* C**44**, 1421–1424.

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* Lists of structure factors, anisotropic thermal parameters, hydrogen-bond distances, least-squares planes, bond lengths, bond angles and torsion angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51312 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.