

Discussion. The molecular structure and atomic labelling scheme are shown in Fig. 1. Atomic coordinates for all non-H atoms are given in Table 1,* and the bond lengths and angles are listed in Table 2.

The structure of compound (III) is very similar to those of (I) and (II). In (I) and (II), the spiro atom is shared by two rings and displays regular sp^3 hybridization, but in (III) three rings share the spiro atom. The dihedral angle between planes through O(1)—C(1)—C(9) and N(1)—C(1)—C(8) is 88.6° , similar to the angles in spirooxazines and spiropyrans [86.4 – 89.6° (Clegg, Norman, Flood, Sallans, Kwak, Kwiatkowski & Lasch, 1991)]. The dihedral angle between planes N(1)—C(1)—C(8) and N(1)—C(1)—C(9) is 53.4° and between planes N(1)—C(1)—C(9) and O(1)—C(1)—C(9) is 23.6° . The C(9)—N(2) bond of compound (III) is a single bond of length 1.424 \AA , clearly different from the C=N double bond, 1.267 \AA , in spirooxazine (Millini, Del Piero, Alle-

grini, Crisci & Malatesta, 1991). Other distances are comparable to those in (I) and (II).

The authors thank the National Science Council of the Republic of China for support of this work (NSC81-0405-E007-17).

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* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55629 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1012]

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Acta Cryst. (1993). **C49**, 511–514

Determination of the Stereochemistry of Oxandran-3-one; a Novel Methyltriterpene from *Oxandra asbeckii* (Annonaceae)

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(Received 10 February 1992; accepted 22 July 1992)

Abstract. (24*R*)-24-Methyl-21,24-oxylanost-9(11)-en-3-one, $C_{31}H_{50}O_2$, $M_r = 454.7$, orthorhombic, $P2_12_12_1$, $a = 7.135$ (3), $b = 17.639$ (4), $c = 21.454$ (7) \AA , $V = 2700.1$ (16) \AA^3 , $Z = 4$, $D_x = 1.12 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.70930 \text{ \AA}$, $\mu = 0.6 \text{ cm}^{-1}$, $F(000) = 1008$, room temperature, $R = 0.052$ for 1519 observed reflections. The structure of oxandran-3-one, a methyltriterpene

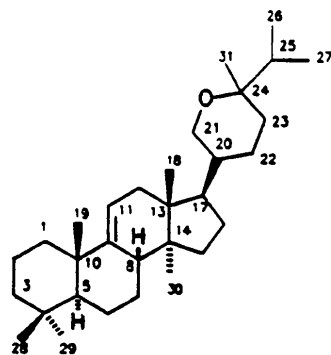
with a novel skeletal structure, has been determined and shown to have the lanostane stereochemistry. There are some apparent distortions of bond lengths and angles in the molecule. C(4)—C(5) and C(16)—C(14) bonds are longer than normal, reflecting ring strain. C(25)—C(26) is apparently anomalously short but this is likely an artefact owing to libration about the C(17)—C(20) and/or C(24)—C(25) bonds.

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Introduction. As part of a continuing investigation of natural products isolated from Guyanese plant

species, we recently completed what we believe is the first phytochemical investigation of *Oxandra asbeckii* (Pulle) R. E. Fries (Annonaceae), a tree with a restricted range in central Guyana (Tinto, Blair, Reynolds & McLean, 1992). Among the compounds isolated were three new methyltriterpenes with a novel skeleton which we called the oxandran skeleton (1).



(1)

The three compounds were 2,3-dioxoxandran (in the enol form), 3-acetoxoxandran-2-one and 3-hydroxyoxandran, the latter being the major product. The 3-hydroxy derivative was also converted to 3-acetoxoxandran and oxandran-3-one.

The basic structures of these triterpenes were determined by two-dimensional NMR methods while the stereochemistry was partially determined by selective ^1H NOE (nuclear Overhauser enhancement) measurements and from vicinal ^1H - ^1H coupling constants. These data suggested the lanostane stereochemistry for C(18) and C(30) of the carbocyclic skeleton [as illustrated in (1)] and that H(20) and C(31) of the tetrahydropyran ring were in a *trans* diaxial arrangement. They also indicated that all three compounds had the same stereochemistry. However, these data did not allow us to determine the relative stereochemistries of the tetrahydropyran ring and the tetracyclic part of the molecule. Consequently, an X-ray crystal-structure determination of oxandran-3-one (chosen because it gave the most suitable crystals) was undertaken in order to establish the total stereochemistry of this new class of compounds.

Experimental. Isolation of 3-hydroxyoxandran and synthesis and recrystallization of oxandran-3-one are described elsewhere (Tinto, Blair, Reynolds & McLean, 1992). Accurate cell dimensions and crystal-orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $10 < \theta < 14^\circ$. A crystal of dimensions $0.1 \times 0.2 \times$

0.3 mm was used to measure intensities of reflections with indices $h = 1$ to 7 , $k = 0$ to 18 , $l = 0$ to 23 , with $2 < 2\theta < 45^\circ$ (Friedel pairs measured), using ω - 2θ scans of ω -scan width $(0.6 + 0.35\tan\theta)^\circ$, and graphite-monochromated Mo $K\alpha$ radiation. Intensities of three reflections (235, 200 and 310), measured every 2 h, showed no evidence of crystal decay. 2356 reflections were measured, and 1778 reflections with $I > 2.5\sigma(I)$ were labelled observed and used in the structure solution and initial refinement. Data were corrected for Lorentz and polarization effects. Space group $P2_12_12_1$ was determined uniquely by the systematic absences ($0h0$ absent if $h = 2n + 1$, $0k0$ absent if $k = 2n + 1$ and $0l0$ absent if $l = 2n + 1$). The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). Refinement was by full-matrix least-squares calculations to minimize $\sum w(F_o - F_c)^2$, initially with isotropic and then with anisotropic thermal parameters for C and O atoms. H atoms were positioned on geometric grounds [$\text{C}-\text{H} = 0.95 \text{ \AA}$, $U(\text{H}) = U(\text{C}) + 0.01 \text{ \AA}^2$] and included (as riding atoms) in the structure-factor calculation. Parallel refinement with the chirality of the molecule reversed gave no significant difference in R factors or molecular geometry. In the final cycles of least squares, hkl and $\bar{h}\bar{k}\bar{l}$ reflections were averaged to yield 2040 unique reflections ($R_{\text{int}} = 0.027$), 1519 of which were observed. Final cycles of least squares included 299 parameters; $R = 0.052$, $wR = 0.071$, goodness of fit = 2.32 and $w = 1/[\sigma(F_o)^2 + 0.0004(F_o)^2]$. The final value for the secondary-extinction coefficient (Larson *et al.*, 1990) was 0.67 (24). Maximum shift/e.s.d. in the final refinement cycle was less than 0.001; density in final difference map was in the range -0.19 to 0.23 e \AA^{-3} ; there were no chemically significant features. Atomic scattering factors and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were carried out on an Apollo computer using *NRCVAX* (Larson *et al.*, 1990) and *SHELXS86* (Sheldrick, 1986). Atomic coordinates* are given in Table 1. Details of molecular geometry are given in Table 2. Fig. 1 is a view of the molecule prepared using *ORTEPII* (Johnson, 1976).

Discussion. The structure as shown in Fig. 1 confirms the lanostane stereochemistry for the carbocyclic skeleton [with C(18) and C(30) *anti*]. It shows a stereochemistry for the tetrahydropyran ring which is

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom coordinates, mean-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55611 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1003]

Table 1. Positional and thermal parameters (\AA^2) with *e.s.d.'s in parentheses*

B_{eq} is the mean of the principal axes of the thermal ellipsoid.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
O(1)	0.7762 (8)	0.4177 (3)	0.02879 (24)	5.8 (3)
O(2)	1.1317 (8)	-0.2529 (3)	0.0870 (3)	6.6 (3)
C(1)	0.9757 (10)	0.2401 (4)	0.0573 (3)	4.1 (3)
C(2)	1.0092 (10)	0.3265 (4)	0.0547 (3)	4.5 (4)
C(3)	0.8273 (10)	0.3683 (4)	0.0643 (3)	3.7 (3)
C(4)	0.7126 (10)	0.3474 (4)	0.1222 (3)	3.3 (3)
C(5)	0.7029 (9)	0.2579 (3)	0.1284 (3)	2.9 (3)
C(6)	0.6021 (10)	0.2322 (4)	0.1872 (3)	3.6 (3)
C(7)	0.5472 (10)	0.1499 (4)	0.1801 (3)	3.9 (3)
C(8)	0.7136 (9)	0.0993 (3)	0.1676 (3)	3.1 (3)
C(9)	0.8363 (9)	0.1291 (3)	0.1159 (3)	2.8 (3)
C(10)	0.8856 (9)	0.2129 (3)	0.1177 (3)	2.9 (3)
C(11)	0.9159 (10)	0.0830 (3)	0.0746 (3)	3.7 (3)
C(12)	0.9065 (11)	-0.0038 (4)	0.0761 (3)	4.3 (3)
C(13)	0.8359 (9)	-0.0322 (3)	0.1381 (3)	3.2 (3)
C(14)	0.6575 (9)	0.0156 (4)	0.1556 (3)	3.2 (3)
C(15)	0.5815 (11)	-0.0276 (4)	0.2117 (3)	4.2 (3)
C(16)	0.6257 (11)	-0.1113 (4)	0.1984 (4)	4.9 (4)
C(17)	0.7581 (10)	-0.1146 (3)	0.1412 (3)	3.5 (3)
C(18)	0.9935 (10)	-0.0221 (4)	0.1858 (3)	4.3 (3)
C(19)	1.0294 (10)	0.2233 (4)	0.1717 (4)	4.7 (4)
C(20)	0.8903 (11)	-0.1813 (3)	0.1438 (4)	4.2 (4)
C(21)	1.0139 (12)	-0.1865 (4)	0.0875 (4)	5.9 (4)
C(22)	0.7830 (10)	-0.2545 (4)	0.1491 (3)	4.9 (4)
C(23)	0.9121 (11)	-0.3245 (4)	0.1452 (3)	4.4 (4)
C(24)	1.0396 (11)	-0.3239 (4)	0.0882 (4)	4.4 (4)
C(25)	1.1919 (12)	-0.3818 (4)	0.0899 (5)	6.5 (5)
C(26)	1.3386 (16)	-0.3675 (6)	0.1302 (8)	13.3 (10)
C(27)	1.1205 (14)	-0.4628 (4)	0.0981 (5)	8.6 (6)
C(28)	0.8036 (11)	0.3882 (4)	0.1789 (3)	4.3 (3)
C(29)	0.5124 (10)	0.3792 (4)	0.1145 (4)	4.6 (4)
C(30)	0.5059 (10)	0.0122 (4)	0.1037 (4)	4.8 (4)
C(31)	0.9294 (18)	-0.3353 (5)	0.0293 (4)	8.4 (6)

consistent with it being derived from a side chain with the lanostane stereochemistry (Shopee, 1964). The stereochemistry at C(24) is *R*.

Most of the C—C single-bond distances in the structure are within the range 1.492 (11)–1.558 (10) Å. The slightly longer C(4)—C(5) and C(13)—C(14) bonds of 1.586 (9) and 1.573 (9) Å (and associated distortions of angles involving these atoms) may indicate some ring strain at these points in the molecule. The C(25)—C(26) bond is unusually short [1.380 (17) Å] but this is likely an artefact arising from the very large thermal parameter [B_{iso} of 13.3 (10) Å²] for C(26). The thermal parameters of C(27) [B_{iso} 8.6 (6) Å²] and C(31) [B_{iso} 8.4 (6) Å²] are also large. These thermal parameters in turn may reflect slight disorder, possibly resulting from libration about the C(24)—C(25) bond and/or the C(17)—C(20) bond. Disorder in this area of the molecule was investigated but multiple sites for C(26), C(27) and C(31) were not detectable from difference maps calculated with these atoms omitted from the final model. We have therefore assumed that there is large thermal displacement associated with these three atoms.

The saturated six-membered rings in the molecule have chair conformations. The unsaturated six-membered ring adopts a half-chair conformation with C(8), C(9), C(11) and C(12) forming a plane [maximum deviation -0.021 (9) Å for C(11)] while

Table 2. Geometric parameters (\AA , °)

O(1)—C(3)	1.213 (9)	C(11)—C(12)	1.532 (9)
O(2)—C(21)	1.442 (9)	C(12)—C(13)	1.507 (10)
O(2)—C(24)	1.414 (9)	C(13)—C(14)	1.573 (9)
C(1)—C(2)	1.543 (9)	C(13)—C(17)	1.557 (9)
C(1)—C(10)	1.525 (9)	C(13)—C(18)	1.532 (10)
C(2)—C(3)	1.507 (11)	C(14)—C(15)	1.524 (9)
C(3)—C(4)	1.533 (10)	C(14)—C(30)	1.555 (10)
C(4)—C(5)	1.586 (9)	C(15)—C(16)	1.538 (10)
C(4)—C(28)	1.556 (10)	C(16)—C(17)	1.549 (10)
C(4)—C(29)	1.543 (10)	C(17)—C(20)	1.510 (9)
C(5)—C(6)	1.521 (9)	C(20)—C(21)	1.498 (11)
C(5)—C(10)	1.543 (9)	C(20)—C(22)	1.505 (10)
C(6)—C(7)	1.511 (10)	C(22)—C(23)	1.543 (11)
C(7)—C(8)	1.510 (9)	C(23)—C(24)	1.524 (11)
C(8)—C(9)	1.507 (9)	C(24)—C(25)	1.492 (11)
C(8)—C(14)	1.550 (9)	C(24)—C(31)	1.501 (13)
C(9)—C(10)	1.520 (9)	C(25)—C(26)	1.380 (17)
C(9)—C(11)	1.330 (9)	C(25)—C(27)	1.527 (11)
C(10)—C(19)	1.558 (10)		
C(21)—O(2)—C(24)	116.6 (6)	C(12)—C(13)—C(17)	117.9 (5)
C(2)—C(1)—C(10)	114.0 (5)	C(12)—C(13)—C(18)	107.8 (6)
C(1)—C(2)—C(3)	110.0 (6)	C(14)—C(13)—C(17)	101.6 (5)
O(1)—C(3)—C(2)	121.6 (6)	C(14)—C(13)—C(18)	111.8 (5)
O(1)—C(3)—C(4)	121.4 (7)	C(17)—C(13)—C(18)	109.9 (5)
C(2)—C(3)—C(4)	116.9 (6)	C(8)—C(14)—C(13)	110.0 (5)
C(3)—C(4)—C(5)	109.3 (5)	C(8)—C(14)—C(15)	115.9 (5)
C(3)—C(4)—C(28)	107.4 (5)	C(8)—C(14)—C(30)	109.6 (5)
C(3)—C(4)—C(29)	108.7 (6)	C(13)—C(14)—C(15)	102.1 (5)
C(5)—C(4)—C(28)	114.4 (5)	C(13)—C(14)—C(30)	111.5 (5)
C(5)—C(4)—C(29)	109.3 (5)	C(15)—C(14)—C(30)	107.4 (6)
C(28)—C(4)—C(29)	107.5 (6)	C(14)—C(15)—C(16)	105.1 (5)
C(4)—C(5)—C(6)	112.7 (5)	C(15)—C(16)—C(17)	107.9 (5)
C(4)—C(5)—C(10)	117.6 (5)	C(13)—C(17)—C(16)	102.5 (5)
C(6)—C(5)—C(10)	111.7 (5)	C(13)—C(17)—C(20)	120.4 (6)
C(5)—C(6)—C(7)	109.0 (5)	C(16)—C(17)—C(20)	112.4 (6)
C(6)—C(7)—C(8)	112.5 (6)	C(17)—C(20)—C(21)	112.7 (6)
C(7)—C(8)—C(9)	112.4 (5)	C(17)—C(20)—C(22)	110.7 (6)
C(7)—C(8)—C(14)	112.9 (5)	C(21)—C(20)—C(22)	108.0 (6)
C(9)—C(8)—C(14)	111.1 (5)	O(2)—C(21)—C(20)	113.5 (6)
C(8)—C(9)—C(10)	117.0 (5)	C(20)—C(22)—C(23)	112.2 (6)
C(8)—C(9)—C(11)	121.7 (5)	C(22)—C(23)—C(24)	113.2 (6)
C(10)—C(9)—C(11)	120.8 (6)	O(2)—C(24)—C(23)	107.3 (6)
C(1)—C(10)—C(5)	108.7 (5)	O(2)—C(24)—C(25)	105.6 (6)
C(1)—C(10)—C(9)	112.5 (5)	O(2)—C(24)—C(31)	110.3 (6)
C(1)—C(10)—C(19)	108.5 (6)	C(23)—C(24)—C(25)	114.2 (7)
C(5)—C(10)—C(9)	108.0 (5)	C(23)—C(24)—C(31)	111.2 (7)
C(5)—C(10)—C(19)	112.7 (5)	C(25)—C(24)—C(31)	108.1 (7)
C(9)—C(10)—C(19)	106.6 (5)	C(24)—C(25)—C(26)	116.3 (8)
C(9)—C(11)—C(12)	125.2 (6)	C(24)—C(25)—C(27)	113.6 (7)
C(11)—C(12)—C(13)	111.5 (6)	C(26)—C(25)—C(27)	110.7 (9)
C(12)—C(13)—C(14)	107.6 (5)		

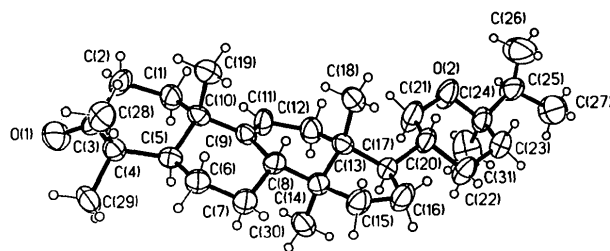


Fig. 1. View of the molecule indicating the atomic labelling scheme. The thermal ellipsoids of the C and O atoms are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary radii.

C(13) and C(14) are 0.418 (13) and -0.416 (13) Å, respectively, out of the plane. The five-membered ring has an envelope conformation; C(14), C(15), C(16) and C(17) define a plane [maximum deviation -0.069 (10) Å for C(15)], with C(13) 0.681 (10) Å from this plane. A plane common to both rings exists

through the atoms C(8), C(9), C(11), C(12), C(15), C(16) and C(17) [maximum deviation 0.081 (9) Å for C(15)] with C(13) 0.394 (7) and C(14) -0.407 (7) Å out of this plane.

Financial support in the form of operating grants from NSERCC (WFR and SM) and an NSERCC-CIDA Research Associateship (WFT) and a CIDA grant to the Centre for Natural Products Chemistry are gratefully acknowledged.

Acta Cryst. (1993). **C49**, 514–517

Functionalized Hydrocarbons with Condensed Ring Skeletons. XI. Tetramethyl Tricyclo[8.4.0.0^{2,7}]tetradeca-1,8-diene-5,5,12,12-tetracarboxylate and its Corresponding Tetradec-8-ene

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(Received 11 July 1991; accepted 29 July 1992)

Abstract. Monoclinic, $\lambda(\text{Cu } K\alpha) = 1.54056 \text{ \AA}$, $Z = 4$, room temperature. (I) (7,10-*cis*)-Tetramethyl tricyclo[8.4.0.0^{2,7}]tetradeca-1,8-diene-5,5,12,12-tetracarboxylate, $\text{C}_{22}\text{H}_{28}\text{O}_8$, $M_r = 420.46$, $P2_1/a$, $a = 7.8478 (4)$, $b = 20.0952 (9)$, $c = 13.3666 (3) \text{ \AA}$, $\beta = 95.680 (2)^\circ$, $V = 2097.60 \text{ \AA}^3$, $D_x = 1.331 \text{ Mg m}^{-3}$, $\mu = 0.80 \text{ mm}^{-1}$, $F(000) = 896$, final $R = 0.052$ for 2840 observed reflections. (II) (1,2-*cis*-1,10-*trans*-2,7-*trans*)-Tetramethyl tricyclo[8.4.0.0^{2,7}]tetradec-8-ene-5,5,12,12-tetracarboxylate, $\text{C}_{22}\text{H}_{30}\text{O}_8$, $M_r = 422.48$, $P2_1/c$, $a = 6.0842 (2)$, $b = 12.7171 (7)$, $c = 27.8011 (16) \text{ \AA}$, $\beta = 93.183 (3)^\circ$, $V = 2147.75 \text{ \AA}^3$, $D_x = 1.307 \text{ Mg m}^{-3}$, $\mu = 0.79 \text{ mm}^{-1}$, $F(000) = 904$, final $R = 0.046$ for 3256 observed reflections. Both compounds (I) and (II) consist of three angularly fused six-membered rings *A*, *B* and *C*. Rings *A* and *C* for structure (I) adopt a chair conformation with C7 and C10 H atoms (IUPAC numbering) being axial, while unsaturated ring *B* prefers a boat-like conformation. Rings *A* and *C* for structure (II) also adopt a chair conformation with C1, C2, C7 and C10 H atoms (IUPAC numbering) being all axial, while the conformation of ring *B* is boat. In compound (II), the relative stereochemistry is *trans* at the *AB* ring junction, *syn* between C1 and C2 H atoms (IUPAC numbering) and *trans* at the *BC* ring junction (abbreviated by TST).

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Introduction. In earlier publications (Michel, Michel-Dewez & Roughton 1989; Drouin, Michel, Xu & Deslongchamps, 1990), we have reported the conformational properties and X-ray data of several steroid-like compounds having *A.B.C.* [6.6.6] tricyclic skeletons. Two new tricyclic compounds (I) and (II), which do not have the methyl substituent on the ring junctions, were synthesized from their macrocyclic precursors (III) and (IV), respectively (Cantin, Xu & Deslongchamps, 1990). The double bonds $\Delta^{3,4}$ and $\Delta^{5,6}$ are both *trans* in the two macrocycles and $\Delta^{11,12}$ is *cis* in (IV). It is expected that the transannular Diels–Alder reaction takes place *via* a boat-like transition state (Lamothe, Ndibwami & Deslongchamps, 1988). Consequently, the conformational strains imposed on the transition state by its olefin geometry, substituents, and ring size determine the relative stereochemistry of the cycloaddition products. From the molecular-model analysis of the transition state, it is expected that 4 + 2 cycloaddition of (III) would give rise to tricyclic product (I) with the two H atoms H(3) and H(6) (crystallographic numbering) on ring *B* being *syn*. Indeed, only one compound was obtained by the transannular Diels–Alder reaction of (III), but the relative stereochemistry could not be determined by conventional spectroscopic data. From a similar molecular-modeling analysis, the transannular Diels–Alder reaction of macrocycle (IV) would produce a