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Structure of Methyl Angolensate

By S. Bamidele Sanni,* H. Behm and Paul T. Beurskens

Crystallography Laboratory, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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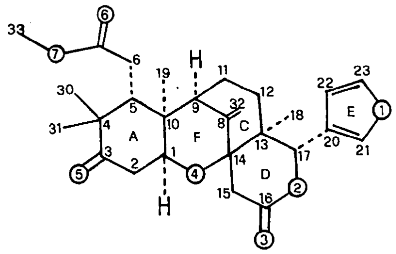
Abstract. 4-(3-Furyl)dodecahydro-4a,7a,9,9-tetramethyl-13-methylene-2,10-dioxo-7,12a-methano-4*H*,-12a*H*-pyrano[4,3-*b*][1]-benzoxocine-8-acetic acid methyl ester, $C_{27}H_{34}O_7$, $M_r = 470{\cdot}56$, tetragonal, $P4_1$, $a = 9{\cdot}8988\,(13)$, $c = 25{\cdot}4152\,(40)$ Å, $V = 2490{\cdot}3\,(7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}255$ Mg m^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}54184$ Å, $\mu(\text{Cu}\,K\alpha) = 0{\cdot}698$ mm^{-1}, $F(000) = 1008$, $T = 290$ K. Final $R = 0{\cdot}034$ for 3090 'observed' reflections and 403 variables. The structure was solved by a combination of direct methods and translation functions. The lactone ring adopts a chair conformation, the second C_5O ring has a twist-boat conformation, and the other six-membered rings have chair conformations. The furan ring is planar. The conformation of the methoxycarbonyl group is synperiplanar.

Introduction. Methyl angolensate, a ring-*B*-seco tetranor-tetracyclic triterpene, was first isolated from the heartwood of *Entandrophragma angolense* and later from other West African timbers (Bevan, Powell, Taylor, Halsall, Toft & Welford, 1967; Chan, Magnus & Mootoo, 1967, and references therein). Its structure (I), proposed by those workers, is based on chemical, spectroscopic (NMR, IR, UV) and biogenetic evidence, but because of some uncertainty an X-ray structure analysis was considered desirable. The numbering in (I), used in the following, is adopted from Bevan *et al.* (1967).



(I)

Experimental. A sample of the title compound from the Chemistry Department of the University of Ibadan, Nigeria, gave suitable single crystals by recrystallization from methanol. A colourless crystal approximately 0·28 × 0·40 × 0·21 mm was used for the measurements. The unit-cell dimensions were determined from the angular settings of 25 reflections with $18 \leq \theta \leq 38°$. The space group was found to be $P4_1$ (No. 76), from systematic absences and the structure determination. The intensities of 13 247 reflections, up to $\theta = 70°$ in the range $-12 \leq h \leq 12$, $-12 \leq k \leq 5$, $-30 \leq l \leq 30$, were measured using the ω–2θ scan technique with a scan angle of 1·50° and a variable scan rate with a maximum scan time of 20 s per reflection. Cu $K\alpha$ radiation was used with a graphite-crystal monochromator on a Nonius CAD-4 single-crystal diffractometer. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 30 min. A systematic drop-off in intensity of 6% during the measurement was observed and corrected. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); an empirical absorption correction was applied, using ψ scans (North, Phillips & Mathews, 1968) (correction factors were in the range 0·938–0·999, with an average of 0·973). Lorentz and polarization corrections were applied, the data were reduced to $|F_o|$ values, symmetry-equivalent reflections were averaged, resulting in 4698 unique reflections (Friedel pairs not merged) with $R_{\text{int}} = \sum(I - \langle I\rangle)/\sum I = 0{\cdot}043$, of which 3090 were observed with $I > 3\sigma(I)$ and $R_{\text{int}} = 0{\cdot}018$.

A *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) run did not give the entire structure, but revealed a chemically reasonable nine-atom fragment which, however, could not be expanded. Application of *DIRDIF* (Beurskens *et al.*, 1982) with this fragment using reciprocal-space translation functions (Beurskens, Gould, Bruins Slot & Bosman, 1987) and automatic expansion gave the positions of all non-hydrogen atoms. From a difference Fourier map all H atoms, except the methyl H atoms, could be located. The methyl groups therefore were refined as idealized rigid groups.

During the final stage, the refinement of all positional parameters and anisotropic temperature factors of the non-hydrogen atoms, of the positional parameters and isotropic temperature factors of the non-methyl H atoms and of the rigid methyl groups with

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* Permanent address: Department of Chemistry, University of Benin, Benin City, Nigeria.

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equal isotropic temperature factors for the three H atoms was carried out in two alternating blocks using *SHELX* (Sheldrick, 1976). The final conventional agreement factors are $R = 0{\cdot}034$ and $wR = 0{\cdot}037$ for the 3090 'observed' reflections and 403 variables. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0{\cdot}0004\,F_o^2]$, $\sigma(F_o)$ from counting statistics. The maximum shift-over-e.s.d. ratios in the final full-matrix least-squares cycle were less than 0·2 and 0·5 for the non-hydrogen and hydrogen atoms respectively, the highest and lowest peaks in the last difference Fourier calculated were +0·16 and −0·23 e Å^{-3}. Some temperature factors were found to be highly anisotropic, but no splitting of atomic positions was observed. It was possible to confirm the absolute configuration of the natural product as given here with a probability of 97% from the calculation of the average product of calculated and observed Bijvoet differences (Noordik, Beurskens, Ottenheijm, Herscheid & Tijhuis, 1978), which results in a value of +3·28(208) based on 1497 Friedel pairs. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Plots were made with *PLUTO* (Motherwell, 1976), and geometrical calculations with *PARST* (Nardelli, 1983).

Discussion. Final positional and equivalent isotropic thermal parameters are given in Table 1,* and bond lengths are in Table 2. The molecular configuration is given in Fig. 1. The crystallographic numbering scheme is given in formula (I). The structural formula of methyl angolensate, proposed by Bevan *et al.* (1967) and Chan *et al.* (1967), as a ring-*B*-seco tetranor-tetracyclic triterpene (I) is confirmed by this structure determination. The absolute stereochemistry of the molecule in the conventional nomenclature is 1*S*, 5*R*, 9*R*, 10*R*, 13*S*, 14*S*, 17*S*.

The sign distributions of the torsion angles for rings *A* and *C* and the lactone ring *D* show that these rings adopt chair conformations. The tetrahydropyran ring *F* has a twist-boat conformation; in Boeyens's (1978) notation, it approaches an $^8T_4$ form. The furan ring *E* is planar to within 0·003 (3) Å. The conformation of the methoxycarbonyl group is synperiplanar and the group is almost perpendicular to rings *A* and *F*. The least-squares plane through ring *F* is almost perpendicular to the planes through rings *C* and *D*. The configuration of atom C18 is α, those of O4 and C19 are *β*.

Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized **U** tensor.

	x	y	z	U_{eq}(Å^2×100)
O1	0·25373 (19)	−0·05759 (19)	0·09800 (8)	10·18 (7)
O2	0·14961 (17)	0·12613 (17)	−0·05684 (7)	8·68 (6)
O3	0·0995 (3)	0·14710 (23)	−0·13982 (8)	12·97 (10)
O4	0·00474 (14)	0·41443 (13)	−0·02831 (6)	6·90 (5)
O5	−0·33480 (23)	0·40162 (27)	0·02696 (13)	14·26 (12)
O6	−0·09674 (20)	0·78285 (17)	0·18616 (7)	9·16 (6)
O7	0·0195 (3)	0·59608 (26)	0·17170 (9)	14·30 (12)
C1	−0·05625 (28)	0·54432 (23)	−0·03584 (10)	8·03 (9)
C2	−0·2083 (3)	0·5213 (3)	−0·03608 (14)	10·62 (13)
C3	−0·2644 (3)	0·4989 (3)	0·01740 (15)	10·18 (13)
C4	−0·2336 (3)	0·60331 (25)	0·05891 (13)	9·84 (11)
C30	−0·2799 (4)	0·5487 (4)	0·11264 (16)	13·72 (17)
C31	−0·3207 (4)	0·7280 (3)	0·04472 (21)	14·04 (17)
C5	−0·07880 (27)	0·62590 (20)	0·06001 (9)	7·65 (8)
C6	−0·0388 (3)	0·73917 (25)	0·09850 (9)	8·76 (10)
C7	−0·0349 (3)	0·6945 (3)	0·15549 (11)	9·35 (11)
C33	−0·0987 (3)	0·7510 (3)	0·24206 (10)	10·31 (11)
C8	0·20000 (26)	0·55564 (24)	−0·03835 (9)	8·22 (9)
C32	0·2800 (4)	0·6155 (3)	−0·07231 (12)	11·78 (13)
C9	0·14892 (27)	0·62155 (24)	0·01135 (9)	8·01 (9)
C10	−0·00588 (26)	0·64582 (23)	0·00615 (9)	7·72 (8)
C11	0·2069 (3)	0·53578 (27)	0·05723 (10)	8·23 (10)
C12	0·18179 (28)	0·38288 (25)	0·05367 (9)	7·12 (8)
C13	0·21496 (21)	0·32269 (23)	−0·00053 (8)	6·77 (7)
C14	0·14610 (23)	0·41324 (23)	−0·04264 (8)	7·20 (8)
C15	0·1567 (4)	0·35024 (28)	−0·09715 (10)	8·66 (11)
C16	0·1306 (3)	0·20289 (27)	−0·09948 (10)	8·93 (10)
C17	0·14978 (24)	0·18218 (23)	−0·00396 (8)	6·70 (7)
C18	0·36782 (25)	0·3156 (3)	−0·00914 (12)	9·37 (10)
C19	−0·0254 (4)	0·78827 (25)	−0·01751 (11)	10·10 (12)
C20	0·21456 (21)	0·07847 (22)	0·02963 (9)	6·99 (8)
C21	0·17186 (27)	0·03915 (25)	0·07743 (11)	7·95 (9)
C22	0·33289 (27)	−0·0009 (3)	0·01925 (14)	9·22 (11)
C23	0·3504 (3)	−0·0782 (3)	0·06123 (14)	10·16 (12)

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

O1—C21	1·359 (3)	C5—C10	1·560 (3)
O1—C23	1·353 (4)	C6—C7	1·515 (4)
O2—C16	1·337 (3)	C8—C32	1·313 (4)
O2—C17	1·454 (3)	C8—C9	1·509 (3)
O3—C16	1·204 (3)	C8—C14	1·511 (3)
O4—C1	1·433 (3)	C9—C10	1·557 (4)
O4—C14	1·446 (3)	C9—C11	1·552 (4)
O5—C3	1·214 (4)	C10—C19	1·545 (3)
O6—C7	1·322 (3)	C11—C12	1·536 (4)
O6—C33	1·455 (3)	C12—C13	1·536 (3)
O7—C7	1·187 (4)	C13—C14	1·553 (3)
C1—C2	1·522 (4)	C13—C17	1·536 (3)
C1—C10	1·548 (3)	C13—C18	1·530 (3)
C2—C3	1·485 (5)	C14—C15	1·523 (3)
C3—C4	1·508 (5)	C15—C16	1·483 (4)
C4—C30	1·539 (5)	C17—C20	1·481 (3)
C4—C31	1·548 (5)	C20—C21	1·344 (4)
C4—C5	1·549 (4)	C20—C22	1·435 (4)
C5—C6	1·540 (3)	C22—C23	1·325 (5)

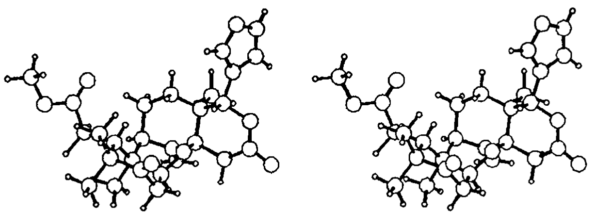

Fig. 1. A stereoscopic view of the molecule.

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* Lists of structure amplitudes, H-atom parameters, anisotropic thermal parameters, all bond angles and bond lengths involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43841 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure and Absolute Configuration of *Cedrela odorata* Substance B (Mexicanolide)

By S. Bamidele Sanni,* H. Behm and Paul T. Beurskens

Crystallography Laboratory, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

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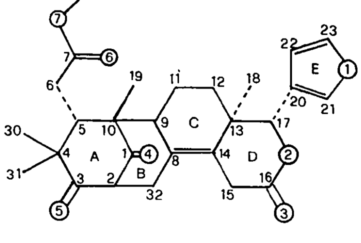
Abstract. 4β-(3-Furyl)-1,4,4a,5,6,6a,7,8α,9,10,11α,12-dodecahydro-4aβ,7α,9,9-tetramethyl-2,10,13-trioxo-7,-11-methano-2*H*-cycloocta[*f*][2]benzopyran-8-acetic acid methyl ester, $C_{27}H_{32}O_7$, $M_r = 468{\cdot}55$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}3274\ (13)$, $b = 10{\cdot}6790\ (12)$, $c = 21{\cdot}6641\ (18)$ Å, $V = 2389{\cdot}3\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}302$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54184$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}727$ mm^{-1}, $F(000) = 1000$, $T = 290$ K. Final $R = 0{\cdot}042$, for 3908 'observed' reflections and 388 variables. The structure was solved with Patterson orientation functions and reciprocal-space translation functions. The six-membered rings *A, B, C* and *D* adopt boat, chair, half-chair and skew-boat conformations respectively, while the furan ring *E* is planar. The conformation of the methoxycarbonyl group is synperiplanar, torsion angle Me—O—C=O 3·2 (4)°.

Introduction. Several years ago, Bevan, Powell & Taylor (1963) isolated two substances, A and B, from the West African timber *Cedrela odorata*. Substance A was shown to be 7-deacetyl-7-oxogedunin (Bevan, Powell & Taylor, 1965), while substance B was assigned the structure (I), which is the same structure as assigned to mexicanolide (Connolly, McCrindle & Overton, 1965) based on chemical and spectroscopic evidence. Adeoye & Bekoe (1965) published an X-ray structure determination of a modified iodoacetate derivate of the title compound ($R = 0{\cdot}18$, visually estimated data), to support the molecular structure of *Cedrela odorata* substance B. We report herewith the crystal and molecular structure and absolute configuration of the title compound. Because of similarities to methyl angolensate (Sanni, Behm & Beurskens, 1987, and references therein), we adopted a similar numbering scheme in (I).



(I)

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* Permanent address: Department of Chemistry, University of Benin, Benin City, Nigeria.

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