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

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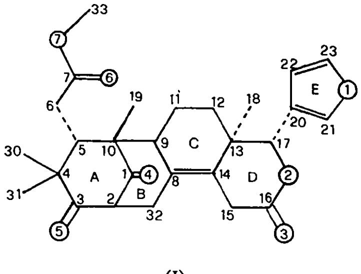
Abstract. 4β-(3-Furyl)-1,4,4a,5,6,6a,7,8α,9,10,11α,12-dodecahydro-4aβ,7α,9,9-tetramethyl-2,10,13-trioxo-7,11-methano-2*H*-cycloocta[*f*][2]benzopyran-8-acetic acid methyl ester, $C_{27}H_{32}O_7$, $M_r = 468{\cdot}55$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}3274$ (13), $b = 10{\cdot}6790$ (12), $c = 21{\cdot}6641$ (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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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 0·23 × 0·42 × 0·29 mm was used for the measurements. The unit-cell dimensions were determined from the angular settings of 25 reflections with $20 \leq \theta \leq 46°$. The intensities of 12 638 reflections, up to $\theta = 70°$ in the range $-12 \leq h \leq 3$, $-13 \leq k \leq 13$, $-26 \leq l \leq 26$, 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 15 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 drop-off of 5% during the measurement was 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 0·922–0·999 with an average of 0·956). Symmetry-equivalent reflections were averaged, $R_{\text{int}} = \sum(I - \langle I \rangle)/\sum I = 0{\cdot}045$, resulting in 4511 unique reflections (Friedel pairs not merged) of which 3908 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied.

The structure could not be solved by direct methods. Therefore a small fragment of five atoms, suspected to be planar and of known geometry (a C—CO—O—C group), was input to a Patterson-rotation-function program (Beurskens, Beurskens, Strumpel & Nordman, 1986), followed by application of reciprocal-space translation functions (Beurskens, Gould, Bruins Slot & Bosman, 1987), and automatically expanded by *DIRDIF* (Beurskens *et al.*, 1982). Isotropic least-squares refinement, using *SHELX* (Sheldrick, 1976), converged at $R = 0{\cdot}12$. In order to establish the absolute configuration of this natural product, we calculated the average product of calculated and observed Bijvoet differences (Noordik, Beurskens, Ottenheijm, Herscheid & Tijhius, 1978) and obtained a value of −4·81 (128) on 1778 Friedel pairs. The structure was therefore inverted before refinement was continued. Additional empirical absorption corrections were applied (Walker & Stuart, 1983), at this stage leading to a further reduction of R to 0·11 (correction factors were in the range 0·872–1·175 with an average of 0·988). The H atoms were located from a difference Fourier, except those bonded to C33 and C32 which were fixed at calculated positions.

Full-matrix least-squares refinement of the positional parameters (except those of H atoms at C33 and C32), the anisotropic temperature factors of the non-hydrogen atoms, and with isotropic temperature factors for the H atoms fixed at 0·060 Å^2, converged at $R = 0{\cdot}042$ and $wR = 0{\cdot}045$ for the 3908 'observed' reflections and 388 variables. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0{\cdot}0004F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift-over-e.s.d. ratios in the final full-matrix least-squares cycle were less than 0·04 and 0·12 for the non-hydrogen and hydrogen atoms respectively, while the highest and lowest peaks in the final difference Fourier were +0·25 and −0·3 e Å^{-3}. 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).

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

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

	x	y	z	U_{eq}(Å^2 × 100)
O1	−0·4706 (3)	−0·4407 (2)	−0·1222 (1)	7·22 (7)
O2	−0·3388 (2)	−0·6459 (1)	−0·2882 (1)	4·96 (5)
O3	−0·2405 (2)	−0·7790 (2)	−0·3488 (1)	6·95 (7)
O4	−0·7816 (2)	−0·3503 (2)	−0·5508 (1)	7·43 (7)
O5	−0·7762 (2)	−0·7448 (2)	−0·4720 (1)	6·91 (7)
O6	−0·7695 (2)	−0·5488 (2)	−0·2664 (1)	6·24 (6)
O7	−0·9631 (2)	−0·4718 (2)	−0·2411 (1)	7·56 (8)
C1	−0·7592 (3)	−0·4144 (2)	−0·5060 (1)	5·02 (7)
C2	−0·7152 (3)	−0·5474 (2)	−0·5116 (1)	4·97 (7)
C3	−0·7923 (3)	−0·6322 (2)	−0·4693 (1)	4·91 (7)
C4	−0·8869 (2)	−0·5707 (2)	−0·4247 (1)	4·99 (7)
C30	−0·9342 (4)	−0·6683 (3)	−0·3778 (1)	7·1 (1)
C31	−1·0054 (3)	−0·5225 (4)	−0·4616 (2)	7·4 (1)
C5	−0·8067 (2)	−0·4642 (2)	−0·3930 (1)	3·94 (6)
C6	−0·8761 (3)	−0·4076 (3)	−0·3368 (1)	5·17 (8)
C7	−0·8609 (2)	−0·4865 (3)	−0·2789 (1)	5·16 (7)
C33	−0·9493 (4)	−0·5334 (5)	−0·1816 (1)	9·6 (1)
C8	−0·5369 (2)	−0·4765 (2)	−0·4367 (1)	4·09 (6)
C32	−0·5686 (3)	−0·5496 (2)	−0·4950 (1)	5·18 (7)
C9	−0·6012 (2)	−0·3491 (2)	−0·4332 (1)	4·18 (6)
C10	−0·7535 (2)	−0·3643 (2)	−0·4402 (1)	4·30 (6)
C11	−0·5537 (2)	−0·2710 (2)	−0·3788 (1)	4·45 (6)
C12	−0·5265 (2)	−0·3481 (2)	−0·3213 (1)	4·00 (6)
C13	−0·4259 (2)	−0·4506 (2)	−0·3340 (1)	3·65 (5)
C14	−0·4585 (2)	−0·5206 (2)	−0·3931 (1)	3·75 (5)
C15	−0·3942 (3)	−0·6483 (2)	−0·3981 (1)	5·39 (7)
C16	−0·3187 (2)	−0·6953 (2)	−0·3442 (1)	4·87 (7)
C17	−0·4378 (2)	−0·5487 (2)	−0·2820 (1)	3·87 (5)
C18	−0·2888 (3)	−0·3953 (2)	−0·3384 (1)	5·09 (7)
C19	−0·8228 (3)	−0·2375 (2)	−0·4385 (1)	5·97 (9)
C20	−0·4221 (2)	−0·4988 (2)	−0·2179 (1)	4·43 (6)
C21	−0·5180 (3)	−0·4861 (3)	−0·1768 (1)	5·51 (7)
C22	−0·3059 (3)	−0·4602 (3)	−0·1878 (1)	6·89 (10)
C23	−0·3429 (4)	−0·4269 (3)	−0·1307 (1)	8·0 (1)

Discussion. Final positional and thermal parameters are given in Table 1;* bond lengths and selected torsion angles are in Table 2. A stereoview of the molecule, showing the molecular configuration, is shown in Fig. 1. The crystallographic numbering scheme is given in formula (I). Our results confirm the molecular structure (I).

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* Lists of structure amplitudes, H-atom coordinates, 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 43842 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

If we define a 'molecular plane' consisting of rings *B*, *C* and *D*, then ring *A* is above this plane fused to ring *B* *via* the axial valencies of C2 and C10. The relative disposition of rings *A* and *C* is *s-cis* with respect to the C9—C10 bond, or, stated alternatively, HC9 and Me19 are both below the 'molecular plane'. HC9 is attached pseudo-axially to C9, while Me19 is attached equatorially to C10. The fusion of rings *C* and *D* is such that Me18 is below the 'molecular plane', attached pseudo-axially to C13. The furan substituent and the acetate group are attached pseudo-equatorially to rings *D* and *A* respectively. The absolute configuration at the various asymmetric centres is established as 2*S*, 5*S*, 9*S*, 10*R*, 13*R*, 17*S*.

Table 2. *Bond lengths* (Å), *endocyclic torsion angles* (°) *and Cremer & Pople* (1975) *puckering parameters*

O1—C21	1·367 (3)	C5—C10	1·577 (3)
O1—C23	1·339 (5)	C6—C7	1·520 (3)
O2—C16	1·339 (3)	C8—C9	1·516 (3)
O2—C17	1·463 (2)	C8—C14	1·333 (3)
O3—C16	1·209 (3)	C8—C32	1·516 (3)
O4—C1	1·211 (3)	C9—C10	1·589 (3)
O5—C3	1·215 (3)	C9—C11	1·526 (3)
O6—C7	1·187 (3)	C10—C19	1·532 (3)
O7—C7	1·345 (3)	C11—C12	1·519 (3)
O7—C33	1·453 (4)	C12—C13	1·534 (3)
C1—C2	1·495 (3)	C13—C14	1·521 (3)
C1—C10	1·524 (3)	C13—C17	1·544 (3)
C2—C3	1·515 (3)	C13—C18	1·538 (3)
C2—C32	1·556 (4)	C14—C15	1·520 (3)
C3—C4	1·523 (3)	C15—C16	1·492 (4)
C4—C5	1·566 (3)	C17—C20	1·497 (3)
C4—C30	1·535 (4)	C20—C21	1·338 (4)
C4—C31	1·550 (4)	C20—C22	1·427 (3)
C5—C6	1·536 (3)	C22—C23	1·343 (5)

C1—C2—C3—C4	−6·5 (3)	$q_2 = 0{\cdot}754\ (3), q_3 = 0{\cdot}049\ (2)$ Å
C2—C3—C4—C5	−48·9 (3)	$Q = 0{\cdot}756\ (3)$ Å
C3—C4—C5—C10	60·2 (2)	$\varphi = -168{\cdot}6\ (2)°$
C4—C5—C10—C1	−16·4 (2)	$\theta = 86{\cdot}3\ (2)°$
C5—C10—C1—C2	−43·2 (3)	Numbering sequence:
C10—C1—C2—C3	56·1 (3)	C1, C2, C3, C4, C5, C10
C1—C10—C9—C8	−64·3 (2)	$q_2 = 0{\cdot}193\ (2), q_3 = 0{\cdot}605\ (2)$ Å
C10—C9—C8—C32	55·6 (2)	$Q = 0{\cdot}635\ (2)$ Å
C9—C8—C32—C2	−45·2 (3)	$\varphi = 106{\cdot}2\ (6)°$
C8—C32—C2—C1	46·5 (3)	$\theta = 17{\cdot}7\ (2)°$
C32—C2—C1—C10	−65·5 (2)	Numbering sequence:
C2—C1—C10—C9	73·2 (2)	C2, C1, C10, C9, C8, C32
C8—C9—C11—C12	−36·6 (3)	$q_2 = 0{\cdot}359\ (2), q_3 = 0{\cdot}286\ (2)$ Å
C9—C11—C12—C13	57·8 (2)	$Q = 0{\cdot}459\ (2)$ Å
C11—C12—C13—C14	−47·1 (2)	$\varphi = -16{\cdot}3\ (3)°$
C12—C13—C14—C8	19·1 (3)	$\theta = 51{\cdot}4\ (3)°$
C13—C14—C8—C9	1·1 (3)	Numbering sequence:
C14—C8—C9—C11	7·3 (3)	C12, C13, C14, C8, C9, C11
O2—C16—C15—C14	19·5 (3)	$q_2 = 0{\cdot}521\ (2), q_3 = 0{\cdot}249\ (2)$ Å
C16—C15—C14—C13	5·4 (3)	$Q = 0{\cdot}577\ (2)$ Å
C15—C14—C13—C17	−44·5 (2)	$\varphi = -33{\cdot}3\ (2)°$
C14—C13—C17—O2	66·0 (2)	$\theta = 64{\cdot}5\ (2)°$
C13—C17—O2—C16	−45·7 (2)	Numbering sequence:
C17—O2—C16—C15	1·6 (3)	O2, C16, C15, C14, C13, C17

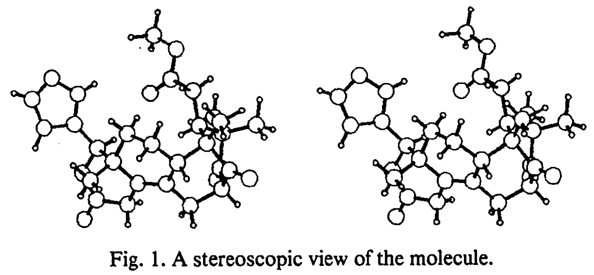

Fig. 1. A stereoscopic view of the molecule.

The furan ring *E* is planar within experimental limits, the maximum deviation from the least-squares plane being 0·003 (3) Å. Ring *D* has a skew-boat conformation approaching the $^{17}S_{13}$ form in the notation of Boeyens (1978). The presence of a double bond between C8 and C14 forces ring *C* to adopt a half-chair conformation. Ring *B* has an approximate chair conformation. A chair form for a six-membered ring with *para*-exocyclic double bonds is unusual. Such a ring normally adopts a boat form (Hazebrock & Oosterhoff, 1951; Mossel, Romer & Havinga, 1963; Mossel & Romers, 1964). In this case, however, the fusion with ring *A* above the 'molecular plane' can only be achieved when ring *B* has a chair conformation. Finally, ring *A* can best be described as a shallow boat, intermediate between the true boat $B_{4,1}$ and the twist-boat $^2T_4$ (Boeyens, 1978). This shape is undoubtedly forced upon ring *A* to avoid steric congestion between the methyl groups on C4 and the atoms of ring *C*. The conformation of the methoxycarbonyl group is synperiplanar [torsion angle C33—O7—C7—O6 3·2 (4)°], the same conformation as in free methyl acetate (Pyckhout, Van Alsenoy & Geise, 1986).

Apart from slight elongations in the most congested area of the molecule (C3, C4, C5, C10, C1, C9) none of the bond lengths and valence angles are outside the ranges normally to be expected.

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Structure of an α,β-Unsaturated Dipeptide, Racemic *N*-[(Phenylmethoxy)carbonyl]-phenylalanyl-Δ^2-phenylalanine

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Abstract. $C_{26}H_{24}N_2O_5$, $M_r = 444\cdot49$, m.p. 466–469 K, triclinic, $P\bar{1}$, $a = 6\cdot418\,(1)$, $b = 13\cdot223\,(2)$, $c = 14\cdot153\,(2)$ Å, $\alpha = 104\cdot73\,(1)$, $\beta = 94\cdot33\,(2)$, $\gamma = 96\cdot54\,(2)°$, $V = 1147\cdot2\,(3)$ Å^3, $Z = 2$, $D_x = 1\cdot287$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 0\cdot01$ mm^{-1}, $F(000) = 468$. Final $R = 0\cdot039$ for 2806 observed $[I \geq 3\sigma(I)]$ reflections measured on a diffractometer at 293 K. The molecules in the crystal form compact 'hydrophilic columns' consisting of intermolecular hydrogen-bonded double chains surrounded by a hydrophobic space composed of phenyl substituents. The conformation of the phenylalanyl residue is close to parallel β-sheet ($\varphi = -89\cdot3$, $\psi = 114\cdot4°$) while the unsaturated residue adopts a left-handed α-helix conformation ($\varphi = 50\cdot4$, $\psi = 21\cdot2°$).

Introduction. α,β-Unsaturated amino acids have been found in many biologically active peptides, most of them having antibiotic properties (Noda, Shimohigashi & Izumiya, 1983). These dehydro amino acids are intermediates in the interchange of natural L-amino acids to their D enantiomers, as D molecules cannot be incorporated directly into the peptide chain (Demain, 1966). That is why a great number of microbial peptides having antibiotic activity contain both α,β-unsaturated and D-amino acid residues. Incorporation of a dehydro amino acid unit into the peptide decreases conformational flexibility and has a stabilizing influence on a β-turn (Aubry, Boussard & Marraud, 1984). The phenomenon has been used in analogues of biologically active peptides to reduce their enzymatic degradation (English & Stammer, 1978).

The structures of several dehydro amino acids [Z-Δ^E-Phe-OEt (Nitz, Holt, Rubin & Stammer, 1981); *N*-acetyl-Δ^Z-Phe-methylamide (Aubry, Allier, Boussard & Marraud, 1985); *N*-Boc-Δ^Z-Leu-OH (Chauhan, Stammer, Norskov-Lauritzen & Newton, 1979); *N*-acetyl-Δ^Z-Phe-OH (Ajò, Cesarin, Granozzi & Busetti, 1981); *N*-acetyl-Δ^Z-Phe-OEt (Ajò, Busetti, Ottenheijm & Plate, 1984); *N*-acetyl-Δ^Z-Pro-OH (Ajò, Busetti, Granozzi & Liakopoulou-Kyriakides, 1984); *N*-acetyl-Δ-Ala-OH (Ajò, Granozzi, Tondello, Del Pra & Zanotti, 1979)] and di- or tripeptides [*N*-acetyl-Δ^Z-Phe-Pro-OH (Ajò, Busetti & Granozzi, 1982); *N*-acetyl-Δ^Z-Phe-Gly-OH (Pieroni, Montagnoli, Fissi, Merlino & Ciardelli, 1975)], mostly *N*-acetylated, have

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