Related literature. γ-Lactones of the oleanan-28-oic acid skeleton have been prepared synthetically by a number of routes leading to the 3-hydroxy-12-oxo, 3,12-dioxo and 3,12-dihydroxy species (Kitagawa, Kitazawa & Yosioka, 1968, 1972; Majumder & Chakraborty, 1979; Majumder & Bagchi, 1983). The 12-hydroxy-3-oxo compound reported here completes the tetrad, although this product was isolated from a natural source.

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Polymorphisme de la (−) Bromo-10 Méthoxycarbonyl-1 Nitro-16 Aspidospermidine-(2*R*,7*R*,16*S*,20*S*,21*S*): Structure d'une Nouvelle Variété

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(*Reçu le* 16 *décembre* 1986, *accepté le* 27 *janvier* 1987)

Abstract. $C_{21}H_{26}BrN_3O_4$, $M_r = 464{\cdot}4$, monoclinic, $P2_1$, $a = 11{\cdot}370\,(2)$, $b = 10{\cdot}529\,(3)$, $c = 8{\cdot}536\,(4)$ Å, $\beta = 90{\cdot}66\,(2)°$, $V = 1021{\cdot}9$ Å^3, $Z = 2$, $D_x = 1{\cdot}509$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2{\cdot}02$ mm^{-1}, $F(000) = 480$, $T = 294$ K, $R = 0{\cdot}053$ for 845 independent reflections $[I > \sigma(I)]$. The crystals of the previously described variety exhibit the orthorhombic $P2_12_12_1$ symmetry and have a density of 1·495 Mg m^{-3}. In the two forms the ring conformations are planar for *A* and *B*, chair for *D* and boat for *E*. For *C*, the conformation is sofa in the monoclinic form and approximately half-chair in the orthorhombic one. Homologous bond lengths and angles are not significantly different, except for the angles relative to atoms fixing substituent groups. The torsion-angle values indicate that the most important differences between the molecules of the two modifications consist of the relative orientations of the methoxycarbonyl, nitro and ethyl groups.

Partie expérimentale. Cristaux obtenus par évaporation d'une solution dans un mélange de $CHCl_3$ et C_2H_5OH. Cristal prismatique: 0,055 × 0,125 × 0,250 mm. Dimensions de la maille sur monocristal avec 25 réflexions telles que $2{,}63 \leq \theta \leq 11{,}73°$. Diffractomètre Enraf–Nonius CAD-4 $0{,}049 \leq (\sin\theta)/\lambda \leq 0{,}527$ Å^{-1}; $0 \leq h \leq 11$, $0 \leq k \leq 11$ et $-8 \leq l \leq 8$. Réflexions de contrôle des intensités: $00\bar{2}$, $2\bar{2}\bar{1}$ et $\bar{1}\bar{2}1$. Diminution de I au cours des mesures: 1,1%, $\sigma(I)/I_{\rm moyen}$: 0,0036. 1327 réflexions indépendantes mesurées, 482 inobservées $[I < \sigma(I)]$. Corrections d'absorption (Coppens, Leiserowitz & Rabinovich, 1965). Valeurs extrêmes du coefficient de transmission: 0,895 et 0,779. Programme *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). H des CH_3: série de Fourier des ΔF; autres H: positions calculées. Affinement sur F, programme à matrice entière. Paramètres affinés: x, y, z de Br, O, N et C, β_{ij} de Br et B de O, N et C; O, N et C affinés en agitation isotrope

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(peu de réflexions observées). $R = 0{,}053$, $wR = 0{,}047$, $S = 1{,}25$, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{\max} = 0{,}04$, $|\Delta\rho|_{\max} = 0{,}41\ (8)\ \text{e Å}^{-3}$. Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974), corrigés des f' et f''. Lorsqu'on change les signes de toutes les coordonnées, on trouve $R = 0{,}059$ et $wR = 0{,}054$. Programmes de calcul du système *SDP* (Frenz, 1982), angles des plans moyens: *Best-Plane Program* (Ito & Sugawara, 1983), angles de torsion: *ORFFE*3 (Busing, Martin & Levy, 1964). Fig. 1: programme *ORTEP* (Johnson, 1965). Les coordonnées atomiques sont rapportées dans le Tableau 1, les principales distances interatomiques et les angles des liaisons dans le Tableau 2.[*] La Fig. 1 représente la molécule vue en perspective et la Fig. 2 une projection de la structure selon [001].

Tableau 1. *Coordonnées atomiques relatives, facteurs de température isotropes* ($B_{\text{éq}}$ *pour* Br) *et écarts-type*

$$B_{\text{éq}} = \tfrac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha).$$

	x	y	z	$B_{\text{éq}}/B_{\text{iso}}$(Å^2)
Br	0,4218 (1)	0,2985 (3)	0,3084 (2)	5,40 (3)
N(1)	0,6252 (9)	0,184 (1)	0,946 (1)	2,8 (2)
C(2)	0,7064 (9)	0,291 (2)	0,967 (1)	2,4 (2)
C(3)	1,041 (1)	0,382 (2)	0,687 (2)	4,2 (3)
N(4)	0,9264 (9)	0,397 (1)	0,758 (1)	3,2 (2)
C(5)	0,860 (1)	0,506 (2)	0,705 (2)	4,3 (3)
C(6)	0,741 (1)	0,484 (1)	0,786 (2)	3,6 (3)
C(7)	0,7284 (9)	0,336 (1)	0,796 (1)	2,2 (3)
C(8)	0,6226 (9)	0,279 (1)	0,712 (1)	2,4 (2)
C(9)	0,582 (1)	0,310 (2)	0,564 (1)	3,3 (2)
C(10)	0,481 (1)	0,254 (1)	0,509 (2)	3,1 (3)
C(11)	0,423 (1)	0,166 (1)	0,602 (2)	3,6 (3)
C(12)	0,464 (1)	0,136 (1)	0,752 (2)	4,2 (3)
C(13)	0,564 (1)	0,196 (1)	0,804 (1)	2,5 (3)
C(14)	1,101 (1)	0,271 (1)	0,759 (2)	4,3 (3)
C(15)	1,027 (1)	0,152 (1)	0,743 (2)	4,0 (3)
C(16)	0,8265 (9)	0,276 (1)	1,043 (1)	2,5 (3)
C(17)	0,897 (1)	0,167 (1)	0,985 (1)	3,3 (3)
C(18)	0,883 (1)	−0,078 (2)	0,787 (2)	6,1 (4)
C(19)	0,830 (1)	0,051 (1)	0,739 (1)	3,5 (3)
C(20)	0,902 (1)	0,163 (1)	0,803 (1)	3,1 (3)
C(21)	0,8488 (9)	0,285 (1)	0,733 (1)	2,4 (2)
N(22)	0,8239 (8)	0,283 (1)	1,223 (1)	4,1 (2)
O(23)	0,7685 (8)	0,3702 (9)	1,278 (1)	5,1 (2)
O(24)	0,8809 (8)	0,208 (1)	1,299 (1)	4,9 (2)
C(25)	0,599 (1)	0,095 (1)	1,060 (2)	3,9 (3)
O(26)	0,6611 (7)	0,1095 (9)	1,1867 (9)	3,7 (2)
C(27)	0,643 (1)	0,018 (2)	1,310 (2)	4,8 (4)
O(28)	0,5259 (8)	0,0127 (9)	1,037 (1)	5,0 (2)

Tableau 2. *Distances interatomiques* (Å), *angles valenciels* (°) *et écarts-type*

Br—C(10)	1,89 (1)	C(10)—C(11)	1,39 (2)
N(1)—C(2)	1,47 (2)	C(11)—C(12)	1,39 (2)
N(1)—C(13)	1,40 (2)	C(12)—C(13)	1,38 (2)
N(1)—C(25)	1,38 (2)	C(14)—C(15)	1,52 (2)
C(2)—C(7)	1,56 (2)	C(15)—C(20)	1,51 (2)
C(2)—C(16)	1,52 (1)	C(16)—C(17)	1,49 (2)
C(3)—N(4)	1,45 (2)	C(16)—N(22)	1,54 (1)
C(3)—C(14)	1,48 (2)	C(17)—C(20)	1,56 (2)
N(4)—C(5)	1,44 (2)	C(18)—C(19)	1,54 (2)
N(4)—C(21)	1,48 (2)	C(19)—C(20)	1,53 (2)
C(5)—C(6)	1,54 (2)	C(20)—C(21)	1,54 (2)
C(6)—C(7)	1,56 (2)	N(22)—O(23)	1,21 (2)
C(7)—C(8)	1,51 (2)	N(22)—O(24)	1,20 (2)
C(7)—C(21)	1,57 (2)	C(25)—O(26)	1,29 (2)
C(8)—C(9)	1,38 (2)	C(25)—O(28)	1,22 (2)
C(8)—C(13)	1,36 (2)	O(26)—C(27)	1,44 (2)
C(9)—C(10)	1,37 (2)		

C(2)—N(1)—C(13)	109,7 (9)	N(1)—C(13)—C(8)	109 (1)
C(2)—N(1)—C(25)	125 (1)	N(1)—C(13)—C(12)	130 (1)
C(13)—N(1)—C(25)	124 (1)	C(8)—C(13)—C(12)	122 (1)
N(1)—C(2)—C(7)	103,5 (9)	C(3)—C(14)—C(15)	111 (1)
N(1)—C(2)—C(16)	122 (1)	C(14)—C(15)—C(20)	116 (1)
C(7)—C(2)—C(16)	106,4 (8)	C(2)—C(16)—C(17)	115 (1)
N(4)—C(3)—C(14)	109 (1)	C(2)—C(16)—N(22)	113,5 (8)
C(3)—N(4)—C(5)	115 (1)	C(17)—C(16)—N(22)	113 (1)
C(3)—N(4)—C(21)	113 (1)	C(16)—C(17)—C(20)	113 (1)
C(5)—N(4)—C(21)	106 (1)	C(18)—C(19)—C(20)	112 (1)
N(4)—C(5)—C(6)	101 (1)	C(15)—C(20)—C(17)	113 (1)
C(5)—C(6)—C(7)	105 (1)	C(15)—C(20)—C(19)	109 (1)
C(2)—C(7)—C(6)	112 (1)	C(15)—C(20)—C(21)	107 (1)
C(2)—C(7)—C(8)	100,6 (8)	C(17)—C(20)—C(19)	110 (1)
C(2)—C(7)—C(21)	111,3 (9)	C(17)—C(20)—C(21)	110 (1)
C(6)—C(7)—C(8)	116 (1)	C(19)—C(20)—C(21)	107 (1)
C(6)—C(7)—C(21)	104,1 (9)	N(4)—C(21)—C(7)	101 (1)
C(8)—C(7)—C(21)	113,2 (9)	N(4)—C(21)—C(20)	111,9 (9)
C(7)—C(8)—C(9)	127 (1)	C(7)—C(21)—C(20)	119,8 (9)
C(7)—C(8)—C(13)	112,2 (9)	C(16)—N(22)—O(23)	116 (1)
C(9)—C(8)—C(13)	121 (1)	C(16)—N(22)—O(24)	119 (1)
C(8)—C(9)—C(10)	119 (1)	O(23)—N(22)—O(24)	125 (1)
Br—C(10)—C(9)	119 (1)	N(1)—C(25)—O(26)	113 (1)
Br—C(10)—C(11)	121 (1)	N(1)—C(25)—O(28)	122 (1)
C(9)—C(10)—C(11)	119 (1)	O(26)—C(25)—O(28)	125 (1)
C(10)—C(11)—C(12)	122 (1)	C(25)—O(26)—C(27)	117 (1)
C(11)—C(12)—C(13)	117 (1)		

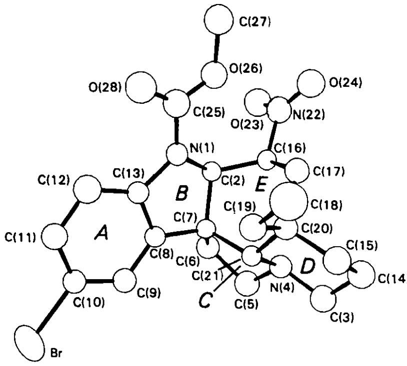

Fig. 1. Vue en perspective de la molécule, numéros attribués aux atomes et lettres utilisées pour nommer les cycles.

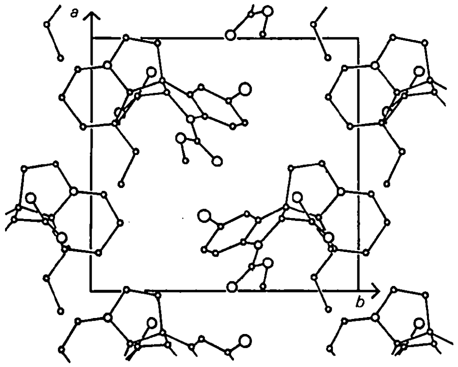

Fig. 2. Représentation de la structure vue parallèlement à l'axe *c*.

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[*] Les listes des facteurs de structure, des distances interatomiques, des angles de torsion, des distances des atomes aux plans moyens, des facteurs d'agitation thermique anisotrope et des paramètres des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 43754: 13 pp.). On peut obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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Acta Cryst. (1987). C**43**, 1233–1235

Structure of a Second Monoclinic Polymorph of Triphenylphosphine Oxide

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(*Received 7 January* 1987; *accepted* 28 *January* 1987)

Abstract. $C_{18}H_{15}OP$, $M_r = 278{\cdot}29$, monoclinic, $P2_1/c$, $a = 15{\cdot}066\ (1)$, $b = 9{\cdot}037\ (2)$, $c = 11{\cdot}296\ (3)$ Å, $\beta = 98{\cdot}47\ (1)°$, $U = 1521{\cdot}2\ (5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}215$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 1{\cdot}7$ cm^{-1}, $F(000) = 584$, $T = 295$ K, $R = 0{\cdot}045$ for 3128 reflections with $I > 2{\cdot}5\sigma(I)$. The torsion angles about the three Ph—P bonds in the second monoclinic polymorph of triphenylphosphine oxide deviate only slightly from those reported for the orthorhombic polymorph and significantly from those in the other monoclinic polymorph.

Experimental. A small batch of crystals of the title compound was obtained as the result of an attempt to crystallize a Pd-containing compound. The true composition of the crystals was established *via* an X-ray structure determination. X-ray data for a yellowish transparent crystal (0·25 × 0·62 × 0·85 mm) mounted on top of a glass fibre were collected on an Enraf–Nonius CAD-4F diffractometer using Zr-filtered Mo $K\alpha$ radiation. Lattice parameters and their e.s.d.'s were derived from the setting angles of 15 reflections ($13 < \theta < 19°$). The space group was determined from the observed systematic absences. A total of 4687 unique reflections ($1{\cdot}37 < \theta < 30°$; $\omega/2\theta$-scan; $-21 \leq h \leq 20$, $-12 \leq k \leq 0$, $0 \leq l \leq 15$) was scanned. Three reference reflections (400, $0\bar{2}0$, 002) showed variations less than 1·5% about the mean and no decay during the 76 h of X-ray exposure time. The data were corrected for Lp but not absorption. The 3128 reflections with $I > 2{\cdot}5\sigma(I)$ were used in the subsequent analysis. The structure was solved by Patterson methods and refined by full-matrix least squares on F (*SHELX*76; Sheldrick, 1976). H atoms were obtained from a difference map. Convergence with anisotropic thermal parameters for the non-hydrogen atoms and individual isotropic parameters for the hydrogen atoms was reached at $R = 0{\cdot}045$ [$wR = 0{\cdot}042$, $w = 1/\sigma^2(F)$, 3128 reflections, 242 parameters, $S = 0{\cdot}51$]. $(\Delta/\sigma)_{\max} = 0{\cdot}5$. A final difference Fourier map did not show features outside the range of $-0{\cdot}33$ and $0{\cdot}39$ e Å^{-3}. Scattering factors of Cromer & Mann (1968) were used. Calculations of the geometry and illustrations by programs of the *EUCLID* package (Spek, 1982). Fig. 1 shows the molecule with adopted numbering and Fig. 2 a projection of the unit-cell contents down the monoclinic b axis. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* Data on the geometry are assembled in Table 2.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43763 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/87/061233-03$01.50