Acta Cryst. (1989). C**45**, 1472–1473

Structure of a Bryonolic Acid Derivative, Acetic 3β-Acetoxy-*D:C*-friedoolean-8-en-29-oic Anhydride

BY HIROSHI NAKAI

Shionogi Research Laboratories, Shionogi & Co. Ltd, Fukushima-ku, Osaka 553, *Japan*

(*Received* 25 *March* 1989; *accepted* 24 *April* 1989)

Abstract. $C_{34}H_{52}O_5$, $M_r = 540{\cdot}78$, monoclinic, $P2_1$, $a = 15{\cdot}412\ (8)$, $b = 7{\cdot}993\ (2)$, $c = 13{\cdot}760\ (7)$ Å, $\beta = 113{\cdot}80\ (3)°$, $V = 1551\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}158$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ(Cu $K\alpha$) = 0·60 mm^{-1}, $F(000) = 592$, $T = 295$ K, $R = 0{\cdot}044$ for 2761 observed reflections [$F_o > 3\sigma(F_o)$]. The ring junctions *A/B*, *C/D* and *D/E* are *trans*, *trans* and *cis*, respectively. The conformations of rings *A*–*C* are chair, half-chair and half-chair, respectively. The *D*–*E* ring adopts a chair–chair conformation which is considerably distorted to relieve the repulsive interaction between Me(27) and C(29)OOCOMe, in contrast to the boat–boat conformation of a bryonolic acid derivative substituted by the tetragonal functional group C(29)H_2OAc [Kamisako, Isoi, Nakai & Shiro (1984). *Acta Cryst.* C**40**, 1013–1015]. The conformation of the *D*–*E* ring agrees very closely with that in the other bryonolic acid derivative having the 29-trigonal functional group, COOMe [Nakai, Shiro, Kamisako, Honda & Isoi (1987). *Acta Cryst.* C**43**, 1779–1782].

Experimental. Colorless plates obtained from acetic anhydride–pyridine. Crystal of dimensions 0·2 × 0·2 × 0·1 mm. Rigaku AFC-5 diffractometer, graphite-monochromatized Cu $K\alpha$. Cell dimensions determined from 2θ angles for 25 reflections in the range $27 < 2\theta < 34°$. Intensities measured up to $2\theta = 140°$ in h −17/18, k 0/9 and l −16/0, ω–2θ scans, ω-scan width $(1{\cdot}1 + 0{\cdot}2\tan\theta)°$, three standard reflections monitored every 100 measurements showed no significant change. 3105 unique reflections measured, 2761 intensities observed [$F_o \le 3\sigma(F_o)$ rejected], no absorption corrections.

Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located on a difference density map. Positional and thermal parameters refined by block-diagonal least squares, isotropic for H and anisotropic for the others. $\Sigma(w|\Delta F|^2)$ minimized, $w = 1/[\sigma^2(F_o) + 0{\cdot}0018|F_o|^2]$, $w = 0$ for 55 reflections with $w^{1/2}|\Delta F| > 3$. Final $R = 0{\cdot}044$, $wR = 0{\cdot}055$, $S = 1{\cdot}0364$. Highest and lowest peaks in final difference

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
C(1)	0·2624 (2)	0·5500 (0)	1·0848 (2)	4·5 (1)
C(2)	0·2923 (2)	0·5024 (4)	0·9953 (2)	4·7 (1)
C(3)	0·3351 (2)	0·3296 (4)	1·0141 (2)	4·1 (1)
C(4)	0·2661 (2)	0·1940 (4)	1·0167 (2)	4·3 (1)
C(5)	0·2282 (2)	0·2489 (3)	1·1008 (2)	3·6 (1)
C(6)	0·1591 (2)	0·1246 (4)	1·1150 (3)	5·4 (1)
C(7)	0·1508 (2)	0·1569 (4)	1·2188 (2)	4·7 (1)
C(8)	0·1517 (2)	0·3399 (3)	1·2482 (2)	3·4 (1)
C(9)	0·1684 (2)	0·4620 (3)	1·1913 (2)	3·5 (1)
C(10)	0·1877 (2)	0·4286 (3)	1·0920 (2)	3·5 (1)
C(11)	0·1687 (2)	0·6443 (3)	1·2216 (2)	4·5 (1)
C(12)	0·1427 (2)	0·6811 (3)	1·3151 (2)	4·1 (1)
C(13)	0·1758 (2)	0·5415 (3)	1·3998 (2)	3·2 (1)
C(14)	0·1256 (2)	0·3777 (3)	1·3425 (2)	3·2 (1)
C(15)	0·1557 (2)	0·2357 (3)	1·4259 (2)	3·8 (1)
C(16)	0·1232 (2)	0·2714 (4)	1·5147 (2)	4·1 (1)
C(17)	0·1514 (2)	0·4417 (3)	1·5711 (2)	3·7 (1)
C(18)	0·1456 (2)	0·5862 (3)	1·4924 (2)	3·2 (1)
C(19)	0·1888 (2)	0·7497 (3)	1·5545 (2)	3·7 (1)
C(20)	0·2813 (2)	0·7432 (4)	1·6571 (2)	4·1(1)
C(21)	0·2827 (2)	0·5912 (4)	1·7240 (2)	4·7 (1)
C(22)	0·2507 (2)	0·4276 (4)	1·6617 (2)	4·2 (1)
C(23)	0·1889 (2)	0·1623 (6)	0·9058 (3)	6·5 (1)
C(24)	0·3263 (3)	0·0344 (5)	1·0586 (4)	7·8 (2)
C(25)	0·0924 (2)	0·4566 (6)	0·9962 (2)	6·2 (1)
C(26)	0·0160 (2)	0·3893 (4)	1·2938 (2)	4·4 (1)
C(27)	0·2837 (2)	0·5244 (3)	1·4369 (2)	3·8 (1)
C(28)	0·0790 (2)	0·4740 (4)	1·6206 (2)	4·8 (1)
C(29)	0·3715 (2)	0·7496 (5)	1·6383 (2)	4·8 (1)
C(30)	0·2851 (2)	0·9030 (5)	1·7227 (2)	5·5 (1)
C(31)	0·4572 (2)	0·2888 (4)	0·9508 (2)	4·7 (1)
C(32)	0·4747 (2)	0·2443 (5)	0·8546 (2)	5·1 (1)
O(33)	0·3652 (1)	0·2891 (3)	0·9290 (1)	4·5 (1)
O(34)	0·5172 (1)	0·3186 (5)	1·0357 (2)	8·0 (1)
O(35)	0·4382 (2)	0·6590 (4)	1·6745 (2)	7·0 (1)
O(36)	0·3692 (2)	0·8817 (4)	1·5712 (2)	6·2 (1)
C(37)	0·4495 (3)	0·9607 (7)	1·5776 (4)	8·8 (2)
O(38)	0·5197 (3)	0·9658 (9)	1·6573 (4)	16·3 (3)
C(39)	0·4359 (5)	1·0242 (15)	1·4727 (8)	18·6 (5)

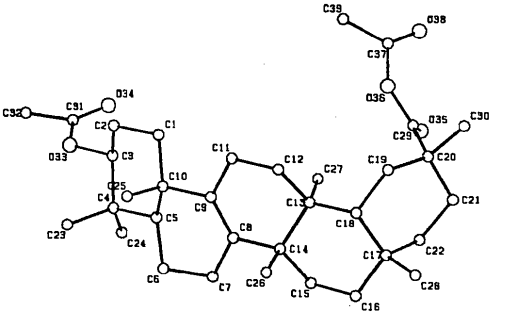

Fig. 1. Perspective view with the atom-numbering system.

0108-2701/89/091472-02$03.00

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

C(1)—C(2)	1·527 (4)	C(14)—C(15)	1·546 (4)
C(1)—C(10)	1·539 (4)	C(14)—C(26)	1·548 (4)
C(2)—C(3)	1·507 (5)	C(15)—C(16)	1·523 (4)
C(3)—C(4)	1·529 (5)	C(16)—C(17)	1·540 (4)
C(3)—O(33)	1·459 (4)	C(17)—C(18)	1·561 (4)
C(4)—C(5)	1·555 (4)	C(17)—C(22)	1·539 (4)
C(4)—C(23)	1·531 (6)	C(17)—C(28)	1·546 (4)
C(4)—C(24)	1·546 (6)	C(18)—C(19)	1·556 (4)
C(5)—C(6)	1·526 (5)	C(19)—C(20)	1·550 (4)
C(5)—C(10)	1·551 (4)	C(20)—C(21)	1·519 (5)
C(6)—C(7)	1·507 (5)	C(20)—C(29)	1·514 (5)
C(7)—C(8)	1·516 (4)	C(20)—C(30)	1·551 (5)
C(8)—C(9)	1·340 (4)	C(21)—C(22)	1·532 (5)
C(8)—C(14)	1·536 (4)	C(29)—O(35)	1·190 (5)
C(9)—C(10)	1·535 (4)	C(29)—O(36)	1·394 (5)
C(9)—C(11)	1·515 (4)	C(31)—C(32)	1·497 (5)
C(10)—C(25)	1·544 (6)	C(31)—O(33)	1·326 (4)
C(11)—C(12)	1·523 (4)	C(31)—O(34)	1·185 (5)
C(12)—C(13)	1·544 (4)	O(36)—C(37)	1·360 (6)
C(13)—C(14)	1·563 (4)	C(37)—O(38)	1·191 (9)
C(13)—C(18)	1·564 (4)	C(37)—C(39)	1·463 (13)
C(13)—C(27)	1·536 (4)		

C(2)—C(1)—C(10)	111·8 (3)	C(8)—C(14)—C(15)	112·4 (3)
C(1)—C(2)—C(3)	110·1 (3)	C(8)—C(14)—C(26)	105·0 (2)
C(2)—C(3)—C(4)	113·2 (3)	C(13)—C(14)—C(15)	107·5 (2)
C(2)—C(3)—O(33)	108·9 (3)	C(13)—C(14)—C(26)	113·6 (3)
C(4)—C(3)—O(33)	108·1 (3)	C(15)—C(14)—C(26)	108·3 (2)
C(3)—C(4)—C(5)	106·9 (3)	C(14)—C(15)—C(16)	111·1 (3)
C(3)—C(4)—C(23)	111·2 (3)	C(15)—C(16)—C(17)	116·9 (3)
C(3)—C(4)—C(24)	106·0 (3)	C(16)—C(17)—C(18)	112·3 (3)
C(5)—C(4)—C(23)	114·5 (3)	C(16)—C(17)—C(22)	109·2 (3)
C(5)—C(4)—C(24)	107·7 (3)	C(16)—C(17)—C(28)	105·2 (2)
C(23)—C(4)—C(24)	110·1 (3)	C(18)—C(17)—C(22)	112·1 (3)
C(4)—C(5)—C(6)	113·8 (3)	C(18)—C(17)—C(28)	109·4 (2)
C(4)—C(5)—C(10)	117·6 (3)	C(22)—C(17)—C(28)	108·3 (3)
C(6)—C(5)—C(10)	109·5 (3)	C(13)—C(18)—C(17)	116·3 (2)
C(5)—C(6)—C(7)	109·9 (3)	C(13)—C(18)—C(19)	115·9 (2)
C(6)—C(7)—C(8)	115·0 (3)	C(17)—C(18)—C(19)	110·4 (2)
C(7)—C(8)—C(9)	122·0 (3)	C(18)—C(19)—C(20)	120·3 (3)
C(7)—C(8)—C(14)	116·0 (3)	C(19)—C(20)—C(21)	111·2 (3)
C(9)—C(8)—C(14)	121·9 (3)	C(19)—C(20)—C(29)	114·4 (3)
C(8)—C(9)—C(10)	123·1 (3)	C(19)—C(20)—C(30)	107·9 (3)
C(8)—C(9)—C(11)	121·3 (3)	C(21)—C(20)—C(29)	109·9 (3)
C(10)—C(9)—C(11)	115·6 (3)	C(21)—C(20)—C(30)	108·5 (3)
C(1)—C(10)—C(5)	107·5 (2)	C(29)—C(20)—C(30)	104·5 (3)
C(1)—C(10)—C(9)	111·5 (3)	C(20)—C(21)—C(22)	114·9 (3)
C(1)—C(10)—C(25)	109·4 (3)	C(17)—C(22)—C(21)	112·4 (3)
C(5)—C(10)—C(9)	107·9 (2)	C(20)—C(29)—O(35)	127·3 (4)
C(5)—C(10)—C(25)	114·5 (3)	C(20)—C(29)—O(36)	111·0 (3)
C(9)—C(10)—C(25)	106·0 (3)	O(35)—C(29)—O(36)	121·7 (4)
C(9)—C(11)—C(12)	116·5 (3)	C(32)—C(31)—O(33)	111·0 (3)
C(11)—C(12)—C(13)	112·3 (3)	C(32)—C(31)—O(34)	124·9 (3)
C(12)—C(13)—C(14)	106·2 (2)	O(33)—C(31)—O(34)	124·1 (3)
C(12)—C(13)—C(18)	109·5 (2)	C(3)—O(33)—C(31)	118·4 (3)
C(12)—C(13)—C(27)	107·4 (2)	C(29)—O(36)—C(37)	122·0 (4)
C(14)—C(13)—C(18)	110·7 (2)	O(36)—C(37)—O(38)	122·7 (6)
C(14)—C(13)—C(27)	110·0 (2)	O(36)—C(37)—C(39)	109·4 (6)
C(18)—C(13)—C(27)	112·8 (2)	O(38)—C(37)—C(39)	127·7 (7)
C(8)—C(14)—C(13)	110·2 (2)		

map are 0·26 and −0·23 e Å^{-3}. Max. Δ/σ in the final cycle 0·2. Atomic scattering factors calculated by $\sum[a_i\exp(-b_i\lambda^{-2}\sin^2\theta)] + c$ $(i = 1,...,4)$ (*International Tables for X-ray Crystallography*, 1974). Calculations performed on FACOM M-730 computer at Shionogi Research Laboratories. The final atomic coordinates and equivalent isotropic temperature factors are given in Table 1. Bond distances and angles are listed in Table 2.* A perspective view of the molecule with the atom-numbering system and a stereoview of the crystal packing drawn using the program *PLUTO* (Motherwell & Clegg, 1978) are presented in Figs. 1 and 2, respectively.

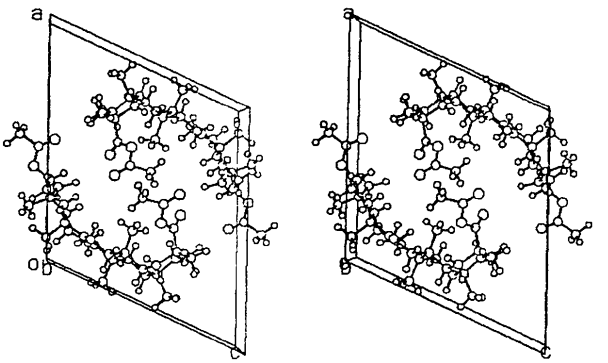

Fig. 2. A stereoview of the unit-cell packing.

Related literature. The structure of the title compound reported here has been discussed in Kamisako, Suwa, Honda, Isoi, Nakai, Shiro & Machida (1987).

The author thanks Professor Wasuke Kamisako, Mukogawa Women's University, for the supply of crystals.

* Lists of structure factors, anisotropic temperature factors of the non-H atoms and atomic coordinates of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51902 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

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

KAMISAKO, W., ISOI, K., NAKAI, H. & SHIRO, M. (1984). *Acta Cryst.* C**40**, 1013–1015.

KAMISAKO, W., SUWA, K., HONDA, C., ISOI, K., NAKAI, H., SHIRO, M. & MACHIDA, K. (1987). *Magn. Reson. Chem.* **25**, 848–855.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN*78. *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). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NAKAI, H., SHIRO, M., KAMISAKO, W., HONDA, C. & ISOI, K. (1987). *Acta Cryst.* C**43**, 1779–1782.