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# Structure of a Bryonolic Acid Derivative, *D:C*-Friedoolean-8-ene-3*β*,29-diol Diacetate, $C_{34}H_{54}O_4$

BY WASUKE KAMISAKO AND KOICHIRO ISOI

*Faculty of Pharmaceutical Sciences, Mukogawa Women's University, 3–16 Edagawa-cho, Nishinomiya, Hyogo 663, Japan*

AND HIROSHI NAKAI AND MOTOO SHIRO

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

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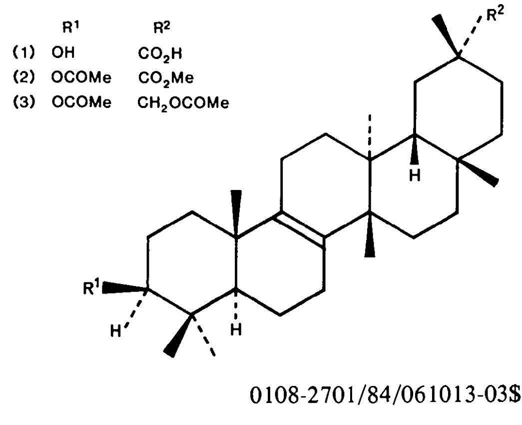
**Abstract.** $M_r$ = 526·8, monoclinic, $C2$, $a$ = 13·547 (1), $b$ = 6·385 (1), $c$ = 36·183 (3) Å, $\beta$ = 92·69 (1)°, $V$ = 3126·1 (6) Å$^3$, $Z$ = 4, $D_x$ = 1·119 Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·5418 Å, $\mu$(Cu $K\alpha$) = 0·56 mm$^{-1}$, $F(000)$ = 1160, $T$ = 295 K, $R$ = 0·038 for 2904 reflections. The compound was derived from bryonolic acid isolated from *Luffa cylindrica* roots (Cucurbitaceae). The ring junctions *A/B, C/D* and *D/E* are respectively *trans*, *trans* and *cis*. The conformations of rings *A–E* are respectively chair, half-chair, half-chair, twist-boat and boat. The twist-boat form of ring *D* is considerably distorted to relieve methyl–methyl and methyl–H interactions.

**Introduction.** The structure of bryonolic acid (1), a triterpenoid which was first isolated from *Brionia dioica* (Cucurbitaceae), has already been proposed as 3*β*-hydroxy-*D:C*-friedoolean-8-en-29-oic acid on the basis of chemical and $^1$H NMR, IR and mass spectral evidence (Biglino, Cattel, Caputo & Nobili, 1969). As part of an investigation on $^{13}$C NMR chemical shifts, we conducted a spectral study of methyl acetylbryonolate (2) and the diacetate of *D:C*-friedoolean-8-ene-3*β*,29-diol (3) which were derived from (1) isolated from *L. cylindrica* roots. We found a complicating substituent effect induced by C(29)-functional group replacement (Kamisako, Suwa, Morimoto & Isoi, 1984), and knowledge of the detailed structure of the triterpenoid was desirable to interpret the spectral data. Thus, the structure determination of (3), crystallized in a suitable form for X-ray work, was undertaken.



| | $R^1$ | $R^2$ |
|---|---|---|
| (1) | OH | $CO_2H$ |
| (2) | OCOMe | $CO_2Me$ |
| (3) | OCOMe | $CH_2OCOMe$ |

**Experimental.** Prismatic colorless crystals grown from benzene solution. Crystal 0·25 × 0·30 × 0·30 mm, Rigaku AFC-5UD diffractometer, graphite-monochromatized Cu $K\alpha$. Cell dimensions from $2\theta$ angles for 20 reflections (35° < $2\theta$ < 46°). Intensities measured up to $2\theta$ = 140° in $h$ 0/16, $k$ 0/7 and $l$ −44/44. Three standard reflections monitored every 100 measurements (±1% variation). 3224 unique reflections measured, 3067 intensities observed $|F_o| > \sigma_1(F_o)$, where $\sigma_1(F_o)$ is the e.s.d. due to counting errors; no absorption corrections. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located on a difference density map. Positional parameters of all atoms and anisotropic thermal parameters of non-H atoms refined by block-diagonal least squares. Temperature factor of each H atom equal to $B_{eq}$ of the bonded atom. $R$ = 0·038, $wR$ = 0·054, $S$ = 1·18 for 2904 observed reflections ($w \neq 0$).* No significant peaks in final difference map, highest peak 0·2 e Å$^{-3}$. $\sum w|\Delta F|^2$ minimized, $w = 1/\sigma^2(F_o)$ for $|F_c| \geq \sigma(F_o)$ and $|\Delta F| < 3\sigma(F_o)$, $w = 0$ otherwise, $\sigma(F_o) = [\sigma_1^2(F_o) + 0{\cdot}00165|F_o|^2]^{1/2}$ (Grant, Killean & Lawrence, 1969). Ratio of final shift to e.s.d. < 0·5. Atomic scattering factors calculated by $\sum[a_i\exp(-b_i\lambda^{-2}\sin^2\theta)] + c$ ($i = 1{\sim}4$) (*International Tables for X-ray Crystallography*, 1974). Calculations performed on a FACOM M-150F computer at Shionogi Research Laboratories.

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* Lists of structure factors, anisotropic temperature factors of the non-H atoms and coordinates of the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39223 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^2$ Å$^2$) *with their e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| C(1) | 2837 (1) | 6207 (5) | 8504 (1) | 367 (4) |
| C(2) | 2762 (1) | 5925 (5) | 8920 (1) | 405 (4) |
| C(3) | 3642 (1) | 4649 (5) | 9074 (1) | 367 (4) |
| C(4) | 4650 (1) | 5627 (5) | 9011 (1) | 363 (4) |
| C(5) | 4676 (1) | 6088 (4) | 8588 (1) | 333 (3) |
| C(6) | 5644 (1) | 7027 (5) | 8471 (1) | 425 (4) |
| C(7) | 5732 (1) | 6683 (5) | 8059 (1) | 425 (5) |
| C(8) | 4788 (1) | 7141 (4) | 7830 (1) | 308 (3) |
| C(9) | 3914 (1) | 7368 (4) | 7983 (1) | 310 (3) |
| C(10) | 3798 (1) | 7323 (4) | 8403 (1) | 313 (3) |
| C(11) | 2981 (1) | 7818 (5) | 7750 (1) | 387 (4) |
| C(12) | 3132 (1) | 8440 | 7350 (1) | 360 (4) |
| C(13) | 3958 (1) | 7161 (4) | 7178 (1) | 287 (3) |
| C(14) | 4929 (1) | 7559 (4) | 7416 (1) | 310 (3) |
| C(15) | 5758 (1) | 6164 (5) | 7265 (1) | 404 (4) |
| C(16) | 5669 (1) | 5623 (5) | 6853 (1) | 445 (5) |
| C(17) | 5078 (1) | 7139 (5) | 6596 (1) | 359 (4) |
| C(18) | 4090 (1) | 7893 (4) | 6771 (1) | 304 (3) |
| C(19) | 3179 (1) | 7308 (5) | 6520 (1) | 368 (4) |
| C(20) | 3225 (1) | 8045 (5) | 6115 (1) | 389 (4) |
| C(21) | 4205 (1) | 7287 (6) | 5954 (1) | 503 (6) |
| C(22) | 4829 (1) | 5984 (5) | 6229 (1) | 461 (5) |
| C(23) | 4857 (2) | 7540 (5) | 9262 (1) | 503 (5) |
| C(24) | 5440 (2) | 3944 (5) | 9106 (1) | 488 (5) |
| C(25) | 3728 (2) | 9634 (5) | 8525 (1) | 440 (5) |
| C(26) | 5249 (1) | 9898 (5) | 7410 (1) | 428 (4) |
| C(27) | 3658 (1) | 4825 (4) | 7199 (1) | 361 (4) |
| C(28) | 5739 (1) | 9008 (5) | 6510 (1) | 491 (5) |
| C(29) | 2342 (2) | 7005 (6) | 5915 (1) | 519 (6) |
| C(30) | 3125 (2) | 10429 (5) | 6090 (1) | 551 (6) |
| C(31) | 3148 (1) | 2624 (5) | 9590 (1) | 445 (5) |
| C(32) | 3225 (3) | 2476 (7) | 10007 (1) | 719 (9) |
| O(33) | 3567 (1) | 4367 (4) | 9472 (1) | 437 (3) |
| O(34) | 2756 (2) | 1352 (5) | 9392 (1) | 655 (5) |
| O(35) | 2282 (1) | 7669 (5) | 5532 (1) | 632 (5) |
| O(36) | 1486 (2) | 7201 (10) | 5342 (1) | 932 (15) |
| O(37) | 832 (2) | 6232 (11) | 5476 (1) | 1687 (25) |
| C(38) | 1502 (3) | 7851 (14) | 4947 (1) | 1125 (20) |

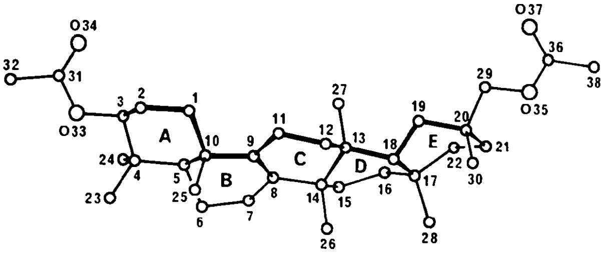

Fig. 1. Perspective view of the molecule with the atom-numbering and ring-labelling systems.

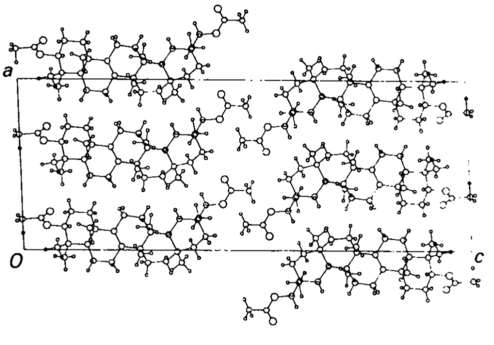

Fig. 2. Projection of the crystal structure along **b**.

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

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·524 (5) | C(13)–C(27) | 1·549 (4) |
| C(1)–C(10) | 1·543 (4) | C(14)–C(15) | 1·553 (4) |
| C(2)–C(3) | 1·527 (5) | C(14)–C(26) | 1·556 (4) |
| C(3)–C(4) | 1·528 (5) | C(15)–C(16) | 1·529 (5) |
| C(3)–O(33) | 1·460 (4) | C(16)–C(17) | 1·540 (5) |
| C(4)–C(5) | 1·561 (4) | C(17)–C(18) | 1·583 (4) |
| C(4)–C(23) | 1·540 (5) | C(17)–C(22) | 1·542 (5) |
| C(4)–C(24) | 1·544 (5) | C(17)–C(28) | 1·533 (5) |
| C(5)–C(6) | 1·520 (4) | C(18)–C(19) | 1·543 (4) |
| C(5)–C(10) | 1·552 (4) | C(19)–C(20) | 1·543 (5) |
| C(6)–C(7) | 1·517 (5) | C(20)–C(21) | 1·552 (5) |
| C(7)–C(8) | 1·519 (4) | C(20)–C(29) | 1·521 (5) |
| C(8)–C(9) | 1·338 (4) | C(20)–C(30) | 1·530 (5) |
| C(8)–C(14) | 1·542 (4) | C(21)–C(22) | 1·522 (5) |
| C(9)–C(10) | 1·535 (4) | C(29)–O(35) | 1·448 (5) |
| C(9)–C(11) | 1·513 (4) | C(31)–C(32) | 1·510 (6) |
| C(10)–C(25) | 1·544 (4) | C(31)–O(33) | 1·329 (4) |
| C(11)–C(12) | 1·524 (3) | C(31)–O(34) | 1·191 (5) |
| C(12)–C(13) | 1·540 (3) | O(35)–O(36) | 1·286 (7) |
| C(13)–C(14) | 1·559 (4) | O(36)–O(37) | 1·201 (9) |
| C(13)–C(18) | 1·563 (4) | O(36)–C(38) | 1·489 (11) |

| | | | |
|---|---|---|---|
| C(2)–C(1)–C(10) | 112·6 (3) | C(1)–C(10)–C(25) | 108·0 (2) |
| C(1)–C(2)–C(3) | 109·6 (3) | C(5)–C(10)–C(9) | 108·9 (2) |
| C(2)–C(3)–C(4) | 114·5 (3) | C(5)–C(10)–C(25) | 114·7 (2) |
| C(2)–C(3)–O(33) | 109·6 (3) | C(9)–C(10)–C(25) | 106·0 (2) |
| C(4)–C(3)–O(33) | 107·6 (3) | C(9)–C(11)–C(12) | 115·6 (2) |
| C(3)–C(4)–C(5) | 106·6 (2) | C(11)–C(12)–C(13) | 112·2 (2) |
| C(3)–C(4)–C(23) | 112·0 (3) | C(12)–C(13)–C(14) | 107·5 (2) |
| C(3)–C(4)–C(24) | 107·3 (3) | C(12)–C(13)–C(18) | 109·9 (2) |
| C(5)–C(4)–C(23) | 114·6 (3) | C(12)–C(13)–C(27) | 107·1 (2) |
| C(5)–C(4)–C(24) | 107·6 (3) | C(14)–C(13)–C(18) | 109·9 (2) |
| C(23)–C(4)–C(24) | 108·4 (3) | C(14)–C(13)–C(27) | 110·3 (2) |
| C(4)–C(5)–C(6) | 114·0 (2) | C(18)–C(13)–C(27) | 112·1 (2) |
| C(4)–C(5)–C(10) | 117·8 (2) | C(8)–C(14)–C(13) | 111·6 (2) |
| C(6)–C(5)–C(10) | 109·5 (2) | C(8)–C(14)–C(15) | 111·6 (2) |
| C(5)–C(6)–C(7) | 109·0 (3) | C(8)–C(14)–C(26) | 103·1 (2) |
| C(6)–C(7)–C(8) | 113·9 (3) | C(13)–C(14)–C(15) | 108·5 (2) |
| C(7)–C(8)–C(9) | 122·3 (3) | C(13)–C(14)–C(26) | 112·2 (2) |
| C(7)–C(8)–C(14) | 115·0 (2) | C(15)–C(14)–C(26) | 109·8 (2) |
| C(9)–C(8)–C(14) | 122·4 (2) | C(14)–C(15)–C(16) | 116·6 (3) |
| C(8)–C(9)–C(10) | 122·8 (2) | C(15)–C(16)–C(17) | 117·5 (3) |
| C(8)–C(9)–C(11) | 121·5 (2) | C(16)–C(17)–C(18) | 112·0 (3) |
| C(10)–C(9)–C(11) | 115·7 (2) | C(16)–C(17)–C(22) | 107·8 (3) |
| C(1)–C(10)–C(5) | 107·5 (2) | C(16)–C(17)–C(28) | 108·7 (3) |
| C(1)–C(10)–C(9) | 111·7 (2) | C(18)–C(17)–C(22) | 109·6 (3) |
| C(18)–C(17)–C(28) | 111·0 (3) | C(20)–C(21)–C(22) | 112·5 (3) |
| C(22)–C(17)–C(28) | 107·7 (3) | C(17)–C(22)–C(21) | 113·2 (3) |
| C(13)–C(18)–C(17) | 115·0 (2) | C(20)–C(29)–O(35) | 109·6 (3) |
| C(13)–C(18)–C(19) | 111·0 (2) | C(32)–C(31)–O(33) | 111·3 (3) |
| C(17)–C(18)–C(19) | 111·0 (2) | C(32)–C(31)–O(34) | 124·5 (4) |
| C(18)–C(19)–C(20) | 114·7 (3) | O(33)–C(31)–O(34) | 124·2 (3) |
| C(19)–C(20)–C(21) | 109·6 (3) | C(3)–O(33)–C(31) | 118·1 (3) |
| C(19)–C(20)–C(29) | 104·6 (3) | C(29)–O(35)–O(36) | 116·8 (4) |
| C(19)–C(20)–C(30) | 110·6 (3) | O(35)–O(36)–O(37) | 121·3 (6) |
| C(21)–C(20)–C(29) | 110·7 (3) | O(35)–O(36)–C(38) | 113·5 (6) |
| C(21)–C(20)–C(30) | 111·3 (3) | O(37)–O(36)–C(38) | 125·1 (7) |
| C(29)–C(20)–C(30) | 109·9 (3) | | |

**Discussion.** Atomic coordinates and equivalent isotropic temperature factors of non-H atoms are listed in Table 1. Bond lengths and angles are given in Table 2. A perspective view with the atom-numbering and ring-labelling systems is shown in Fig. 1. The absolute configuration of the molecule was determined on the basis of the α configuration of the C(27) methyl group. A projection of the crystal structure is presented in Fig. 2.

The ring junctions *A/B*, *C/D* and *D/E* are respectively *trans*, *trans* and *cis*. Rings *A–C* adopt the chair, half-chair and half-chair conformations, respectively, though they are somewhat deformed. Ring *D* is in a twist-boat form considerably distorted to relieve the repulsive interactions of Me(C14)···Me(C17) and

Me(C13)$\cdots$H(C16-$\alpha$): the inner bond angles of atoms C(15), C(16), C(17) and C(18) [116·6 (3), 117·5 (3), 112·0 (3) and 115·0 (2)°] and the endocyclic torsion angles of the C(16)—C(17) and C(17)—C(18) bonds [−42·9 (3) and 5·9 (3)°] deviate widely from the respective normal values. Ring *E*, in contrast, closely approximates a regular boat form.

The conformations of the *D* and *E* rings of (3) are boat–boat as in triterpenes having a similar *D–E* ring skeleton, *e.g.* epifriedelinol (Laing, Burke-Laing, Bartho & Weeks, 1977), and not chair–chair as found in campanulin (Mo, 1977). Because of the conformational dependency of the $^{13}$C chemical shifts (Dalling & Grant, 1972), the $^{13}$C NMR spectral data of (2) and (3) indicate that their *D–E* ring conformations in $CHCl_3$ solution are different from one another, and, assuming that the conformation of (3) in the crystalline state is retained in solution, the *D–E* ring of (2) probably takes, not the boat–boat form, but another one, such as the chair–chair form in solution.

The authors wish to thank Professor Giuseppe Biglino, Università degli Studi di Torino, for the authentic sample of bryonolic acid.

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# Photochromic and Thermochromic Compounds. I. Structures of (*E*) and (*Z*) Isomers of 2-Isopropylidene-3-[1-(2-methyl-5-phenyl-3-thienyl)ethylidene]succinic Anhydride, $C_{20}H_{18}O_3S$, and the Photoproduct 7,7a-Dihydro-4,7,7,7a-tetramethyl-2-phenylbenzo[*b*]thiophene-5,6-dicarboxylic Anhydride (*P*), $C_{20}H_{18}O_3S$

By M. Kaftory

*Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel*

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**Abstract.** $M_r = 338{\cdot}42$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, room temperature. (*Z*): monoclinic, $P2_1$, $a = 14{\cdot}449$ (7), $b = 7{\cdot}619$ (4), $c = 8{\cdot}014$ (4) Å, $\beta = 94{\cdot}83$ (2)°, $U = 879{\cdot}10$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}278$ g cm$^{-3}$, $\mu = 1{\cdot}88$ cm$^{-1}$, $F(000) = 356$, $R = 0{\cdot}063$, 1156 reflections. (*E*): monoclinic, $P2_1$, $a = 14{\cdot}295$ (7), $b = 7{\cdot}620$ (4), $c = 8{\cdot}317$ (4) Å, $\beta = 104{\cdot}21$ (2)°, $U = 878{\cdot}23$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}279$ g cm$^{-3}$, $\mu = 1{\cdot}89$ cm$^{-1}$, $F(000) = 356$, $R = 0{\cdot}048$, 1500 reflections. (*P*): monoclinic, $P2_1/n$, $a = 16{\cdot}604$ (8), $b = 7{\cdot}490$ (4), $c = 14{\cdot}113$ (7) Å, $\beta = 106{\cdot}59$ (2)°, $U = 1682{\cdot}08$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}336$ g cm$^{-3}$, $\mu = 1{\cdot}97$cm$^{-1}$, $F(000) = 712$, $R = 0{\cdot}073$, 1810 reflections. The (*E*) and (*Z*) isomers crystallize in the monoclinic chiral space group $P2_1$. The pale-violet (*E*) isomer undergoes reversible photochemical reaction to yield (*P*) which crystallizes in the monoclinic achiral space group $P2_1/n$.

**Introduction.** Among the many classes of photochromic compounds the fulgides, first discovered and studied by Stobbe & Eckert (1905) and Stobbe (1911), are important for their relative stability. Although the first compounds of the fulgide system showed reversible photochemical properties they were unstable during repeated irradiation. Reinvestigation of the properties of some of those compounds (Heller & Szewczyk, 1974; Darcy, Hart & Heller, 1978) showed that thermal H shifts are involved in the process after the cyclization takes place, and therefore the reversibility of the process is halted during repeated irradiation. Efforts were made to improve the properties of the fulgide system in order to obtain thermally stable photochemically fatigue-resistant photochromic compounds (Darcy, Heller, Strydom & Whitall 1981; Heller & Oliver, 1981; Heller & Langan, 1981).

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