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# A diterpenoid from *Isodon japonica* var. glaucocalyx

**Xing-Ke Ma,[a] Zhi-An He[b] and Su-Ping Bai[c]***

[a]Department of Chemistry, Zhoukou Normal University, Zhoukou, Henan 466000, People's Republic of China, [b]Department of Laboratory Medicine, Xinxiang Medical University, Xinxiang, Henan 453000, People's Republic of China, and [c]Pharmacy College, Xinxiang Medical University, Xinxiang, Henan 453000, People's Republic of China
Correspondence e-mail: baisuping@xxmu.edu.cn

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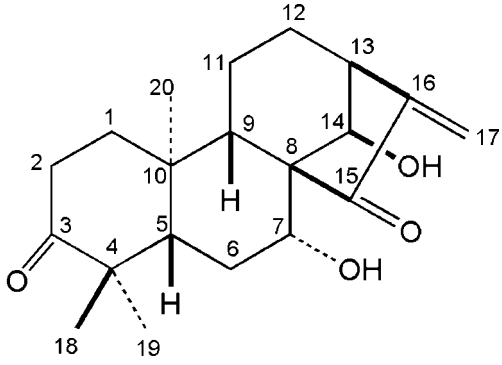
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.044; $wR$ factor = 0.127; data-to-parameter ratio = 10.1.

The title compound, 7$\alpha$,14$\beta$-dihydroxy-*ent*-kaur-16-ene-3,5-dione or glaucocalyxin A, $C_{20}H_{28}O_4$, a natural *ent*-kaurane diterpenoid, is composed of four rings with the expected *cis* and *trans* junctions. In the crystal structure, the molecules are linked together by O—H···O hydrogen bonds to form double chains running along the shortest cell axis.

## Related literature

For related literature, see: Allen *et al.* (1987); Kim *et al.* (1992); Sun *et al.* (2001).




## Experimental

### Crystal data

$C_{20}H_{28}O_4$
$M_r$ = 332.42
Orthorhombic, $P2_12_12_1$
$a$ = 6.6349 (19) Å
$b$ = 10.659 (4) Å
$c$ = 24.586 (7) Å
$V$ = 1738.8 (10) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 (2) K
0.41 × 0.20 × 0.18 mm

### Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: none
17081 measured reflections
2298 independent reflections
1946 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.056

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.127
$S$ = 1.00
2298 reflections
228 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.16 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2O···O4$^{i}$ | 0.94 (3) | 1.83 (3) | 2.765 (3) | 171 (3) |
| O4—H4O···O2 | 0.84 (4) | 1.85 (4) | 2.641 (3) | 156 (4) |

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

Data collection: *RAPID-AUTO* (Rigaku, 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1995); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2095).

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# supplementary materials

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# A diterpenoid from *Isodon japonica* var. glaucocalyx

**X.-K. Ma, Z.-A. He and S.-P. Bai**

## Comment

The title compound(I), is a natural *ent*-kaurane diterpenoid isolated from the medicinal plant Isodon japonica var. glaucocalyx. This plant has been used as antibacterial, inflammation-diminishing and stomachic agents. The compound (I) has been isolated previously from the same source and its structure was postulated from spectroscopic methods (Kim *et al.*,1992). In order to further confirm the structure and conformation of (I), a crystal structure analysis has been undertaken.

The X-ray crystallographic analysis confirms the previously proposed molecular structure of (I). Fig.1 shows its conformation: two carbonyl groups locate at C3 and C15, while two hydrogen groups adopt α,β-orientations at C7 and C14 respectively. There is a *trans* junction between ring A (C1—C5/C10) and ring B (C5—C10); *cis* junctions are present between ring B and ring C (C8/C9/C11—C14), and ring C and ring D (C8/C13—C16).

Bond lengths and angles are within expected ranges (Allen *et al.*, 1987), with average values (Å): C$sp^3$—C$sp^3$ = 1.541 (3), C$sp^3$—C$sp^2$ = 1.517 (4), C$sp^2$—C$sp^2$ (in C═C—C═O) = 1.500 (4), C═C = 1.326 (4), C═O = 1.209 (3), C$sp^3$—O = 1.432 (3). Rings B and C have chair conformations, with average torsion angles of 54.6 (2) ° and 55.8 °, respectively. Ring A adopts a twist-boat conformation and ring D shows an evenlope conformation; the flap atom, C14, lies 0.69 (1) Å from the plane defined by atoms C8, C15, C16 and C13.

The molecule contains seven chiral centers at C5(*R*), C7(*R*), C8(*R*), C9(S), C10(*R*), C13(*R*) and C14(*R*). Although the absolute configuration could not be reliably determined from anomalous dispersion effects, the negative optical rotation showed this compound to be in the *ent*- kaurane series as reported in genus Isodon (Sun *et al.*,2001), rather than in the kaurane series, and so allowed us to assign the correct configuration. In the crystal structure the molecules are linked by O—H···O hydrogen bonds, to form double chains running along the shortest cell axis, a. (Table 1 and Fig. 2).

## Experimental

The dried and crushed leaves of Isodon japonica var. glaucocalyx (10 kg, collected from Hui Prefecture, Henan Province, China) were extracted four times with $Me_2CO/H_2O$ (7:3, *v*/*v*) at room temperature over a period of seven days. The extract was filtered and the solvent was removed under reduced pressure. The residue was then partitioned between water and AcOEt. After removal of the solvent, the AcOEt residue was separated by repeated silica gel (200–300 mesh) column chromatography and recrystallization from $CHCl_3/Me_2CO$(10:1), giving 900 mg of compound (I) (m.p. 493–495 K. Optical rotation: $[\alpha]_D^{20}$ −183 ° (c 1/2, $CHCl_3$). Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the compound (I) in $Me_2CO$ at room temperature.

### Refinement

All H atoms were included in calculated positions and refined as riding atoms, with C—H = 0.96 Å ($CH_3$), 0.93 and 0.97 Å ($CH_2$), and 0.98 Å (CH), and with $U_{iso}$(H) = 1.2 $U_{eq}$(C). In the absence of significant anomalous scattering effects, Friedel pairs were merged. The choice of enantiomer was based on comparison of the optical rotation with that of related compounds with known stereochemistry.

### Figures

Fig. 1. A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

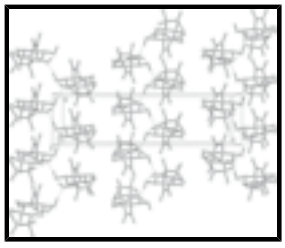

Fig. 2. The crystal packing of (I), viewed along the *b* axis. O—H···O hydrogen bonds are shown as dashed lines.

### 7α,14β-dihydroxy-*ent*-kaur-16-ene-3,5-dione

*Crystal data*

| | |
|---|---|
| $C_{20}H_{28}O_4$ | $D_x$ = 1.270 Mg m$^{-3}$ |
| $M_r$ = 332.42 | Melting point: 493 K |
| Orthorhombic, $P2_12_12_1$ | Mo $K\alpha$ radiation<br>λ = 0.71073 Å |
| Hall symbol: P 2ac 2ab | Cell parameters from 13908 reflections |
| *a* = 6.6349 (19) Å | θ = 3.1–27.5º |
| *b* = 10.659 (4) Å | μ = 0.09 mm$^{-1}$ |
| *c* = 24.586 (7) Å | *T* = 293 (2) K |
| *V* = 1738.8 (10) Å$^3$ | Block, colourless |
| *Z* = 4 | 0.41 × 0.20 × 0.18 mm |
| $F_{000}$ = 720 | |

*Data collection*

| | |
|---|---|
| Rigaku R-AXIS RAPID diffractometer | 1946 reflections with $I > 2\sigma(I)$ |
| Radiation source: Rotating Anode | $R_{int}$ = 0.056 |
| Monochromator: graphite | $\theta_{max}$ = 27.5º |
| *T* = 293(2) K | $\theta_{min}$ = 3.1º |
| ω scans | *h* = −8→8 |

Absorption correction: none
17081 measured reflections
2298 independent reflections

$k = -13 \rightarrow 13$
$l = -31 \rightarrow 31$

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.127$

$S = 1.00$

2298 reflections

228 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2 + 0.1982P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.30$ e Å$^{-3}$

$\Delta\rho_{min} = -0.16$ e Å$^{-3}$

Extinction correction: none

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on $F^2$, conventional *R*-factors *R* are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on F, and *R*-factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.6082 (4) | 0.8582 (2) | 0.68057 (9) | 0.0771 (8) |
| O2 | 0.1990 (3) | 0.39429 (17) | 0.49532 (6) | 0.0379 (4) |
| O3 | −0.1915 (3) | 0.32770 (18) | 0.57763 (8) | 0.0441 (5) |
| O4 | 0.3435 (3) | 0.19761 (17) | 0.54776 (8) | 0.0439 (5) |
| C1 | 0.2273 (5) | 0.6432 (3) | 0.70138 (10) | 0.0479 (7) |
| H1A | 0.0821 | 0.6336 | 0.7034 | 0.057* |
| H1B | 0.2830 | 0.6163 | 0.7359 | 0.057* |
| C2 | 0.2764 (5) | 0.7819 (3) | 0.69317 (12) | 0.0563 (8) |
| H2A | 0.1662 | 0.8217 | 0.6738 | 0.068* |
| H2B | 0.2884 | 0.8221 | 0.7284 | 0.068* |
| C3 | 0.4674 (5) | 0.8012 (2) | 0.66199 (10) | 0.0477 (7) |
| C4 | 0.4690 (5) | 0.7467 (2) | 0.60447 (9) | 0.0406 (6) |
| C5 | 0.3202 (4) | 0.6329 (2) | 0.60206 (8) | 0.0309 (5) |
| H5 | 0.1860 | 0.6700 | 0.5977 | 0.037* |
| C6 | 0.3501 (4) | 0.5498 (2) | 0.55213 (8) | 0.0311 (5) |
| H6A | 0.3604 | 0.6019 | 0.5199 | 0.037* |
| H6B | 0.4748 | 0.5030 | 0.5558 | 0.037* |
| C7 | 0.1754 (3) | 0.4593 (2) | 0.54579 (8) | 0.0295 (5) |
| H7 | 0.0501 | 0.5078 | 0.5443 | 0.035* |
| C8 | 0.1644 (3) | 0.3699 (2) | 0.59436 (8) | 0.0257 (4) |
| C9 | 0.1505 (3) | 0.4486 (2) | 0.64833 (8) | 0.0302 (5) |
| H9 | 0.0210 | 0.4924 | 0.6457 | 0.036* |
| C10 | 0.3093 (3) | 0.5555 (2) | 0.65574 (8) | 0.0300 (5) |
| C11 | 0.1273 (4) | 0.3612 (3) | 0.69854 (10) | 0.0429 (6) |
| H11A | 0.1696 | 0.4070 | 0.7307 | 0.052* |
| H11B | −0.0144 | 0.3412 | 0.7029 | 0.052* |
| C12 | 0.2459 (5) | 0.2384 (3) | 0.69599 (10) | 0.0477 (7) |
| H12A | 0.1948 | 0.1812 | 0.7234 | 0.057* |
| H12B | 0.3865 | 0.2551 | 0.7041 | 0.057* |
| C13 | 0.2304 (4) | 0.1762 (2) | 0.63987 (11) | 0.0407 (6) |
| H13 | 0.2960 | 0.0938 | 0.6395 | 0.049* |
| C14 | 0.3249 (3) | 0.2652 (2) | 0.59796 (9) | 0.0322 (5) |
| H14 | 0.4551 | 0.2977 | 0.6104 | 0.039* |
| C15 | −0.0298 (3) | 0.2914 (2) | 0.59443 (9) | 0.0316 (5) |
| C16 | 0.0144 (4) | 0.1678 (3) | 0.62099 (13) | 0.0478 (7) |
| C17 | −0.1289 (6) | 0.0875 (3) | 0.63508 (14) | 0.0688 (10) |
| H17A | −0.2634 | 0.1069 | 0.6286 | 0.083* |
| H17B | −0.0949 | 0.0117 | 0.6515 | 0.083* |
| C18 | 0.3899 (7) | 0.8516 (3) | 0.56763 (12) | 0.0642 (10) |
| H18A | 0.2557 | 0.8739 | 0.5785 | 0.077* |
| H18B | 0.3883 | 0.8230 | 0.5306 | 0.077* |
| H18C | 0.4761 | 0.9235 | 0.5706 | 0.077* |
| C19 | 0.6851 (5) | 0.7164 (3) | 0.58732 (14) | 0.0623 (9) |
| H19A | 0.6878 | 0.6962 | 0.5493 | 0.075* |
| H19B | 0.7335 | 0.6461 | 0.6079 | 0.075* |

| | | | | |
|---|---|---|---|---|
| H19C | 0.7697 | 0.7879 | 0.5940 | 0.075* |
| C20 | 0.5169 (4) | 0.5082 (2) | 0.67412 (11) | 0.0414 (6) |
| H20A | 0.6002 | 0.5784 | 0.6837 | 0.050* |
| H20B | 0.5791 | 0.4624 | 0.6450 | 0.050* |
| H20C | 0.5012 | 0.4543 | 0.7051 | 0.050* |
| H2O | 0.071 (5) | 0.370 (3) | 0.4827 (12) | 0.049 (8)* |
| H4O | 0.291 (6) | 0.244 (4) | 0.5241 (14) | 0.076 (12)* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.104 (2) | 0.0781 (16) | 0.0495 (11) | −0.0581 (16) | −0.0082 (12) | −0.0065 (11) |
| O2 | 0.0415 (10) | 0.0446 (9) | 0.0275 (7) | −0.0064 (8) | 0.0001 (7) | −0.0110 (7) |
| O3 | 0.0261 (8) | 0.0535 (11) | 0.0527 (10) | −0.0042 (9) | −0.0007 (8) | −0.0091 (9) |
| O4 | 0.0473 (11) | 0.0401 (10) | 0.0443 (10) | 0.0112 (9) | 0.0062 (9) | −0.0119 (8) |
| C1 | 0.0565 (17) | 0.0494 (15) | 0.0376 (12) | −0.0154 (13) | 0.0139 (13) | −0.0167 (12) |
| C2 | 0.076 (2) | 0.0440 (15) | 0.0485 (15) | −0.0072 (15) | 0.0103 (15) | −0.0207 (13) |
| C3 | 0.0726 (19) | 0.0325 (13) | 0.0379 (13) | −0.0175 (14) | −0.0048 (13) | −0.0050 (10) |
| C4 | 0.0582 (16) | 0.0316 (12) | 0.0321 (11) | −0.0162 (13) | −0.0016 (11) | −0.0012 (9) |
| C5 | 0.0351 (12) | 0.0291 (10) | 0.0284 (10) | −0.0040 (10) | −0.0003 (9) | −0.0034 (9) |
| C6 | 0.0387 (12) | 0.0303 (10) | 0.0243 (9) | −0.0089 (10) | 0.0034 (9) | 0.0009 (9) |
| C7 | 0.0296 (10) | 0.0325 (11) | 0.0265 (9) | −0.0017 (10) | −0.0005 (9) | −0.0047 (9) |
| C8 | 0.0229 (10) | 0.0284 (10) | 0.0260 (9) | −0.0021 (9) | 0.0017 (8) | −0.0043 (8) |
| C9 | 0.0289 (11) | 0.0328 (11) | 0.0289 (10) | −0.0029 (10) | 0.0065 (9) | −0.0049 (9) |
| C10 | 0.0329 (11) | 0.0321 (11) | 0.0250 (9) | −0.0067 (10) | 0.0023 (9) | −0.0051 (9) |
| C11 | 0.0488 (14) | 0.0479 (14) | 0.0321 (11) | −0.0142 (13) | 0.0120 (11) | 0.0004 (11) |
| C12 | 0.0571 (17) | 0.0456 (14) | 0.0406 (13) | −0.0095 (13) | 0.0029 (13) | 0.0152 (12) |
| C13 | 0.0417 (13) | 0.0283 (11) | 0.0520 (14) | −0.0016 (11) | 0.0021 (12) | 0.0049 (10) |
| C14 | 0.0269 (11) | 0.0339 (12) | 0.0357 (11) | 0.0007 (10) | 0.0021 (9) | −0.0062 (9) |
| C15 | 0.0251 (11) | 0.0360 (12) | 0.0337 (10) | −0.0052 (10) | 0.0041 (9) | −0.0094 (10) |
| C16 | 0.0392 (14) | 0.0375 (13) | 0.0669 (17) | −0.0096 (12) | 0.0030 (13) | 0.0031 (13) |
| C17 | 0.065 (2) | 0.0606 (19) | 0.081 (2) | −0.0317 (18) | −0.0093 (18) | 0.0210 (18) |
| C18 | 0.107 (3) | 0.0366 (14) | 0.0493 (16) | −0.0186 (18) | −0.0143 (18) | 0.0071 (13) |
| C19 | 0.0580 (18) | 0.068 (2) | 0.0604 (17) | −0.0345 (17) | 0.0166 (15) | −0.0077 (16) |
| C20 | 0.0380 (13) | 0.0431 (14) | 0.0432 (13) | −0.0094 (12) | −0.0094 (11) | 0.0064 (11) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C3 | 1.205 (3) | C9—C11 | 1.554 (3) |
| O2—C7 | 1.430 (2) | C9—C10 | 1.562 (3) |
| O2—H2O | 0.94 (3) | C9—H9 | 0.9800 |
| O3—C15 | 1.213 (3) | C10—C20 | 1.535 (3) |
| O4—C14 | 1.434 (3) | C11—C12 | 1.529 (4) |
| O4—H4O | 0.84 (4) | C11—H11A | 0.9700 |
| C1—C2 | 1.527 (4) | C11—H11B | 0.9700 |
| C1—C10 | 1.558 (3) | C12—C13 | 1.534 (4) |
| C1—H1A | 0.9700 | C12—H12A | 0.9700 |
| C1—H1B | 0.9700 | C12—H12B | 0.9700 |
| C2—C3 | 1.495 (4) | C13—C16 | 1.509 (4) |

| | | | |
|---|---|---|---|
| C2—H2A | 0.9700 | C13—C14 | 1.534 (3) |
| C2—H2B | 0.9700 | C13—H13 | 0.9800 |
| C3—C4 | 1.529 (3) | C14—H14 | 0.9800 |
| C4—C19 | 1.529 (4) | C15—C16 | 1.500 (4) |
| C4—C18 | 1.531 (4) | C16—C17 | 1.325 (4) |
| C4—C5 | 1.566 (3) | C17—H17A | 0.9300 |
| C5—C6 | 1.527 (3) | C17—H17B | 0.9300 |
| C5—C10 | 1.558 (3) | C18—H18A | 0.9600 |
| C5—H5 | 0.9800 | C18—H18B | 0.9600 |
| C6—C7 | 1.516 (3) | C18—H18C | 0.9600 |
| C6—H6A | 0.9700 | C19—H19A | 0.9600 |
| C6—H6B | 0.9700 | C19—H19B | 0.9600 |
| C7—C8 | 1.529 (3) | C19—H19C | 0.9600 |
| C7—H7 | 0.9800 | C20—H20A | 0.9600 |
| C8—C15 | 1.537 (3) | C20—H20B | 0.9600 |
| C8—C14 | 1.545 (3) | C20—H20C | 0.9600 |
| C8—C9 | 1.572 (3) | | |
| C7—O2—H2O | 108.7 (17) | C5—C10—C1 | 107.96 (19) |
| C14—O4—H4O | 105 (3) | C20—C10—C9 | 113.58 (19) |
| C2—C1—C10 | 114.3 (2) | C5—C10—C9 | 108.58 (17) |
| C2—C1—H1A | 108.7 | C1—C10—C9 | 106.63 (18) |
| C10—C1—H1A | 108.7 | C12—C11—C9 | 115.4 (2) |
| C2—C1—H1B | 108.7 | C12—C11—H11A | 108.4 |
| C10—C1—H1B | 108.7 | C9—C11—H11A | 108.4 |
| H1A—C1—H1B | 107.6 | C12—C11—H11B | 108.4 |
| C3—C2—C1 | 112.5 (2) | C9—C11—H11B | 108.4 |
| C3—C2—H2A | 109.1 | H11A—C11—H11B | 107.5 |
| C1—C2—H2A | 109.1 | C11—C12—C13 | 111.9 (2) |
| C3—C2—H2B | 109.1 | C11—C12—H12A | 109.2 |
| C1—C2—H2B | 109.1 | C13—C12—H12A | 109.2 |
| H2A—C2—H2B | 107.8 | C11—C12—H12B | 109.2 |
| O1—C3—C2 | 122.2 (2) | C13—C12—H12B | 109.2 |
| O1—C3—C4 | 122.5 (3) | H12A—C12—H12B | 107.9 |
| C2—C3—C4 | 115.3 (2) | C16—C13—C12 | 111.5 (2) |
| C3—C4—C19 | 110.0 (2) | C16—C13—C14 | 102.6 (2) |
| C3—C4—C18 | 105.5 (2) | C12—C13—C14 | 108.0 (2) |
| C19—C4—C18 | 108.2 (3) | C16—C13—H13 | 111.5 |
| C3—C4—C5 | 108.96 (19) | C12—C13—H13 | 111.5 |
| C19—C4—C5 | 114.7 (2) | C14—C13—H13 | 111.5 |
| C18—C4—C5 | 109.1 (2) | O4—C14—C13 | 107.62 (19) |
| C6—C5—C10 | 112.34 (18) | O4—C14—C8 | 111.89 (18) |
| C6—C5—C4 | 113.44 (19) | C13—C14—C8 | 101.75 (18) |
| C10—C5—C4 | 114.07 (17) | O4—C14—H14 | 111.7 |
| C6—C5—H5 | 105.3 | C13—C14—H14 | 111.7 |
| C10—C5—H5 | 105.3 | C8—C14—H14 | 111.7 |
| C4—C5—H5 | 105.3 | O3—C15—C16 | 127.0 (2) |
| C7—C6—C5 | 110.63 (18) | O3—C15—C8 | 124.6 (2) |
| C7—C6—H6A | 109.5 | C16—C15—C8 | 108.4 (2) |
| C5—C6—H6A | 109.5 | C17—C16—C15 | 122.8 (3) |

| | | | |
|---|---|---|---|
| C7—C6—H6B | 109.5 | C17—C16—C13 | 129.7 (3) |
| C5—C6—H6B | 109.5 | C15—C16—C13 | 105.5 (2) |
| H6A—C6—H6B | 108.1 | C16—C17—H17A | 120.0 |
| O2—C7—C6 | 108.30 (18) | C16—C17—H17B | 120.0 |
| O2—C7—C8 | 112.40 (18) | H17A—C17—H17B | 120.0 |
| C6—C7—C8 | 110.64 (17) | C4—C18—H18A | 109.5 |
| O2—C7—H7 | 108.5 | C4—C18—H18B | 109.5 |
| C6—C7—H7 | 108.5 | H18A—C18—H18B | 109.5 |
| C8—C7—H7 | 108.5 | C4—C18—H18C | 109.5 |
| C7—C8—C15 | 112.33 (18) | H18A—C18—H18C | 109.5 |
| C7—C8—C14 | 117.52 (17) | H18B—C18—H18C | 109.5 |
| C15—C8—C14 | 100.63 (18) | C4—C19—H19A | 109.5 |
| C7—C8—C9 | 109.23 (17) | C4—C19—H19B | 109.5 |
| C15—C8—C9 | 103.89 (16) | H19A—C19—H19B | 109.5 |
| C14—C8—C9 | 112.18 (17) | C4—C19—H19C | 109.5 |
| C11—C9—C10 | 114.28 (19) | H19A—C19—H19C | 109.5 |
| C11—C9—C8 | 110.87 (18) | H19B—C19—H19C | 109.5 |
| C10—C9—C8 | 116.61 (17) | C10—C20—H20A | 109.5 |
| C11—C9—H9 | 104.5 | C10—C20—H20B | 109.5 |
| C10—C9—H9 | 104.5 | H20A—C20—H20B | 109.5 |
| C8—C9—H9 | 104.5 | C10—C20—H20C | 109.5 |
| C20—C10—C5 | 112.43 (19) | H20A—C20—H20C | 109.5 |
| C20—C10—C1 | 107.4 (2) | H20B—C20—H20C | 109.5 |
| C10—C1—C2—C3 | −28.6 (4) | C2—C1—C10—C5 | −28.6 (3) |
| C1—C2—C3—O1 | −120.8 (3) | C2—C1—C10—C9 | −145.1 (3) |
| C1—C2—C3—C4 | 60.8 (4) | C11—C9—C10—C20 | 52.7 (3) |
| O1—C3—C4—C19 | 28.0 (4) | C8—C9—C10—C20 | −78.8 (2) |
| C2—C3—C4—C19 | −153.5 (3) | C11—C9—C10—C5 | 178.57 (19) |
| O1—C3—C4—C18 | −88.5 (4) | C8—C9—C10—C5 | 47.0 (3) |
| C2—C3—C4—C18 | 89.9 (3) | C11—C9—C10—C1 | −65.3 (3) |
| O1—C3—C4—C5 | 154.5 (3) | C8—C9—C10—C1 | 163.1 (2) |
| C2—C3—C4—C5 | −27.1 (3) | C10—C9—C11—C12 | −97.4 (3) |
| C3—C4—C5—C6 | −164.4 (2) | C8—C9—C11—C12 | 36.9 (3) |
| C19—C4—C5—C6 | −40.7 (3) | C9—C11—C12—C13 | −43.5 (3) |
| C18—C4—C5—C6 | 80.8 (3) | C11—C12—C13—C16 | −49.4 (3) |
| C3—C4—C5—C10 | −34.1 (3) | C11—C12—C13—C14 | 62.6 (3) |
| C19—C4—C5—C10 | 89.7 (3) | C16—C13—C14—O4 | −72.6 (2) |
| C18—C4—C5—C10 | −148.8 (2) | C12—C13—C14—O4 | 169.6 (2) |
| C10—C5—C6—C7 | 61.0 (2) | C16—C13—C14—C8 | 45.2 (2) |
| C4—C5—C6—C7 | −167.78 (19) | C12—C13—C14—C8 | −72.7 (2) |
| C5—C6—C7—O2 | 173.36 (18) | C7—C8—C14—O4 | −49.4 (3) |
| C5—C6—C7—C8 | −63.0 (2) | C15—C8—C14—O4 | 72.9 (2) |
| O2—C7—C8—C15 | −68.3 (2) | C9—C8—C14—O4 | −177.24 (17) |
| C6—C7—C8—C15 | 170.46 (18) | C7—C8—C14—C13 | −164.03 (19) |
| O2—C7—C8—C14 | 47.7 (3) | C15—C8—C14—C13 | −41.8 (2) |
| C6—C7—C8—C14 | −73.5 (2) | C9—C8—C14—C13 | 68.1 (2) |
| O2—C7—C8—C9 | 176.95 (18) | C7—C8—C15—O3 | −33.0 (3) |
| C6—C7—C8—C9 | 55.7 (2) | C14—C8—C15—O3 | −158.9 (2) |
| C7—C8—C9—C11 | 176.91 (19) | C9—C8—C15—O3 | 84.9 (3) |

| | | | |
|---|---|---|---|
| C15—C8—C9—C11 | 56.9 (2) | C7—C8—C15—C16 | 149.7 (2) |
| C14—C8—C9—C11 | −51.0 (2) | C14—C8—C15—C16 | 23.9 (2) |
| C7—C8—C9—C10 | −50.0 (2) | C9—C8—C15—C16 | −92.3 (2) |
| C15—C8—C9—C10 | −170.04 (19) | O3—C15—C16—C17 | −8.3 (5) |
| C14—C8—C9—C10 | 82.1 (2) | C8—C15—C16—C17 | 168.9 (3) |
| C6—C5—C10—C20 | 75.4 (2) | O3—C15—C16—C13 | −173.6 (2) |
| C4—C5—C10—C20 | −55.5 (3) | C8—C15—C16—C13 | 3.6 (3) |
| C6—C5—C10—C1 | −166.4 (2) | C12—C13—C16—C17 | −78.6 (4) |
| C4—C5—C10—C1 | 62.8 (3) | C14—C13—C16—C17 | 166.1 (3) |
| C6—C5—C10—C9 | −51.1 (3) | C12—C13—C16—C15 | 85.3 (3) |
| C4—C5—C10—C9 | 177.98 (19) | C14—C13—C16—C15 | −30.0 (3) |
| C2—C1—C10—C20 | 92.8 (3) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2O···O4$^{i}$ | 0.94 (3) | 1.83 (3) | 2.765 (3) | 171 (3) |
| O4—H4O···O2 | 0.84 (4) | 1.85 (4) | 2.641 (3) | 156 (4) |

Symmetry codes: (i) *x*−1/2, −*y*+1/2, −*z*+1.

**Fig. 1**

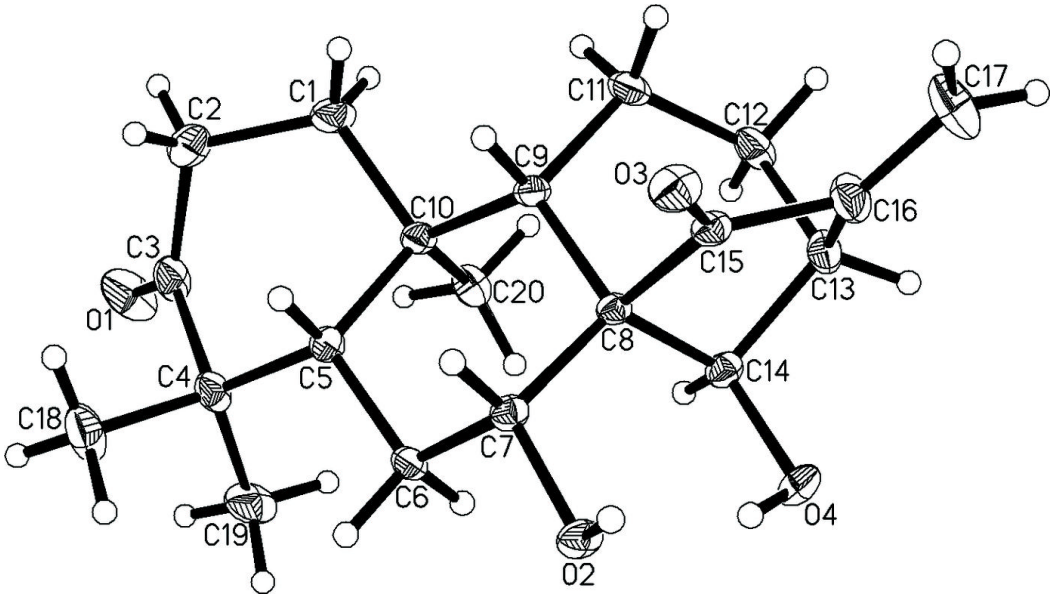
C1
C2
C3
O1
C4
C5
C6
C7
C8
C9
C10
C11
C12
C13
C14
C15
C16
C17
C18
C19
C20
O2
O3
O4

**Fig. 2**