# Crystal structure of a photobiologically active brominated angular pyranocoumarin: bromo-hydroxy-seselin

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The title compound, $C_{14}H_{13}BrO_3$ [systematic name: rac-(9S,10R)-9-bromo-10-hydroxy-8,8-dimethyl-9,10-dihydro-2H,8H-pyrano[2,3-f]chromen-2-one], is a substituted pyranocoumarin, obtained by bromination of seselin [8,8-dimethyl-2H,8H-pyrano[2,3-f]chromen-2-one], which was isolated from the Indian herb Trachyspermum stictocarpum (Aajmod). The pyrano ring has a distorted half-chair conformation and its mean plane is inclined to the coumarin mean plane by 1.6 (2)°. In the crystal, molecules are linked by pairs of O—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(16)$ ring motif. The dimers stack along the a-axis direction and are linked by offset $\pi$–$\pi$ interactions, forming columns [intercentroid distance = 3.514 (4) Å].

## 1. Chemical context

The title compound, rac-(9S,10R)-9-bromo-10-hydroxy-8,8-dimethyl-9,10-dihydro-2H,8H-pyrano[2,3-f]chromen-2-one, is a substituted product of the angular pyranocoumarin seselin, with a bromine atom and a hydroxy group at the asymmetric carbon atoms C3 and C4 in the pyrano ring (see Fig. 1). This class of pyranocoumarins have absorption bands in the near UV region due to the presence of an extended conjugated enone system and exhibit photomutagenic (Appendino et al., 2004) and photocarcinogenic properties, binding with purin bases of DNA in living cells to yield photoadducts (Filomena et al., 2009). Based on this property, these compounds are employed to treat numerous inflammatory skin diseases such as atopic dermatitis and pigment disorders such as vitiligo and psoriasis on exposure to ultraviolet (UV) radiation in photodynamic therapy (PDT). As a result of their strong ability to absorb UV radiation, this class of molecules are also utilized as photoprotective agents to prevent the absorption of harmful UV radiation by the skin in the form of a variety of sun-screening lotions, widely used in dermatological applications in the cosmetic and pharmaceutical industries (Chen et al., 2007, 2009). In addition, in vitro antiproliferative activity and in vivo phototoxicity of the parent molecule has been reported against numerous cancer cell lines, including HL60, A431 (Conconi et al., 1998). These classes of coumarins have been used successfully in combination with ultraviolet irradiation to treat psoriasis and vitiligo and have been found to inhibit proliferation in human hepatocellular carcinoma cell lines (March et al., 1993). Experimental results revealed that their phototoxicity is exerted via Diels–Alder reactions,
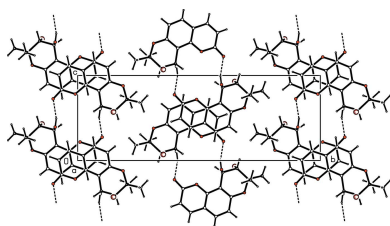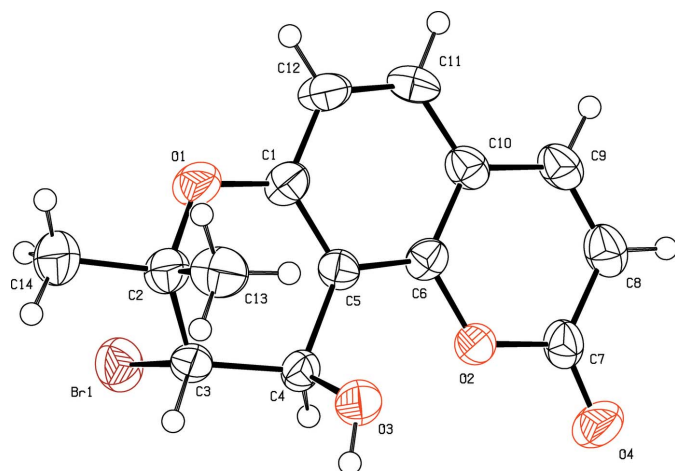
binding to the double bond of a purin base of DNA in living cells with double bonds of the coumarin, to yield mono- and di-adducts (Conforti *et al.*, 2009). Recently, this type of molecule has been combined with a porphyrin to obtain a scaffold-type macromolecule and employed to study of its interaction (host–guest interaction) with fullerenes, such as $C_{60}$ and $C_{70}$ in supramolecular chemistry (Banerjee *et al.*, 2014; Ghosh *et al.*, 2014). The molecular tweezers containing a coumarin moiety showed better quantum yield and fluorescence absorption due to the presence of the extended conjugated enone of pyranocoumarin. As part of our studies in this area, we now describe the synthesis and structure of the title compound.
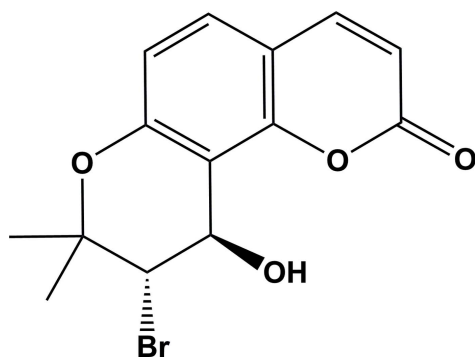


## 2. Structural commentary

The title compound, Fig. 1, belongs to a class of naturally occurring pyranocoumarins, known as psoralenes. It is an angular isomer of the substituted pyranocoumarin seselin [8,8-dimethyl-2*H*,8*H*-pyrano[2,3-*f*]chromen-2-one], whose crystal structure has been reported (Kato, 1970; Bauri *et al.*, 2006). It is composed of three different ring systems, *viz.* benzene, pyrone and pyrano, with $(CH_3)_2$, Br and OH substituents located at the C2, C3 and C4 positions, respectively, see Fig. 1. The C5—C6—C10—C9 and O2—C6—C10—C11 torsion

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

| D—H···A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|
| O3—H3O···O4$^i$ | 0.81 (2) | 1.95 (3) | 2.734 (7) | 162 (8) |

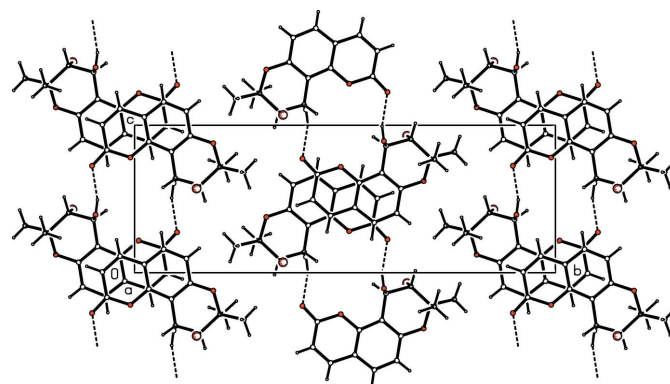Symmetry code: (i) $-x, -y, -z + 1$.

angles are almost the same, *viz.* 178.6 (6) and 178.3 (5)°, respectively, indicating that these rings are almost coplanar. The pyrano ring (O1/C1–C5) has a distorted half-chair conformation [puckering parameters: amplitude $(Q)$ = 0.443 (7) Å, $\theta = 132.7$ (9)°, $\varphi = 91.7$ (11)°], probably due to ring flexibility and the presence of the substituents. Its mean plane is inclined to the mean plane of the coumarin ring by 1.6 (2)°. There are two asymmetric centres at positions C3 and C4 in the molecule (Fig. 1). The present study of the title racemic compound revealed that the relative configuration of atoms C3 and C4 to be *S* and *R*, respectively.

## 3. Supramolecular features

In the crystal, molecules are linked by pairs of O—H···O hydrogen bonds, forming inversion dimers with an $R_2^2(16)$ ring motif (Table 1 and Fig. 2). The dimers stack along the *a*-axis direction and are linked by offset $\pi$–$\pi$ interactions, forming columns [$Cg2\cdots Cg2(-x + 1, -y, -z + 2)$ = 3.514 (4) Å, interplanar distance = 3.422 (3) Å, slippage = 0.798 Å; $Cg2$ is the centroid of the O2/C6–C10 ring].

## 4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.38, last update November 2016; Groom *et al.*, 2016) gave more than 25 hits for the pyranocoumarin structure. They include two reports of the crystal structure of seselin [CSD refcodes AMYROL (Kato, 1970) and AMYROL01 (Bauri *et al.*, 2006)], and a number of structures with various substi-

**Figure 1**
The molecular structure of the title compound, with the atom labelling and displacement ellipsoids drawn at the 50% probability level



**Figure 2**
A view along the *a* axis of the crystal packing of the title compound, with hydrogen bonds shown as dashed lines (see Table 1).

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{14}H_{13}BrO_4$ |
| $M_r$ | 325.15 |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Temperature (K) | 299 |
| $a, b, c$ (Å) | 6.9573 (6), 23.465 (2), 8.3435 (7) |
| $\beta$ (°) | 100.79 (1) |
| $V$ (Å³) | 1338.0 (2) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 3.08 |
| Crystal size (mm) | $0.44 \times 0.20 \times 0.16$ |
| | |
| Data collection | |
| Diffractometer | Oxford Diffraction Xcalibur Sapphire CCD detector |
| Absorption correction | Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009) |
| $T_{min}, T_{max}$ | 0.344, 0.639 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 4521, 2392, 2063 |
| $R_{int}$ | 0.022 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.602 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.063, 0.202, 1.12 |
| No. of reflections | 2392 |
| No. of parameters | 175 |
| No. of restraints | 1 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}, \Delta\rho_{min}$ (e Å$^{-3}$) | 1.25, −1.02 |

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

tuents at the C3 and C4 atoms; many of which are natural products.

## 5. Synthesis and crystallization

The compound seselin was isolated as a colourless crystalline solid from the methanol extract of *T. stictocarpum* (in local dialect known as *Aajmod*) by means of column chromatography over $SiO_2$ gel, by gradient elution with a mixture of a binary solvent system of hexane and ethyl acetate. It was purified by reverse-phase high-pressure liquid chromatography followed by crystallization to yield a colourless solid. This compound was then brominated using NBS in aqueous tetrahydrofuran (THF) in a 1:1 ratio at room temperature with continuous mechanical stirring over a period of 12 h. The reaction was quenched with ice-cold water and extracted with diethyl ether to yield the crude product. This was then purified by column chromatography over $SiO_2$ with gradient solvent elution to yield the title compound. Colourless rod-like crystals were obtained after recrystallization three times from ethyl acetate:hexane (1:4) solution at room temperature.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydroxyl H atom was located in a difference Fourier map and refined with $U_{iso}(H) = 1.2U_{eq}(O)$. The C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.93–0.98 Å with $U_{iso}(H) = 1.2U_{eq}(C)$.

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# supporting information

## Crystal structure of a photobiologically active brominated angular pyranocoumarin: bromo-hydroxy-seselin

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**Computing details**

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

**rac-(9*S*,10*R*)-9-Bromo-10-hydroxy-8,8-dimethyl-9,10-dihydro-2*H*,8*H*-pyrano[2,3-*f*]chromen-2-one**

*Crystal data*

| | |
|---|---|
| $C_{14}H_{13}BrO_4$ | $F(000) = 656$ |
| $M_r = 325.15$ | $D_x = 1.614$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: -P 2yn | Cell parameters from 3332 reflections |
| $a = 6.9573$ (6) Å | $\theta = 2.5–27.4°$ |
| $b = 23.465$ (2) Å | $\mu = 3.08$ mm$^{-1}$ |
| $c = 8.3435$ (7) Å | $T = 299$ K |
| $\beta = 100.79$ (1)° | Rod, colourless |
| $V = 1338.0$ (2) Å$^3$ | $0.44 \times 0.20 \times 0.16$ mm |
| $Z = 4$ | |

*Data collection*

| | |
|---|---|
| Oxford Diffraction Xcalibur Sapphire CCD detector diffractometer | 4521 measured reflections |
| | 2392 independent reflections |
| | 2063 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int} = 0.022$ |
| Graphite monochromator | $\theta_{max} = 25.4°$, $\theta_{min} = 2.6°$ |
| Rotation method data acquisition using $\omega$ scans. | $h = -8 \rightarrow 8$ |
| Absorption correction: multi-scan | $k = -20 \rightarrow 28$ |
| (CrysAlis RED; Oxford Diffraction, 2009) | $l = -10 \rightarrow 6$ |
| $T_{min} = 0.344$, $T_{max} = 0.639$ | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.063$ | Secondary atom site location: difference Fourier map |
| $wR(F^2) = 0.202$ | |
| $S = 1.12$ | Hydrogen site location: inferred from neighbouring sites |
| 2392 reflections | |
| 175 parameters | H atoms treated by a mixture of independent and constrained refinement |
| 1 restraint | |

$w = 1/[\sigma^2(F_o^2) + (0.0969P)^2 + 6.1833P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$

$\Delta\rho_{max} = 1.25$ e Å$^{-3}$
$\Delta\rho_{min} = -1.02$ e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2$ &gt; $2\text{sigma}(F^2)$ 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 (Å²)*

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.2945 (9) | 0.1326 (3) | 0.9293 (8) | 0.0385 (14) |
| C2 | 0.2080 (10) | 0.2030 (3) | 0.7183 (8) | 0.0439 (15) |
| C3 | 0.2309 (9) | 0.1564 (3) | 0.5932 (8) | 0.0370 (14) |
| H3 | 0.1538 | 0.1673 | 0.4870 | 0.044* |
| C4 | 0.1631 (8) | 0.0972 (3) | 0.6392 (7) | 0.0337 (13) |
| H4 | 0.2193 | 0.0678 | 0.5787 | 0.040* |
| C5 | 0.2295 (8) | 0.0878 (3) | 0.8222 (7) | 0.0323 (13) |
| C6 | 0.2285 (8) | 0.0340 (3) | 0.8890 (8) | 0.0327 (13) |
| C7 | 0.1645 (9) | −0.0657 (3) | 0.8329 (8) | 0.0392 (15) |
| C8 | 0.2141 (10) | −0.0764 (3) | 1.0051 (9) | 0.0450 (16) |
| H8 | 0.2076 | −0.1135 | 1.0430 | 0.054* |
| C9 | 0.2692 (10) | −0.0345 (3) | 1.1120 (8) | 0.0415 (15) |
| H9 | 0.3007 | −0.0427 | 1.2229 | 0.050* |
| C10 | 0.2804 (9) | 0.0233 (3) | 1.0572 (8) | 0.0367 (14) |
| C11 | 0.3418 (10) | 0.0693 (3) | 1.1591 (8) | 0.0425 (15) |
| H11 | 0.3787 | 0.0635 | 1.2709 | 0.051* |
| C12 | 0.3486 (11) | 0.1233 (3) | 1.0959 (8) | 0.0462 (16) |
| H12 | 0.3897 | 0.1537 | 1.1653 | 0.055* |
| C13 | −0.0073 (12) | 0.2122 (3) | 0.7295 (10) | 0.0554 (19) |
| H13A | −0.0167 | 0.2418 | 0.8069 | 0.066* |
| H13B | −0.0602 | 0.1775 | 0.7641 | 0.066* |
| H13C | −0.0797 | 0.2230 | 0.6244 | 0.066* |
| C14 | 0.2986 (14) | 0.2596 (3) | 0.6815 (11) | 0.062 (2) |
| H14A | 0.4356 | 0.2543 | 0.6823 | 0.075* |
| H14B | 0.2819 | 0.2871 | 0.7629 | 0.075* |
| H14C | 0.2353 | 0.2730 | 0.5760 | 0.075* |
| O1 | 0.3137 (7) | 0.18705 (19) | 0.8778 (6) | 0.0473 (12) |
| O2 | 0.1716 (6) | −0.01003 (17) | 0.7824 (5) | 0.0366 (10) |
| O3 | −0.0446 (7) | 0.0926 (2) | 0.6070 (6) | 0.0455 (11) |
| H3O | −0.078 (11) | 0.089 (4) | 0.510 (3) | 0.055* |
| O4 | 0.1163 (8) | −0.1010 (2) | 0.7257 (6) | 0.0562 (14) |

| Br1 | 0.50492 (10) | 0.14733 (3) | 0.57070 (9) | 0.0528 (3) |

**Atomic displacement parameters (Å²)**

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.038 (3) | 0.034 (3) | 0.041 (4) | −0.001 (3) | 0.000 (3) | −0.002 (3) |
| C2 | 0.057 (4) | 0.031 (3) | 0.041 (4) | −0.001 (3) | 0.000 (3) | 0.003 (3) |
| C3 | 0.039 (3) | 0.038 (3) | 0.028 (3) | −0.005 (2) | −0.009 (2) | 0.008 (3) |
| C4 | 0.033 (3) | 0.032 (3) | 0.034 (3) | −0.005 (2) | 0.000 (2) | 0.003 (3) |
| C5 | 0.030 (3) | 0.034 (3) | 0.030 (3) | 0.001 (2) | −0.001 (2) | 0.006 (3) |
| C6 | 0.028 (3) | 0.032 (3) | 0.036 (3) | 0.002 (2) | −0.001 (2) | 0.001 (3) |
| C7 | 0.038 (3) | 0.035 (3) | 0.043 (4) | −0.001 (3) | 0.004 (3) | 0.011 (3) |
| C8 | 0.044 (4) | 0.044 (4) | 0.047 (4) | 0.002 (3) | 0.008 (3) | 0.015 (3) |
| C9 | 0.044 (4) | 0.045 (4) | 0.034 (3) | 0.004 (3) | 0.004 (3) | 0.012 (3) |
| C10 | 0.034 (3) | 0.043 (4) | 0.032 (3) | 0.003 (3) | 0.003 (2) | 0.007 (3) |
| C11 | 0.048 (4) | 0.053 (4) | 0.024 (3) | 0.006 (3) | 0.000 (3) | 0.001 (3) |
| C12 | 0.055 (4) | 0.045 (4) | 0.034 (4) | −0.001 (3) | −0.003 (3) | −0.010 (3) |
| C13 | 0.068 (5) | 0.046 (4) | 0.051 (4) | 0.013 (4) | 0.007 (4) | 0.000 (3) |
| C14 | 0.087 (6) | 0.041 (4) | 0.056 (5) | −0.013 (4) | 0.006 (4) | 0.008 (4) |
| O1 | 0.063 (3) | 0.033 (2) | 0.041 (3) | −0.003 (2) | −0.005 (2) | 0.000 (2) |
| O2 | 0.043 (2) | 0.031 (2) | 0.032 (2) | −0.0022 (18) | −0.0017 (18) | 0.0054 (18) |
| O3 | 0.040 (2) | 0.052 (3) | 0.040 (3) | −0.008 (2) | −0.005 (2) | 0.006 (2) |
| O4 | 0.079 (4) | 0.033 (2) | 0.048 (3) | −0.008 (2) | −0.011 (3) | 0.000 (2) |
| Br1 | 0.0432 (4) | 0.0606 (5) | 0.0542 (5) | −0.0072 (3) | 0.0085 (3) | 0.0069 (4) |

**Geometric parameters (Å, º)**

| | | | |
|---|---|---|---|
| C1—O1 | 1.362 (8) | C7—O2 | 1.376 (7) |
| C1—C12 | 1.388 (10) | C7—C8 | 1.435 (10) |
| C1—C5 | 1.399 (9) | C8—C9 | 1.336 (10) |
| C2—O1 | 1.444 (8) | C8—H8 | 0.9300 |
| C2—C14 | 1.526 (9) | C9—C10 | 1.438 (9) |
| C2—C13 | 1.533 (11) | C9—H9 | 0.9300 |
| C2—C3 | 1.540 (9) | C10—C11 | 1.391 (9) |
| C3—C4 | 1.538 (8) | C11—C12 | 1.375 (10) |
| C3—Br1 | 1.962 (7) | C11—H11 | 0.9300 |
| C3—H3 | 0.9800 | C12—H12 | 0.9300 |
| C4—O3 | 1.424 (7) | C13—H13A | 0.9600 |
| C4—C5 | 1.526 (8) | C13—H13B | 0.9600 |
| C4—H4 | 0.9800 | C13—H13C | 0.9600 |
| C5—C6 | 1.381 (8) | C14—H14A | 0.9600 |
| C6—O2 | 1.372 (7) | C14—H14B | 0.9600 |
| C6—C10 | 1.404 (9) | C14—H14C | 0.9600 |
| C7—O4 | 1.220 (8) | O3—H3O | 0.81 (2) |
| | | | |
| O1—C1—C12 | 116.1 (6) | C9—C8—C7 | 121.6 (6) |
| O1—C1—C5 | 122.9 (6) | C9—C8—H8 | 119.2 |
| C12—C1—C5 | 121.0 (6) | C7—C8—H8 | 119.2 |

| | | | |
|---|---|---|---|
| O1—C2—C14 | 104.7 (6) | C8—C9—C10 | 120.6 (6) |
| O1—C2—C13 | 108.3 (6) | C8—C9—H9 | 119.7 |
| C14—C2—C13 | 109.6 (6) | C10—C9—H9 | 119.7 |
| O1—C2—C3 | 109.9 (5) | C11—C10—C6 | 117.7 (6) |
| C14—C2—C3 | 112.5 (6) | C11—C10—C9 | 124.5 (6) |
| C13—C2—C3 | 111.5 (6) | C6—C10—C9 | 117.8 (6) |
| C4—C3—C2 | 113.3 (5) | C12—C11—C10 | 120.5 (6) |
| C4—C3—Br1 | 105.9 (4) | C12—C11—H11 | 119.7 |
| C2—C3—Br1 | 111.6 (4) | C10—C11—H11 | 119.7 |
| C4—C3—H3 | 108.6 | C11—C12—C1 | 120.5 (6) |
| C2—C3—H3 | 108.6 | C11—C12—H12 | 119.7 |
| Br1—C3—H3 | 108.6 | C1—C12—H12 | 119.7 |
| O3—C4—C5 | 106.5 (5) | C2—C13—H13A | 109.5 |
| O3—C4—C3 | 111.7 (5) | C2—C13—H13B | 109.5 |
| C5—C4—C3 | 109.4 (5) | H13A—C13—H13B | 109.5 |
| O3—C4—H4 | 109.7 | C2—C13—H13C | 109.5 |
| C5—C4—H4 | 109.7 | H13A—C13—H13C | 109.5 |
| C3—C4—H4 | 109.7 | H13B—C13—H13C | 109.5 |
| C6—C5—C1 | 117.1 (5) | C2—C14—H14A | 109.5 |
| C6—C5—C4 | 120.9 (5) | C2—C14—H14B | 109.5 |
| C1—C5—C4 | 122.0 (5) | H14A—C14—H14B | 109.5 |
| O2—C6—C5 | 116.7 (5) | C2—C14—H14C | 109.5 |
| O2—C6—C10 | 120.2 (5) | H14A—C14—H14C | 109.5 |
| C5—C6—C10 | 123.1 (6) | H14B—C14—H14C | 109.5 |
| O4—C7—O2 | 116.1 (6) | C1—O1—C2 | 118.1 (5) |
| O4—C7—C8 | 126.6 (6) | C6—O2—C7 | 122.5 (5) |
| O2—C7—C8 | 117.3 (6) | C4—O3—H3O | 107 (6) |
| | | | |
| O1—C2—C3—C4 | 56.8 (7) | O2—C7—C8—C9 | −1.5 (10) |
| C14—C2—C3—C4 | 173.0 (6) | C7—C8—C9—C10 | 0.1 (10) |
| C13—C2—C3—C4 | −63.4 (7) | O2—C6—C10—C11 | 178.3 (5) |
| O1—C2—C3—Br1 | −62.7 (6) | C5—C6—C10—C11 | −2.3 (9) |
| C14—C2—C3—Br1 | 53.5 (7) | O2—C6—C10—C9 | −0.7 (9) |
| C13—C2—C3—Br1 | 177.1 (5) | C5—C6—C10—C9 | 178.6 (6) |
| C2—C3—C4—O3 | 76.8 (6) | C8—C9—C10—C11 | −178.0 (7) |
| Br1—C3—C4—O3 | −160.5 (4) | C8—C9—C10—C6 | 1.0 (9) |
| C2—C3—C4—C5 | −40.8 (7) | C6—C10—C11—C12 | 0.8 (10) |
| Br1—C3—C4—C5 | 81.9 (5) | C9—C10—C11—C12 | 179.8 (7) |
| O1—C1—C5—C6 | 176.0 (6) | C10—C11—C12—C1 | −0.1 (11) |
| C12—C1—C5—C6 | −2.3 (9) | O1—C1—C12—C11 | −177.4 (6) |
| O1—C1—C5—C4 | −3.7 (9) | C5—C1—C12—C11 | 0.9 (11) |
| C12—C1—C5—C4 | 178.1 (6) | C12—C1—O1—C2 | −161.8 (6) |
| O3—C4—C5—C6 | 74.4 (7) | C5—C1—O1—C2 | 19.9 (9) |
| C3—C4—C5—C6 | −164.7 (5) | C14—C2—O1—C1 | −166.3 (6) |
| O3—C4—C5—C1 | −105.9 (6) | C13—C2—O1—C1 | 76.9 (7) |
| C3—C4—C5—C1 | 14.9 (8) | C3—C2—O1—C1 | −45.2 (8) |
| C1—C5—C6—O2 | −177.6 (5) | C5—C6—O2—C7 | 179.9 (5) |
| C4—C5—C6—O2 | 2.1 (8) | C10—C6—O2—C7 | −0.7 (8) |

| | | | |
|---|---|---|---|
| C1—C5—C6—C10 | 3.1 (9) | O4—C7—O2—C6 | −178.2 (6) |
| C4—C5—C6—C10 | −177.3 (6) | C8—C7—O2—C6 | 1.8 (8) |
| O4—C7—C8—C9 | 178.5 (7) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H⋯*A* | *D*—H | H⋯*A* | *D*⋯*A* | *D*—H⋯*A* |
|---|---|---|---|---|
| O3—H3*O*⋯O4[i] | 0.81 (2) | 1.95 (3) | 2.734 (7) | 162 (8) |

Symmetry code: (i) −*x*, −*y*, −*z*+1.