# Alpinumisoflavone

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The title compound, $C_{20}H_{16}O_5$, {systematic name: 5-hydroxy-7-(4-hydroxyphenyl)-2,2-dimethyl-2$H$,6$H$-benzo[1,2-$b$:5,4-$b'$]-dipyran-6-one}, was obtained by demethylation of the biologically active related compound, 4-$O$-methylalpinumiso-flavone. The molecular structure of the title compound is characterized by a fused tricyclic system that contains an approximately planar benzopyrone ring fragment. The six membered pyran ring adopts a half-chair conformation. Both ring systems show an out-of-plane twist. The dihedral angle between the mean plane of the benzopyrone system and the benzene ring is 54.29 (3)°. The molecules are linked by O—H···O hydrogen bonds, forming a molecular tape running along the $b$ axis.

## Related literature

For related compounds, see: Kingsford-Adaboh et al. (2001, 2006). For ring puckering analysis, see: Cremer & Pople (1975).
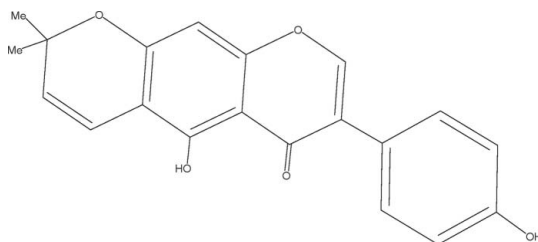


## Experimental

### Crystal data

| | |
|---|---|
| $C_{20}H_{16}O_5$ | $V = 1603.13\ (7)$ Å$^3$ |
| $M_r = 336.34$ | $Z = 4$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 13.8333\ (3)$ Å | $\mu = 0.10$ mm$^{-1}$ |
| $b = 5.92699\ (17)$ Å | $T = 93\ (2)$ K |
| $c = 19.8352\ (4)$ Å | $0.53 \times 0.45 \times 0.43$ mm |
| $\beta = 99.6806\ (7)°$ | |

### Data collection

| | |
|---|---|
| Rigaku R-AXIS RAPIDII diffractometer | 30574 measured reflections |
| Absorption correction: multi-scan (ABSCOR; Higashi, 1995) | 4676 independent reflections |
| | 4296 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.771$, $T_{max} = 0.958$ | $R_{int} = 0.036$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.123$ | |
| $S = 1.04$ | $\Delta\rho_{max} = 0.51$ e Å$^{-3}$ |
| 4676 reflections | $\Delta\rho_{min} = -0.26$ e Å$^{-3}$ |
| 237 parameters | |

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2$O$···O3 | 0.92 (2) | 1.76 (2) | 2.6023 (10) | 152.2 (17) |
| O5—H5$O$···O3$^i$ | 0.871 (18) | 1.943 (18) | 2.7823 (10) | 161.4 (17) |

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

Data collection: PROCESS-AUTO (Rigaku/MSC, 2004); cell refinement: PROCESS-AUTO ; data reduction: CrystalStructure (Rigaku/MSC, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: CrystalStructure and PLATON (Spek, 2003).

## References

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# supporting information

## Alpinumisoflavone

**Jerry Joe Ebow Kingsley Harrison, Youhei Tabuchi, Hiroyuki Ishida and Robert Kingsford-Adaboh**

### S1. Comment

The 4-*O*-methylalpinumisoflavone, *O*,*O*-dimethylalpinumisoflavone and 5-*O*-methyl-4-*O*-(3-methylbut-2-en-1-yl)alpinumisoflavone are some of the solvent-extracted compounds from the rootbark and seeds of *Milletia thonningii* whose crystal structures have been studied for obtaining fundamental information on their chemical and biological properties (Kingsford-Adaboh *et al.*, 2001, 2006). These compounds have shown considerable brine shrimp lethality (Kingsford-Adaboh *et al.*, 2006).

In the present work, single crystals of alpinumisoflavone suitable for X-ray diffraction were obtained by demethylation of 4-*O*-methylalpinumisoflavone using cold BCl$_3$. The crystals isolated from the crude extract were usually of poor quality. Therefore we decided to modify 4-*O*-methylalpinumisoflavone chemically by demethylation (Scheme 2) hoping that a new compound would yield crystals of a better quality. This turned to be true. The molecular structure of the title compound differs from 4-*O*-methylalpinumisoflavone only in the replacement of the methoxy group by the hydroxyl on the benzene ring D.

The molecular structure of the title compound is characterized by a tricyclic fused ring system, A/B/C, and a benzene ring D (Fig. 1). The benzopyrone ring fragment, B/C, is planar and it is twisted out of plane with respect to the benzene ring D. The outer six-membered ring A is deformed into a half-chair conformation, with Cremer & Pople (1975) parameters $q_2$, $q_3$ and $\varphi_2$ of 0.2342 (9), -0.1148 (9) Å and 220.4 (2)°, respectively.

The presence of the hydroxyl group proximal to the keto group on the ring C permits the formation of a relatively stronger intramolecular O—H⋯O hydrogen bond (Table 1). This distance is comparable to the intramolecular contact distance equal to 1.724 (17) Å in 4-*O*-methylalpinumisoflavone which is the closest related compound in the studied series (Kingsford-Adaboh *et al.*, 2001, 2006). The corresponding distances observed in other members of the series are longer (*ca* 2.3 Å; Kingsford-Adaboh *et al.*, 2006).

The observed intramolecular contact is affected by the coplanar arrangement between the hydroxyl and the carbonyl groups in the pertinent part of the molecule. This is demonstrated by the observed torsion angle C9—C8—C7—O2 = -1.19 (13)° in the title structure. The largest deviation from the coplanarity in the series is observed in *O*,*O*-dimethyl-alpinumisoflavone with the corresponding angle equal to -12.83 (18)° (Kingsford-Adaboh *et al.*, 2001). The intermolecular O—H⋯O hydrogen bond (Table 1), where the terminal OH group of the benzene ring D serves as a proton donor to the carbonyl oxygen atom, is observed to play an important role in the molecular bonding in the crystal structure (Tab. 1, Fig. 2).

## S2. Experimental

Alpinumisoflavone was obtained from the demethylation of 4-O-methylalpinumisoflavone. Solvent extraction of 4-O-methylalpinumisoflavone from the pulverized root bark of Milletia thonningii followed similar procedure as described in our earlier work (Kingsford-Adaboh et al., 2001). A cold solution of BCl$_3$ in chloroform (-78 °C) was added slowly to about 15 ml of a chloroform solution of 4-O-methylalpinumisoflavone (200 mg, 0.571 mmol) cooled to -78 °C using dry ice and acetone mixture. The solution was stirred for about 10 min under argon atmosphere. 30 ml of water was added slowly and the resulting yellowish mixture was extracted with chloroform three times. The combined extracts were washed with water twice and then dried over anhydrous sodium sulphate. After evaporation of the solvent under vacuum, the residue was chromatographed on a silica gel using petroleum ether and ethylacetate mixture in the ratio of between 8/1 and 5/1 as the mobile phase. The product was recrystallized from acetonitrile. The demethylation yield (159.6 mg about 80%, m.p. 486 K). The product was confirmed by $^{13}$C NMR spectra of both the reactants and the product.)

## S3. Refinement

All the H atoms were located in the difference Fourier map. The H atoms that have been attached to the C atoms were constrained in idealized geometry while the hydroxyl H atoms were freely isotropically refined. C$_{methyl}$—H= 0.98 Å allowing for rotation around the C—C bond with $U_{iso}(H_{methyl}) = 1.5U_{eq}(C_{methyl})$. C$_{aryl}$—H = 0.95 Å with $U_{iso}(H_{aryl}) = 1.2U_{eq}(C_{aryl})$.
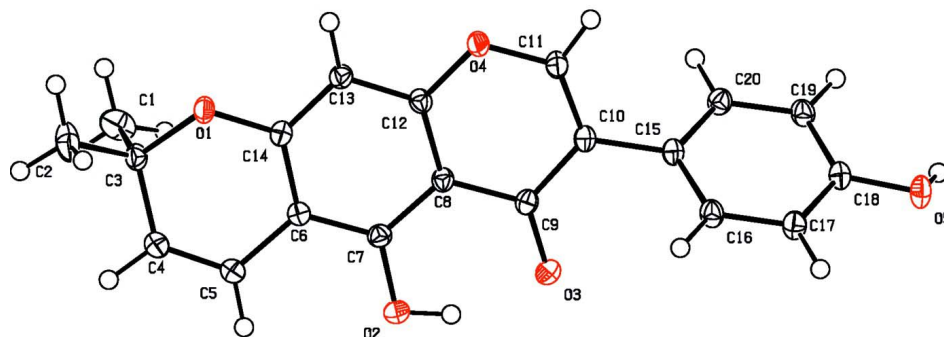


**Figure 1**

The molecular structure of the title compound. The displacement ellipsoids are drawn at the 50% probability level.
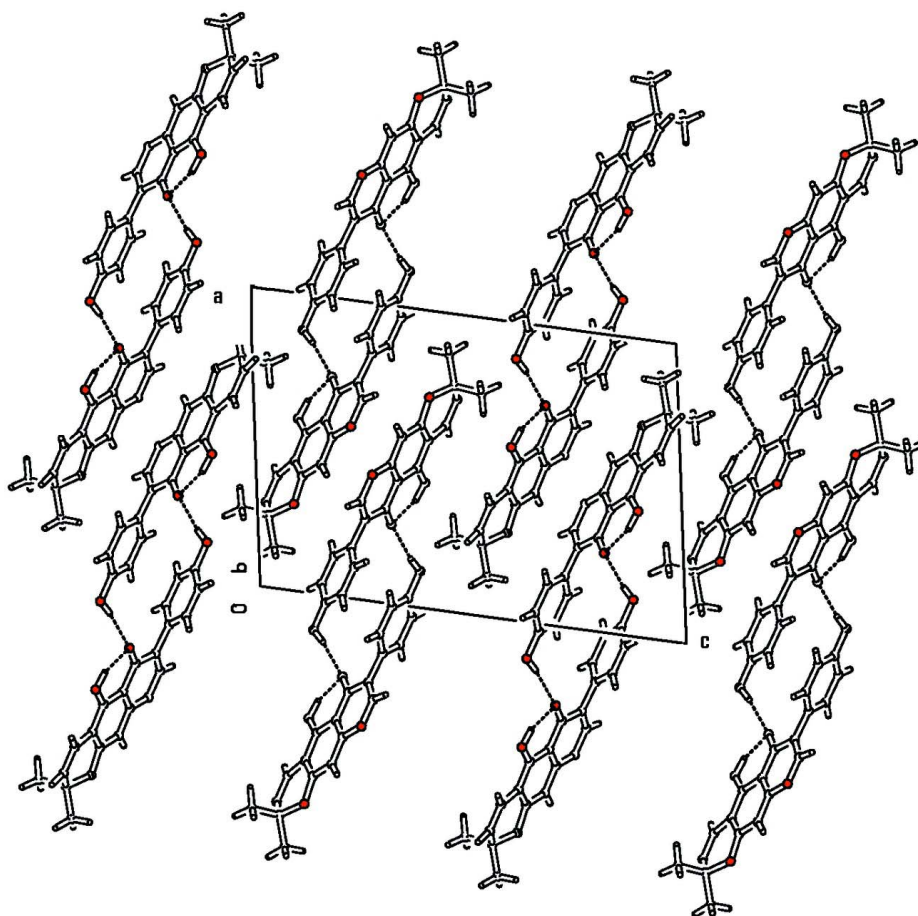
**Figure 2**

Crystal packing viewed on the *a-c* plane. Hydrogen bonds are shown as broken lines.

**5-hydroxy-7-(4-hydroxyphenyl)-2,2- dimethyl-2*H*,6*H*-benzo[1,2 - *b*:5,4 - *b′*]dipyran-6-one**

*Crystal data*

| | |
|---|---|
| $C_{20}H_{16}O_5$ | $F(000) = 704.00$ |
| $M_r = 336.34$ | $D_x = 1.393$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Melting point: 486 K |
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å |
| $a = 13.8333$ (3) Å | Cell parameters from 27371 reflections |
| $b = 5.92699$ (17) Å | $\theta = 3.0–30.0°$ |
| $c = 19.8352$ (4) Å | $\mu = 0.10$ mm$^{-1}$ |
| $\beta = 99.6806$ (7)° | $T = 93$ K |
| $V = 1603.13$ (7) Å$^3$ | Block, yellow |
| $Z = 4$ | $0.53 \times 0.45 \times 0.43$ mm |

*Data collection*

| | |
|---|---|
| Rigaku R-AXIS RAPIDII diffractometer | 4676 independent reflections |
| Detector resolution: 10.00 pixels mm$^{-1}$ | 4296 reflections with $I > 2\sigma(I)$ |
| $\omega$ scans | $R_{int} = 0.036$ |
| Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995) | $\theta_{max} = 30.0°$, $\theta_{min} = 3.3°$ |
| | $h = -19 \rightarrow 17$ |
| $T_{min} = 0.771$, $T_{max} = 0.958$ | $k = -8 \rightarrow 8$ |
| 30574 measured reflections | $l = -27 \rightarrow 27$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | Hydrogen site location: difference Fourier map |
| $wR(F^2) = 0.123$ | H atoms treated by a mixture of independent and constrained refinement |
| $S = 1.04$ | |
| 4676 reflections | $w = 1/[\sigma^2(F_o^2) + (0.0785P)^2 + 0.3851P]$ |
| 237 parameters | where $P = (F_o^2 + 2F_c^2)/3$ |
| 0 restraints | $(\Delta/\sigma)_{max} < 0.001$ |
| 54 constraints | $\Delta\rho_{max} = 0.51$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{min} = -0.26$ e Å$^{-3}$ |
| | Extinction correction: *SHELXL*, Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2$\theta$)]$^{-1/4}$ |
| | Extinction coefficient: 0.015 (2) |

*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 $F^2 > \sigma(F^2)$ 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. Although there were present diffractions that violated the space-group-systematic absences the average $I/\sigma$ values for *h*0*l* with l = 2n and for l =2n+1 were 25.6 and 0.8, respectively. This indicates presence of the *c* glide plane. Thus we selected $P2_1/c$. We have also refined the structure with $P2_1$. All atoms except H completely fit to the *c* and *i* symmetries. The reflections that should be absent for $P2_1/c$ might be accidentally observed. Probably some of them were diffractions from small ice particles (frost) generated in the X-ray beam path.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.70895 (5) | 0.49566 (11) | 0.41410 (3) | 0.01881 (15) |
| O2 | 0.42098 (5) | 0.04434 (11) | 0.39657 (4) | 0.02165 (16) |
| O3 | 0.26668 (5) | 0.18561 (11) | 0.31384 (3) | 0.02019 (15) |
| O4 | 0.42341 (4) | 0.74216 (11) | 0.27339 (3) | 0.01861 (15) |
| O5 | −0.12257 (5) | 0.49357 (12) | 0.12202 (4) | 0.02212 (16) |
| C1 | 0.74810 (9) | 0.50860 (18) | 0.53739 (5) | 0.0300 (2) |
| H1A | 0.7776 | 0.6578 | 0.5344 | 0.045* |
| H1B | 0.7814 | 0.4307 | 0.5784 | 0.045* |
| H1C | 0.6784 | 0.5257 | 0.5401 | 0.045* |
| C2 | 0.86499 (7) | 0.3562 (2) | 0.46408 (6) | 0.0312 (2) |

| H2A | 0.8685 | 0.2740 | 0.4217 | 0.047* |
| H2B | 0.9035 | 0.2764 | 0.5028 | 0.047* |
| H2C | 0.8915 | 0.5086 | 0.4611 | 0.047* |
| C3 | 0.75883 (6) | 0.37155 (15) | 0.47438 (4) | 0.01759 (17) |
| C4 | 0.71488 (7) | 0.14234 (16) | 0.47920 (5) | 0.0231 (2) |
| H4 | 0.7539 | 0.0268 | 0.5033 | 0.028* |
| C5 | 0.62256 (7) | 0.09525 (16) | 0.45064 (5) | 0.02201 (19) |
| H5 | 0.5948 | −0.0474 | 0.4580 | 0.026* |
| C6 | 0.56482 (6) | 0.26353 (14) | 0.40815 (4) | 0.01600 (17) |
| C7 | 0.46669 (6) | 0.23138 (14) | 0.37950 (4) | 0.01593 (17) |
| C8 | 0.41581 (6) | 0.38972 (14) | 0.33266 (4) | 0.01501 (16) |
| C9 | 0.31511 (6) | 0.35590 (14) | 0.30076 (4) | 0.01544 (16) |
| C10 | 0.27298 (6) | 0.53058 (15) | 0.25305 (4) | 0.01599 (16) |
| C11 | 0.32922 (6) | 0.71046 (16) | 0.24342 (4) | 0.01798 (17) |
| H11 | 0.3000 | 0.8244 | 0.2130 | 0.022* |
| C12 | 0.46784 (6) | 0.58219 (14) | 0.31783 (4) | 0.01550 (17) |
| C13 | 0.56476 (6) | 0.62234 (15) | 0.34640 (4) | 0.01663 (17) |
| H13 | 0.5977 | 0.7550 | 0.3357 | 0.020* |
| C14 | 0.61209 (6) | 0.46139 (15) | 0.39122 (4) | 0.01554 (16) |
| C15 | 0.16979 (6) | 0.52188 (15) | 0.21756 (4) | 0.01598 (17) |
| C16 | 0.13347 (6) | 0.33720 (15) | 0.17706 (4) | 0.01859 (18) |
| H16 | 0.1757 | 0.2145 | 0.1715 | 0.022* |
| C17 | 0.03611 (7) | 0.33194 (16) | 0.14484 (5) | 0.01923 (18) |
| H17 | 0.0121 | 0.2060 | 0.1174 | 0.023* |
| C18 | −0.02636 (6) | 0.51134 (15) | 0.15274 (4) | 0.01714 (17) |
| C19 | 0.00911 (6) | 0.69858 (15) | 0.19145 (5) | 0.01829 (17) |
| H19 | −0.0328 | 0.8227 | 0.1959 | 0.022* |
| C20 | 0.10686 (6) | 0.70239 (15) | 0.22366 (4) | 0.01783 (17) |
| H20 | 0.1311 | 0.8300 | 0.2502 | 0.021* |
| H2O | 0.3584 (15) | 0.054 (3) | 0.3729 (10) | 0.057 (5)* |
| H5O | −0.1591 (13) | 0.580 (3) | 0.1428 (9) | 0.046 (4)* |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0133 (3) | 0.0231 (3) | 0.0186 (3) | −0.0020 (2) | −0.0014 (2) | 0.0047 (2) |
| O2 | 0.0188 (3) | 0.0184 (3) | 0.0268 (3) | −0.0039 (2) | 0.0009 (3) | 0.0060 (2) |
| O3 | 0.0156 (3) | 0.0197 (3) | 0.0251 (3) | −0.0029 (2) | 0.0029 (2) | 0.0019 (2) |
| O4 | 0.0145 (3) | 0.0206 (3) | 0.0195 (3) | −0.0014 (2) | −0.0006 (2) | 0.0063 (2) |
| O5 | 0.0133 (3) | 0.0288 (4) | 0.0226 (3) | 0.0034 (2) | −0.0018 (2) | −0.0033 (3) |
| C1 | 0.0459 (6) | 0.0234 (5) | 0.0193 (4) | 0.0037 (4) | 0.0018 (4) | −0.0028 (3) |
| C2 | 0.0159 (4) | 0.0492 (7) | 0.0277 (5) | 0.0032 (4) | 0.0010 (4) | 0.0116 (4) |
| C3 | 0.0160 (4) | 0.0206 (4) | 0.0149 (3) | 0.0002 (3) | −0.0010 (3) | 0.0012 (3) |
| C4 | 0.0228 (4) | 0.0178 (4) | 0.0258 (4) | 0.0007 (3) | −0.0043 (4) | 0.0024 (3) |
| C5 | 0.0217 (4) | 0.0165 (4) | 0.0253 (4) | −0.0008 (3) | −0.0031 (3) | 0.0030 (3) |
| C6 | 0.0156 (4) | 0.0158 (4) | 0.0162 (4) | 0.0000 (3) | 0.0013 (3) | 0.0007 (3) |
| C7 | 0.0157 (4) | 0.0154 (4) | 0.0170 (4) | −0.0010 (3) | 0.0035 (3) | 0.0006 (3) |
| C8 | 0.0126 (3) | 0.0173 (4) | 0.0153 (3) | 0.0000 (3) | 0.0027 (3) | 0.0006 (3) |

| C9 | 0.0131 (3) | 0.0179 (4) | 0.0157 (3) | 0.0001 (3) | 0.0036 (3) | −0.0012 (3) |
|----|-----------|-----------|-----------|-----------|-----------|-----------|
| C10 | 0.0129 (3) | 0.0194 (4) | 0.0156 (3) | 0.0011 (3) | 0.0022 (3) | −0.0005 (3) |
| C11 | 0.0139 (4) | 0.0219 (4) | 0.0175 (4) | 0.0009 (3) | 0.0008 (3) | 0.0025 (3) |
| C12 | 0.0149 (4) | 0.0174 (4) | 0.0144 (3) | 0.0008 (3) | 0.0027 (3) | 0.0020 (3) |
| C13 | 0.0147 (4) | 0.0182 (4) | 0.0169 (4) | −0.0017 (3) | 0.0023 (3) | 0.0022 (3) |
| C14 | 0.0135 (3) | 0.0185 (4) | 0.0145 (3) | −0.0008 (3) | 0.0020 (3) | −0.0005 (3) |
| C15 | 0.0126 (3) | 0.0197 (4) | 0.0155 (3) | 0.0014 (3) | 0.0020 (3) | 0.0000 (3) |
| C16 | 0.0158 (4) | 0.0200 (4) | 0.0196 (4) | 0.0036 (3) | 0.0020 (3) | −0.0027 (3) |
| C17 | 0.0167 (4) | 0.0213 (4) | 0.0188 (4) | 0.0019 (3) | 0.0006 (3) | −0.0037 (3) |
| C18 | 0.0135 (4) | 0.0219 (4) | 0.0157 (3) | 0.0018 (3) | 0.0015 (3) | 0.0007 (3) |
| C19 | 0.0154 (4) | 0.0193 (4) | 0.0203 (4) | 0.0035 (3) | 0.0033 (3) | −0.0008 (3) |
| C20 | 0.0153 (4) | 0.0188 (4) | 0.0195 (4) | 0.0007 (3) | 0.0032 (3) | −0.0024 (3) |

*Geometric parameters (Å, º)*

| | | | |
|----|----|----|----|
| O1—C14 | 1.3558 (10) | C6—C7 | 1.3937 (11) |
| O1—C3 | 1.4728 (10) | C6—C14 | 1.4105 (12) |
| O2—C7 | 1.3474 (10) | C7—C8 | 1.4210 (11) |
| O2—H2O | 0.92 (2) | C8—C12 | 1.4062 (11) |
| O3—C9 | 1.2623 (10) | C8—C9 | 1.4438 (11) |
| O4—C11 | 1.3512 (10) | C9—C10 | 1.4565 (12) |
| O4—C12 | 1.3680 (10) | C10—C11 | 1.3522 (12) |
| O5—C18 | 1.3714 (10) | C10—C15 | 1.4824 (11) |
| O5—H5O | 0.871 (18) | C11—H11 | 0.9500 |
| C1—C3 | 1.5186 (13) | C12—C13 | 1.3856 (11) |
| C1—H1A | 0.9800 | C13—C14 | 1.3904 (12) |
| C1—H1B | 0.9800 | C13—H13 | 0.9500 |
| C1—H1C | 0.9800 | C15—C20 | 1.3973 (11) |
| C2—C3 | 1.5190 (13) | C15—C16 | 1.4001 (12) |
| C2—H2A | 0.9800 | C16—C17 | 1.3907 (11) |
| C2—H2B | 0.9800 | C16—H16 | 0.9500 |
| C2—H2C | 0.9800 | C17—C18 | 1.3956 (12) |
| C3—C4 | 1.4980 (13) | C17—H17 | 0.9500 |
| C4—C5 | 1.3366 (12) | C18—C19 | 1.3911 (12) |
| C4—H4 | 0.9500 | C19—C20 | 1.3952 (11) |
| C5—C6 | 1.4549 (12) | C19—H19 | 0.9500 |
| C5—H5 | 0.9500 | C20—H20 | 0.9500 |
| | | | |
| C14—O1—C3 | 119.91 (7) | O3—C9—C8 | 121.81 (8) |
| C7—O2—H2O | 105.4 (12) | O3—C9—C10 | 122.26 (7) |
| C11—O4—C12 | 118.85 (7) | C8—C9—C10 | 115.93 (7) |
| C18—O5—H5O | 110.0 (12) | C11—C10—C9 | 118.38 (8) |
| C3—C1—H1A | 109.5 | C11—C10—C15 | 119.43 (8) |
| C3—C1—H1B | 109.5 | C9—C10—C15 | 122.13 (7) |
| H1A—C1—H1B | 109.5 | O4—C11—C10 | 125.64 (8) |
| C3—C1—H1C | 109.5 | O4—C11—H11 | 117.2 |
| H1A—C1—H1C | 109.5 | C10—C11—H11 | 117.2 |
| H1B—C1—H1C | 109.5 | O4—C12—C13 | 116.33 (7) |

| | | | |
|---|---|---|---|
| C3—C2—H2A | 109.5 | O4—C12—C8 | 120.45 (7) |
| C3—C2—H2B | 109.5 | C13—C12—C8 | 123.22 (8) |
| H2A—C2—H2B | 109.5 | C12—C13—C14 | 117.57 (8) |
| C3—C2—H2C | 109.5 | C12—C13—H13 | 121.2 |
| H2A—C2—H2C | 109.5 | C14—C13—H13 | 121.2 |
| H2B—C2—H2C | 109.5 | O1—C14—C13 | 116.35 (7) |
| O1—C3—C4 | 111.41 (7) | O1—C14—C6 | 121.10 (7) |
| O1—C3—C1 | 107.68 (7) | C13—C14—C6 | 122.37 (8) |
| C4—C3—C1 | 109.62 (8) | C20—C15—C16 | 118.66 (8) |
| O1—C3—C2 | 104.61 (7) | C20—C15—C10 | 119.76 (8) |
| C4—C3—C2 | 111.49 (8) | C16—C15—C10 | 121.57 (7) |
| C1—C3—C2 | 111.90 (9) | C17—C16—C15 | 120.50 (8) |
| C5—C4—C3 | 122.11 (8) | C17—C16—H16 | 119.7 |
| C5—C4—H4 | 118.9 | C15—C16—H16 | 119.7 |
| C3—C4—H4 | 118.9 | C16—C17—C18 | 120.10 (8) |
| C4—C5—C6 | 119.65 (8) | C16—C17—H17 | 120.0 |
| C4—C5—H5 | 120.2 | C18—C17—H17 | 120.0 |
| C6—C5—H5 | 120.2 | O5—C18—C19 | 122.17 (8) |
| C7—C6—C14 | 118.38 (8) | O5—C18—C17 | 117.68 (8) |
| C7—C6—C5 | 123.00 (8) | C19—C18—C17 | 120.14 (8) |
| C14—C6—C5 | 118.46 (8) | C18—C19—C20 | 119.37 (8) |
| O2—C7—C6 | 118.43 (8) | C18—C19—H19 | 120.3 |
| O2—C7—C8 | 120.39 (7) | C20—C19—H19 | 120.3 |
| C6—C7—C8 | 121.18 (8) | C19—C20—C15 | 121.19 (8) |
| C12—C8—C7 | 117.25 (7) | C19—C20—H20 | 119.4 |
| C12—C8—C9 | 120.73 (7) | C15—C20—H20 | 119.4 |
| C7—C8—C9 | 122.02 (8) | | |
| | | | |
| C14—O1—C3—C4 | 31.87 (11) | C11—O4—C12—C8 | −0.83 (12) |
| C14—O1—C3—C1 | −88.36 (10) | C7—C8—C12—O4 | −179.76 (7) |
| C14—O1—C3—C2 | 152.45 (8) | C9—C8—C12—O4 | 0.74 (12) |
| O1—C3—C4—C5 | −24.52 (13) | C7—C8—C12—C13 | 0.13 (13) |
| C1—C3—C4—C5 | 94.56 (11) | C9—C8—C12—C13 | −179.37 (8) |
| C2—C3—C4—C5 | −140.97 (10) | O4—C12—C13—C14 | −179.35 (7) |
| C3—C4—C5—C6 | 5.75 (15) | C8—C12—C13—C14 | 0.76 (13) |
| C4—C5—C6—C7 | −176.66 (9) | C3—O1—C14—C13 | 163.91 (7) |
| C4—C5—C6—C14 | 7.97 (14) | C3—O1—C14—C6 | −20.89 (12) |
| C14—C6—C7—O2 | −178.87 (7) | C12—C13—C14—O1 | 174.83 (7) |
| C5—C6—C7—O2 | 5.75 (13) | C12—C13—C14—C6 | −0.31 (13) |
| C14—C6—C7—C8 | 1.94 (13) | C7—C6—C14—O1 | −175.92 (7) |
| C5—C6—C7—C8 | −173.44 (8) | C5—C6—C14—O1 | −0.33 (12) |
| O2—C7—C8—C12 | 179.31 (7) | C7—C6—C14—C13 | −1.02 (13) |
| C6—C7—C8—C12 | −1.51 (12) | C5—C6—C14—C13 | 174.57 (8) |
| O2—C7—C8—C9 | −1.19 (13) | C11—C10—C15—C20 | −53.12 (12) |
| C6—C7—C8—C9 | 177.98 (7) | C9—C10—C15—C20 | 124.00 (9) |
| C12—C8—C9—O3 | −179.25 (8) | C11—C10—C15—C16 | 126.14 (9) |
| C7—C8—C9—O3 | 1.27 (13) | C9—C10—C15—C16 | −56.74 (12) |
| C12—C8—C9—C10 | 0.40 (12) | C20—C15—C16—C17 | −1.39 (13) |

| | | | |
|---|---|---|---|
| C7—C8—C9—C10 | −179.08 (7) | C10—C15—C16—C17 | 179.35 (8) |
| O3—C9—C10—C11 | 178.22 (8) | C15—C16—C17—C18 | −0.07 (14) |
| C8—C9—C10—C11 | −1.43 (12) | C16—C17—C18—O5 | −177.52 (8) |
| O3—C9—C10—C15 | 1.07 (13) | C16—C17—C18—C19 | 1.62 (14) |
| C8—C9—C10—C15 | −178.58 (7) | O5—C18—C19—C20 | 177.44 (8) |
| C12—O4—C11—C10 | −0.31 (13) | C17—C18—C19—C20 | −1.67 (13) |
| C9—C10—C11—O4 | 1.47 (14) | C18—C19—C20—C15 | 0.18 (13) |
| C15—C10—C11—O4 | 178.70 (8) | C16—C15—C20—C19 | 1.34 (13) |
| C11—O4—C12—C13 | 179.27 (7) | C10—C15—C20—C19 | −179.39 (8) |

*Hydrogen-bond geometry (Å, º)*

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| O2—H2$O$$\cdots$O3 | 0.92 (2) | 1.76 (2) | 2.6023 (10) | 152.2 (17) |
| O5—H5$O$$\cdots$O3[i] | 0.871 (18) | 1.943 (18) | 2.7823 (10) | 161.4 (17) |

Symmetry code: (i) −$x$, $y$+1/2, −$z$+1/2.