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# 16-*O*-Methylcafestol

**Xia-Li Liao,[a] Xiao-Zhen Chen,[a] Kai-Bei Yu[b] and Guo-You Li[a]***

[a]Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, People's Republic of China, and [b]Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, People's Republic of China
Correspondence e-mail: ligy@cib.ac.cn

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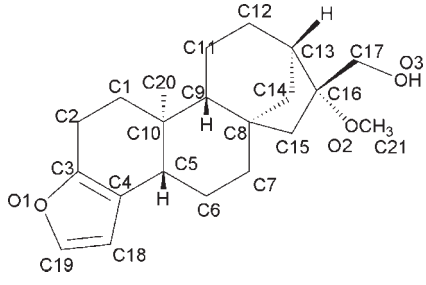
Key indicators: single-crystal X-ray study; $T$ = 93 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.031; $wR$ factor = 0.069; data-to-parameter ratio = 9.5.

The title compound [systematic name: (3b*S*,5a*S*,7*R*,8*R*,10a*R*,-10b*S*)-7-methoxy-10b-methyl-3b,4,5,6,7,8,9,10,10a,10b,11,12--dodecahydro-5a,8-methano-5a*H*-cycloheptal[5,6]naphtho-[2,1-*b*]furan-7-methanol], $C_{21}H_{30}O_3$, was isolated from the beans of *Coffea robusta*. The molecule contains five fused rings including a furan ring. The two six-membered rings are in chair conformations, but the third six-membered ring and the five-membered aliphatic ring adopt envelope conformations. Intermolecular O—H···O hydrogen bonding is present in the crystal structure.

## Related literature

For related structures, see: Beattie & Mills (1955); Djerassi *et al.* (1959); Finnegan & Djerassi (1960); Scott *et al.* (1962); Ducruix *et al.* (1977); Chakrabarti & Venkatesan (1981). For a total synthesis of cafestol, see: Corey *et al.* (1987). For the absolute configuration of a related compound, see: Djerassi *et al.* (1953). For the relative configuration, see: Scharnhop & Winterhalter (2009).




## Experimental

### *Crystal data*

$C_{21}H_{30}O_3$ $M_r$ = 330.45
Monoclinic, $P2_1$
$a$ = 10.6399 (9) Å
$b$ = 7.0001 (5) Å
$c$ = 11.5765 (12) Å
$\beta$ = 92.640 (5)°
$V$ = 861.31 (13) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.08 mm$^{-1}$
$T$ = 93 K
0.50 × 0.33 × 0.20 mm

### *Data collection*

Rigaku SPIDER diffractometer
6921 measured reflections
2116 independent reflections
1961 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.029

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.069
$S$ = 1.00
2116 reflections
223 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.15 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H3*O*···O2$^{i}$ | 0.81 (3) | 1.97 (3) | 2.7479 (19) | 163 (3) |

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

Data collection: *RAPID-AUTO* (Rigaku, 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors are grateful to the analytical staff of Chengdu Institute of Biology, CAS, for measuring the NMR spectra.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2727).

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# supporting information

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## 16-*O*-Methylcafestol

**Xia-Li Liao, Xiao-Zhen Chen, Kai-Bei Yu and Guo-You Li**

### S1. Comment

*Coffea robusta* is a species of coffee which has its origins in western Africa. As a part of our research on the bioactive constituents in coffee, the title compound was isolated. Its relative configuration was obtained from ESI-MS and NMR analyses, which were compared with a recent report (Scharnhop *et al.*, 2009), and confirmed by Single-crystal X-ray diffraction study. The molecule of the title compound contains a five-ring system A/B/C/D/E(Fig. 1). There is a *trans* junction between ring A(C1—C5/C10)and ring B(C5—C10). *Cis* junction are present between ring B and ring C(C8—C9/C11—C14) and ring C and ring D(C8/C13—C16). Ring A and D are both in envelope-like conformations, with C10 and C16 at the flap, respectively. Ring B and C both adopt chair conformations. The furan ring E(C5—C6/C18—C19/O1), of course, is planar. Intermolecular O—H···O hydrogen bonding helps to stabilize the crystal structure(Fig. 2).

### S2. Experimental

The powdered seeds of *Coffea robusta* were extracted with cyclohexane and filtered. The filtrate was evaporated under reduced pressure. Then the residue was hydrolyzed with KOH in EtOH and extracted with *tert*-Butyl methyl ether(TBME). The extract was chromatograhed over Silica gel column with eluent of petroleum ether/ethyl acetate(3:1) to provide the title compound as white solid. It was recrystallized in acetone to afford suitable crystals for Single-crystal X-ray diffraction analysis.

### S3. Refinement

Hydroxyl H atom was located in a difference Fourier map and was refined isotropically. Other H atoms were located geometrically with C—H = 0.95-1.00 Å, and were refined in riding mode with $U_{iso}(H) = 1.2U_{eq}(C)$. The absolute configuration could not be determined from the X-ray analysis, owing to the absence of significant anomalous scattering, and Friedel pairs were merged. The absolute configuration was assigned by a comparison between the measured Optical Rotatory Power ($[\alpha]^{24}_{D}$ = -121° (c=0.4, $CHCl_3$)) and a previous work (For Cafestol: $[\alpha]^{24}_{D}$ = -97° ($CHCl_3$)) (Djerassi *et al.*, 1953).

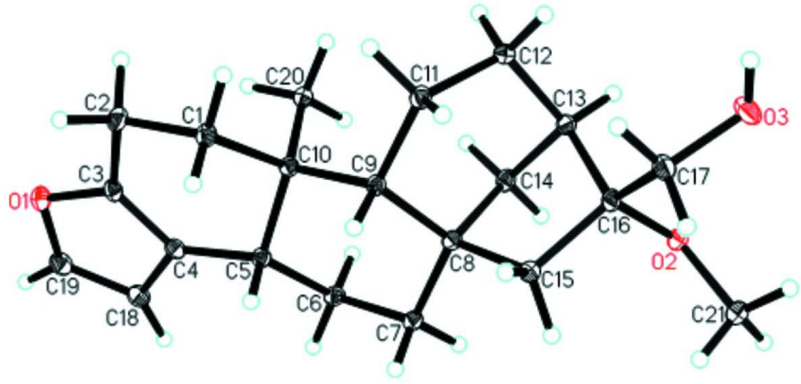


**Figure 1**

View of the title molecule showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

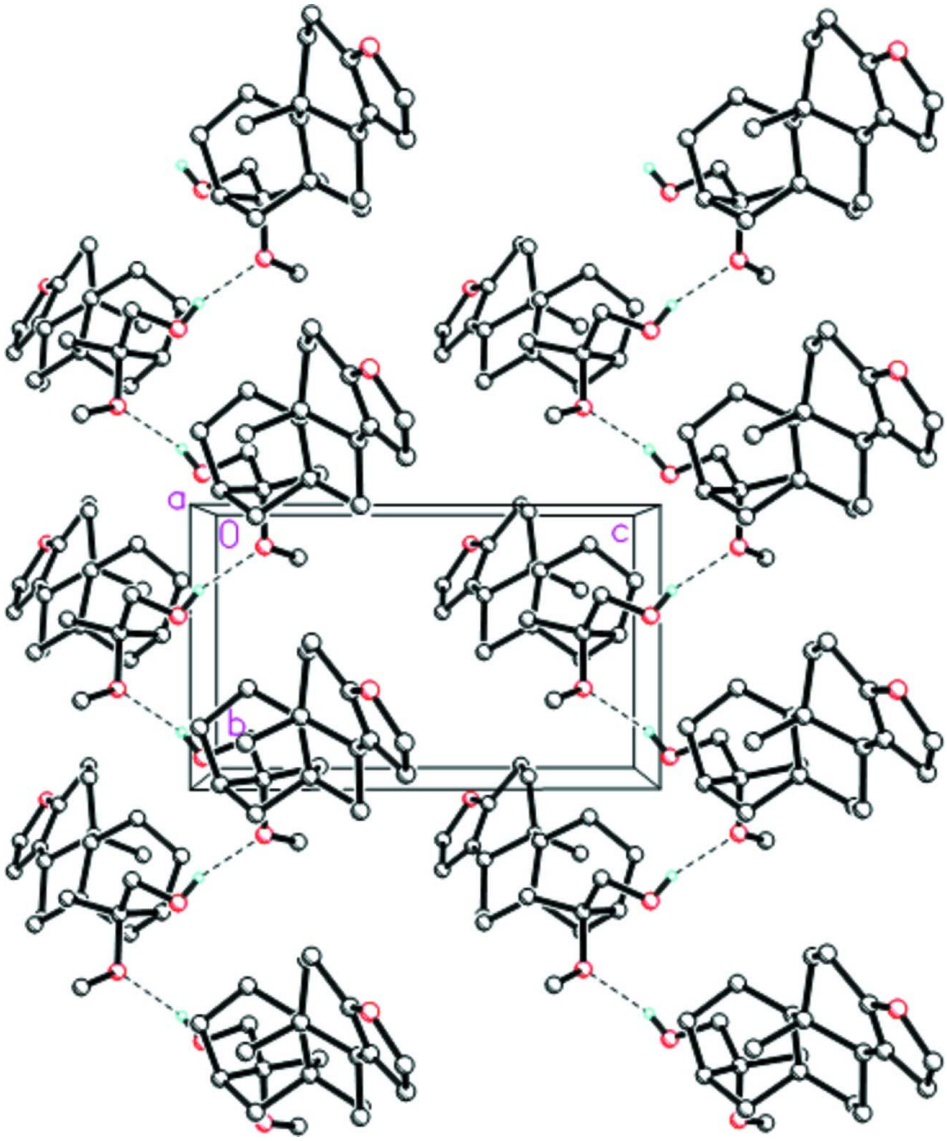


**Figure 2**

The crystal packing of the title molecule, viewed down the a axis. H atoms were omitted for clarity.

**(3b*S*,5a*S*,7*R*,8*R*,10a*R*,10b*S*)- 7-methoxy-10b-methyl-3b,4,5,6,7,8,9,10,10a,10b,11,12-dodecahydro-5a,8-methano- 5a*H*-cycloheptal[5,6]naphtho[2,1-*b*]furan-7-methanol**

*Crystal data*

$C_{21}H_{30}O_3$
$M_r = 330.45$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 10.6399\ (9)$ Å
$b = 7.0001\ (5)$ Å
$c = 11.5765\ (12)$ Å
$\beta = 92.640\ (5)°$
$V = 861.31\ (13)$ Å$^3$
$Z = 2$
$F(000) = 360$
$D_x = 1.274$ Mg m$^{-3}$
Melting point: 448 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2892 reflections
$\theta = 3.4–27.5°$
$\mu = 0.08$ mm$^{-1}$
$T = 93$ K
Prism, colorless
0.50 × 0.33 × 0.20 mm

*Data collection*

Rigaku SPIDER diffractometer
Radiation source: Rotating Anode
Graphite monochromator
$\omega$ scans
6921 measured reflections
2116 independent reflections
1961 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
$h = -12 \rightarrow 13$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 13$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.069$
$S = 1.00$
2116 reflections
223 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2 + 0.16P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å$^{-3}$
$\Delta\rho_{min} = -0.15$ e Å$^{-3}$

*Special details*

**Experimental**. $^{13}$C NMR (150 MHz, $CDCl_3$, $\delta$, p.p.m.): 148.8(C3), 140.6(C19), 120.1(C4), 108.3(C18), 87.0(C16), 60.5(C17), 52.1(C5), 49.1(C15), 48.9(C21), 44.4(C8), 44.3(C9), 41.5(C13), 41.0(C7), 38.7(C10), 37.8(C14), 35.8(C1), 25.7(C12), 23.1(C6), 20.6(C2), 19.2(C11), 13.3(C20).

**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 $F^2 > \sigma(F^2)$ 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 | 0.09240 (11) | 0.1142 (2) | 0.60603 (10) | 0.0202 (3) |
| O2 | 0.91263 (11) | 0.64850 (18) | 0.83888 (10) | 0.0180 (3) |
| O3 | 1.04079 (14) | 0.3897 (2) | 0.97682 (12) | 0.0259 (3) |
| C1 | 0.41584 (16) | 0.0015 (3) | 0.73392 (16) | 0.0173 (4) |
| H1A | 0.4554 | −0.0512 | 0.6651 | 0.021* |
| H1B | 0.4492 | −0.0705 | 0.8022 | 0.021* |
| C2 | 0.27216 (16) | −0.0310 (3) | 0.72069 (16) | 0.0196 (4) |
| H2A | 0.2544 | −0.1577 | 0.6857 | 0.024* |
| H2B | 0.2349 | −0.0272 | 0.7975 | 0.024* |
| C3 | 0.21656 (16) | 0.1217 (3) | 0.64550 (14) | 0.0167 (4) |
| C4 | 0.27270 (16) | 0.2813 (3) | 0.60818 (14) | 0.0159 (4) |
| C5 | 0.41066 (16) | 0.3158 (3) | 0.63354 (15) | 0.0148 (4) |
| H5 | 0.4551 | 0.2495 | 0.5707 | 0.018* |
| C6 | 0.45291 (16) | 0.5236 (3) | 0.62997 (15) | 0.0174 (4) |

| | | | | |
|---|---|---|---|---|
| H6A | 0.4238 | 0.5930 | 0.6983 | 0.021* |
| H6B | 0.4167 | 0.5865 | 0.5594 | 0.021* |
| C7 | 0.59643 (16) | 0.5269 (3) | 0.62984 (15) | 0.0175 (4) |
| H7A | 0.6254 | 0.6613 | 0.6279 | 0.021* |
| H7B | 0.6238 | 0.4632 | 0.5589 | 0.021* |
| C8 | 0.65845 (16) | 0.4275 (3) | 0.73580 (14) | 0.0148 (4) |
| C9 | 0.60201 (16) | 0.2259 (2) | 0.75520 (15) | 0.0141 (4) |
| H9 | 0.6291 | 0.1485 | 0.6881 | 0.017* |
| C10 | 0.45483 (16) | 0.2142 (3) | 0.74799 (15) | 0.0145 (4) |
| C11 | 0.66860 (16) | 0.1311 (3) | 0.86261 (14) | 0.0175 (4) |
| H11A | 0.6107 | 0.0350 | 0.8935 | 0.021* |
| H11B | 0.7433 | 0.0617 | 0.8367 | 0.021* |
| C12 | 0.71155 (17) | 0.2649 (3) | 0.96239 (15) | 0.0188 (4) |
| H12A | 0.6400 | 0.2854 | 1.0127 | 0.023* |
| H12B | 0.7793 | 0.2009 | 1.0094 | 0.023* |
| C13 | 0.75979 (16) | 0.4604 (3) | 0.92313 (15) | 0.0161 (4) |
| H13 | 0.7822 | 0.5436 | 0.9912 | 0.019* |
| C14 | 0.65661 (17) | 0.5522 (3) | 0.84587 (15) | 0.0167 (4) |
| H14A | 0.6765 | 0.6872 | 0.8288 | 0.020* |
| H14B | 0.5740 | 0.5457 | 0.8817 | 0.020* |
| C15 | 0.80304 (16) | 0.4041 (3) | 0.72158 (14) | 0.0166 (4) |
| H15A | 0.8227 | 0.2716 | 0.6986 | 0.020* |
| H15B | 0.8319 | 0.4923 | 0.6614 | 0.020* |
| C16 | 0.86878 (16) | 0.4516 (3) | 0.84003 (15) | 0.0159 (4) |
| C17 | 0.97698 (17) | 0.3184 (3) | 0.87504 (15) | 0.0198 (4) |
| H17A | 0.9441 | 0.1887 | 0.8897 | 0.024* |
| H17B | 1.0362 | 0.3099 | 0.8117 | 0.024* |
| C18 | 0.17903 (17) | 0.3819 (3) | 0.53822 (16) | 0.0201 (4) |
| H18 | 0.1897 | 0.4990 | 0.4983 | 0.024* |
| C19 | 0.07310 (17) | 0.2766 (3) | 0.54064 (16) | 0.0213 (4) |
| H19 | −0.0046 | 0.3101 | 0.5023 | 0.026* |
| C20 | 0.39111 (16) | 0.2962 (3) | 0.85393 (15) | 0.0181 (4) |
| H20A | 0.4278 | 0.2371 | 0.9244 | 0.022* |
| H20B | 0.3007 | 0.2690 | 0.8475 | 0.022* |
| H20C | 0.4043 | 0.4347 | 0.8573 | 0.022* |
| C21 | 1.01924 (17) | 0.6855 (3) | 0.77196 (17) | 0.0233 (4) |
| H21A | 1.0082 | 0.6217 | 0.6968 | 0.028* |
| H21B | 1.0953 | 0.6368 | 0.8129 | 0.028* |
| H21C | 1.0275 | 0.8235 | 0.7601 | 0.028* |
| H3O | 1.052 (2) | 0.302 (4) | 1.021 (2) | 0.043 (8)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0154 (6) | 0.0215 (7) | 0.0235 (7) | −0.0012 (6) | −0.0020 (5) | −0.0019 (6) |
| O2 | 0.0194 (6) | 0.0162 (7) | 0.0184 (6) | −0.0047 (5) | 0.0000 (5) | 0.0010 (5) |
| O3 | 0.0326 (8) | 0.0219 (8) | 0.0221 (7) | −0.0020 (6) | −0.0116 (6) | 0.0034 (6) |
| C1 | 0.0173 (9) | 0.0132 (9) | 0.0210 (9) | −0.0003 (7) | −0.0024 (7) | 0.0013 (7) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0195 (9) | 0.0148 (9) | 0.0245 (10) | −0.0037 (7) | −0.0004 (7) | 0.0005 (7) |
| C3 | 0.0129 (8) | 0.0196 (9) | 0.0172 (8) | −0.0006 (8) | −0.0015 (6) | −0.0029 (8) |
| C4 | 0.0178 (9) | 0.0166 (9) | 0.0135 (8) | 0.0014 (7) | 0.0009 (6) | −0.0031 (7) |
| C5 | 0.0152 (8) | 0.0135 (9) | 0.0157 (8) | −0.0008 (7) | 0.0002 (6) | −0.0001 (7) |
| C6 | 0.0190 (9) | 0.0149 (9) | 0.0181 (9) | −0.0007 (7) | −0.0007 (7) | 0.0046 (7) |
| C7 | 0.0180 (9) | 0.0169 (9) | 0.0174 (9) | −0.0043 (7) | −0.0002 (7) | 0.0034 (7) |
| C8 | 0.0156 (8) | 0.0135 (8) | 0.0154 (8) | −0.0015 (7) | 0.0008 (6) | 0.0010 (7) |
| C9 | 0.0145 (8) | 0.0129 (8) | 0.0148 (9) | −0.0011 (7) | 0.0007 (6) | −0.0016 (7) |
| C10 | 0.0156 (8) | 0.0123 (8) | 0.0154 (9) | −0.0008 (7) | −0.0009 (7) | 0.0012 (7) |
| C11 | 0.0181 (9) | 0.0138 (8) | 0.0204 (9) | −0.0018 (8) | −0.0016 (7) | 0.0021 (8) |
| C12 | 0.0204 (9) | 0.0207 (10) | 0.0152 (9) | −0.0047 (8) | −0.0016 (7) | 0.0031 (8) |
| C13 | 0.0187 (9) | 0.0160 (9) | 0.0135 (8) | −0.0038 (7) | 0.0007 (7) | −0.0025 (7) |
| C14 | 0.0170 (9) | 0.0132 (8) | 0.0199 (9) | −0.0024 (7) | 0.0018 (7) | −0.0026 (7) |
| C15 | 0.0164 (8) | 0.0181 (9) | 0.0155 (8) | −0.0021 (7) | 0.0014 (6) | −0.0003 (7) |
| C16 | 0.0168 (9) | 0.0133 (9) | 0.0176 (9) | −0.0038 (7) | −0.0011 (7) | −0.0005 (7) |
| C17 | 0.0199 (9) | 0.0204 (10) | 0.0189 (9) | −0.0016 (8) | −0.0030 (7) | −0.0015 (8) |
| C18 | 0.0207 (9) | 0.0206 (10) | 0.0190 (9) | 0.0023 (8) | −0.0006 (7) | −0.0002 (8) |
| C19 | 0.0182 (9) | 0.0253 (10) | 0.0201 (9) | 0.0035 (8) | −0.0024 (7) | 0.0001 (8) |
| C20 | 0.0167 (8) | 0.0204 (9) | 0.0171 (9) | −0.0037 (8) | 0.0007 (7) | 0.0000 (8) |
| C21 | 0.0212 (9) | 0.0271 (11) | 0.0215 (10) | −0.0078 (8) | 0.0002 (7) | 0.0039 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C19 | 1.376 (2) | C9—C10 | 1.566 (2) |
| O1—C3 | 1.379 (2) | C9—H9 | 1.0000 |
| O2—C21 | 1.427 (2) | C10—C20 | 1.539 (2) |
| O2—C16 | 1.455 (2) | C11—C12 | 1.540 (2) |
| O3—C17 | 1.423 (2) | C11—H11A | 0.9900 |
| O3—H3O | 0.81 (3) | C11—H11B | 0.9900 |
| C1—C2 | 1.546 (2) | C12—C13 | 1.538 (3) |
| C1—C10 | 1.552 (2) | C12—H12A | 0.9900 |
| C1—H1A | 0.9900 | C12—H12B | 0.9900 |
| C1—H1B | 0.9900 | C13—C14 | 1.526 (3) |
| C2—C3 | 1.484 (3) | C13—C16 | 1.542 (2) |
| C2—H2A | 0.9900 | C13—H13 | 1.0000 |
| C2—H2B | 0.9900 | C14—H14A | 0.9900 |
| C3—C4 | 1.347 (3) | C14—H14B | 0.9900 |
| C4—C18 | 1.439 (2) | C15—C16 | 1.547 (2) |
| C4—C5 | 1.503 (2) | C15—H15A | 0.9900 |
| C5—C6 | 1.524 (3) | C15—H15B | 0.9900 |
| C5—C10 | 1.557 (2) | C16—C17 | 1.522 (3) |
| C5—H5 | 1.0000 | C17—H17A | 0.9900 |
| C6—C7 | 1.527 (2) | C17—H17B | 0.9900 |
| C6—H6A | 0.9900 | C18—C19 | 1.348 (3) |
| C6—H6B | 0.9900 | C18—H18 | 0.9500 |
| C7—C8 | 1.533 (2) | C19—H19 | 0.9500 |
| C7—H7A | 0.9900 | C20—H20A | 0.9800 |
| C7—H7B | 0.9900 | C20—H20B | 0.9800 |

| | | | |
|---|---|---|---|
| C8—C14 | 1.546 (2) | C20—H20C | 0.9800 |
| C8—C9 | 1.554 (2) | C21—H21A | 0.9800 |
| C8—C15 | 1.563 (2) | C21—H21B | 0.9800 |
| C9—C11 | 1.552 (2) | C21—H21C | 0.9800 |

| | | | |
|---|---|---|---|
| C19—O1—C3 | 105.49 (14) | C9—C11—H11A | 108.1 |
| C21—O2—C16 | 116.12 (14) | C12—C11—H11B | 108.1 |
| C17—O3—H3O | 107.8 (19) | C9—C11—H11B | 108.1 |
| C2—C1—C10 | 114.20 (14) | H11A—C11—H11B | 107.3 |
| C2—C1—H1A | 108.7 | C13—C12—C11 | 114.28 (14) |
| C10—C1—H1A | 108.7 | C13—C12—H12A | 108.7 |
| C2—C1—H1B | 108.7 | C11—C12—H12A | 108.7 |
| C10—C1—H1B | 108.7 | C13—C12—H12B | 108.7 |
| H1A—C1—H1B | 107.6 | C11—C12—H12B | 108.7 |
| C3—C2—C1 | 108.51 (15) | H12A—C12—H12B | 107.6 |
| C3—C2—H2A | 110.0 | C14—C13—C12 | 107.89 (15) |
| C1—C2—H2A | 110.0 | C14—C13—C16 | 101.10 (14) |
| C3—C2—H2B | 110.0 | C12—C13—C16 | 114.82 (15) |
| C1—C2—H2B | 110.0 | C14—C13—H13 | 110.9 |
| H2A—C2—H2B | 108.4 | C12—C13—H13 | 110.9 |
| C4—C3—O1 | 110.95 (16) | C16—C13—H13 | 110.9 |
| C4—C3—C2 | 127.93 (15) | C13—C14—C8 | 102.08 (14) |
| O1—C3—C2 | 121.11 (16) | C13—C14—H14A | 111.4 |
| C3—C4—C18 | 106.28 (15) | C8—C14—H14A | 111.4 |
| C3—C4—C5 | 120.92 (16) | C13—C14—H14B | 111.4 |
| C18—C4—C5 | 132.55 (17) | C8—C14—H14B | 111.4 |
| C4—C5—C6 | 115.76 (15) | H14A—C14—H14B | 109.2 |
| C4—C5—C10 | 110.29 (14) | C16—C15—C8 | 106.93 (13) |
| C6—C5—C10 | 112.40 (14) | C16—C15—H15A | 110.3 |
| C4—C5—H5 | 105.9 | C8—C15—H15A | 110.3 |
| C6—C5—H5 | 105.9 | C16—C15—H15B | 110.3 |
| C10—C5—H5 | 105.9 | C8—C15—H15B | 110.3 |
| C5—C6—C7 | 108.12 (15) | H15A—C15—H15B | 108.6 |
| C5—C6—H6A | 110.1 | O2—C16—C17 | 110.11 (14) |
| C7—C6—H6A | 110.1 | O2—C16—C13 | 102.62 (14) |
| C5—C6—H6B | 110.1 | C17—C16—C13 | 116.09 (15) |
| C7—C6—H6B | 110.1 | O2—C16—C15 | 109.12 (14) |
| H6A—C6—H6B | 108.4 | C17—C16—C15 | 114.21 (15) |
| C6—C7—C8 | 112.69 (14) | C13—C16—C15 | 103.85 (14) |
| C6—C7—H7A | 109.1 | O3—C17—C16 | 109.38 (16) |
| C8—C7—H7A | 109.1 | O3—C17—H17A | 109.8 |
| C6—C7—H7B | 109.1 | C16—C17—H17A | 109.8 |
| C8—C7—H7B | 109.1 | O3—C17—H17B | 109.8 |
| H7A—C7—H7B | 107.8 | C16—C17—H17B | 109.8 |
| C7—C8—C14 | 112.44 (15) | H17A—C17—H17B | 108.2 |
| C7—C8—C9 | 111.91 (14) | C19—C18—C4 | 106.20 (17) |
| C14—C8—C9 | 111.97 (14) | C19—C18—H18 | 126.9 |
| C7—C8—C15 | 110.65 (13) | C4—C18—H18 | 126.9 |

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| C14—C8—C15 | 101.29 (13) | C18—C19—O1 | 111.06 (16) |
| C9—C8—C15 | 108.00 (14) | C18—C19—H19 | 124.5 |
| C11—C9—C8 | 109.82 (14) | O1—C19—H19 | 124.5 |
| C11—C9—C10 | 116.03 (14) | C10—C20—H20A | 109.5 |
| C8—C9—C10 | 115.59 (14) | C10—C20—H20B | 109.5 |
| C11—C9—H9 | 104.7 | H20A—C20—H20B | 109.5 |
| C8—C9—H9 | 104.7 | C10—C20—H20C | 109.5 |
| C10—C9—H9 | 104.7 | H20A—C20—H20C | 109.5 |
| C20—C10—C1 | 108.40 (15) | H20B—C20—H20C | 109.5 |
| C20—C10—C5 | 112.40 (14) | O2—C21—H21A | 109.5 |
| C1—C10—C5 | 106.25 (14) | O2—C21—H21B | 109.5 |
| C20—C10—C9 | 114.45 (14) | H21A—C21—H21B | 109.5 |
| C1—C10—C9 | 108.50 (14) | O2—C21—H21C | 109.5 |
| C5—C10—C9 | 106.46 (14) | H21A—C21—H21C | 109.5 |
| C12—C11—C9 | 116.73 (16) | H21B—C21—H21C | 109.5 |
| C12—C11—H11A | 108.1 | | |

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| C10—C1—C2—C3 | 40.0 (2) | C11—C9—C10—C1 | −65.34 (19) |
| C19—O1—C3—C4 | 0.62 (19) | C8—C9—C10—C1 | 163.96 (14) |
| C19—O1—C3—C2 | 179.58 (16) | C11—C9—C10—C5 | −179.33 (14) |
| C1—C2—C3—C4 | −10.1 (3) | C8—C9—C10—C5 | 49.96 (19) |
| C1—C2—C3—O1 | 171.15 (15) | C8—C9—C11—C12 | 33.6 (2) |
| O1—C3—C4—C18 | −1.1 (2) | C10—C9—C11—C12 | −99.74 (18) |
| C2—C3—C4—C18 | −179.94 (18) | C9—C11—C12—C13 | −36.3 (2) |
| O1—C3—C4—C5 | −176.03 (15) | C11—C12—C13—C14 | 55.56 (19) |
| C2—C3—C4—C5 | 5.1 (3) | C11—C12—C13—C16 | −56.3 (2) |
| C3—C4—C5—C6 | −157.29 (16) | C12—C13—C14—C8 | −70.78 (16) |
| C18—C4—C5—C6 | 29.3 (3) | C16—C13—C14—C8 | 50.07 (16) |
| C3—C4—C5—C10 | −28.3 (2) | C7—C8—C14—C13 | −160.51 (14) |
| C18—C4—C5—C10 | 158.29 (18) | C9—C8—C14—C13 | 72.48 (16) |
| C4—C5—C6—C7 | −167.16 (13) | C15—C8—C14—C13 | −42.38 (16) |
| C10—C5—C6—C7 | 64.86 (18) | C7—C8—C15—C16 | 138.40 (15) |
| C5—C6—C7—C8 | −58.46 (19) | C14—C8—C15—C16 | 18.98 (18) |
| C6—C7—C8—C14 | −77.13 (19) | C9—C8—C15—C16 | −98.79 (16) |
| C6—C7—C8—C9 | 49.9 (2) | C21—O2—C16—C17 | 53.11 (19) |
| C6—C7—C8—C15 | 170.41 (15) | C21—O2—C16—C13 | 177.30 (14) |
| C7—C8—C9—C11 | 179.55 (14) | C21—O2—C16—C15 | −72.99 (18) |
| C14—C8—C9—C11 | −53.16 (18) | C14—C13—C16—O2 | 76.47 (16) |
| C15—C8—C9—C11 | 57.52 (17) | C12—C13—C16—O2 | −167.70 (14) |
| C7—C8—C9—C10 | −46.8 (2) | C14—C13—C16—C17 | −163.39 (15) |
| C14—C8—C9—C10 | 80.45 (18) | C12—C13—C16—C17 | −47.6 (2) |
| C15—C8—C9—C10 | −168.87 (14) | C14—C13—C16—C15 | −37.17 (17) |
| C2—C1—C10—C20 | 57.47 (19) | C12—C13—C16—C15 | 78.65 (18) |
| C2—C1—C10—C5 | −63.55 (19) | C8—C15—C16—O2 | −97.88 (16) |
| C2—C1—C10—C9 | −177.68 (14) | C8—C15—C16—C17 | 138.41 (16) |
| C4—C5—C10—C20 | −64.11 (19) | C8—C15—C16—C13 | 11.01 (19) |
| C6—C5—C10—C20 | 66.70 (18) | O2—C16—C17—O3 | 49.13 (19) |
| C4—C5—C10—C1 | 54.31 (18) | C13—C16—C17—O3 | −66.9 (2) |

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| C6—C5—C10—C1 | −174.88 (14) | C15—C16—C17—O3 | 172.30 (15) |
| C4—C5—C10—C9 | 169.83 (14) | C3—C4—C18—C19 | 1.1 (2) |
| C6—C5—C10—C9 | −59.36 (18) | C5—C4—C18—C19 | 175.23 (18) |
| C11—C9—C10—C20 | 55.9 (2) | C4—C18—C19—O1 | −0.8 (2) |
| C8—C9—C10—C20 | −74.85 (19) | C3—O1—C19—C18 | 0.1 (2) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3*O*···O2$^{i}$ | 0.81 (3) | 1.97 (3) | 2.7479 (19) | 163 (3) |

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