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L-Menthyl ester of highly estrogenic (-)-(*Z*)-bisdehydrodoisynolic acid 3-methyl ether

P. D. Robinson, Y. Hou, C. Y. Meyers, S. Adler, W. J. Banz and T. A. Winters

Abstract

The absolute structure of the highly estrogenic carboxylic acid (-)-(*Z*)-bisdehydrodoisynolic acid has been obtained *via* the crystal structure of the *L*-menthyl ester of its 3-methyl ether [*L*-menthyl (-)-3-methoxy-13-methyl-14-ethyl-11,12,13(S),14(*R*)- tetrahydrophenanthrene 13-carboxylate, $C_{29}H_{40}O_3$]. The *Z* (*cis*), 13(S),14(*R*) geometry of the tetrahydrophenanthrene moiety, near coplanarity of the three fused rings whose singular out-of-plane C atom holds the carboxyl group, and large torsion angle separating the *cis* carboxyl and ethyl substituents of this ring, may contribute to the compound's considerable estrogenicity while also being responsible for its poor binding affinity for estradiol receptors.

Experimental

The diastereomeric *L*-menthyl esters of racemic *Z*-bisdehydrodoisynolic acid 3-methyl ether and the corresponding enantiomeric *Z*-bisdehydrodoisynolic acid 3-methyl ethers were prepared by the method reported by Rometsch & Miescher (1947). The diastereomeric *L*-menthyl esters were isolated in a 1:1 molar ratio as a solid mixture; 10.8 g, 92.3%. Recrystallization, first from acetone, then from methanol, provided the pure diastereomers. The *L*-menthyl ester of the (-) enantiomer melted at 385–386 K [lit. (Rometsch & Miescher, 1947) 386 K]. These crystals were used for the X-ray analysis. Ester hydrolysis of this diastereomer, followed by ether cleavage, produced the phenolic (-)-bisdehydrodoisynolic acid, which darkens in air; recrystallization from various solvents consistently produced twinned crystals unsuitable for X-ray diffraction.

Refinement

The orientations of the methyl group H atoms were determined by the circular Fourier method available in *SHELXL97* (Sheldrick, 1997). All H atoms are riding.

Computing details

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *TEXSAN SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* LS and *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN ORTEP* (Johnson, 1965); software used to prepare material for publication: *TEXSAN*, *SHELXL97* and *PLATON* (Spek, 1990).

_L_-menthyl (-)-3-methoxy-13-methyl-14-ethyl-11,12,13(S)14(_R_)- tetrahydrophenanthrene 13-carboxylateIUPAC: _L_-menthyl (-)-(1_R_,2S)-1-ethyl-7-methoxy-2-methyl- 1,2,3,4-tetrahydrophenanthrene-2-carboxylate

CIF access

Crystal data

$C_{29}H_{40}O_3$	$V = 2667.3\ (5)\ Å^3$
$M_r = 436.61$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$
$a = 10.9185\ (11)$ Å	$\mu = 0.07\ mm^{-1}$
$b = 28.281\ (4)$ Å	$T = 296$ K
$c = 8.6380\ (7)$ Å	$0.41 \times 0.35 \times 0.33$ mm

Data collection

Rigaku AFC-5S diffractometer	$R_{int} = 0.0$
Absorption correction: none	3 standard reflections
3004 measured reflections	every 150 reflections
3004 independent reflections	intensity decay: 0.0%
1046 reflections with $I > 2\sigma(I)$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.121$	$\Delta\rho_{max} = 0.10\ e\ Å^{-3}$
$S = 0.96$	$\Delta\rho_{min} = -0.11\ e\ Å^{-3}$
3004 reflections	Absolute structure: ascertained from the known absolute configuration of the L-menthyl moiety
296 parameters	Flack parameter: 3 (3)

Table 1
Selected geometric parameters (°)

C8—C9—C11—C12	4.2 (6)	C9—C11—C12—C13	−31.1 (6)
C11—C9—C8—C14	−6.3 (6)	C9—C8—C14—C13	34.1 (5)
C17—C13—C14—C15	−53.3 (5)	C18—C13—C14—C15	−171.2 (4)

Acknowledgements

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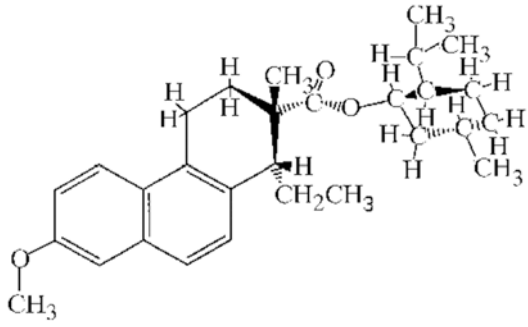
CIF access

Scheme 1



supplementary materials

_L_-menthyl (-)-3-methoxy-13-methyl-14-ethyl-11,12,13(S)14(_R_)- tetrahydrophenanthrene 13-carboxylateIUPAC: _L_-menthyl (-)-(1_R_,2S)-1-ethyl-7-methoxy-2-methyl- 1,2,3,4-tetrahydrophenanthrene-2-carboxylate

Crystal data

$C_{29}H_{40}O_3$	$D_x = 1.087$ Mg m^{-3}
$M_r = 436.61$	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 24 reflections
$a = 10.9185$ (11) Å	$\theta = 9.0$–9.9^o
$b = 28.281$ (4) Å	$\mu = 0.07$ mm^{-1}
$c = 8.6380$ (7) Å	$T = 296$ K
$V = 2667.3$ (5) Å^3	Prism, colorless
$Z = 4$	0.41 × 0.35 × 0.33 mm
$F_{000} = 952$	

Data collection

Rigaku AFC-5S diffractometer	$R_{int} = 0.0$
Radiation source: X-ray tube	$\theta_{max} = 27.5^o$
Monochromator: graphite	$\theta_{min} = 2.0^o$
$T = 296$ K	$h = 0 \rightarrow 13$
ω scans (rate 4° min^{-1} in ω)	$k = 0 \rightarrow 36$
Absorption correction: none	$l = 0 \rightarrow 11$
3004 measured reflections	3 standard reflections
3004 independent reflections	every 150 reflections
1046 reflections with $I > 2\sigma(I)$	intensity decay: 0.0%

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$(\Delta/\sigma)_{max} = <0.001$
$wR(F^2) = 0.121$	$\Delta\rho_{max} = 0.10$ e Å^{-3}
$S = 0.96$	$\Delta\rho_{min} = -0.11$ e Å^{-3}
3004 reflections	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
296 parameters	Extinction coefficient: 0.0046 (6)
Primary atom site location: structure-invariant direct methods	Absolute structure: ascertained from the known absolute configuration of the L-menthyl moiety
Secondary atom site location: difference Fourier map	Flack parameter: 3 (3)
Hydrogen site location: inferred from neighbouring sites	

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.1462 (4)	0.55699 (15)	0.4523 (4)	0.1098 (11)
O2	−0.0292 (3)	0.19288 (12)	0.2321 (4)	0.1033 (12)
O3	0.1448 (3)	0.18495 (12)	0.3667 (3)	0.0810 (9)
C1	0.0204 (4)	0.4451 (2)	0.3338 (6)	0.0905 (15)
C2	0.0421 (5)	0.4920 (2)	0.3498 (6)	0.0926 (15)
C3	0.1333 (5)	0.5089 (2)	0.4508 (6)	0.0885 (14)
C4	0.2002 (4)	0.4777 (2)	0.5355 (6)	0.0866 (14)
C5	0.1783 (4)	0.4287 (2)	0.5221 (6)	0.0788 (14)
C6	0.2472 (4)	0.3948 (2)	0.6071 (6)	0.0831 (14)
C7	0.2264 (4)	0.3479 (2)	0.5918 (5)	0.0819 (14)
C8	0.1363 (4)	0.33015 (17)	0.4892 (5)	0.0717 (12)
C9	0.0686 (4)	0.36095 (19)	0.4020 (5)	0.0723 (13)
C10	0.0886 (4)	0.4106 (2)	0.4192 (5)	0.0751 (13)
C11	−0.0201 (4)	0.34396 (18)	0.2801 (5)	0.0934 (15)
C12	−0.0355 (4)	0.29037 (18)	0.2691 (5)	0.0897 (15)
C13	0.0804 (4)	0.26326 (18)	0.3124 (5)	0.0717 (12)
C14	0.1159 (4)	0.27725 (15)	0.4786 (4)	0.0722 (13)
C15	0.0217 (4)	0.25991 (16)	0.6001 (4)	0.0844 (13)
C16	0.0721 (5)	0.2567 (2)	0.7641 (5)	0.127 (2)
C17	0.0562 (5)	0.2103 (2)	0.2980 (5)	0.0790 (14)
C18	0.1866 (4)	0.27446 (16)	0.1994 (5)	0.0883 (14)
C19	0.2482 (5)	0.5762 (2)	0.5321 (7)	0.132 (2)
C1'	0.0704 (4)	0.06602 (19)	0.5420 (6)	0.0955 (16)
C2'	0.0809 (4)	0.11930 (18)	0.5262 (5)	0.0889 (15)
C3'	0.1315 (4)	0.13363 (18)	0.3696 (5)	0.0785 (13)
C4'	0.2580 (4)	0.11238 (16)	0.3387 (5)	0.0758 (13)
C5'	0.2504 (4)	0.05855 (17)	0.3565 (6)	0.0951 (15)
C6'	0.1948 (5)	0.04373 (18)	0.5103 (6)	0.1027 (17)
C7'	0.0168 (5)	0.0517 (2)	0.6985 (6)	0.135 (2)
C8'	0.3113 (4)	0.12841 (18)	0.1830 (5)	0.0888 (15)
C9'	0.4418 (4)	0.10941 (19)	0.1623 (6)	0.1107 (18)
C10'	0.2320 (4)	0.1154 (2)	0.0435 (5)	0.127 (2)
H1	−0.0402	0.4351	0.2656	0.109*
H2	−0.0042	0.5135	0.2931	0.111*
H4	0.2606	0.4887	0.6024	0.104*
H7	0.2725	0.3267	0.6501	0.098*
H10a	0.2678	0.1283	−0.0489	0.190*
H10b	0.1512	0.1282	0.0571	0.190*
H10c	0.2271	0.0817	0.0346	0.190*
H11a	0.0070	0.3556	0.1802	0.112*
H11b	−0.0996	0.3579	0.3009	0.112*
H12a	−0.1015	0.2807	0.3372	0.108*
H12b	−0.0587	0.2821	0.1641	0.108*
H14	0.1941	0.2618	0.5020	0.087*
H15a	−0.0478	0.2813	0.5999	0.101*

H15b	−0.0078	0.2289	0.5694	0.101*
H16a	0.1413	0.2358	0.7656	0.190*
H16b	0.0097	0.2448	0.8320	0.190*
H16c	0.0969	0.2876	0.7981	0.190*
H18a	0.2584	0.2573	0.2302	0.132*
H18b	0.2036	0.3078	0.2016	0.132*
H18c	0.1636	0.2653	0.0964	0.132*
H19a	0.2434	0.5679	0.6397	0.198*
H19b	0.2479	0.6100	0.5218	0.198*
H19c	0.3225	0.5638	0.4889	0.198*
H1'	0.0139	0.0549	0.4616	0.115*
H2'a	0.0007	0.1334	0.5402	0.107*
H2'b	0.1342	0.1313	0.6070	0.107*
H3'	0.0747	0.1237	0.2880	0.094*
H4'	0.3130	0.1240	0.4199	0.091*
H5'a	0.2012	0.0457	0.2730	0.114*
H5'b	0.3320	0.0453	0.3479	0.114*
H6	0.3078	0.4051	0.6747	0.100*
H6'a	0.2506	0.0524	0.5930	0.123*
H6'b	0.1862	0.0096	0.5116	0.123*
H7'a	0.0718	0.0611	0.7797	0.203*
H7'b	0.0057	0.0180	0.7014	0.203*
H7'c	−0.0608	0.0670	0.7130	0.203*
H8'	0.3169	0.1630	0.1860	0.107*
H9'a	0.4389	0.0758	0.1462	0.166*
H9'b	0.4890	0.1162	0.2533	0.166*
H9'c	0.4791	0.1243	0.0742	0.166*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.108 (3)	0.111 (3)	0.110 (3)	−0.008 (2)	0.011 (3)	0.018 (2)
O2	0.075 (2)	0.135 (3)	0.099 (3)	−0.021 (2)	−0.019 (2)	0.012 (2)
O3	0.0692 (19)	0.098 (3)	0.076 (2)	−0.0056 (18)	−0.0079 (18)	−0.0040 (19)
C1	0.070 (3)	0.115 (4)	0.087 (4)	0.008 (3)	−0.001 (3)	0.009 (4)
C2	0.078 (4)	0.115 (5)	0.085 (4)	0.016 (3)	−0.003 (3)	0.023 (3)
C3	0.070 (3)	0.111 (5)	0.084 (4)	0.003 (4)	0.015 (3)	0.021 (4)
C4	0.066 (3)	0.118 (5)	0.076 (4)	−0.005 (3)	0.003 (3)	0.003 (3)
C5	0.048 (3)	0.119 (5)	0.069 (3)	0.003 (3)	−0.002 (3)	0.002 (3)
C6	0.047 (2)	0.129 (4)	0.073 (3)	0.003 (3)	−0.016 (3)	−0.002 (3)
C7	0.063 (3)	0.116 (4)	0.066 (3)	0.009 (3)	−0.012 (3)	0.007 (3)
C8	0.054 (2)	0.106 (4)	0.055 (3)	0.005 (3)	−0.006 (3)	0.005 (3)
C9	0.052 (2)	0.105 (4)	0.059 (3)	0.011 (3)	−0.008 (3)	0.009 (3)
C10	0.055 (3)	0.108 (4)	0.062 (3)	0.018 (3)	−0.001 (3)	0.015 (3)
C11	0.077 (3)	0.130 (5)	0.074 (3)	0.014 (3)	−0.019 (3)	0.001 (3)
C12	0.074 (3)	0.123 (4)	0.072 (3)	0.000 (3)	−0.013 (3)	0.008 (3)
C13	0.055 (3)	0.106 (4)	0.054 (3)	0.002 (3)	−0.002 (2)	0.001 (3)
C14	0.056 (3)	0.113 (4)	0.047 (3)	0.010 (3)	−0.008 (2)	0.008 (3)

C15	0.081 (3)	0.114 (4)	0.059 (3)	0.010 (3)	0.005 (3)	0.005 (3)
C16	0.138 (5)	0.187 (6)	0.055 (3)	0.006 (5)	−0.005 (3)	0.026 (4)
C17	0.064 (3)	0.119 (5)	0.054 (3)	0.002 (4)	0.004 (3)	0.005 (3)
C18	0.083 (3)	0.122 (4)	0.060 (3)	−0.005 (3)	0.004 (3)	0.005 (3)
C19	0.122 (5)	0.123 (5)	0.150 (6)	−0.035 (4)	0.007 (5)	0.003 (4)
C1'	0.082 (4)	0.120 (4)	0.085 (4)	−0.022 (3)	0.004 (3)	0.010 (3)
C2'	0.070 (3)	0.132 (4)	0.065 (3)	−0.006 (3)	0.010 (3)	−0.006 (3)
C3'	0.061 (3)	0.112 (4)	0.063 (3)	−0.012 (3)	0.005 (3)	−0.009 (3)
C4'	0.060 (3)	0.101 (4)	0.066 (3)	−0.009 (3)	0.005 (3)	−0.013 (3)
C5'	0.074 (3)	0.108 (4)	0.102 (4)	−0.007 (3)	0.010 (3)	−0.012 (3)
C6'	0.091 (4)	0.108 (4)	0.109 (4)	−0.005 (3)	0.006 (4)	0.014 (4)
C7'	0.123 (5)	0.177 (6)	0.105 (5)	−0.014 (4)	0.024 (4)	0.035 (4)
C8'	0.073 (3)	0.126 (4)	0.066 (3)	−0.010 (3)	0.007 (3)	−0.009 (3)
C9'	0.071 (3)	0.169 (5)	0.093 (4)	−0.010 (4)	0.020 (3)	−0.007 (4)
C10'	0.098 (4)	0.221 (6)	0.061 (3)	−0.015 (4)	0.003 (3)	−0.014 (4)

Geometric parameters (Å, °)

O1—C3	1.368 (5)	C2'—H2'b	0.9700
O1—C19	1.419 (6)	C2—H2	0.9300
O2—C17	1.199 (5)	C3'—H3'	0.9800
O3—C17	1.343 (5)	C4—H4	0.9300
O3—C3'	1.459 (5)	C4'—H4'	0.9800
C1—C2	1.354 (6)	C5'—H5'a	0.9700
C1—C10	1.433 (6)	C5'—H5'b	0.9700
C1'—C2'	1.517 (6)	C6—H6	0.9300
C1'—C6'	1.523 (6)	C6'—H6'a	0.9700
C1'—C7'	1.528 (6)	C6'—H6'b	0.9700
C2—C3	1.406 (6)	C7'—H7'a	0.9600
C2'—C3'	1.517 (5)	C7'—H7'b	0.9600
C3—C4	1.359 (6)	C7'—H7'c	0.9600
C3'—C4'	1.530 (6)	C7—H7	0.9300
C4—C5	1.412 (6)	C9'—H9'a	0.9600
C4'—C5'	1.533 (6)	C9'—H9'b	0.9600
C4'—C8'	1.534 (6)	C9'—H9'c	0.9600
C5—C10	1.418 (6)	C10'—H10a	0.9600
C5—C6	1.422 (6)	C10'—H10b	0.9600
C5'—C6'	1.519 (6)	C10'—H10c	0.9600
C6—C7	1.352 (6)	C11—H11a	0.9700
C7—C8	1.415 (5)	C11—H11b	0.9700
C8—C9	1.369 (5)	C8'—H8'	0.9800
C8—C14	1.515 (5)	C12—H12a	0.9700
C8'—C10'	1.529 (6)	C12—H12b	0.9700
C8'—C9'	1.533 (5)	C14—H14	0.9800
C9—C10	1.429 (6)	C15—H15a	0.9700
C9—C11	1.509 (5)	C15—H15b	0.9700
C11—C12	1.528 (5)	C16—H16a	0.9600
C12—C13	1.526 (5)	C16—H16b	0.9600
C13—C17	1.525 (6)	C16—H16c	0.9600

C13—C14	1.539 (5)	C18—H18a	0.9600
C13—C18	1.548 (5)	C18—H18b	0.9600
C14—C15	1.549 (5)	C18—H18c	0.9600
C15—C16	1.522 (6)	C19—H19a	0.9600
C1—H1	0.9300	C19—H19b	0.9600
C1'—H1'	0.9800	C19—H19c	0.9600
C2'—H2'a	0.9700		
C3—O1—C19	117.8 (5)	C6'—C5'—H5'a	109.1
C17—O3—C3'	117.9 (4)	C4'—C5'—H5'a	109.1
C2—C1—C10	121.6 (5)	C6'—C5'—H5'b	109.1
C2'—C1'—C6'	109.1 (4)	C4'—C5'—H5'b	109.1
C2'—C1'—C7'	111.8 (5)	C7—C6—H6	119.2
C6'—C1'—C7'	113.0 (5)	C5—C6—H6	119.2
C1—C2—C3	121.3 (5)	H5'a—C5'—H5'b	107.8
C3'—C2'—C1'	111.9 (4)	C5'—C6'—H6'a	108.9
C4—C3—O1	125.8 (6)	C1'—C6'—H6'a	108.9
C4—C3—C2	119.6 (5)	C5'—C6'—H6'b	108.9
O1—C3—C2	114.5 (6)	C1'—C6'—H6'b	108.9
O3—C3'—C2'	108.5 (4)	H6'a—C6'—H6'b	107.7
O3—C3'—C4'	107.3 (4)	C6—C7—H7	119.2
C2'—C3'—C4'	112.3 (4)	C8—C7—H7	119.2
C3—C4—C5	120.2 (5)	C1'—C7'—H7'a	109.5
C3'—C4'—C5'	108.9 (4)	C1'—C7'—H7'b	109.5
C3'—C4'—C8'	112.3 (4)	H7'a—C7'—H7'b	109.5
C5'—C4'—C8'	113.7 (4)	C1'—C7'—H7'c	109.5
C4—C5—C10	121.5 (5)	H7'a—C7'—H7'c	109.5
C4—C5—C6	122.1 (5)	H7'b—C7'—H7'c	109.5
C10—C5—C6	116.5 (5)	C10'—C8'—H8'	107.2
C6'—C5'—C4'	112.6 (4)	C9'—C8'—H8'	107.2
C7—C6—C5	121.5 (5)	C4'—C8'—H8'	107.2
C5'—C6'—C1'	113.5 (4)	C8'—C9'—H9'a	109.5
C6—C7—C8	121.6 (5)	C8'—C9'—H9'b	109.5
C9—C8—C7	119.7 (5)	H9'a—C9'—H9'b	109.5
C9—C8—C14	121.0 (4)	C8'—C9'—H9'c	109.5
C7—C8—C14	119.3 (4)	H9'a—C9'—H9'c	109.5
C10'—C8'—C9'	110.5 (4)	H9'b—C9'—H9'c	109.5
C10'—C8'—C4'	113.9 (3)	C8'—C10'—H10a	109.5
C9'—C8'—C4'	110.6 (4)	C8'—C10'—H10b	109.5
C8—C9—C10	119.0 (4)	H10a—C10'—H10b	109.5
C8—C9—C11	121.9 (4)	C8'—C10'—H10c	109.5
C10—C9—C11	118.9 (4)	H10a—C10'—H10c	109.5
C5—C10—C9	121.6 (4)	H10b—C10'—H10c	109.5
C5—C10—C1	115.9 (5)	C9—C11—H11a	108.4
C9—C10—C1	122.5 (5)	C12—C11—H11a	108.4
C9—C11—C12	115.4 (4)	C9—C11—H11b	108.4
C13—C12—C11	113.1 (4)	C12—C11—H11b	108.4
C17—C13—C12	109.3 (4)	H11a—C11—H11b	107.5
C17—C13—C14	111.9 (4)	C13—C12—H12a	109.0
C12—C13—C14	108.0 (4)	C11—C12—H12a	109.0

C17—C13—C18	106.2 (4)	C13—C12—H12b	109.0
C12—C13—C18	111.3 (3)	C11—C12—H12b	109.0
C14—C13—C18	110.3 (3)	H12a—C12—H12b	107.8
C8—C14—C13	110.3 (3)	C8—C14—H14	107.3
C8—C14—C15	111.7 (4)	C13—C14—H14	107.3
C13—C14—C15	112.5 (3)	C15—C14—H14	107.3
C16—C15—C14	114.1 (4)	C16—C15—H15a	108.7
O2—C17—O3	123.4 (5)	C14—C15—H15a	108.7
O2—C17—C13	125.3 (5)	C16—C15—H15b	108.7
O3—C17—C13	111.4 (4)	C14—C15—H15b	108.7
C2—C1—H1	119.2	H15a—C15—H15b	107.6
C2'—C1'—H1'	107.6	C15—C16—H16a	109.5
C6'—C1'—H1'	107.6	C15—C16—H16b	109.5
C7'—C1'—H1'	107.6	H16a—C16—H16b	109.5
C10—C1—H1	119.2	C15—C16—H16c	109.5
C1—C2—H2	119.4	H16a—C16—H16c	109.5
C3—C2—H2	119.4	H16b—C16—H16c	109.5
C3'—C2'—H2'a	109.2	C13—C18—H18a	109.5
C1'—C2'—H2'a	109.2	C13—C18—H18b	109.5
C3'—C2'—H2'b	109.2	H18a—C18—H18b	109.5
C1'—C2'—H2'b	109.2	C13—C18—H18c	109.5
H2'a—C2'—H2'b	107.9	H18a—C18—H18c	109.5
O3—C3'—H3'	109.6	H18b—C18—H18c	109.5
C2'—C3'—H3'	109.6	O1—C19—H19a	109.5
C4'—C3'—H3'	109.6	O1—C19—H19b	109.5
C3—C4—H4	119.9	H19a—C19—H19b	109.5
C5—C4—H4	119.9	O1—C19—H19c	109.5
C3'—C4'—H4'	107.2	H19a—C19—H19c	109.5
C5'—C4'—H4'	107.2	H19b—C19—H19c	109.5
C8'—C4'—H4'	107.2		
C8—C9—C11—C12	4.2 (6)	C3'—C4'—C8'—C9'	175.7 (4)
C11—C9—C8—C14	−6.3 (6)	C5'—C4'—C8'—C9'	−60.1 (5)
C17—C13—C14—C15	−53.3 (5)	C7—C8—C9—C10	−1.4 (6)
C9—C11—C12—C13	−31.1 (6)	C14—C8—C9—C10	178.2 (4)
C9—C8—C14—C13	34.1 (5)	C7—C8—C9—C11	174.1 (4)
C18—C13—C14—C15	−171.2 (4)	C4—C5—C10—C9	178.1 (4)
C10—C1—C2—C3	0.4 (7)	C6—C5—C10—C9	0.0 (6)
C6'—C1'—C2'—C3'	55.5 (6)	C4—C5—C10—C1	−1.5 (6)
C7'—C1'—C2'—C3'	−178.8 (4)	C6—C5—C10—C1	−179.7 (4)
C19—O1—C3—C4	9.1 (7)	C8—C9—C10—C5	1.2 (6)
C19—O1—C3—C2	−170.4 (4)	C11—C9—C10—C5	−174.5 (4)
C1—C2—C3—C4	−0.8 (7)	C8—C9—C10—C1	−179.2 (4)
C1—C2—C3—O1	178.7 (4)	C11—C9—C10—C1	5.1 (6)
C17—O3—C3'—C2'	−98.7 (4)	C2—C1—C10—C5	0.7 (6)
C17—O3—C3'—C4'	139.8 (4)	C2—C1—C10—C9	−178.9 (5)
C1'—C2'—C3'—O3	−177.1 (4)	C10—C9—C11—C12	179.7 (4)
C1'—C2'—C3'—C4'	−58.6 (5)	C11—C12—C13—C17	−180.0 (4)
O1—C3—C4—C5	−179.5 (4)	C11—C12—C13—C14	58.2 (5)
C2—C3—C4—C5	0.0 (7)	C11—C12—C13—C18	−63.0 (5)

O3—C3'—C4'—C5'	174.5 (3)	C7—C8—C14—C13	−146.3 (4)
C2'—C3'—C4'—C5'	55.4 (5)	C9—C8—C14—C15	−91.8 (4)
O3—C3'—C4'—C8'	−58.6 (5)	C7—C8—C14—C15	87.8 (4)
C2'—C3'—C4'—C8'	−177.8 (4)	C17—C13—C14—C8	−178.7 (4)
C3—C4—C5—C10	1.2 (7)	C12—C13—C14—C8	−58.5 (4)
C3—C4—C5—C6	179.2 (4)	C18—C13—C14—C8	63.4 (5)
C3'—C4'—C5'—C6'	−52.8 (5)	C12—C13—C14—C15	67.0 (4)
C8'—C4'—C5'—C6'	−178.8 (4)	C8—C14—C15—C16	−76.2 (5)
C4—C5—C6—C7	−179.1 (5)	C13—C14—C15—C16	159.1 (4)
C10—C5—C6—C7	−1.0 (6)	C3'—O3—C17—O2	−4.2 (6)
C4'—C5'—C6'—C1'	54.0 (5)	C3'—O3—C17—C13	176.9 (3)
C2'—C1'—C6'—C5'	−53.7 (6)	C12—C13—C17—O2	14.9 (6)
C7'—C1'—C6'—C5'	−178.7 (4)	C14—C13—C17—O2	134.4 (4)
C5—C6—C7—C8	0.8 (7)	C18—C13—C17—O2	−105.3 (5)
C6—C7—C8—C9	0.5 (6)	C12—C13—C17—O3	−166.3 (3)
C6—C7—C8—C14	−179.1 (4)	C14—C13—C17—O3	−46.8 (5)
C3'—C4'—C8'—C10'	−59.1 (5)	C18—C13—C17—O3	73.6 (4)
C5'—C4'—C8'—C10'	65.0 (5)		