

tion. The disorder of the chloride ion [Cl(4)] probably acts cooperatively with that of the cation, since the hydrogen bonds to one of the mirror-related positions of Cl(4) are significantly shorter and more linear than those to the other position.

Finally, while we have been satisfied to depict only one of the chloride ions [Cl(4)] as accompanying the cation in its disorder, the high anisotropy of the thermal motions of the remaining chloride ions and the ammonium group (Table 2) suggests that they, too, may show some displacement disorder. In particular, the ammonium ion would find itself surrounded by a more regular tetrahedron of chloride ions if it were displaced by about 0.2 Å [corresponding to $(U_{33}-U_{22})^{1/2}$] to one or the other side of the mirror plane. However, many of the other anisotropies cannot be explained without assuming a very complicated pattern of disorder that certainly cannot be proven with the data at hand.

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The Crystal and Molecular Structure of Briarein A, a Diterpenoid from the Gorgonian *Briareum asbestinum*

BY J. E. BURKS, DICK VAN DER HELM, C. Y. CHANG AND L. S. CIERESZKO

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73019, USA

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The crystal structure of briarein A, a chlorine-substituted diterpenoid, isolated from *Briareum asbestinum*, has been determined and refined by three-dimensional least-squares techniques with data taken at -160°C . The molecule crystallizes in the space group $P2_12_12_1$, with unit-cell dimensions (at -160°C) $a = 11.661$ (4), $b = 26.26$ (2) and $c = 10.355$ (6) Å. The final R value for all 3668 reflections is 0.042. The molecule has fused 6- and 10-membered rings, a lactone ring, five acetate groups, chlorine substitution and a non-planar diene group. The absolute configuration has been determined.

Introduction

In 1960 we reported the occurrence, in octocorals from the Caribbean area, of a number of crystalline compounds which appeared to be lactones (Ciereszko, Sif-

ford & Weinheimer, 1960). The lactones isolated from gorgonians of the genera *Eunicea* and *Pseudoplexaura* are cembranolides, those from the genus *Pterogorgia*, polymethylene butenolides (Ciereszko & Karns, 1973; Schmitz, Lorange & Ciereszko, 1969). *Briareum*

asbestinum, a scleraxonian octocoral, yielded a complex mixture of polyacylated diterpenes, shown by mass spectrometry to contain chlorine (Hyde, 1966). B. Tursch of the Université Libre de Bruxelles encountered these chlorinated diterpenoids, the 'briareins', when he extracted *Briareum* for gorgosterol (Ciereszko, Johnson, Schmidt & Koons, 1968; Hale, Leclercq, Tursch, Djerassi, Gross, Weinheimer, Gupta & Scheuer, 1970). A recent doctoral thesis from Brussels reports on the structures of briareins A, B, C and D (Bartholome, 1974). The present report deals with the structure of briarein A determined by X-ray diffraction.

We are interested in the diterpenoid compounds of octocorals because we feel that these compounds serve as a defense against predation and against settling by larval forms. The octocorals are successful in an environment in which there is intense competition for suitable settling space. The diterpenoid compounds are toxic to a variety of organisms, and affect the ciliary activity of protozoans and larval forms (Perkins & Ciereszko, 1970, 1973, 1974; Hadfield, 1975).

Experimental

Briareum asbestinum (Pallas), a gorgonian, suborder Scleraxonia, subclass Octocorallia, class Anthozoa, phylum Coelenterata (= Cnidaria), was collected by hand near South Cay, off Port Royal, Jamaica. The cleaned animals were drained, cut into small pieces and dried within 12 hours in a stream of warm air. The dried material was crushed to a powder, defatted with *n*-hexane at room temperature, and extracted with benzene in a continuous percolator-extractor (Ciereszko, 1966) to yield an extract which gave colorless crystals upon concentration *in vacuo*. The crystals (9.4 g from 4.7 kg *Briareum*) were washed with benzene and ether, and a portion was chromatographed on silica gel H, eluted with chloroform-ether, 40/50 v.v., to yield five compounds detected by thin-layer chromatography. The major component, constituting 50% of the sample and being the second to be eluted from the column, is identical with the briarein A of Bartholome (1974) by

Table 1. Crystallographic data

Formula $C_{30}H_{39}O_{13}Cl$	Cell dimensions* ($-160^{\circ}C$)
F.W. 643.10	$a = 11.661 (4) \text{ \AA}$
Space group $P2_12_12_1$	$b = 26.26 (2)$
$\mu = 16.34 \text{ cm}^{-1} (\text{Cu } K\alpha)$	$c = 10.355 (6)$
$V(\text{at } 25^{\circ}C) = 3256 \text{ \AA}^3$	$V = 3170.9 \text{ \AA}^3$
$\rho_{\text{calc}}(25^{\circ}C) = 1.312 \text{ g cm}^{-3}$	$Z = 4$
$\rho_{\text{obs}}(25^{\circ}C) = 1.318 (\text{C}_6\text{H}_{14}/\text{CCl}_4)$	

* Determined by least-squares fit to the $+2\theta$ and -2θ values of 47 reflections taken from all octants of reciprocal space.

IR, ^1H NMR, ^{13}C NMR and UV. A sample was re-crystallized from ethyl acetate to obtain crystals for the X-ray analysis.

An orthorhombic crystal ($0.48 \times 0.22 \times 0.10 \text{ mm}$) was selected for data collection at $-160^{\circ}C$ with the expectation that the low-temperature data would improve the effectiveness of the direct methods to be used for the structure solution. Unit-cell-dimension data (Table 1) (Cu $K\alpha_1$ radiation, $\lambda = 1.54051 \text{ \AA}$) and integrated X-ray intensity data (Cu $K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$, Ni-filtered) were collected on a Nonius CAD-4 automatic diffractometer. The mosaic spread of the crystal was 0.7° . The space group was determined uniquely as $P2_12_12_1$ from systematic absences. All 3668 independent reflections with $2\theta \leq 150^{\circ}$ were measured by a $\theta-2\theta$ scan technique with variable scan width ($1.0 + 0.1 \tan \theta$) $^{\circ}$. A variable receiving aperture was used, ($4.0 + 0.86 \tan \theta$) mm, while the height was constant at 6.0 mm. The maximum scan time for each intensity measurement was 60 s, with 40 s used for scanning the peak and 10 s each used for scanning the left and right background. An intensity monitor reflection decreased 3% during the data collection. A total of 212 intensities were considered indistinguishable from background having $I \leq 1.4\sigma(I)$ and they were assigned a value equal to the square root of the total count, *i.e.* peak plus background. Lorentz, polarization and absorption corrections were applied to the data. For the absorption corrections, the program of Coppens, Leiserowitz & Rabinovich (1965) was used. The program employs the numerical integration method of Gauss and in this case 216 sampling points were taken. Values for the transmission coefficients ranged from 0.601 to 0.848. Each amplitude was assigned an experimental weight based on counting statistics (van der Helm, Ealick & Burks, 1975) with an instability factor of 0.04.

Structure determination and refinement

The intensities were placed on an absolute scale with the results of a Wilson plot (Wilson, 1942) and normalized structure factors, $|E|$, were derived. The Cl position was obtained from an interpretation of the Patterson synthesis. All C and O positions were obtained from the combined use of heavy-atom methods and direct methods; in the latter case the *MULTAN* program (Germain, Main & Woolfson, 1971) was used. After block-diagonal (9×9 or 4×4) least-squares refinement a difference Fourier map was calculated from which the H positions were determined. Most C atoms and the H atoms were refined, except the H atoms of one disordered methyl group, with isotropic temperature factors. The Cl atom, all O atoms and those C atoms which showed anisotropy in the difference Fourier synthesis were refined with anisotropic

temperature factors. 23 reflections, considered most sensitive to the anomalous dispersion of Cl scattering, were used to measure differences in I_+ and I_- (Bijvoet, Peerdeman & van Bommel, 1951) in order to establish the absolute configuration of the compound. The results of 21 reflections agreed with the absolute configuration shown in the figures, while one showed no indication and one showed the opposite configuration. The observed intensities were corrected for the anomalous dispersion of Cl (Patterson, 1963). The least-squares refinement was terminated when all shifts

were less than 0.5 of the corresponding estimated standard deviation. The final R value ($= \sum |kF_o| - |F_c| / \sum |kF_o|$) is 0.042 for all 3668 reflections. In the structure factor analysis the average value of $w_F \Delta F^2$ did not show significant variation with either $|F_o|$ or $\sin \theta/\lambda$. A final difference Fourier map showed a peak of $-0.35 \text{ e } \text{Å}^{-3}$ on the Cl position, a peak of $0.37 \text{ e } \text{Å}^{-3}$ in the middle of the C(5)–C(6) bond, while all other peaks were less than $0.3 \text{ e } \text{Å}^{-3}$. Final parameters are shown in Tables 2, 3 and 4.*

Atomic scattering factors for Cl, C and O were taken from *International Tables for X-ray Crystallography* (1974) and those for H atoms from Stewart, Davidson & Simpson (1965). All least-squares refinements were done with the block-diagonal least-squares program of Ahmed (1966).

Table 2. Positional and isotropic thermal parameters for chlorine, oxygen and carbon atoms

Calculated standard deviations for last digit are listed in parentheses.

	$x (\times 10^4)$	$y (\times 10^5)$	$z (\times 10^4)$	$B (\text{Å}^2 \times 10^2)$
Cl	6040.6 (6)	39032 (3)	-1565.2 (7)	*
O(1)	4804 (2)	38893 (7)	1097 (2)	*
O(2)	5048 (2)	28623 (7)	-1044 (2)	*
O(3)	7041 (2)	39200 (7)	4657 (2)	*
O(4)	4727 (2)	44575 (6)	4382 (2)	*
O(5)	2288 (2)	42224 (7)	4289 (2)	*
O(6)	2177 (2)	34080 (7)	2906 (2)	*
O(7)	5019 (2)	26889 (6)	2516 (2)	*
O(8)	3398 (2)	28506 (7)	-2119 (2)	*
O(9)	7402 (2)	46758 (8)	3688 (2)	*
O(10)	5151 (2)	49600 (8)	6073 (2)	*
O(11)	1200 (2)	44524 (9)	5989 (2)	*
O(12)	546 (2)	33777 (9)	4097 (2)	*
O(13)	3978 (2)	21827 (7)	1211 (2)	*
C(1)	4557 (2)	33709 (9)	833 (2)	133 (4)
C(2)	5554 (2)	31058 (10)	71 (3)	155 (4)
C(3)	6545 (2)	34466 (10)	-390 (3)	162 (4)
C(4)	7187 (2)	36914 (9)	716 (3)	154 (4)
C(5)	7402 (2)	33216 (10)	1769 (3)	156 (4)
C(6)	6998 (2)	33294 (9)	2974 (3)	149 (4)
C(7)	6296 (2)	37367 (9)	3610 (3)	144 (4)
C(8)	5168 (2)	35616 (9)	4311 (2)	117 (4)
C(9)	4804 (2)	40033 (9)	5195 (3)	141 (4)
C(10)	3669 (2)	39170 (10)	5878 (2)	*
C(11)	2674 (2)	37793 (9)	5007 (3)	150 (4)
C(12)	2974 (2)	33693 (9)	4009 (2)	131 (4)
C(13)	4148 (2)	34812 (9)	3334 (2)	107 (3)
C(14)	4271 (2)	31113 (9)	2180 (2)	122 (4)
C(15)	3512 (2)	33107 (10)	-79 (3)	*
C(16)	3935 (3)	29908 (9)	-1190 (3)	*
C(17)	2964 (3)	38052 (11)	-556 (3)	*
C(18)	7584 (3)	41664 (10)	713 (3)	*
C(19)	5466 (2)	31062 (10)	5190 (3)	*
C(20)	2846 (2)	28392 (10)	4597 (3)	*
C(21)	7535 (3)	43874 (11)	4570 (3)	205 (5)
C(22)	8228 (3)	44861 (13)	5774 (4)	*
C(23)	4941 (2)	49131 (10)	4945 (3)	163 (4)
C(24)	4873 (3)	53295 (10)	3974 (3)	*
C(25)	1489 (3)	45071 (12)	4884 (3)	241 (5)
C(26)	998 (3)	48896 (13)	3961 (4)	*
C(27)	1028 (3)	34187 (10)	3073 (3)	198 (4)
C(28)	441 (3)	34974 (15)	1798 (3)	*
C(29)	4719 (2)	22307 (9)	2010 (3)	156 (4)
C(30)	5425 (3)	18157 (10)	2603 (3)	*

* These atoms were refined anisotropically (Table 3).

Description and discussion of the structure

A stereo view (Johnson, 1965) of a single molecule is given in Fig. 1. Bond distances, bond angles and conformational angles are given in Figs. 2 and 3. The fusion of a 6- and a 10-membered ring is also shown in eunicellin (Kennard, Watson, Riva di Sanseverino, Tursch, Bosmans & Djerassi, 1968), a diterpenoid isolated from *Eunicella stricta*. Briarein A (BAC A) differs from eunicellin in the position of the ring fusion, lacks the ether O, and possesses an additional acetate group, a Cl substitution, a double bond in the 10-membered ring, and a γ -lactone ring.

BAC A is but one of a series of closely related compounds isolated from *Briareum asbestinum* (Hyde, 1966; Bartholome, 1974) all containing a Cl substitution. The major difficulty in obtaining the correct structure from spectroscopic and classical organic methods was the failure to establish the double-bond system C(6) C(5) C(4) C(18). No conjugated double-bond system was observed in the UV spectrum, and indeed the conformational angle for this system is observed as 68.9° (Fig. 3), rather than a value close to 0° , destroying the possibility for conjugation between C(4)=C(18) and C(5)=C(6).

The lactone group is *cis*. The endocyclic double bond in the 10-membered ring is *cis*. The 6-membered ring is in a chair conformation. The conformational angles of the lactone, 10- and 6-membered rings are given in Fig. 3; they show that considerable strain exists in the 10-membered ring. The absolute configuration is C(1)(*R*), C(2)(*R*), C(3)(*S*), C(7)(*S*), C(8)(*R*), C(9)(*S*), C(11)(*R*), C(12)(*S*), C(13)(*S*), C(14)(*S*), C(15)(*R*), and

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32092 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

is shown in Figs. 1, 2 and 3. All distances between quaternary and tertiary C atoms C(1)–C(2), C(1)–C(15), C(7)–C(8), C(8)–C(13), C(12)–C(13) and C(1)–C(14) are long (1.550–1.575 Å). All other bond distances and bond angles are normal. C–H bond distances vary between 0.91 and 1.06 Å with an average of 0.98 Å. The O(1)–H bond is 0.79 Å and is involved in an intramolecular hydrogen bond to the Cl atom. The H(11)···Cl distance is 2.45 Å, the O(1)···Cl distance is 3.11 Å, falling in the range of average O···Cl hydrogen-bond distances (Clark, 1963), and the O(1)–H(11)···Cl angle is 141°. No

intermolecular hydrogen bonding is observed, and there are no intermolecular distances among C, O or Cl atoms less than 3.30 Å.

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Table 3. Anisotropic thermal parameters

Thermal parameters ($\times 10^4$) are of the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	324 (3)	283 (3)	193 (3)	-23 (3)	18 (3)	48 (3)
O(1)	272 (9)	150 (7)	184 (8)	-31 (8)	40 (8)	1 (7)
O(2)	265 (10)	241 (10)	200 (9)	-29 (8)	23 (8)	-54 (8)
O(3)	202 (9)	217 (7)	260 (10)	-43 (8)	-76 (8)	2 (8)
O(4)	238 (9)	122 (7)	141 (8)	-5 (7)	-16 (7)	8 (7)
O(5)	210 (9)	171 (7)	249 (10)	36 (7)	16 (8)	25 (8)
O(6)	156 (8)	238 (7)	203 (9)	-8 (7)	-16 (7)	16 (8)
O(7)	180 (8)	119 (7)	196 (8)	7 (6)	-32 (7)	3 (7)
O(8)	393 (11)	238 (10)	182 (9)	-67 (9)	-44 (9)	-21 (8)
O(9)	351 (12)	272 (10)	359 (12)	-110 (9)	-12 (10)	0 (9)
O(10)	577 (14)	252 (10)	209 (10)	-102 (10)	-35 (11)	-59 (8)
O(11)	430 (14)	465 (14)	378 (13)	141 (11)	110 (12)	-103 (12)
O(12)	216 (10)	458 (14)	348 (11)	-36 (9)	72 (9)	21 (10)
O(13)	317 (10)	196 (7)	311 (11)	-12 (9)	-80 (9)	-56 (8)
C(10)	270 (12)	178 (10)	130 (11)	4 (10)	11 (10)	-14 (10)
C(15)	212 (12)	213 (10)	150 (11)	-14 (10)	-15 (10)	7 (10)
C(16)	319 (14)	164 (10)	160 (11)	-54 (11)	3 (12)	24 (9)
C(17)	320 (15)	272 (14)	266 (14)	54 (12)	-79 (13)	2 (12)
C(18)	278 (14)	234 (14)	286 (15)	-21 (12)	17 (13)	45 (12)
C(19)	234 (12)	171 (10)	202 (12)	1 (10)	-66 (11)	39 (10)
C(20)	225 (12)	199 (10)	207 (12)	-29 (10)	22 (11)	23 (10)
C(22)	360 (17)	367 (17)	441 (20)	-105 (14)	-150 (16)	-28 (16)
C(24)	393 (17)	150 (10)	340 (15)	-17 (12)	3 (14)	19 (11)
C(26)	489 (20)	311 (17)	576 (23)	125 (16)	-3 (20)	45 (16)
C(28)	207 (14)	615 (21)	349 (17)	2 (15)	-50 (13)	34 (17)
C(30)	325 (14)	150 (10)	342 (16)	47 (11)	-24 (13)	17 (11)

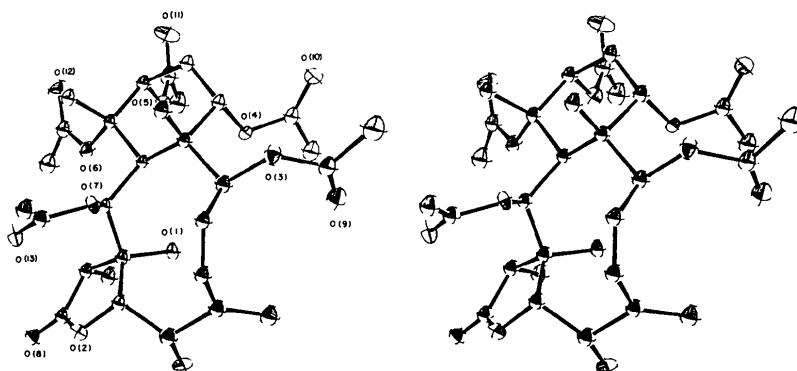


Fig. 1. Stereo view of single molecule.

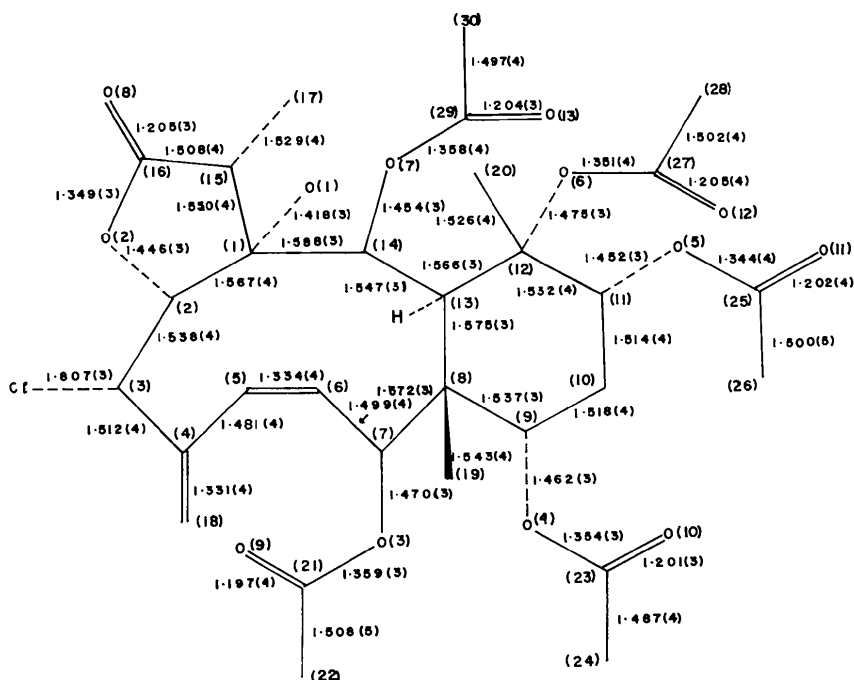


Fig. 2. Bond distances in BAC A.

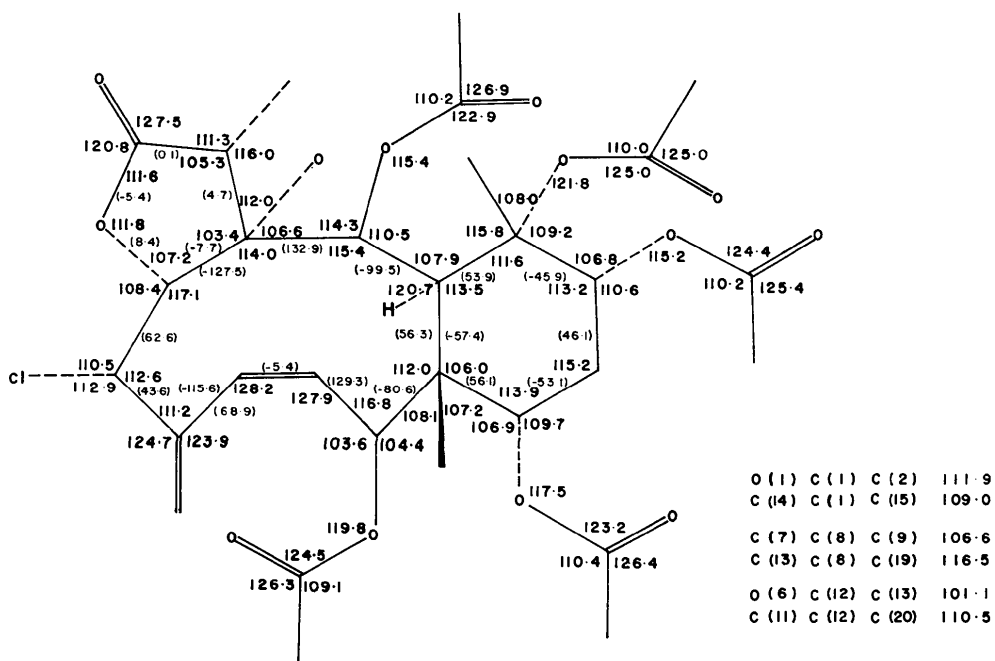


Fig. 3. Bond angles and, in parentheses, conformational angles in BAC A. Standard deviations for the bond angles are between 0.2 and 0.3°. All conformational angles are internal ones for the rings with the exception of C(18)C(4)C(5)C(6) (68.9°).

Table 4. Positional parameters ($\times 10^3$) and isotropic temperature factors ($\times 10$) for hydrogen atoms

	x	y	z	B (\AA^2)
H(11)	494 (3)	402 (1)	42 (3)	22 (7)
H(21)	592 (2)	284 (1)	56 (3)	6 (5)
H(31)	707 (3)	324 (1)	-91 (3)	22 (7)
H(51)	783 (3)	299 (1)	155 (3)	27 (7)
H(61)	723 (3)	305 (1)	356 (3)	27 (7)
H(71)	611 (3)	403 (1)	299 (3)	20 (6)
H(91)	536 (2)	407 (1)	583 (3)	11 (5)
H(101)	340 (3)	421 (1)	635 (3)	27 (7)
H(102)	375 (2)	366 (1)	651 (3)	15 (6)
H(111)	206 (3)	368 (1)	558 (3)	22 (7)
H(131)	401 (2)	384 (1)	291 (3)	8 (5)
H(141)	352 (2)	297 (1)	204 (2)	4 (5)
H(151)	288 (3)	311 (1)	33 (4)	30 (8)
H(171)	356 (3)	404 (1)	-105 (3)	30 (8)
H(172)	265 (3)	401 (1)	23 (3)	25 (7)
H(173)	230 (4)	369 (2)	-107 (4)	51 (10)
H(181)	800 (3)	429 (1)	149 (3)	24 (7)
H(182)	745 (3)	437 (1)	-5 (3)	26 (7)
H(191)	620 (2)	318 (1)	563 (3)	14 (6)
H(192)	489 (3)	307 (1)	588 (4)	31 (8)
H(193)	551 (2)	279 (1)	472 (3)	16 (6)
H(201)	207 (3)	278 (1)	482 (3)	21 (7)
H(202)	317 (3)	256 (1)	406 (3)	23 (7)
H(203)	324 (3)	280 (1)	541 (3)	19 (6)
H(221)	876 (3)	476 (2)	559 (5)	53 (10)
H(222)	759 (4)	456 (2)	646 (5)	67 (13)
H(223)	869 (4)	421 (2)	603 (4)	56 (11)
H(241)	555 (3)	534 (1)	356 (4)	46 (10)
H(242)	426 (3)	529 (1)	345 (4)	40 (9)
H(243)	497 (3)	567 (1)	439 (4)	46 (10)
H(261)	161 (3)	505 (1)	348 (4)	42 (9)
H(262)	48 (3)	473 (2)	340 (4)	48 (10)
H(263)	73 (4)	515 (2)	458 (5)	63 (12)
*H(281)	80	330	100	50
*H(282)	-40	340	190	50
*H(283)	20	390	170	50
*H(284)	80	370	115	50
*H(285)	-30	360	195	50
*H(286)	40	320	135	50
H(301)	621 (3)	186 (1)	258 (4)	32 (8)
H(302)	524 (3)	177 (1)	354 (4)	40 (9)
H(303)	519 (3)	150 (1)	214 (3)	33 (8)

* Hydrogen atom locations with 50% occupancy.

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