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CRYSTAL STRUCTURES OF TWO MACROCYCLIC DITERPENOID PHOTOPRODUCTS

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Abstract—The crystal structures of two macrocyclic diterpenoid photoproducts, the chemistry of which has been described in the preceding paper have been determined at 295 K.

Compounds I ($C_{20}H_{26}O_3$) and II ($C_{22}H_{30}O_4$) are both orthorhombic, $P2_12_12_1$. In I, $a = 24.18(1)$, $b = 11.841(5)$, $c = 5.984(2)$ Å, $Z = 4$, the structure being refined by least squares to a residual of 0.063 for 1234 "observed" reflections. For II, $a = 24.30(1)$, $b = 9.413(5)$, $c = 9.149(5)$ Å, $Z = 4$ ($R = 0.070$, 982 "observed" reflections).

The preceding paper[1] has described the chemical evidence for the nature of the photoproducts derived from bertyadionol and a derivative of its congener "Diterpene D", denoted **2** and **19** respectively. In both cases some doubt existed as to the stereochemistry about the cyclopropane ring junction and for this reason, as well as the novelty of **2**, a crystal structure determination by X-ray diffraction was considered desirable in each case. In a previous paper[2] we have reported the structural characterisation of other bertyadionol derivatives and the numbering scheme adopted in the present paper follows that already defined for compound **1** in that paper.

CRYSTALLOGRAPHY

Cell dimensions were determined in each case by a least squares fit of the angular prameters of 15 reflections centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set was then collected using a conventional $2\theta/\theta$ scan, for I, in the range $2\theta < 45°$, yielding 1350 reflections, 1234 of which with $I > 2\sigma(I)$ were considered "observed", and II, in the range $2\theta < 40°$, yielding 1186 reflections, 982 with $I > 2\sigma(I)$ being considered "observed", and used in the structure solution and refinement. No correction was applied for absorption in either case; in both structures neutral atom scattering factors were used, O, C corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[3-5] Monochromatic Mo(K_α) radiation was used for both structures ($\lambda = 0.71069$ Å), T being 295(1)K.

Crystal data: I: $C_{20}H_{26}O_3$, $M = 314.4$, orthorhombic, $P2_12_12_1$, (D_2^4, No. 19), $a = 24.18(1)$, $b = 11.841(5)$, $c = 5.984(2)$ Å, $U = 1713(1)$ Å,[3] $D_m = 1.22(1)$, $D_c(Z = 4) = 1.22$ g.cm^{-3}, $F(000) = 690$, $\mu_{MoK\alpha} = 0.86$ cm^{-1}. Crystal size $0.35 \times 0.35 \times 0.35$ mm.

II: $C_{22}H_{30}O_4$, $M = 374.5$, orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 24.30(1)$, $b = 9.413(5)$, $c = 9.149(5)$ Å, $U = 2093(2)$ Å,[3] $D_m = 1.19(1)$, $D_c(Z = 4) = 1.19$ g cm^{-3}, $F(000) = 808$, $\mu_{MoK\alpha} = 0.90$ cm^{-1}, crystal size $0.21 \times 0.08 \times 0.08$ mm.

Both structures were solved using the MULTAN program[6] package, subsequent processing being carried out using the X-ray 72 program system implemented on a CYBER 73 computer.[7] The structures were refined by 9×9 block diagonal least squares; where the C or O atoms had hydrogen atoms attached, the positional parameters of these were also included in the block.

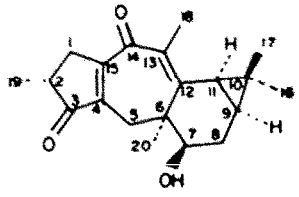
Non-hydrogen anisotropic thermal parameters were of the form

$$\exp(-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*))$$

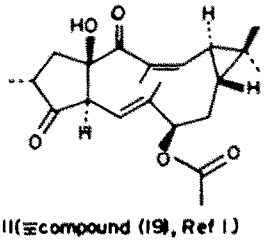
H atoms thermal motion being constrained at a value estimated by consideration of the motion of the parent C or O atom. Refinement converged when parameter shifts were $<0.2\sigma$. Final residuals were 0.063(I); 0.070(II); $R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{1/2}$ being 0.070(I), 0.068(II). In a weighting scheme of the form $w = (\sigma^2(F_o) + n \times 10^{-4}(F_o)^2)^{-1}$, the appropriate values of n were found to be 3(I), 3(II). Tables of structure amplitudes, thermal parameters and hydrogen atom parameters are deposited with the Editor.

DISCUSSION

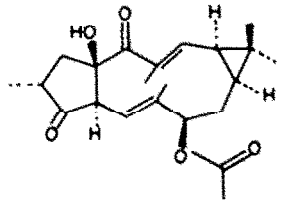
In each case the crystal lattice is comprised of discrete molecular units, the asymmetric unit in each case being a



I (≡compound (2), Ref 1)



II (≡compound (19), Ref 1)



III (≡compound (1), Ref. 2)

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single molecule. In I, the only notable intermolecular interaction is from the hydroxylic H(7b) to a nearby ketonic O(3) $(1-x,\ \frac{1}{2}+y,\ 1\frac{1}{2}-z)$ at 1.85(7) Å, while in II a similar interaction is found between H(15) and O(3) $(\frac{1}{2}-x,\ 2-y,\ z-\frac{1}{2})$, 2.20(13) Å. The structures derived have been presented and discussed chemically in the preceding paper; it remains to make a few comments concerning unusual features of the molecular geometries and stereochemistries of the two molecules.

I. The structure determination establishes the origin of this compound from a transannular bond formation between C(6) and C(12). On the assumption that the chirality throughout the remainder of the molecule is unchanged during the photochemical reaction, the chirality of C(6) is assigned as *S*. Although this assumption is reasonable (and the diagrams in this paper are drawn in conformity with the proposed chirality based on it and chemical evidence), it is not absolutely certain in view of the fact that the structure solution shows the dispositions of C(2) and C(19) to be at the centres of gravity of abnormally large thermal ellipsoids enveloping the atomic positions of the two possible epimeric forms. This in turn suggests that the lattice is comprised of an epimeric mixture of the two possible configurations at C(2). Epimerisation of this centre is known to occur readily.[1] However, the relative chiralities of C(7), C(9), and C(11) remain constant so that the conclusion seems reasonable.

II. The structure determination shows that the double bond between C(12) and C(13) in the precursor, compound (18) in the original paper, has isomerized to a *Z* configuration. Whereas chemical and spectroscopic evidence could not be used easily to assign the stereochemistry about C(9) and C(11), the structure determination has shown that surprisingly C(9) has undergone epimerization. The resultant strain in the C(9)–C(15) sequence of skeleton results in an unusual disposition of CO(14) which is twisted considerably relative to the plane of the C(12)–C(13) double bond and which was predicted from spectroscopic considerations. Again the absolute configuration shown is based on the previous chemistry.

Table 1. Non-hydrogen atom fractional cell coordinates, $\times 10^4$

I				II			
Atom	x	y	z	Atom	x	y	z
C(1)	3479(3)	2512(6)	3029(14)	C(1)	1728(5)	6808(13)	0325(14)
C(2)	3675(2)	2197(5)	5408(15)	C(2)	1537(5)	7751(11)	1623(14)
C(3)	4051(3)	3190(5)	5951(12)	C(3)	2069(4)	8356(11)	2174(13)
O(3)	4383(2)	3216(3)	7470(9)	O(3)	2101(3)	9206(8)	3163(8)
C(4)	3923(2)	4151(4)	4481(11)	C(4)	2550(4)	7731(12)	1327(14)
C(5)	4166(3)	5287(5)	4859(11)	C(5)	3082(4)	8516(13)	1293(13)
C(6)	4286(2)	5987(5)	2787(11)	C(6)	3564(5)	7936(11)	1706(12)
C(7)	4645(2)	7041(5)	3447(12)	C(7)	4116(4)	8689(13)	1546(15)
O(7)	5080(2)	6634(4)	4886(10)	O(7)	4026(2)	10198(8)	1344(8)
C(8)	4303(3)	7965(5)	4559(11)	C(71)	4372(5)	11063(13)	2041(18)
C(9)	3948(2)	8477(5)	2681(11)	O(71)	4795(4)	10625(10)	2601(16)
C(10)	3325(2)	8404(5)	2573(11)	C(72)	4252(5)	12557(13)	1777(14)
C(11)	3682(3)	7620(5)	1166(12)	C(8)	4476(7)	8171(13)	0237(22)
C(12)	3751(2)	6372(5)	1630(10)	C(9)	4200(4)	8270(12)	-1260(14)
C(13)	3362(2)	5672(5)	0897(10)	C(10)	4395(5)	7263(12)	-2475(17)
C(14)	3353(2)	4423(5)	0962(10)	C(11)	3822(5)	7139(12)	-1836(14)
O(14)	3122(2)	3891(3)	-0502(8)	C(12)	3346(5)	7504(15)	-2790(13)
C(15)	3594(2)	3764(5)	2836(10)	C(13)	2810(4)	7187(11)	-2575(13)
C(16)	3031(4)	9316(7)	1317(16)	C(14)	2628(4)	6539(11)	-1157(13)
C(17)	2999(3)	7927(6)	4468(15)	O(14)	2745(3)	5377(8)	-0786(10)
C(18)	2837(3)	6113(6)	-0278(13)	C(15)	2256(5)	7493(11)	-0172(12)
C(19)	3855(3)	1115(6)	5952(17)	O(15)	2111(4)	8834(10)	-0790(11)
C(20)	4640(3)	5318(6)	1136(4)	C(16)	4486(7)	7859(17)	-3970(16)
				C(17)	4815(5)	6028(16)	-1990(21)
				C(18)	2361(6)	7511(14)	-3709(15)
				C(19)	1199(4)	7008(12)	2812(16)
				C(20)	3653(5)	6431(12)	2272(16)

Table 2. Interatomic distances and angles (Å, deg.) with least squares estimated standard deviations in the final digit in parentheses. Values for II follow those for I

C(1) - C(2)	1.55(1), 1.54(1)	C(71) - C(72)	- , 1.45(2)
C(1) - C(15)	1.51(1), 1.50(2)	C(7) - C(8)	1.52(1), 1.56(2)
C(2) - C(3)	1.52(1), 1.50(2)	C(8) - C(9)	1.54(1), 1.51(2)
C(2) - C(19)	1.39(1), 1.53(2)	C(9) - C(10)	1.51(1), 1.54(2)
C(3) - O(3)	1.21(1), 1.21(1)	C(9) - C(11)	1.50(1), 1.51(2)
C(3) - C(4)	1.47(1), 1.52(2)	C(10) - C(16)	1.50(1), 1.48(2)
C(4) - C(15)	1.35(1), 1.56(2)	C(10) - C(17)	1.49(1), 1.64(2)
C(4) - C(5)	1.49(1), 1.49(2)	C(10) - C(11)	1.52(1), 1.52(2)
C(5) - C(6)	1.52(1), 1.35(2)	C(11) - C(12)	1.51(1), 1.48(2)
C(6) - C(7)	1.57(2), 1.52(2)	C(12) - C(13)	1.36(1), 1.35(2)
C(6) - C(12)	1.54(1), -	C(13) - C(14)	1.48(1), 1.50(2)
C(6) - C(20)	1.53(1), 1.52(2)	C(13) - C(18)	1.50(1), 1.53(2)
C(7) - O(7)	1.44(1), 1.45(1)	C(14) - O(14)	1.21(1), 1.18(1)
O(7) - C(71)	- , 1.34(1)	C(14) - C(15)	1.48(1), 1.55(2)
C(71) - O(71)	- , 1.22(2)	C(15) - O(15)	- , 1.43(1)
C(2) - C(1) - C(15)	104.5(6), 104.4(9)	C(10) - C(9) - C(11)	60.7(4), 59.6(8)
C(1) - C(2) - C(3)	101.2(6), 102.4(9)	C(8) - C(9) - C(11)	114.3(5), 123.0(11)
C(1) - C(2) - C(19)	122.3(7), 116.7(9)	C(9) - C(10) - C(16)	117.0(6), 118.9(11)
C(19) - C(2) - C(3)	118.4(7), 112.4(10)	C(9) - C(10) - C(17)	121.1(6), 115.1(12)
C(2) - C(3) - O(3)	125.1(6), 123.8(10)	C(9) - C(10) - C(11)	59.5(4), 58.9(8)
C(2) - C(3) - C(4)	110.2(6), 110.1(10)	C(16) - C(10) - C(17)	113.8(6), 116.1(12)
O(3) - C(3) - C(4)	126.6(6), 126.1(10)	C(16) - C(10) - C(11)	115.6(6), 121.4(12)
C(3) - C(4) - C(5)	121.8(6), 119.0(10)	C(17) - C(10) - C(11)	119.3(5), 114.3(11)
C(3) - C(4) - C(15)	107.4(5), 98.8(8)	C(9) - C(11) - C(10)	59.8(4), 61.5(8)
C(5) - C(4) - C(15)	130.8(6), 116.6(10)	C(9) - C(11) - C(12)	120.1(5), 121.5(11)
C(4) - C(5) - C(6)	116.5(5), 123.0(11)	C(10) - C(11) - C(12)	123.8(5), 118.1(11)
C(5) - C(6) - C(7)	109.5(5), 123.2(10)	C(11) - C(12) - C(6)	117.7(5), -
C(5) - C(6) - C(12)	111.6(5), -	C(11) - C(12) - C(13)	117.1(5), 128.4(12)
C(5) - C(6) - C(20)	110.6(5), 126.9(11)	C(6) - C(12) - C(13)	125.1(5) -
C(7) - C(6) - C(12)	110.0(4), -	C(12) - C(13) - C(14)	125.9(5), 119.7(10)
C(7) - C(6) - C(20)	105.4(5), 109.7(10)	C(12) - C(13) - C(18)	121.9(5), 123.2(11)
C(20) - C(6) - C(12)	109.5(5), -	C(18) - C(13) - C(14)	112.0(5), 117.0(9)
C(6) - C(7) - O(7)	106.7(5), 109.5(8)	C(14) - C(15) - C(4)	127.3(5), 109.1(9)
C(6) - C(7) - C(8)	112.4(5), 114.9(11)	C(1) - C(15) - C(4)	112.7(5), 100.6(9)
O(7) - C(7) - C(8)	112.0(6), 106.4(10)	C(1) - C(15) - O(15)	- , 106.5(9)
C(7) - O(7) - C(71)	- , 116.9(9)	C(4) - C(15) - O(15)	- , 109.1(9)
O(7) - C(71) - O(71)	- , 121.4(11)	C(14) - C(15) - O(15)	- , 114.7(9)
O(7) - C(71) - C(72)	, 113.3(11)	C(14) - C(15) - C(4)	127.3(5), 115.4(9)
O(71) - C(71) - C(72)	, 124.3(11)	C(15) - C(14) - C(13)	123.5(5), 116.5(9)
C(7) - C(8) - C(9)	105.4(5), 116.0(13)	C(15) - C(14) - O(14)	116.9(5), 120.4(11)
C(8) - C(9) - C(10)	124.4(5), 119.2(11)	C(13) - C(14) - O(14)	119.4(5), 123.1(10)

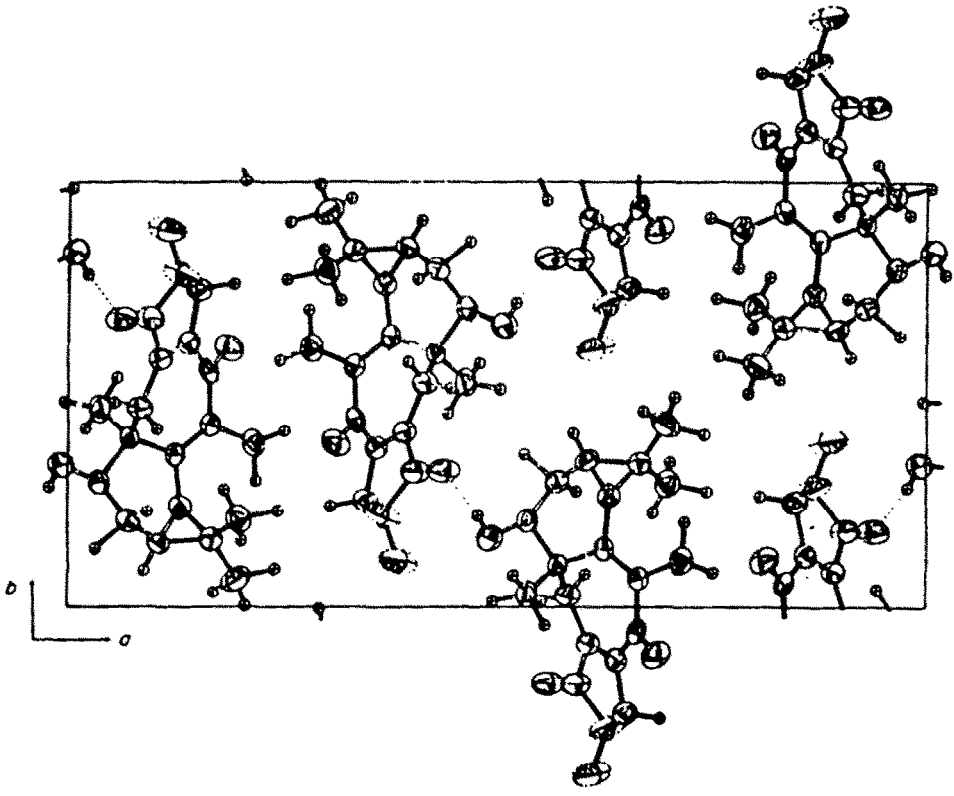


Fig. 1. Unit cell contents of I, projected down *c*, showing 50% thermal ellipsoids; hydrogen atom radii are arbitrarily set at 0.1 Å. Hydrogen bonds are shown by dotted lines; the atoms represented by dotted ellipsoids appear to be disordered.

Table 3. Torsion angles within the non-hydrogen skeleton in degrees for I, II and III. Values for the carboxylate group in II are omitted

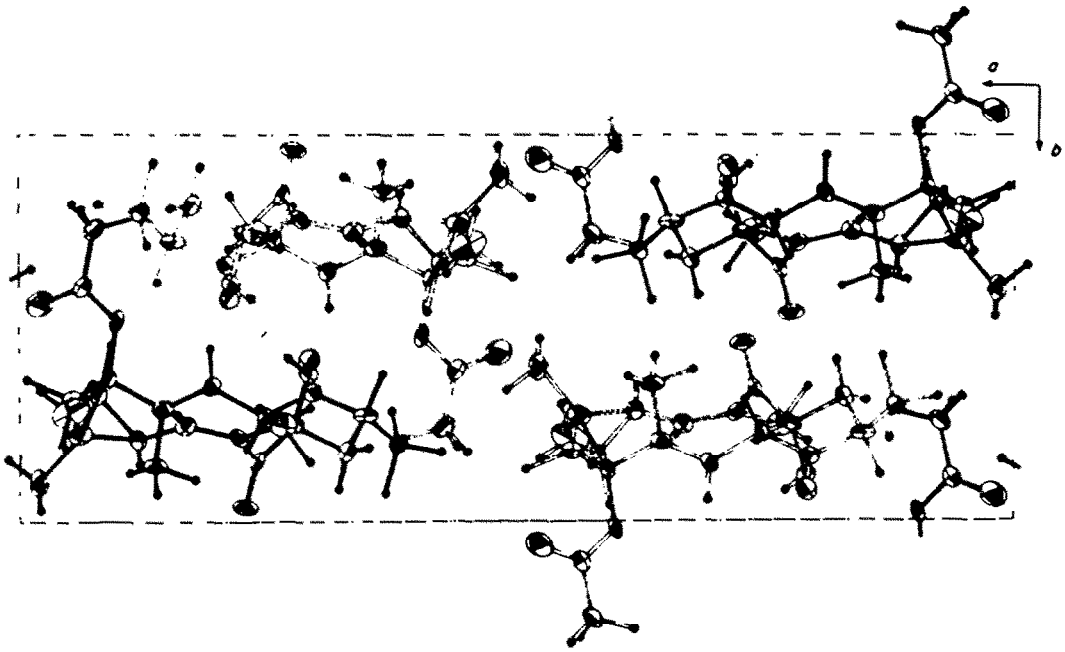
	I	II	III
C(15) - C(1) - C(2) - C(19)	-153.0	-161.2	-160.9
C(15) - C(1) - C(2) - C(3)	-18.7	-26.5	-35.3
C(1) - C(2) - C(3) - O(3)	-165.2	177.0	-162.2
C(1) - C(2) - C(3) - C(4)	19.4	-3.8	16.5
C(19) - C(2) - C(3) - O(3)	-28.7	-56.7	-35.1
C(19) - C(2) - C(3) - C(4)	155.9	122.6	143.6
C(2) - C(3) - C(4) - C(5)	170.6	158.4	136.8
C(2) - C(3) - C(4) - C(15)	-12.3	31.1	8.5
O(3) - C(3) - C(4) - C(5)	-6.8	-22.4	-44.5
O(3) - C(3) - C(4) - C(15)	172.2	-149.7	-172.8
C(3) - C(4) - C(5) - C(6)	146.6	124.5	128.3
C(15) - C(4) - C(5) - C(6)	-29.7	-116.8	-110.7
C(3) - C(4) - C(15) - C(1)	1.0	46.3	-29.7
C(3) - C(4) - C(15) - C(14)	-179.5	167.5	-150.3
C(5) - C(4) - C(15) - C(1)	-175.7	175.3	-154.9
C(5) - C(4) - C(15) - C(14)	3.9	-63.5	84.5
C(4) - C(5) - C(6) - C(7)	-168.8	174.4	175.4
C(4) - C(5) - C(6) - C(20)	-53.1	0.3	0.0
C(4) - C(5) - C(6) - C(12)	69.1	-	-

Table 3. (*Contd.*)

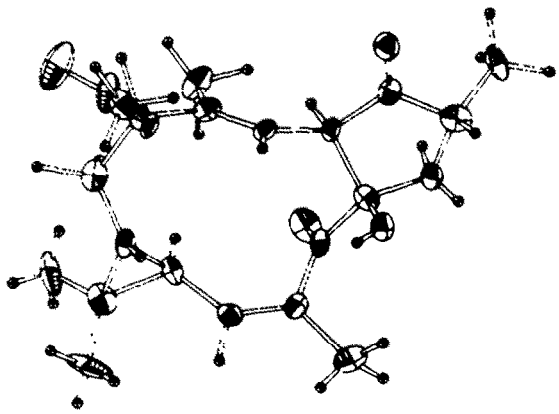
	I	II	III
C(5) - C(6) - C(7) - C(8)	-77.0	-102.6	-63.5
C(20) - C(6) - C(7) - C(8)	164.0	72.8	112.4
C(12) - C(6) - C(7) - C(8)	46.0	-	-
C(5) - C(6) - C(7) - O(7)	46.1	17.9	54.0
C(20) - C(6) - C(7) - O(7)	-72.8	-166.7	-130.1
C(12) - C(6) - C(7) - O(7)	169.2	-	-
C(5) - C(6) - C(12) - C(11)	126.6	-	-
C(5) - C(6) - C(12) - C(13)	-56.4	-	-
C(7) - C(6) - C(12) - C(11)	4.8	-	-
C(7) - C(6) - C(12) - C(13)	-178.2	-	-
C(20) - C(6) - C(12) - C(11)	-110.6	-	-
C(20) - C(6) - C(12) - C(13)	66.3	-	-
C(6) - C(7) - C(8) - C(9)	-71.7	56.7	-71.5
O(7) - C(7) - C(8) - C(9)	168.1	-64.9	168.2
C(7) - C(8) - C(9) - C(10)	114.5	-154.7	157.9
C(7) - C(8) - C(9) - C(11)	44.5	-84.0	82.7
C(8) - C(9) - C(10) - C(11)	-100.8	113.5	-114.2
C(8) - C(9) - C(10) - C(16)	153.9	-135.8	160.0
C(8) - C(9) - C(10) - C(17)	7.1	9.0	-4.6
C(11) - C(9) - C(10) - C(16)	-105.2	110.7	-105.9
C(11) - C(9) - C(10) - C(17)	107.9	-104.5	109.6
C(9) - C(10) - C(11) - C(12)	108.0	112.1	107.7
C(16) - C(10) - C(11) - C(12)	-144.4	5.5	-145.4
C(17) - C(10) - C(11) - C(12)	-2.0	-141.1	-2.0
C(16) - C(10) - C(11) - C(9)	107.6	-106.6	106.9
C(17) - C(10) - C(11) - C(9)	-110.9	106.8	-109.7
C(8) - C(9) - C(11) - C(12)	3.2	146.7	-0.6
C(8) - C(9) - C(11) - C(10)	117.2	-106.2	112.6
C(10) - C(9) - C(11) - C(12)	-114.0	-107.1	-113.1
C(9) - C(11) - C(12) - C(6)	-30.0	-	-
C(9) - C(11) - C(12) - C(13)	152.8	-124.1	-142.1
C(10) - C(11) - C(12) - C(6)	101.9	-	-
C(10) - C(11) - C(12) - C(13)	80.9	164.4	147.4
C(6) - C(12) - C(13) - C(18)	-178.3	-	-
C(11) - C(12) - C(13) - C(18)	-1.3	-174.6	-7.6
C(6) - C(12) - C(13) - C(14)	-3.8	-	-
C(11) - C(12) - C(13) - C(14)	173.2	7.8	169.8
C(12) - C(13) - C(14) - O(14)	-147.1	-68.7	168.2
C(18) - C(13) - C(14) - O(14)	27.8	113.5	-14.2
C(12) - C(13) - C(14) - C(15)	38.1	112.5	-18.4
C(18) - C(13) - C(14) - C(15)	-147.0	-65.3	159.2
C(13) - C(14) - C(15) - C(4)	13.9	120.2	-63.7

Table 3. (*Contd.*)

	I	II	III
O(14) - C(14) - C(15) - C(4)	-171.2	-61.0	109.7
C(13) - C(14) - C(15) - C(1)	-166.5	-128.8	-178.4
O(14) - C(14) - C(15) - C(1)	8.4	51.0	-5.0
C(14) - C(15) - C(1) - C(2)	-167.1	162.9	-161.4
C(4) - C(15) - C(1) - C(2)	13.2	45.8	-41.0
O(14) - C(14) - C(15) - O(15)	-	-175.4	-128.5
C(13) - C(14) - C(15) - O(15)	-	3.4	58.0
C(5) - C(4) - C(15) - O(15)	-	-63.4	-38.2
C(3) - C(4) - C(15) - O(15)	-	65.6	87.0
C(2) - C(1) - C(15) - O(15)	-	-68.4	-74.8



(a)



(b)

Fig. 2. (a) Unit cell contents of II, projected down *c* (20% ellipsoids). (b) A single molecule of II, projected normal to the molecular "plane" (20% ellipsoids).

The torsion angles within I and II are compared with each other and with III in Table 3. The reader should note that in the original report of the structure determination of III, the signs of some of the torsion angles are in error and the opportunity is taken to correct them.

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