FIRST ISOLATION AND DETERMINATION OF THREE HUMULENE TRIEPOXIDES

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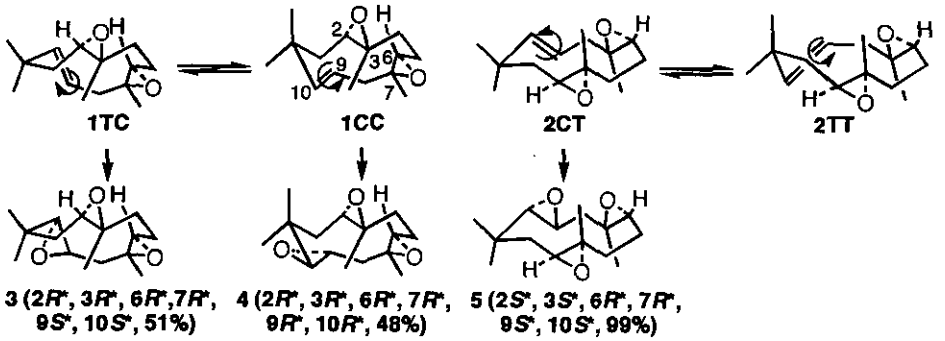
Abstract-The epoxidation of (9*E*)-(2*R**, 3*R**, 6*R**, 7*R**)-2,3;6,7-diepoxy-3,7,11,11-tetramethylcycloundec-9-ene (**1TC**) with *m*-CPBA gave two triepoxides, (2*R**, 3*R**, 6*R**, 7*R**, 9*S**, 10*S**)- and (2*R**, 3*R**, 6*R**, 7*R**, 9*R**, 10*R**)-2,3;6,7;9,10-triepoxy-3,7,11,11-tetramethylcycloundecane (**3** and **4**), in the ratio of **3** : **4** = 52 : 48. The epoxidation of (9*E*)-(2*S**, 3*S**, 6*R**, 7*R**)-2,3;6,7-diepoxy-3,7,11,11-tetramethylcycloundec-9-ene (**2CT**) gave only one triepoxide, (2*S**, 3*S**, 6*R**, 7*R**, 9*S**, 10*S**)-2,3;6,7;9,10-triepoxy-3,7,11,11-tetramethylcycloundecane (**5**). The configurations for **4** and **5** were determined by X-Ray crystallography.

It has been reported[1] that the configuration of africanol and bicyclohumulenone derived form the transannular cyclization products of humulene 9,10-epoxide, are very similar to two conformers, CT and CC, of the four possible conformers (CT, CC, TC and TT) of the original epoxide. In the epoxidation reaction of another monoepoxide, humulene 6,7-epoxide, we have reported[2] that the TC and CT conformations determined by X-Ray crystallography of the 2,3;6,7-diepoxide products (**1TC** and **2CT**[3], Scheme 1) also showed two (TC and CT) of the four possible conformers of the 6,7-epoxide. Thus the configuration (conformation) of the product in the epoxidation and cyclization reactions suggests the possible conformers of the original epoxide. On the basis of this concept, in connection with these studies, we planned to investigate the four possible configurations of humulene 2,3;6,7;9,10-triepoxide, (2*R**, 3*R**, 6*R**, 7*R**, 9*S**, 10*S**) (**3**), (2*R**, 3*R**, 6*R**, 7*R**, 9*R**, 10*R**) (**4**), (2*S**, 3*S**, 6*R**, 7*R**, 9*S**, 10*S**) (**5**) and (2*S**, 3*S**, 6*R**, 7*R**, 9*R**, 10*R**), that have been considered for the triepoxide derived from humulene by the epoxidation of **1TC** and **2CT** because four possible conformers (CT, CC, TC and TT) of humulene were suggested by the force field calculation[4] and that the epoxidation of three *trans*-endocyclic double bonds in humulene takes place at the successive 6,7-, 2,3-, and 9,10-positions. If the 9,10-double bond plane of **1TC** and **2CT** rotates freely during the course of the epoxidation as shown in Scheme 1, the four configurations of the triepoxide do possibly occur, but no experimental evidence has been obtained so far. In order to clarify the possible configuration of the triepoxides, we investigated the triepoxides prepared

by the further epoxidation of the 9,10-double bond in the diepoxides (**1TC** and **2CT**). In this study, we succeeded in the separation and isolation of triepoxides with three new different configurations (**3**, **4**, and **5**).



Scheme 1. T and C denote parallel and crossed arrangement of two bonds (6,7- and 9,10-bond) against 2,3-bond, respectively. The first and second symbols of **1** and **2** represent arrangement of 2,3- and 9,10-bonds, and of 2,3- and 6,7-bonds, respectively.

The epoxidation of **1TC**[2] with *m*-chloroperbenzoic acid (1.2 eq., *m*-CPBA) in dry CH_2Cl_2 at 0 °C under an argon atmosphere gave crude crystals, the chromatographic separation (ethyl acetate / benzene = 1 / 9, v / v) of which produced a mixture of humulene 2,3;6,7;9,10-triepoxides (**3** and **4**, 99 %). The mixture of **3** and **4** (**3** : **4** = 52 : 48, ratio was calculated from the HPLC peak areas) was separated into **3** (mp 157-158 °C, 39.3 % from **1**) and **4** (mp 126-127 °C, 41.2 % from **1**) by HPLC using the 7.8 x 300 mm column of μPORASIL (Waters, ethyl acetate / hexane = 3 / 17, v / v). The complete configuration of **4** was determined as (2*R**, 3*R**, 6*R**, 7*R**, 9*R**, 10*R**) that originated from the possible CC conformer of **1** by X-Ray crystallography (Figure 1) of its single crystal. Although no single crystal was obtained for **3**, **3** was thought as a stereoisomer of the triepoxide (**4**) because the HRMS of **3** showed the same molecular formula of $C_{15}H_{24}O_3$ as that of **4** and two COSY (H-H and C-H) spectra of **3** showed the existence of the same partial structures (Figure 2) as those of **4**. These observations together with the possibility of the existence of two conformers (**1TC** and **1CC**) due to the rotation of the *trans*-9,10-double bond plane indicated that **1TC** gave **3** and its configuration was (2*R**, 3*R**, 6*R**, 7*R**, 9*S**, 10*S**). On the other hand, the epoxidation reaction of **2CT**[2] isolated together with **1TC** from the epoxidation product of humulene 6,7-epoxide was carried out in the same way described above to give a unique triepoxide (mp 118-120 °C, **5**, 99 %), the

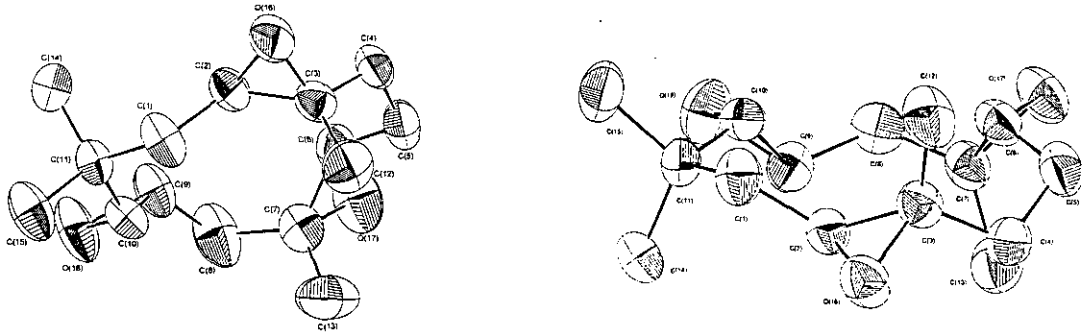


Figure 1. Perspective views of **4** (left)[5] and **5** (right). Hydrogen atoms were omitted.

(2*S**, 3*S**, 6*R**, 7*R**, 9*S**, 10*S**) configuration of which was determined by X-Ray crystallography (Figure 1). The configuration showed that **5** was produced only from **2CT**, one of the two possible conformers (CT and TT) in **2**.

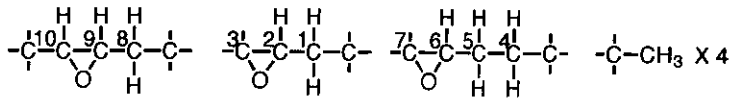


Figure 2. Partial structures of **3**.

Thus, the three new configurations, (2*R**, 3*R**, 6*R**, 7*R**, 9*S**, 10*S**), (2*R**, 3*R**, 6*R**, 7*R**, 9*R**, 10*R**) and (2*S**, 3*S**, 6*R**, 7*R**, 9*S**, 10*S**) of the humulene triepoxides (**3**, **4** and **5**) isolated from the epoxidation products of **1TC** and **2CT**, were first determined by X-Ray crystallography and spectroscopy. The above results suggested that, in the course of the epoxidation reaction, **1TC** maintained the CC conformation by the rotation of the 9,10-double bond plane; the conformation of **2CT** was of greater advantage than that of **2TT**, and three conformations (TC, CC and CT) of humulene 2,3;6,7-diepoxide existed.

EXPERIMENTAL SECTION

Melting points were determined in open capillaries and uncorrected. NMR spectra were measured using a JEOL JNN-EX 270 FT-NMR spectrometer (270 MHz for ^{1}H, 67.5 MHz for ^{13}C). Chemical shifts are reported in δ units relative to internal Me_4Si. TLC: pre-coated TLC plates, silica gel 60 F-254 (Merck). Adsorption chromatography: silica gel 60, 70-230 mesh ASTM (Merck). HPLC: model 6000A solvent delivery system (Waters), differential refractometer R 401 (Waters).

(2*R**, 3*R**, 6*R**, 7*R**, 9*S**, 10*S**)- and (2*R**, 3*R**, 6*R**, 7*R**, 9*R**, 10*R**)-2,3;6,7;9,10-Triepoxy-3,7,11,11-tetramethylcycloundecane (**3** and **4**): To a stirred solution of (9*E*)-(2*R**, 3*R**, 6*R**, 7*R**)-2,3;6,7-diepoxy-3,7,11,11-tetramethylcycloundec-9-ene (**1TC**, 50 mg, 0.21 mmol) in dry dichloromethane (2 mL) under an argon atmosphere at 0 °C was added 44 mg (0.25 mmol) of *m*-chloroperbenzoic acid (minimum 70 %). After stirring for 5 h at rt the epoxidation was complete. To the reaction mixture were added 10 mL of water, 3 mL of 1 M sodium hydroxide solution and 1 mL of 10 % (g / v) sodium thiosulfate solution, and then the mixture was extracted three times with dichloromethane. The extracts were washed with 1 M sodium hydroxide solution and water, and dried over anhydrous magnesium sulfate. Removal of the solvent yielded a crystalline mass, of which separation by silica gel column chromatography (ethyl acetate / benzene = 1 / 9, v / v) gave 53 mg (99 %) of a mixture of **3** and **4** (**3** : **4** = 52 : 48). The ratio was calculated from the HPLC peak areas. Furthermore, the mixture was separated into **3** (21 mg, 39.3 %) and **4** (22 mg, 41.2 %) by HPLC using the 7.8 x 300 mm column of μPORASIL {Waters, eluent: ethyl acetate / hexane = 3 / 17 (v / v), rate of flow = 2.0 mL / min}.

3; ^{1}H NMR ($CDCl_3$) δ: 0.70 (1H, dd, *J* = 9.4, 13.2 Hz, H-8), 0.74, 1.21, 1.33, 1.41 (each 3H, s), 1.28 (1H, ddd, *J* = 3.7, 13.5, 13.8 Hz, H-4), 1.46 (1H, dddd, *J* = 2.8, 10.6, 13.8, 14.5 Hz, H-5), 1.60 (2H,

d, J = 4 Hz, H_2-1), 2.21 (1H, ddt, J = 1.3, 14.5, 3.7 Hz, H-5), 2.26 (1H, ddd, J = 2.8, 3.7, 13.5 Hz, H-4), 2.62 (1H, dd, J = 1.3, 10.6 Hz, H-6), 2.67 (1H, d, J = 2.3 Hz, H-10), 2.79 (1H, dd, J = 3.3, 13.2 Hz, H-8), 2.79 (1H, ddd, J = 2.3, 3.1, 9.4 Hz, H-9), 2.89 (1H, t, J = 4 Hz, H-2); ^{13}C NMR ($CDCl_3$) δ: 17.2, 18.4, 23.2, 27.2 (each q), 24.7 (t, C-5), 32.7 (s), 36.5 (t, C-4), 41.1 (t, C-1), 43.5 (t, C-8), 50.9 (d, C-9), 59.6 (d, C-2), 60.1 (s), 63.6(s), 63.6 (d, C-6), 64.7 (d, C-10); mp 157-158 °C; HRMS (FD): m/z 252.1763 (M^+, $C_{15}H_{24}O_3$ requires 252.1726). *Anal.* Calcd for $C_{15}H_{24}O_3$: C 71.39; H 9.59. Found: C 71.27, H 9.58.

4; ^{1}H NMR ($CDCl_3$) δ: 0.87, 1.14, 1.28, 1.36 (each 3H, s), 1.27 (1H, dt, J = 3.3, 13.5 Hz, H-4), 1.49 (1H, ddt, J = 3.0, 10.0, 13.5 Hz, H-5), 1.55 (1H, dd, J = 2.6, 14.5 Hz, H-8), 1.67 (1H, dd, J = 7.9, 15.5 Hz, H-1), 1.74 (1H, dd, J = 2.0, 15.5 Hz, H-1), 2.08 (1H, dddd, J = 1.7, 3.3, 4.6, 13.5 Hz, H-5), 2.26 (1H, ddd, J = 3.0, 4.6, 13.5 Hz, H-4), 2.30 (1H, dd, J = 5.6, 14.5 Hz, H-8), 2.53 (1H, d, J = 2.6 Hz, H-10), 2.75 (1H, dd, J = 2.0, 7.6 Hz, H-2), 2.88 (1H, dd, J = 1.7, 10.0 Hz, H-6), 2.90 (1H, dt, J = 2.6, 5.6 Hz, H-9); ^{13}C NMR ($CDCl_3$) δ: 16.4 (q), 17.8 (q), 20.7 (q), 23.7 (t, C-5), 29.7 (q), 33.4 (s), 36.5 (t, C-4), 38.7 (t, C-1), 40.7 (t, C-8), 51.7 (d, C-9), 59.0(s), 60.5 (s), 60.6 (d, C-6), 60.8 (d, C-2), 63.4 (d, C-10); mp 126-127 °C; HRMS (EI): m/z 252.1713 (M^+, $C_{15}H_{24}O_3$ requires 252.1726). *Anal.* Calcd for $C_{15}H_{24}O_3$: C 71.39; H 9.59. Found: C 71.29, H 9.64.

(2*S**, 3*S**, 6*R**, 7*R**, 9*S**, 10*S**)-2,3;6,7;9,10-Triepoxy-3,7,11,11-tetramethylcycloundecane (**5**): Epoxidation of (9*E*)-(2*S**, 3*S**, 6*R**, 7*R**)-2,3;6,7-diepoxy-3,7,11,11-tetramethylcycloundec-9-ene (**2CT**, 50 mg, 0.21 mmol) with 44 mg (0.25 mmol) of *m*-chloroperbenzoic acid (minimum 70 %) in dry dichloromethane (2 mL) under an argon atmosphere at 0 °C for 4 h, extractive workup and chromatographic separation were carried out in the same manner described above to give 53 mg (99 %) of a crystalline mass, which was recrystallized from 0.3 mL of benzene to give 46 mg of pure crystals of **5** and evaporation of the filtrate produced 7 mg of crystals. HPLC {7.8 x 300 mm column of μPORASIL (Waters), eluent: ethyl acetate / hexane = 3 / 7 (v / v), rate of flow = 2.0 mL / min} of the two crystals showed a single peak and their NMR spectra were the same.

5; ^{1}H NMR ($CDCl_3$) δ: 0.74 (1H, dd, J = 10.5, 12.9 Hz), 0.88, 1.11, 1.36, 1.38 (each 3H, s), 1.12 (1H, m), 1.43 (1H, m), 1.63 (1H, dd, J = 6.6, 15.5 Hz), 1.71 (1H, dd, J = 2.0, 15.5 Hz), 2.16 (1H, m), 2.26 (1H, m), 2.34 (1H, d, J = 2.0 Hz), 2.65 (1H, dd, J = 2.0, 6.6 Hz), 2.73 (1H, dd, J = 2.6, 12.9 Hz), 2.74 (1H, m), 2.94 (1H, ddd, J = 2.0, 2.6, 10.5 Hz); ^{13}C NMR ($CDCl_3$) δ: 16.6, 17.2, 18.0 (each q), 25.6 (t, C-5), 28.7 (q), 33.2 (s), 35.0 (t, C-4), 37.8 (t, C-1), 43.6 (t, C-8), 52.8 (d, C-9), 57.8 (s), 59.5 (d, C-6), 60.0 (s), 61.4 (d, C-2), 65.7 (d, C-10); mp 118-120 °C; HRMS (EI): m/z 252.1722 (M^+, $C_{15}H_{24}O_3$ requires 252.1726). *Anal.* Calcd for $C_{15}H_{24}O_3$: C 71.39; H 9.59. Found: C 71.31, H 9.56.

X-Ray crystallography of **4** and **5**: The X-Ray crystallography of single crystals of **4** and **5** obtained by recrystallization from 20 % (v / v) ethyl acetate / hexane was carried out on a MAC Science MXC3k four-circle diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71073 Å) using a ω-2θ scan technique. A total of 1920 and 3299 independent reflections was collected for compounds (**4**) and (**5**), respectively. Both structures were solved by the direct method (SIR 92) and refined by the full-matrix least-

squares method. All the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (C-H: 0.96 Å) with isotropic thermal parameters fixed at 1.1 times those of the carbon atoms to which they are covalently bonded. Crystal data **4**: $C_{15}H_{24}O_3$, F.W. = 252.40, orthorhombic, space group $P2_12_12_1$, a = 8.894(1) Å, b = 18.997(3) Å, c = 8.571(1) Å, V = 1448.2(4) Å^3, Z = 4, D_{calc} = 1.157 g/cm^3, μ(MoKα) = 0.736 cm^{-1}, R = 0.054, Rw = 0.065 (weighting scheme, $w = \exp(10\sin^2\theta/\lambda^2)/(\sigma^2(F)+0.001F^2)$, 1396 observed reflections [$I > 2\sigma(I)$] used in the refinement. Crystal data **5**: $C_{15}H_{24}O_3$, F.W. = 252.40, monoclinic, space group $P2_1/n$, a = 9.389(2) Å, b = 27.453(3) Å, c = 5.778(1) Å, β = 105.59(1)°, V = 1434.5(4) Å^3, Z = 4, D_{calc} = 1.168 g/cm^3, μ(MoKα) = 0.743 cm^{-1}, R = 0.069, Rw = 0.079 (weighting scheme, $w = \exp(10\sin^2\theta/\lambda^2)/(\sigma^2(F)+0.001F^2)$, 1821 observed reflections [$I > 2\sigma(I)$] used in the refinement. All the calculations were carried out a SUN SPARK 10 work station (Cryatan-GM program system provided by MAC Science).

The fractional atomic coordinates of **4** and **5** are listed in Table 1 and the bond lengths and angles in Table 2.

Table 1. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters with Esd's in Parentheses for the Non-Hydrogen Atoms of Compounds (**4**) and (**5**).

Compoud **4**					Compound **5**				
Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]	Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
O(16)	0.86159(9)	0.07846(4)	0.12514(9)	0.0662(4)	O(17)	1.12082(11)	0.21315(4)	1.66145(18)	0.0594(5)
O(18)	1.36980(10)	0.21240(4)	0.41024(13)	0.0795(5)	O(16)	0.97400(10)	0.07135(4)	0.91329(17)	0.0588(5)
O(17)	1.17820(11)	0.00451(5)	0.68075(13)	0.0843(5)	O(18)	0.61624(11)	0.15872(4)	1.45231(23)	0.0719(6)
C(3)	0.86610(9)	0.07084(5)	0.29213(12)	0.0498(4)	C(2)	0.89120(12)	0.09242(5)	1.06641(22)	0.0461(5)
C(11)	1.15898(10)	0.21824(4)	0.21540(12)	0.0479(4)	C(6)	1.09605(13)	0.16941(5)	1.51451(22)	0.0471(6)
C(6)	1.11107(11)	0.01385(5)	0.52875(13)	0.0555(5)	C(7)	0.99160(13)	0.21059(5)	1.45345(22)	0.0466(6)
C(9)	1.30116(11)	0.14398(5)	0.42679(14)	0.0583(5)	C(9)	0.73287(13)	0.17707(5)	1.35546(24)	0.0486(6)
C(4)	0.89443(11)	-0.00475(5)	0.34278(13)	0.0566(4)	C(10)	0.71827(13)	0.12475(5)	1.39273(22)	0.0474(6)
C(5)	0.95461(12)	-0.01432(5)	0.50715(14)	0.0598(5)	C(11)	0.65330(12)	0.08705(5)	1.20293(22)	0.0471(5)
C(10)	1.21133(10)	0.20502(4)	0.37981(12)	0.0501(4)	C(3)	1.05335(12)	0.08769(5)	1.15329(21)	0.0452(5)
C(2)	0.98636(10)	0.10872(4)	0.20964(13)	0.0505(4)	C(5)	1.21075(13)	0.15738(6)	1.38641(27)	0.0555(6)
C(7)	1.15208(12)	0.07416(5)	0.62468(12)	0.0567(5)	C(4)	1.14766(13)	0.13190(5)	1.14560(23)	0.0499(6)
C(1)	1.00014(10)	0.18807(5)	0.19661(16)	0.0609(5)	C(13)	0.99108(17)	0.24526(6)	1.25400(30)	0.0642(7)
C(14)	1.26564(16)	0.18834(6)	0.09283(15)	0.0733(7)	C(8)	0.84848(15)	0.20673(5)	1.52558(24)	0.0538(6)
C(15)	1.14847(14)	0.29914(5)	0.19419(17)	0.0734(6)	C(1)	0.78194(14)	0.05966(5)	1.14091(29)	0.0563(6)
C(8)	1.29751(16)	0.11365(7)	0.58793(18)	0.0809(7)	C(12)	1.12262(16)	0.04746(6)	1.32321(33)	0.0662(8)
C(12)	0.74285(14)	0.10857(7)	0.37670(19)	0.0761(6)	C(15)	0.56669(16)	0.05072(7)	1.31690(34)	0.0709(8)
C(13)	1.0374(2)	0.1166(1)	0.7100(2)	0.095(1)	C(14)	0.55009(14)	0.10940(7)	0.97822(26)	0.0605(7)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond Lengths (Å) and Angles (deg) of Compounds (**4**) and (**5**).

	4	**5**		**4**	**5**		**4**	**5**
O(16) - C(3)	1.439(2)	1.458(2)	C(6) - C(7)	1.457(2)	1.476(2)	C(3) - C(2)	1.470(2)	1.475(2)
O(18) - C(9)	1.443(2)	1.447(2)	C(9) - C(8)	1.497(2)	1.495(2)	C(11) - C(10)	1.505(2)	1.513(2)
O(17) - C(6)	1.444(2)	1.454(2)	C(2) - C(1)	1.517(2)	1.511(2)	C(11) - C(14)	1.525(2)	1.524(2)
C(3) - C(4)	1.521(2)	1.510(2)	C(7) - C(13)	1.492(3)	1.493(3)	C(6) - C(5)	1.502(2)	1.499(2)
C(3) - C(12)	1.497(2)	1.504(3)	O(16) - C(2)	1.444(2)	1.447(2)	C(9) - C(10)	1.465(2)	1.464(2)
C(11) - C(1)	1.533(2)	1.545(2)	O(18) - C(10)	1.440(2)	1.444(2)	C(4) - C(5)	1.518(2)	1.528(2)
C(11) - C(15)	1.550(2)	1.541(3)	O(17) - C(7)	1.427(2)	1.462(2)	C(7) - C(8)	1.528(2)	1.514(2)

	4	**5**		**4**	**5**
C(3) - O(16) - C(2)	61.3(1)	61.0(1)	C(9) - O(18) - C(10)	61.1(1)	60.9(1)
C(6) - O(17) - C(7)	61.0(1)	60.8(1)	O(16) - C(3) - C(4)	112.5(1)	112.0(1)
O(16) - C(3) - C(2)	59.5(1)	59.1(1)	O(16) - C(3) - C(12)	114.4(1)	114.5(2)
C(4) - C(3) - C(2)	118.6(1)	118.6(2)	C(4) - C(3) - C(12)	115.8(1)	117.1(2)
C(2) - C(3) - C(12)	122.1(1)	120.8(2)	C(10) - C(11) - C(1)	108.7(1)	108.3(1)

C(10) - C(11) - C(14)	113.0(1)	112.5(2)	C(10) - C(11) - C(15)	107.1(1)	106.8(2)
C(1) - C(11) - C(14)	111.2(1)	110.8(2)	C(1) - C(11) - C(15)	107.6(1)	108.6(2)
C(14) - C(11) - C(15)	109.0(1)	109.6(2)	O(17) - C(6) - C(5)	116.8(1)	116.6(2)
O(17) - C(6) - C(7)	58.9(1)	59.9(1)	C(5) - C(6) - C(7)	125.6(1)	124.8(2)
O(18) - C(9) - C(10)	59.4(1)	59.5(1)	O(18) - C(9) - C(8)	116.5(2)	115.2(2)
C(10) - C(9) - C(8)	123.1(1)	121.2(2)	C(3) - C(4) - C(5)	115.9(1)	115.4(2)
C(6) - C(5) - C(4)	113.5(1)	113.4(2)	O(18) - C(10) - C(11)	117.1(1)	116.8(2)
O(18) - C(10) - C(9)	59.6(1)	59.7(1)	C(11) - C(10) - C(9)	123.9(1)	126.9(2)
O(16) - C(2) - C(3)	59.2(1)	59.9(1)	O(16) - C(2) - C(1)	114.9(1)	117.0(2)
C(3) - C(2) - C(1)	125.5(1)	124.6(2)	O(17) - C(7) - C(6)	60.1(1)	59.3(1)
O(17) - C(7) - C(8)	112.8(1)	112.3(2)	O(17) - C(7) - C(13)	116.6(2)	115.7(2)
C(6) - C(7) - C(8)	118.8(1)	117.6(2)	C(6) - C(7) - C(13)	122.1(2)	122.4(2)
C(8) - C(7) - C(13)	114.5(2)	116.0(2)	C(11) - C(1) - C(2)	116.0(1)	114.2(2)
C(9) - C(8) - C(7)	113.4(2)	113.5(2)			

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5 Perspective view of **4** depicted in Figure 1 is the inverse of the original.

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