

structures: direct methods in *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *MolEN LSFM*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *MolEN BTABLE PTABLE CIF*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and unit-cell diagrams have been deposited with the IUCr (Reference: CR1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

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## Triterpenoide. VII.† Über die Struktur von neuen 2-oxa- und 1,2-seco-Derivaten des Oleanolsäuremethylesters

ANDRZEJ GZELLA, URSZULA WRZECIONO\*  
UND LUCJUSZ ZAPRUTKO

*Lehrstuhl für Organische Chemie der Medizinischen,  
Karol-Marcinkowski-Akademie Poznań,  
ul. Grunwaldzka 6, 60-780 Poznań, Polen*

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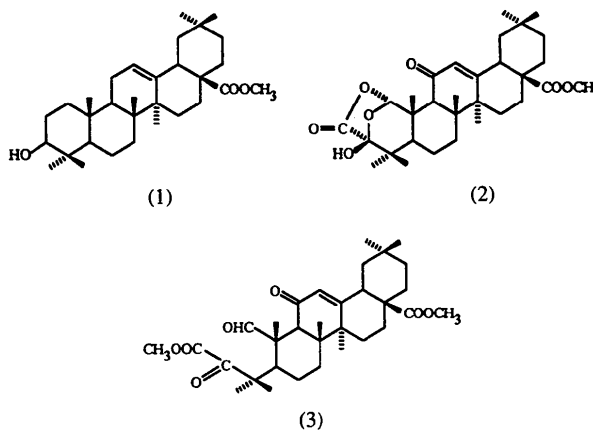
### Abstract

The X-ray crystal structure analysis of 3 $\beta$ -hydroxy-28-methoxy-11,28-dioxo-2-oxaolean-12-ene-3,1-carbolactone, (2), and dimethyl 1,3,11-trioxo-1,2-secoolean-12-

ene-2,28-dioate, (3), confirms the structure of (2) and (3) previously derived by spectroscopic methods. The hydroxyl group at C(3) in (2) and the side chain at C(5) in (3) are in equatorial positions. In (3), the C(1)=O(4) carbonyl group is antiperiplanar with respect to the C(25) methyl group, the C(3)=O(1) carbonyl group synperiplanar relative to the C(5)—C(6) bond and antiperiplanar to the C(2)=O(3) carbonyl group. In both compounds, C(28), O(6), O(7) and C(31) in the C(17) ester group are coplanar; the torsion angles C(18)—C(17)—C(28)—O(6) are quite different. The position of the ester group in (2) is stabilized by an intermolecular hydrogen bond. In both compounds, ring C has a slightly distorted sofa conformation; all other rings have deformed chair conformations. Rings D and E are *cis*-fused.

### Kommentar

Die Einwirkung von Chromtrioxyd auf Oleanolsäuremethylester (1) in Eisessig unter Zusatz von Schwefelsäure führt neben anderen Oleanolsäurederivaten zur Verbindung (2). Bei Behandlung mit Diazomethan erfolgt eine Umwandlung von (2) zu (3) (Zaprutko, 1994b).



Aufgrund spektroskopischer Untersuchungen (IR, MS, <sup>1</sup>H-, <sup>13</sup>C-, <sup>2</sup>D-NMR) hat Zaprutko (1994b) für diese Verbindungen die im Schema aufgeführten Strukturen vorgeschlagen. In dieser Mitteilung werden die Strukturen von (2) and (3) durch Röntgenstrukturanalysen bestätigt.

Die Laktonebrücke in (2) mit der mit dem C(3) Atom benachbarten Carbonylgruppe verbindet C(1) und C(3). Die an das zuletzt genannte C Atom gebundene Hydroxylgruppe nimmt die äquatoriale, die Carbonylgruppe des Laktoneinges die axiale Lage ein.

Der Ring A von (2), in dem das O(2) Atom eine Methylengruppe ersetzt, liegt in einer verzerrten Sesselform vor.

Die C(1)=O(4) Carbonylgruppe in (3) nimmt eine antiperiplanare Stellung zur C(25) Methylgruppe

† 6. Mitteilung: Zaprutko (1994a).

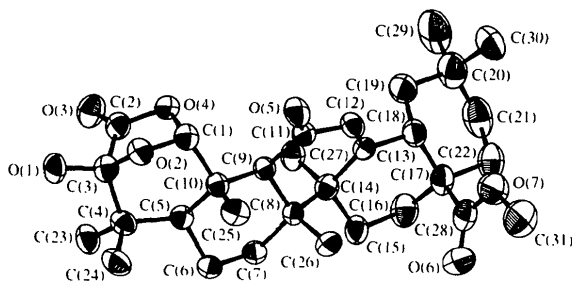


Fig. 1. Molekülstruktur von (2) (Wahrscheinlichkeitsniveau der Ellipsoide 50%).

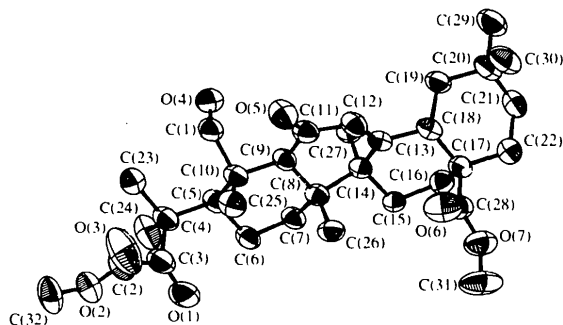


Fig. 2. Molekülstruktur von (3) (Wahrscheinlichkeitsniveau der Ellipsoide 50%).

ein. Die am C(5) haftende Seitenkette liegt in der äquatorialen Lage vor. Die C(3)=O(1) Carbonylgruppe liegt synperiplanar zur C(5)—C(6) Bindung und anti-clinal zur C(2)=O(3) Carbonylgruppe.

C(28), O(6), O(7) und C(31) der Estergruppe am C(17) Atom sind in (2) und (3) koplanar. Die Torsionswinkel C(18)—C(17)—C(28)—O(6) unterscheiden sich in beiden Verbindungen bedeutend voneinander und betragen 129.7 (6) [Verbindung (2)] und  $-8.8 (8)^\circ$  [Verbindung (3)]. Die Stellung der Estergruppe in (2) wird durch die intermolekulare Wasserstoffbrücke O(1)···O(6<sup>i</sup>) stabilisiert [O(1)···O(6<sup>i</sup>) = 2.798 (6), O(6<sup>i</sup>)—H(O1) = 1.97 (6) Å, O(1)—H(O1)···O(6<sup>i</sup>) = 175 (6) $^\circ$ ; (i)  $x, 1 + y, z$ ].

Die relativ großen Bindungswinkel C(4)—C(5)—C(10) von 115.3 (4) $^\circ$  im Ring A von (2) wie auch C(8)—C(9)—C(10) von 116.3 (4) [Verbindung (2)] und 119.0 (4) $^\circ$  [Verbindung (3)] in den Ringen B wird durch die sterische Abstoßung zwischen den axialen Methylgruppen C(24), C(25) und C(26) in (2) bzw. C(25) und C(26) in (3) hervorgerufen. Die nicht bindenden C-Atomabstände zwischen den Methylgruppen C(24)/C(25) und C(25)/C(26) betragen in (2) entsprechend 3.349 (8) und 3.210 (8) Å, in (3) zwischen den C(25)/C(26) Atomen 3.306 (7) Å. Ähnliche Beobachtungen haben wir bereits für andere Oleanolsäurederivate beschrieben (Zaprutko, Gzella & Wrzeciono, 1990).

Aus den Torsionswinkeln geht hervor, daß die Ringe B, D und E von (2) und (3) in deformierter Sesselform, der Ring C in gering verzerrter Sofa-Konformation vorliegen. Die Asymmetrie-Parameter betragen  $\Delta C_s^{12} = 6.1$ ,  $\Delta C_2^{12,13} = 22.8$ ,  $|\Phi| = 189.4^\circ$  [Verbindung (2)] und  $\Delta C_s^{12} = 2.1$ ,  $\Delta = C_2^{11,12} = 25.8$ ,  $|\Phi| = 176.0^\circ$  [Verbindung (3)]. Die Ringe D und E sind cis verknüpft. Die Ebenenwinkel von 60.3 (2) [Verbindung (2)] und 54.8 (1) $^\circ$  [Verbindung (3)] entsprechen dieser Ringverknüpfung.

Die Packung der Verbindungen (2) und (3) in der Elementarzelle sind in den Fig. 3 und 4 dargestellt.

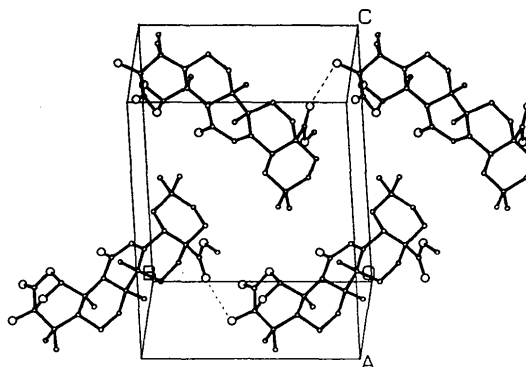


Fig. 3. Kristallstruktur von (2); die Wasserstoffbrückenbindungen sind durch gestrichelte Linien gekennzeichnet.

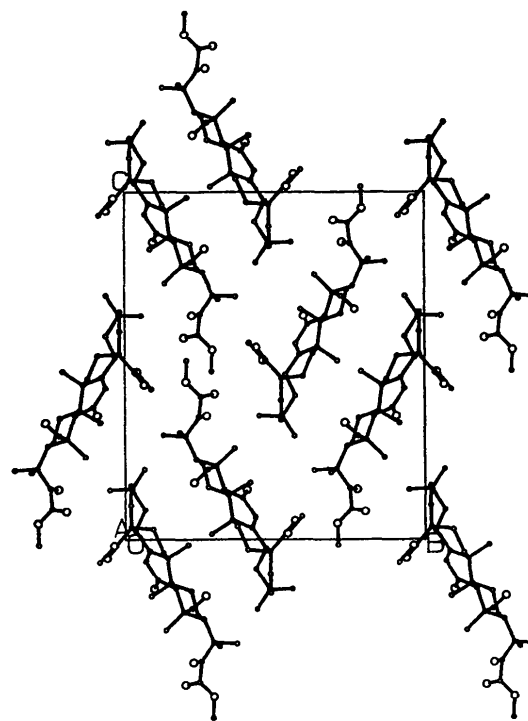


Fig. 4. Kristallstruktur von (3).

**Experimentelles**

Die Herstellung der (2) und (3) wurde von Zaprutko (1994b) beschrieben.

**Verbindung (2)***Kristalldaten*C<sub>31</sub>H<sub>44</sub>O<sub>7</sub>M<sub>r</sub> = 528,68

Monoklin

P2<sub>1</sub>

a = 7,491 (1) Å

b = 12,188 (2) Å

c = 15,744 (3) Å

β = 97,95 (1)°

V = 1423,6 (4) Å<sup>3</sup>

Z = 2

D<sub>x</sub> = 1,233 Mg m<sup>-3</sup>

Cu Kα Strahlung

λ = 1,54178 Å

Gitterparameter aus 15

Reflexen

θ = 11–15°

μ = 0,613 mm<sup>-1</sup>

T = 293 K

Prismen

0,50 × 0,25 × 0,20 mm

Farblos

C(20)	0,6295 (11)	-0,1548 (6)	0,5357 (4)	0,073 (5)
C(21)	0,7327 (9)	-0,2571 (7)	0,5127 (4)	0,080 (5)
C(22)	0,6713 (8)	-0,3002 (5)	0,4223 (4)	0,066 (4)
C(23)	1,0819 (6)	0,4247 (5)	0,0972 (3)	0,051 (3)
C(24)	0,8191 (7)	0,3994 (5)	-0,0182 (3)	0,056 (3)
C(25)	0,5078 (6)	0,2400 (5)	0,0537 (3)	0,046 (3)
C(26)	0,6287 (7)	-0,0003 (5)	0,1226 (3)	0,047 (3)
C(27)	0,9005 (7)	0,0787 (5)	0,3499 (3)	0,048 (3)
C(28)	0,5757 (8)	-0,2599 (5)	0,2696 (4)	0,054 (4)
C(29)	0,4327 (11)	-0,1816 (7)	0,5416 (4)	0,091 (5)
C(30)	0,7183 (12)	-0,1110 (8)	0,6229 (4)	0,098 (6)
C(31)	0,2898 (9)	-0,3254 (7)	0,2037 (4)	0,087 (5)
O(1)	0,8031 (5)	0,5906 (4)	0,0888 (2)	0,053 (2)
O(2)	0,5840 (4)	0,4628	0,1077 (2)	0,043 (2)
O(3)	0,9256 (5)	0,5255 (4)	0,2679 (2)	0,059 (2)
O(4)	0,6822 (4)	0,4158 (4)	0,2459 (2)	0,043 (2)
O(5)	0,3288 (4)	0,2047 (4)	0,2157 (2)	0,051 (2)
O(6)	0,6388 (6)	-0,2879 (4)	0,2074 (3)	0,075 (3)
O(7)	0,4013 (5)	-0,2710 (5)	0,2748 (2)	0,075 (3)

Tabelle 2. Geometrische Parameter (Å, °) für (2)

C(1)—O(2)	1,407 (6)	C(11)—O(5)	1,219 (5)
C(1)—O(4)	1,471 (5)	C(11)—C(12)	1,480 (7)
C(1)—C(10)	1,538 (6)	C(12)—C(13)	1,328 (7)
C(2)—C(3)	1,546 (7)	C(13)—C(14)	1,530 (6)
C(2)—O(3)	1,193 (6)	C(13)—C(18)	1,527 (6)
C(2)—O(4)	1,353 (6)	C(14)—C(15)	1,562 (7)
C(3)—O(1)	1,390 (6)	C(14)—C(27)	1,561 (6)
C(3)—O(2)	1,438 (6)	C(15)—C(16)	1,537 (7)
C(3)—C(4)	1,535 (7)	C(16)—C(17)	1,536 (8)
C(4)—C(5)	1,558 (7)	C(17)—C(18)	1,529 (7)
C(4)—C(23)	1,545 (6)	C(17)—C(22)	1,567 (7)
C(4)—C(24)	1,539 (7)	C(17)—C(28)	1,526 (7)
C(5)—C(6)	1,524 (6)	C(18)—C(19)	1,564 (7)
C(5)—C(10)	1,560 (6)	C(19)—C(20)	1,533 (8)
C(6)—C(7)	1,526 (7)	C(20)—C(21)	1,536 (10)
C(7)—C(8)	1,545 (6)	C(20)—C(29)	1,537 (9)
C(8)—C(9)	1,558 (6)	C(20)—C(30)	1,526 (10)
C(8)—C(14)	1,593 (6)	C(21)—C(22)	1,527 (8)
C(8)—C(26)	1,560 (6)	C(28)—O(6)	1,195 (6)
C(9)—C(10)	1,558 (6)	C(28)—O(7)	1,327 (6)
C(9)—C(11)	1,510 (6)	C(31)—O(7)	1,460 (7)
C(10)—C(25)	1,558 (6)		
O(2)—C(1)—O(4)	104,2 (4)	C(1)—C(10)—C(5)	106,9 (4)
C(10)—C(1)—O(2)	111,0 (4)	C(5)—C(10)—C(9)	105,3 (4)
C(3)—C(2)—O(4)	107,2 (4)	C(9)—C(11)—C(12)	116,1 (4)
C(1)—O(2)—C(3)	102,7 (3)	C(11)—C(12)—C(13)	124,2 (4)
C(2)—C(3)—O(2)	99,8 (4)	C(12)—C(13)—C(14)	121,3 (4)
C(4)—C(3)—O(2)	110,2 (4)	C(14)—C(13)—C(18)	120,6 (4)
C(3)—C(4)—C(5)	106,3 (4)	C(8)—C(14)—C(13)	108,4 (4)
C(1)—O(4)—C(2)	106,2 (4)	C(13)—C(14)—C(15)	112,2 (4)
C(4)—C(5)—C(10)	115,3 (4)	C(14)—C(15)—C(16)	114,5 (4)
C(6)—C(5)—C(10)	109,9 (4)	C(15)—C(16)—C(17)	113,2 (4)
C(5)—C(6)—C(7)	108,6 (4)	C(16)—C(17)—C(18)	110,8 (4)
C(6)—C(7)—C(8)	114,3 (4)	C(18)—C(17)—C(22)	110,5 (4)
C(7)—C(8)—C(9)	111,7 (4)	C(13)—C(18)—C(17)	112,1 (4)
C(9)—C(8)—C(14)	106,8 (3)	C(17)—C(18)—C(19)	113,0 (5)
C(8)—C(9)—C(10)	116,3 (4)	C(18)—C(19)—C(20)	113,0 (5)
C(8)—C(9)—C(11)	109,4 (4)	C(19)—C(20)—C(21)	108,3 (5)

**Verbindung (3)***Kristalldaten*C<sub>32</sub>H<sub>46</sub>O<sub>7</sub>M<sub>r</sub> = 542,71

Orthorhombisch

P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>

a = 7,709 (1) Å

b = 18,293 (2) Å

c = 21,082 (3) Å

V = 2973,4 (7) Å<sup>3</sup>

Z = 4

Cu Kα Strahlung

λ = 1,54178 Å

Gitterparameter aus 15

Reflexen

θ = 10–15°

μ = 0,598 mm<sup>-1</sup>

T = 293 K

Prismen

0,40 × 0,30 × 0,20 mm

*Datensammlung*Syntex P2<sub>1</sub> Diffraktometer

θ/2θ Abtastung

Absorptionskorrektur:

keine

2282 gemessene Reflexe

2032 unabhängige Reflexe

1899 beobachtete Reflexe

[I ≥ 1,96σ(I)]

R<sub>int</sub> = 0,0457*Verfeinerung*

Verfeinerung auf F

R = 0,044

wR = 0,050

S = 5,2148

1899 Reflexe

347 Parameter

H-Atom Parameter nicht

verfeinert ausser O(1)—H

w = 1/σ<sup>2</sup>(F)(Δ/σ)<sub>max</sub> = 0,02θ<sub>max</sub> = 57,5°

h = -8 → 8

k = 0 → 13

l = 0 → 17

2 Kontrollreflexe

gemessen nach je 100

Reflexen

Intensitätsschwankung:

&lt;2%

Δρ<sub>max</sub> = 0,18 e Å<sup>-3</sup>Δρ<sub>min</sub> = -0,19 e Å<sup>-3</sup>Extinktionskorrektur: F<sub>c</sub>' =F<sub>c</sub>(1 - 0,0001x F<sub>c</sub>/sinθ)

Extinktionskoeffizient:

x = 0,0673 (1)

Atomformfaktoren aus

SHELX76 (Sheldrick,

1976)

Tabelle 1. Atomkoordinaten und isotrope äquivalente Verschiebungsparameter (Å<sup>2</sup>) für (2)

$$U_{\text{äq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U <sub>äq</sub>
C(1)	0,5692 (6)	0,3784 (5)	0,1674 (3)	0,040 (3)
C(2)	0,8098 (7)	0,4817 (5)	0,2201 (3)	0,044 (3)
C(3)	0,7737 (6)	0,4871 (5)	0,1211 (3)	0,043 (3)
C(4)	0,8784 (6)	0,3984 (5)	0,0794 (3)	0,043 (3)
C(5)	0,8397 (6)	0,2880 (5)	0,1232 (3)	0,036 (3)
C(6)	0,9158 (6)	0,1841 (5)	0,0880 (3)	0,043 (3)
C(7)	0,9273 (6)	0,0951 (5)	0,1567 (3)	0,045 (3)
C(8)	0,7471 (6)	0,0714 (5)	0,1906 (3)	0,036 (3)
C(9)	0,6452 (6)	0,1791 (4)	0,2068 (3)	0,034 (2)
C(10)	0,6392 (6)	0,2691 (5)	0,1361 (3)	0,035 (3)
C(11)	0,4657 (6)	0,1509 (5)	0,2347 (3)	0,038 (3)
C(12)	0,4629 (6)	0,0531 (5)	0,2901 (3)	0,044 (3)
C(13)	0,6033 (6)	-0,0126 (5)	0,3118 (3)	0,040 (3)
C(14)	0,7841 (6)	0,0085 (5)	0,2800 (3)	0,040 (3)
C(15)	0,8898 (7)	-0,0999 (5)	0,2693 (3)	0,048 (3)
C(16)	0,8735 (8)	-0,1868 (5)	0,3387 (4)	0,059 (4)
C(17)	0,6776 (7)	-0,2106 (5)	0,3513 (3)	0,050 (3)
C(18)	0,5831 (7)	-0,1059 (5)	0,3746 (3)	0,048 (3)
C(19)	0,6475 (8)	-0,0662 (6)	0,4683 (3)	0,061 (4)

$D_x = 1,215 \text{ Mg m}^{-3}$   
 $D_m = 1,21 (1) \text{ Mg m}^{-3}$   
 Schwebemethode in  
 $\text{CCl}_4/\text{C}_6\text{H}_{14}$ -Lösung

Farblos

C(30)	0,0311 (9)	0,4460 (3)	0,3568 (3)	0,087 (4)
C(31)	-0,6039 (10)	0,4120 (4)	0,5661 (4)	0,107 (6)
C(32)	0,0776 (10)	0,7915 (4)	1,0156 (3)	0,089 (5)

## Datensammlung

Syntex  $P2_1$  Diffraktometer  
 $\theta/2\theta$  Abtastung  
 Absorptionskorrektur:  
 keine  
 2354 gemessene Reflexe  
 2287 unabhängige Reflexe  
 1880 beobachtete Reflexe  
 $[I \geq 1,96\sigma(I)]$   
 $\theta_{\text{max}} = 57,5^\circ$

$h = 0 \rightarrow 8$   
 $k = 0 \rightarrow 19$   
 $l = 0 \rightarrow 22$   
 2 Kontrollreflexe  
 gemessen nach je 100  
 Reflexen  
 Intensitätsschwankung:  
 $< 2\%$

## Verfeinerung

Verfeinerung auf  $F$   
 $R = 0,050$   
 $wR = 0,046$   
 $S = 3,8027$   
 1880 Reflexe  
 352 Parameter  
 H-Atom Parameter nicht  
 verfeinert  
 $w = 1/\sigma^2(F)$   
 $(\Delta/\sigma)_{\text{max}} = 0,002$

$\Delta\rho_{\text{max}} = 0,15 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0,18 \text{ e } \text{Å}^{-3}$   
 Extinktionskorrektur:  $F_c' =$   
 $F_c(1 - 0,0001xF_c/\sin\theta)$   
 Extinktionskoeffizient:  
 $x = 0,0113 (5)$   
 Atomformfaktoren aus  
 SHELX76 (Sheldrick,  
 1976)

Tabelle 3. Atomkoordinaten und isotrope äquivalente Verschiebungsparameter ( $\text{Å}^2$ ) für (3)

$$U_{\text{äq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	$x$	$y$	$z$	$U_{\text{äq}}$
O(1)	-0,2181 (6)	0,7259 (3)	0,8560 (2)	0,095 (4)
O(2)	-0,0131 (6)	0,7935 (2)	0,9542 (2)	0,076 (3)
O(3)	0,1407 (8)	0,6983 (3)	0,9198 (2)	0,125 (4)
O(4)	0,3023 (5)	0,7683	0,6632 (2)	0,070 (3)
O(5)	0,2842 (5)	0,5954 (2)	0,6435 (2)	0,075 (3)
O(6)	-0,2700 (6)	0,4361 (2)	0,5534 (2)	0,094 (3)
O(7)	-0,5357 (6)	0,4605 (2)	0,5174 (2)	0,083 (3)
C(1)	0,2656 (7)	0,7220 (3)	0,7016 (2)	0,058 (4)
C(2)	0,0342 (10)	0,7451 (4)	0,9121 (3)	0,074 (5)
C(3)	-0,0746 (9)	0,7524 (4)	0,8524 (3)	0,070 (4)
C(4)	-0,0051 (7)	0,7955 (3)	0,7970 (2)	0,057 (3)
C(5)	-0,0412 (7)	0,7603 (3)	0,7302 (2)	0,051 (3)
C(6)	-0,2314 (7)	0,7400 (3)	0,7199 (2)	0,053 (3)
C(7)	-0,2701 (6)	0,7208 (3)	0,6500 (2)	0,053 (3)
C(8)	-0,1669 (6)	0,6533 (3)	0,6282 (2)	0,045 (3)
C(9)	0,0256 (6)	0,6689 (3)	0,6426 (2)	0,045 (3)
C(10)	0,0787 (7)	0,6940 (3)	0,7114 (2)	0,049 (3)
C(11)	0,1420 (8)	0,6083 (3)	0,6186 (2)	0,057 (4)
C(12)	0,0830 (7)	0,5668 (3)	0,5633 (2)	0,059 (4)
C(13)	-0,0666 (7)	0,5794 (3)	0,5331 (2)	0,046 (3)
C(14)	-0,1853 (6)	0,6415 (3)	0,5540 (2)	0,043 (3)
C(15)	-0,3776 (6)	0,6265 (3)	0,5371 (2)	0,043 (3)
C(16)	-0,4022 (7)	0,5929 (3)	0,4709 (2)	0,053 (3)
C(17)	-0,3035 (7)	0,5201 (3)	0,4653 (2)	0,051 (3)
C(18)	-0,1065 (7)	0,5336 (3)	0,4747 (2)	0,049 (3)
C(19)	-0,0181 (7)	0,5662 (3)	0,4152 (2)	0,057 (3)
C(20)	-0,0530 (8)	0,5218 (3)	0,3544 (2)	0,065 (4)
C(21)	-0,2484 (8)	0,5180 (3)	0,3449 (3)	0,068 (4)
C(22)	-0,3410 (8)	0,4814 (3)	0,4013 (3)	0,068 (4)
C(23)	0,1889 (8)	0,8140 (3)	0,8081 (2)	0,070 (4)
C(24)	-0,1033 (8)	0,8698 (3)	0,8008 (3)	0,082 (4)
C(25)	0,0793 (7)	0,6338 (3)	0,7624 (2)	0,065 (4)
C(26)	-0,2337 (7)	0,5848 (3)	0,6640 (2)	0,057 (3)
C(27)	-0,1292 (6)	0,7102 (3)	0,5152 (2)	0,049 (3)
C(28)	-0,3621 (8)	0,4675 (3)	0,5178 (3)	0,064 (4)
C(29)	0,0314 (9)	0,5641 (3)	0,2983 (2)	0,081 (4)

Tabelle 4. Geometrische Parameter ( $\text{Å}, ^\circ$ ) für (3)

C(1)—O(4)	1,205 (6)	C(11)—C(12)	1,465 (7)
C(1)—C(10)	1,543 (7)	C(12)—C(13)	1,337 (6)
C(2)—O(2)	1,305 (7)	C(13)—C(14)	1,524 (6)
C(2)—O(3)	1,197 (7)	C(13)—C(18)	1,521 (6)
C(2)—C(3)	1,518 (8)	C(14)—C(15)	1,549 (6)
C(3)—O(1)	1,210 (7)	C(14)—C(27)	1,562 (6)
C(3)—C(4)	1,508 (7)	C(15)—C(16)	1,536 (6)
C(4)—C(5)	1,573 (6)	C(16)—C(17)	1,538 (7)
C(4)—C(23)	1,551 (7)	C(17)—C(18)	1,552 (7)
C(4)—C(24)	1,559 (8)	C(17)—C(22)	1,551 (7)
C(5)—C(6)	1,529 (7)	C(17)—C(28)	1,535 (7)
C(5)—C(10)	1,576 (7)	C(18)—C(19)	1,547 (6)
C(6)—C(7)	1,543 (6)	C(19)—C(20)	1,540 (7)
C(7)—C(8)	1,538 (6)	C(20)—C(21)	1,522 (8)
C(8)—C(9)	1,541 (6)	C(20)—C(29)	1,557 (7)
C(8)—C(14)	1,587 (6)	C(20)—C(30)	1,531 (7)
C(8)—C(26)	1,551 (6)	C(21)—C(22)	1,541 (7)
C(9)—C(10)	1,575 (6)	C(28)—O(6)	1,182 (7)
C(9)—C(11)	1,513 (7)	C(28)—O(7)	1,344 (7)
C(10)—C(25)	1,539 (7)	C(32)—O(2)	1,471 (6)
C(11)—O(5)	1,238 (6)	C(31)—O(7)	1,456 (7)
C(2)—O(2)—C(32)	116,7 (5)	C(5)—C(10)—C(9)	107,7 (4)
O(4)—C(1)—C(10)	122,8 (5)	C(9)—C(11)—C(12)	117,5 (5)
O(2)—C(2)—O(3)	125,8 (6)	C(11)—C(12)—C(13)	123,9 (5)
O(2)—C(2)—C(3)	110,5 (6)	C(12)—C(13)—C(14)	120,6 (5)
O(3)—C(2)—C(3)	123,6 (6)	C(14)—C(13)—C(18)	121,5 (4)
O(1)—C(3)—C(2)	114,8 (6)	C(8)—C(14)—C(13)	109,4 (4)
C(2)—C(3)—C(4)	119,4 (6)	C(13)—C(14)—C(15)	112,1 (4)
O(1)—C(3)—C(4)	125,6 (6)	C(14)—C(15)—C(16)	113,4 (4)
C(3)—C(4)—C(5)	114,6 (5)	C(15)—C(16)—C(17)	110,7 (4)
C(4)—C(5)—C(10)	115,9 (4)	C(16)—C(17)—C(18)	109,6 (4)
C(6)—C(5)—C(10)	109,9 (4)	C(18)—C(17)—C(22)	111,4 (4)
C(5)—C(6)—C(7)	112,1 (4)	C(13)—C(18)—C(17)	112,8 (4)
C(6)—C(7)—C(8)	111,6 (4)	C(17)—C(18)—C(19)	112,9 (4)
C(7)—C(8)—C(9)	106,9 (4)	C(18)—C(19)—C(20)	113,2 (4)
C(9)—C(8)—C(14)	107,8 (4)	C(19)—C(20)—C(21)	107,9 (5)
C(8)—C(9)—C(10)	119,0 (4)	C(20)—C(21)—C(22)	112,1 (5)
C(8)—C(9)—C(11)	111,8 (4)	C(17)—C(22)—C(21)	112,8 (4)
C(1)—C(10)—C(5)	109,0 (4)		

Bei Datenreduktion wurde die Lorentz- und die Polarisationskorrektur durchgeführt. Die Strukturen beider Verbindungen wurden mit direkten Methoden unter Verwendung des Programms SHELXS86 (Sheldrick, 1986) gelöst. Die Kohlenstoff- und Sauerstoff-Atome wurden anisotrop verfeinert, wobei die *full-matrix least-squares* Methode und das Programm SHELX76 (Sheldrick, 1976) verwendet wurde. Das Wasserstoff-Atom O(1)—H in (2) wurde aus Differenz-Fourier Synthese ermittelt und isotrop verfeinert, die Lagen der übrigen Wasserstoff-Atome wurden in beiden Strukturen geometrisch berechnet. Die Zeichnungen wurden anhand der Programme PLUTO (Motherwell & Clegg, 1978) und ORTEPII (Johnson, 1976) angefertigt.

Die Listen der Strukturparameter, anisotropen Verschiebungsparameter, H-Atom Koordinaten und vollständigen geometrischen Daten sind bei der IUCr (Aktzeichen: SE1056) hinterlegt. Kopien sind erhältlich durch The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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### Product of an *S<sub>N</sub>2'* Ring-Opening Reaction, (1*R*\*,2*R*\*,3*R*\*,4*R*\*,7*R*\*)-2,4,7-Trimethylcyclohept-5-ene-1,3-diol

JOHN COLUCCI, CHRISTOPHER GAJDA, MARK LAUTENS AND ALAN J. LOUGH

*Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1*

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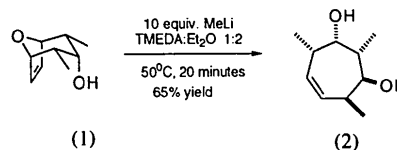
#### Abstract

The relative stereochemistry of the title compound, C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>, has been confirmed. The geometry of the seven-membered ring indicates that it is strained. Molecules are linked by O—H···O hydrogen bonds [O···O 2.796 (3) and 2.816 (3) Å] about independent  $\bar{4}$  inversion sites to form infinite columns with two independent ( $\cdots$ O—H···O—H···)<sub>2</sub> rings.

#### Comment

It has been shown that treatment of the [3.2.1]-oxabicyclic compound (1), 2,7-dimethyl-3,6-epoxycyclohept-4-enol, with excess methyllithium in TMEDA (*N,N,N',N'*-tetramethylethylenediamine) can promote a formal *S<sub>N</sub>2'* ring-opening reaction to yield the cycloheptene compound (2) (Lautens, Abd-El-Aziz & Lough, 1990). It was noted, however, that this ring opening could be accomplished only if the stereochemistry of the hydroxyl group was *endo* and if it was unprotected. Other organolithium compounds reacted much more generally. Earlier studies established that *tert*-butyllithium reacted exclusively from the *exo* face of the olefin. It was essential, therefore, to determine if methyllithium would attack from the same face in spite of this peculiar 'alkoxide effect'. The crystal structure of compound (2) did, indeed, show that attack occurred, as it did with other organolithiums, from the *exo* face of the olefin only. It is with the knowledge of the relative

substitution pattern of the five substituents on cycloheptene ring of (2) that our ongoing syntheses of natural products such as ionomycin and bourgeanic acid can be undertaken.



The cycloheptene ring of the title molecule (Fig. 1) adopts a chair-type conformation with atoms C1, C7, C3 and C4 forming a plane [mean deviation 0.022 (2) Å]. Atom C2 is 0.686 (4) Å 'above' this plane and atoms C5 and C6 are -0.919 (4) and -0.939 (4) Å, respectively, 'below' this plane. The strain present in the molecule is reflected in the deviations from standard values of the internal angles of the cycloheptene ring, which, on the principles of hybridization, are all slightly larger than would be expected. The most prominent deviations are shown by the angle C5—C6—C7 [127.1 (3)°] for an *sp*<sup>2</sup>-hybridized C atom and the angle C2—C1—C7 [117.9 (2)°] for an *sp*<sup>3</sup>-hybridized C atom.

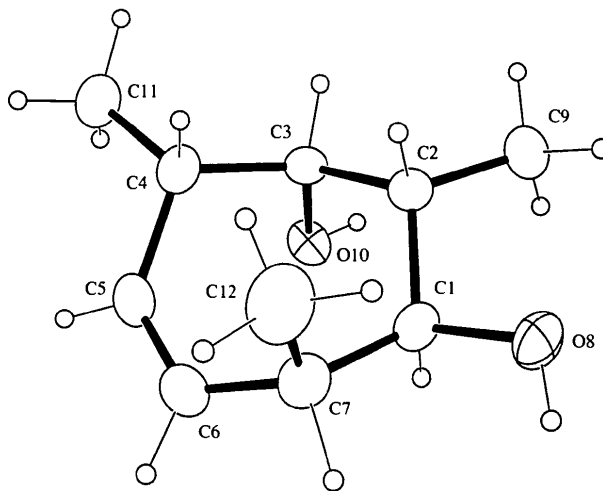


Fig. 1. A view of compound (2) with the crystallographic numbering scheme. Displacement ellipsoids are at the 25% level and H atoms are shown as spheres of arbitrary size.

Hydrogen-bonded ( $\cdots$ O—H···O—H···)<sub>2</sub> rings are formed by molecules related by fourfold inversion centers. Both of the hydroxyl groups present in the molecule are involved in this type of cyclic hydrogen bonding, alternating about different  $\bar{4}$  centers which are situated every  $\frac{1}{2}$  unit cell along the *z* direction (a virtue of the *I*-centering). Molecules are linked *via* this hydrogen bonding to produce infinite columns (see Fig. 2). The unique close intermolecular distances are O8···O8( $\frac{1}{4}-y, \frac{1}{4}+x, \frac{1}{4}-z$ ) 2.796 (3) Å and O10···O10( $\frac{1}{4}-y, \frac{1}{4}+x, -\frac{3}{4}-z$ ) 2.816 (3) Å.