Instrumental Achievements

Crystal Structure of (5*R**)-5-[(1*R**)-[2-(Dimethoxymethyl)-6-methoxyphenyl][(trimethylsilyl)oxy]methyl}-5-hydroxy-2,4,4-trimethyl-3-oxocyclohex-1-en-1-yl Pivaloate

Sachiyo KAMEI, Yasuyuki TAKENAKA, Yoshii SAKAI, Yuji OHASHI,
Koichi TSURUTA, Yoshiaki HORIGUCHI and Isao KUWAJIMA

Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152, Japan

Single crystal X-ray analysis of the title compound, which was synthesized in the course of a synthetic study of taxol (a congener of taxane diterpenes), has been performed to elucidate the relative stereochemistry at C(1) and C(2) atoms and the conformation around the C(2)–C(3) single bond.

Figure 1 shows the scheme of the reaction, which will

Fig. 1 Reaction scheme: Piv=pivaloyl; TMS=trimethylsilyl; DMAP=4-*N,N*-dimethylaminopyridine.

Table 1 Crystal and experimental data

Formula: C ₂₈ H ₄₄ O ₈ Si	
Formula weight=536.7	
Crystal size=0.35×0.30×0.30 mm	
Crystal color: colorless	
Crystal description: parallelepiped	
Crystal system: orthorhombic	
Space group: <i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Z</i> =4
<i>a</i> =12.249(6) Å	<i>α</i> =90°
<i>b</i> =25.617(1)	<i>β</i> =90
<i>c</i> =9.881(1)	<i>γ</i> =90
<i>V</i> =3100(2) Å ³	
<i>D_x</i> =1.15 g/cm ³	
Radiation: graphite monochromated Cu K _α	
<i>μ</i> for Cu K _α radiation=10.03 cm ⁻¹	
2θ range: 0° through 125°	
<i>R</i> =0.110	
No. of reflections measured=2728	
No. of reflexions used=1820	
Measurement: Rigaku AFC-4	
Program system: TEXSAN ²	
Structure determination: direct method (SHELX ³)	
Refinement: full-matrix (SHELX ³)	

Table 2 Positional and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)	occ.
Si	0.2812(3)	0.2309(1)	0.5372(4)	6.3(1)	
O(1)	0.3779(7)	0.1999(3)	0.6209(9)	5.6(2)	
O(2)	0.6505(8)	0.0429(4)	0.9219(9)	7.0(3)	
O(3)	0.566(1)	0.0342(4)	1.117(1)	8.7(4)	
O(4)	0.4357(9)	0.1065(4)	0.4976(9)	7.2(3)	
O(5)	0.5707(7)	0.1656(3)	0.6796(9)	6.1(3)	
O(6)	0.700(1)	0.2249(5)	0.963(1)	10.3(4)	
O(7)	0.224(2)	0.0942(6)	1.002(1)	7.3(3)	0.59(1)
O(8)	0.069(1)	0.1236(6)	0.893(2)	6.8(3)	0.59(1)
O(9)	0.140(2)	0.0793(8)	0.970(2)	7.3(3)	0.41(1)
O(10)	0.149(2)	0.1674(6)	0.880(3)	6.8(3)	0.41(1)
C(1)	0.4937(9)	0.1568(5)	0.785(1)	4.9(3)	
C(2)	0.375(1)	0.1639(4)	0.726(1)	4.7(3)	
C(3)	0.314(1)	0.1131(5)	0.682(1)	4.9(3)	
C(4)	0.347(1)	0.0860(5)	0.574(1)	5.8(4)	
C(5)	0.291(1)	0.0417(5)	0.521(2)	7.2(5)	
C(6)	0.201(1)	0.0269(6)	0.599(2)	7.9(6)	
C(7)	0.173(1)	0.0507(6)	0.713(2)	6.8(4)	
C(8)	0.227(1)	0.0950(5)	0.755(1)	5.8(4)	
C(9)	0.1852(9)	0.1174(5)	0.885(1)	6.2(3)	
C(11)	0.638(1)	0.1888(7)	0.936(1)	7.1(5)	
C(12)	0.676(1)	0.1322(6)	0.956(2)	7.2(5)	
C(13)	0.614(1)	0.0965(6)	0.911(1)	6.1(4)	
C(14)	0.510(1)	0.1008(4)	0.842(1)	4.7(3)	
C(15)	0.520(1)	0.1974(4)	0.899(1)	5.2(3)	
C(16)	0.453(1)	0.1882(5)	1.029(1)	5.7(4)	
C(17)	0.508(2)	0.2523(4)	0.850(2)	7.6(5)	
C(18)	0.778(1)	0.1255(8)	1.030(2)	9.1(6)	
C(19)	0.464(1)	0.0874(9)	0.368(2)	9.1(6)	
C(20)	0.209(2)	0.2749(7)	0.655(2)	9.5(6)	
C(21)	0.354(2)	0.2667(8)	0.407(2)	8.9(6)	
C(22)	0.183(1)	0.1850(6)	0.460(2)	8.1(5)	
C(23)	0.619(1)	0.0157(5)	1.026(1)	5.6(4)	
C(24)	0.663(2)	-0.0396(7)	1.029(2)	8.1(5)	
C(25)	0.649(2)	-0.0656(8)	1.156(2)	10.2(7)	
C(26)	0.776(3)	-0.044(1)	0.991(5)	26(3)	
C(27)	0.606(3)	-0.071(1)	0.929(3)	19(2)	
C(28)	0.197(3)	0.116(1)	1.129(2)	10.5(8)	0.59(1)
C(29)	0.025(2)	0.161(1)	0.801(3)	7.0(5)	0.59(1)
C(30)	0.139(5)	0.087(2)	1.112(3)	10.5(8)	0.41(1)
C(31)	0.037(2)	0.166(2)	0.836(5)	7.0(5)	0.41(1)

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} (a_i \cdot a_j).$$

be reported elsewhere in detail.¹ It should be noted that the title compound (**2**) exists in two conformational isomers and these are not interconvertible to each other at room temperature. The ¹H NMR spectra have suggested that these are rotational isomers around the C(2)–C(3) single bond. These conformational isomers are separable by silica gel column chromatography (20% ethyl acetate/hexane), and the more polar isomer (**2-1**) was used for the X-ray analysis.

Crystal and experimental data are listed in Table 1. The crystal decomposed during the data collection. The intensities of 3 standard reflections measured every 50 reflections were decreased to 0.72 compared with their initial values. A decay correction was, therefore, applied. The dimethoxymethyl group has a disordered structure. These atoms were refined with the same isotropic thermal parameters between the corresponding atoms. The site occupancy factors of each atom converged to 0.59(1) and 0.41(1). The *R* value is somewhat high owing to the decomposition of the crystal during the measurement. Hydrogen atoms were treated as rigid groups with the fixed thermal parameters, except that the atoms in the disordered methoxyl groups were not included. No absorption and extinction corrections were applied. The final fractional coordinates and equivalent isotropic temperature factors are given in Table 2. C(10) is not allocated in order to be consistent with the numbering of taxane diterpenes.

The molecular structure is shown in Fig. 2. The analysis has revealed the relative stereochemistry to be C1*R** and C2*R**, and the conformation around the C(2)–C(3) bond to be *P* [torsion angle of O(1)–C(2)–C(3)–C(4)=57(2)°].

Fig. 2 ORTEP⁴ drawing with the numbering of atoms. Thermal ellipsoids scale to enclose 20% probability. Hydrogen atoms are omitted.

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