Instrumental Achievements

Crystal Structure of *Exo*-(5*R**,6*R**,11*S**,12*S**)-5,6,11,12-tetrahydro-4,11,12-trimethoxy-9,13,13-trimethyl-5-[(triethylsilyl)oxy]-6,10-methano-8(7*H*)-benzocyclodecenone

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Single crystal X-ray analysis of the title compound, synthesized in the course of a synthetic study toward taxinine (a congener of taxane diterpenes), has been performed to elucidate the conformation of the eight-membered ring and the relative stereochemistry at C(1),

C(2), C(9), and C(10) atoms.

The detailed process of synthesis has been already reported.¹ Figure 1 shows the scheme of the reaction. Tricyclic compounds were obtained by treating the natural 2 α type reactant **1** with titanium tetrachloride. The major product **2** was examined by the X-ray method. Crystal and experimental data are listed in Table 1. Hydrogen atoms were treated as rigid groups with the fixed thermal parameters. A residual peak of the height of 0.83 eÅ⁻³ was found at 0.32 Å from C(20) atom on the difference map. The C(20) atom was therefore treated as a disordered structure, but the peak was not diminished. So it was treated as an ordered structure. No absorption and extinction corrections were applied. The final fractional coordinates and equivalent isotropic temperature factors are given in Table 2. The molecular structure is shown in Fig. 2. The analysis has revealed the eight-membered ring to be in a chair-boat-like conformation that makes the whole molecule *exo* and the relative stereochemistry to be C1*R**, C2*R**, C9*S**, and C10*S**. The methoxy groups at 9 and 10 are 9 β , 10 α which are the most stable in *exo* conformation. Two minor products obtained **3**, **4** were found to be in *endo* conformation with 9 α , 10 β and 9 α , 10 α by ¹H NMR. The steric and electrostatic repulsion between 2-triethylsilyloxy and 4-methoxy group might be responsible for the predominant formation of the *exo* isomer **2**.

Table 1 Crystal and experimental data

Formula: C ₂₇ H ₄₂ O ₅ Si
Formula weight=474.7
Crystal size=0.3×0.2×0.2 mm
Crystal color: colorless
Crystal description: parallelepiped
Crystal system: monoclinic
Space group: C2/c Z=8
a=19.490(3) Å α =90°
b=10.764(3) β =102.67(1)
c=26.694(5) γ =90
V=5464(3) Å ³
D _x =1.15 g/cm ³
Radiation: graphite monochromated Cu K α
μ for Cu K α radiation=9.97 cm ⁻¹
2 θ range: 0° through 125°
R=0.085
No. of reflections measured=4623
No. of reflections used=2571
Measurement: Rigaku AFC-4
Program system: TEXSAN ²
Structure determination: direct method
Refinement: full matrix (SHELX ³)

Fig. 1 Reaction scheme.

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

Atom	x	y	z	B_{eq}
Si	0.32234(9)	0.2311(2)	0.1618(1)	5.0(1)
O(1)	0.3436(2)	0.3419(4)	0.1248(2)	3.9(1)
O(2)	0.4983(2)	0.6738(5)	0.1336(2)	5.6(2)
O(3)	0.1576(2)	0.4677(4)	0.0546(2)	5.0(1)
O(4)	0.4808(2)	0.2301(5)	0.0554(2)	6.5(2)
O(5)	0.4153(2)	0.6823(5)	0.1975(2)	5.6(2)
C(1)	0.3189(3)	0.4143(6)	0.0340(2)	3.7(2)
C(2)	0.2930(3)	0.4026(5)	0.0852(2)	3.5(2)
C(3)	0.2677(3)	0.5234(5)	0.1051(2)	3.4(2)
C(4)	0.1958(3)	0.5509(6)	0.0880(2)	3.7(2)
C(5)	0.1659(3)	0.6582(6)	0.1035(2)	4.2(2)
C(6)	0.2089(3)	0.7407(7)	0.1347(3)	5.0(2)
C(7)	0.2794(3)	0.7176(6)	0.1512(2)	4.5(2)
C(8)	0.3107(3)	0.6099(6)	0.1375(2)	3.8(2)
C(9)	0.3909(3)	0.6017(6)	0.1558(2)	3.9(2)
C(10)	0.4279(3)	0.6409(6)	0.1126(2)	3.8(2)
C(11)	0.4214(3)	0.5339(5)	0.0757(2)	3.4(2)
C(12)	0.4604(3)	0.4302(6)	0.0869(2)	3.8(2)
C(13)	0.4395(3)	0.3160(6)	0.0558(2)	4.4(2)
C(14)	0.3636(3)	0.3019(6)	0.0275(2)	4.3(2)
C(15)	0.3623(3)	0.5312(6)	0.0276(2)	3.8(2)
C(16)	0.3157(3)	0.6497(6)	0.0168(2)	4.2(2)
C(17)	0.3934(3)	0.5212(7)	-0.0209(2)	5.1(2)
C(18)	0.5208(3)	0.4100(7)	0.1321(3)	4.8(2)
C(19)	0.4081(4)	0.631(1)	0.2456(3)	7.6(3)
C(20)	0.5244(6)	0.760(1)	0.1098(6)	13.4(6)
C(21)	0.0874(3)	0.4988(7)	0.0321(3)	5.6(2)
C(22)	0.3037(5)	0.0816(8)	0.1248(4)	8.3(3)
C(23)	0.3670(7)	0.0138(9)	0.1130(5)	11.7(5)
C(24)	0.2426(5)	0.269(1)	0.1848(4)	10.2(4)
C(25)	0.2435(7)	0.374(1)	0.2202(5)	14.1(7)
C(26)	0.3996(4)	0.2151(9)	0.2144(3)	7.6(3)
C(27)	0.3955(6)	0.118(1)	0.2552(4)	10.7(4)

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

Fig. 2 ORTEP⁴ drawing with the numbering of atoms. Thermal ellipsoids scaled to enclose 30% probability. Hydrogen atoms are omitted.

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