Supporting Information

First Synthesis and Structural Elucidation of (-)-Presphaerene

Jongkook Lee* and Jiyong Hong

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Table 1. ¹H NMR comparison of natural and synthetic (-)-presphaerene (**1**), and 7-*epi*-presphaerene (**1'**)

Protons at Carbon No.
	(-)-presphaerene (1)	Sphaeroane	7- <i>epi</i> -presphaerene (1')
	Synthetic (-)-presphaerene (1) (500 MHz, CDCl ₃)	Natural (-)-presphaerene ^{2c} (270 MHz, The used solvent was not reported)	Synthetic (-)-7- <i>epi</i> -presphaerene (1') (500 MHz, CDCl ₃)
1, 2, 3, 5, 6, 18	2.03-1.93 (m, 2H), 1.90-1.77 (m, 4H), 1.74-1.66 (m, 2H), 1.44-1.33 (m, 2H)	The protons attached to these carbons were not reported.	1.93-1.82 (m, 4H), 1.82-1.72 (m, 2H), 1.65 (td, J = 14.0, 1.0 Hz, 1H), 1.47-1.30 (m, 3H)
7	3.09-3.04 (m, 1H)	2.92 (m, 1H)	3.05-2.98 (m, 1H)
10	3.20 (dd, J = 12.2, 5.6 Hz, 1H)	3.26 (dd, J = 11, 7 Hz, 1H)	3.14 (dd, J = 12.6, 5.2 Hz, 1H)
11	6.92 (s, 1H)	7.02 (br s, 1H)	6.95 (s, 1H)
13	6.87 (d, J = 7.4 Hz, 1H)	6.94 (d, J = 5.7 Hz, 1H)	6.97 (d, J = 7.8 Hz, 1H)
14	6.94 (d, J = 7.5 Hz, 1H)	7.06 (d, J = 5.7 Hz, 1H)	7.10 (d, J = 7.8 Hz, 1H)
15	2.28 (s, 3H)	2.32 (s, 3H)	2.36 (s, 3H)
16	1.31 (d, J = 7.6 Hz, 3H)	1.30 (d, J = 6.8 Hz, 3H)	1.34 (d, J = 7.0 Hz, 3H)
17	0.51 (s, 3H)	0.48 (s, 3H)	0.40 (s, 3H)
19	0.93 (d, J = 6.5 Hz, 3H)	0.94 (d, J = 7 Hz, 3H)	0.92 (d, J = 6.5 Hz, 3H)
20	0.90 (d, J = 6.6 Hz, 3H)	0.88 (d, J = 7 Hz, 3H)	0.90 (d, J = 6.6 Hz, 3H)
In contrast to natural and synthetic (-)-presphaerene (1), the singlet peak of the proton at C11 of 7- <i>epi</i> -presphaerene (1'), the 7-(α)-methyl isomer, showed up at the most upfield.

FIGURE 1. The most stable conformation of *endo*-olefin **26** by a systematic Monte Carlo conformational search and subsequent energy minimization using MM2 calculation.¹⁷

FIGURE 2. The most stable conformation of *exo*-olefin **27** by a systematic Monte Carlo conformational search and subsequent energy minimization using MM2 calculation.¹⁷

JK-VIII-39-A

UK-VII-39-B / 1H

JK-VII-39-B

JK-VI-36

JK-VII-82 / 1H

JK-VII-79

JK-VII-85

JK-VI-88 / 1H

JK-VII-88

JK-VII-89 / 1H

JK-VII-90 / 1H

JK-VII-90

JK-VI1-92 / 1H

JK-VII-92

JK-VII-95 / 1H

Major / 1H

Minor / 1H

THIRD

jk-vi-98-a

JK-VII-6

JK-VII-84

jk-v11-28

JK-VII-28

JK-VIII-26

jk-vii-31-b

jk-vii-31-a

135 degree

75 MHz DEPT NMR, CDCl₃

7

ALUM	1608.9088 msec
PREDL	10.00000 msec
INITI	1000.0000 msec
RESOL	0.62 Hz
PW1	9.20 usec
ORNUC	13C
ORBR0	75.45 MHz
ORBR1	125840.00 Hz
RGAIN	28
PW2	16.50 usec
ORBR2	11.00 usec
ORBR3	145.00 Hz
ORBR4	1H
ORBR5	300.40 MHz
ORBR6	131150.00 Hz
ORBR7	45.0 usec
ORBR8	0
ORBR9	
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ORBR169

300-75 MHz ^1H - ^{13}C COSY NMR, CDCl_3

UCPLAT	38.9 usec		
DEAD	39.9 usec		
INVL	72.4 usec		
TTMES	160 times		
DUMKY	4 times		
PD	1.2000 sec		
ACQIM	37.0688 msec		
PRIEL	10.00000 msec		
ININT	1000.0000 msec		
RESOL	26.98 Hz		
PM1	9.20 usec		
ORNIC	13C		
ORFPO	75.45 MHz		
ORSTT	125374.47 Hz		
RGAIN	26		
CLFRQ	2399.2 Hz		
CLPMT	128 points		
TD0AT	128 points		
CLINT1	5.00 usec		
CLINT2	208.4 usec		
PM3	11.00 usec		
CONST	145.00 Hz		
IRJNC	1H		
IRFQ	300.40 MHz		
IRFST	130746.34 Hz		
IRPRW	45.0 usec		
IRRNS	0		
SCANS	160 times		
SLVNT	CDCl3		
SPINNING	13 Hz		
TEMP	25.0 C

JK-VI-28

$\theta = 135^\circ$

$\theta = 90^\circ$

^{13}C NMR

5

75 MHz DEPT NMR, CDCl_3

7-*epi*-presphaerene(1')
500-125 MHz ^1H - ^{13}C COSY NMR, CDCl_3

[illegible]

JK-VII-31-B

$\theta = 135^\circ$

$\theta = 90^\circ$

7-*epi*-presphaerene(1')
500 MHz DEPT NMR, CDCl₃

$\theta = 45^\circ$

jk-vi-31a

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Current Data Parameters
)KVL131a
NAME          2
EXPNO        1
PROCNO
```

(-)-presphaerene (1)
500 MHz ^1H - ^1H COSY NMR, CDCl_3

F1 - Acquisition parameters	
DO	0.0000350 sec
NO	0.0002562 sec
TD	1
TO	S16
F1	500.1318 MHz
F1RES	7.47678 Hz
SM	7.714 ppm
F2 - Processing parameters	
S1	S12
SR	500.130018 MHz
SRM	S16
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
F1 - Processing parameters	
S1	1024
SR	0
SRM	500.130018 MHz
SSB	S16
LB	0.00 Hz
GB	0
2D NMR plot parameters	
CX2	15.00 cm
CX1	15.00 cm
PD2	7.456 ppm
PD1	37.467 Hz
PR2	-105.86 Hz
PR1	7.463 ppm
FLD	374.75 Hz
FLD0	-0.221 ppm
FH1	-110.46 Hz
FH2	0.14467 ppm/cm
F2PCAN	257.2163 Hz/cm
F1PCAN	0.15467 ppm/cm
F2PCAN	257.2163 Hz/cm

400-100 MHz ^1H - ^{13}C COSY NMR, CDCl_3

JK-VII-31-A

$\theta = 135^\circ$

$\theta = 90^\circ$

$\theta = 45^\circ$

(-)-presphaerene (1)

100 MHz DEPT NMR, CDCl_3

MAJOR-2

MINOR-3

300 MHz ¹H NOE NMR

thind-3

JK-VII-31-B