Supporting Information

**Towards a total Synthesis of the novel polyketide
natural product Spiculoic Acid A**

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(-)-16:

$[\alpha]_D^{24} = -10.0$ (*c* 1.2, CHCl₃).

IR (neat) 3435, 2964, 1740, 1243, 1037 cm⁻¹.

¹H NMR (300MHz, CDCl₃): δ 4.14-4.01 (m, 2H), 3.57-3.45 (m, 2H), 2.06 (s, 3H), 2.01-1.95 (m, 1H), 0.95 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (75MHz, CDCl₃): 171.6, 66.1, 64.3, 35.3, 20.8, 13.4.

HRMS (ES) *m/z* calcd for C₆H₁₂O₃Na (M+Na)⁺: 155.0684, found 155.0683.

(-)-18:

$[\alpha]_D^{24} = -1.57$ (*c* 8.87, CHCl₃).

IR (neat) 2952, 2885, 1725, 1658, 1043 cm⁻¹.

¹H NMR (300MHz, CDCl₃): δ 6.94 (dd, *J* = 7.5Hz 16.2Hz, 1H), 5.88 (d, *J* = 16.8Hz, 1H) 4.58 (s, 2H), 3.70 (s, 3H), 3.45 (d, *J* = 6.3Hz, 2H), 3.32 (s, 3H), 2.63-2.51(m, 1H), 1.07 (d, *J* = 6.6 Hz, 3H).

¹³C NMR (75MHz, CDCl₃): 166.9, 155.2, 120.6, 96.4, 71.3, 55.2, 51.3, 36.6, 15.9.

HRMS (ES) *m/z* calcd for C₉H₁₆O₄Na (M+Na)⁺: 211.0946, found 211.0952.

(-)-19:

$[\alpha]_D^{25} = -6.19$ (*c* 1.13, CHCl₃).

IR (neat) 3418, 2931, 2875, 1109, 1042 cm⁻¹.

¹H NMR (300MHz, CDCl₃): δ 5.69-5.65 (m, 2H), 4.60 (s, 2H), 3.42-3.38 (m, 2H), 3.34 (s, 3H), 2.51-2.42 (m, 1H), 1.67 (brs, 1H), 1.03 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (75MHz, CDCl₃): 135.0, 128.9, 96.4, 72.4, 63.6, 55.1, 36.4, 16.8.

HRMS (ES) *m/z* calcd for C₈H₁₆O₃Na (M+Na)⁺: 183.0997, found 183.0994.

(-)-21:

$[\alpha]_D^{27} = -10.4$ (*c* 1.64, CHCl₃).

IR (neat) 3045, 2963, 2930, 1040 cm⁻¹.

¹H NMR (300MHz, CDCl₃): δ 4.63 (s, 2H), 3.97-3.93 (m, 2H), 3.78-3.54 (m, 4H), 3.38 (s, 3H), 3.33 (brs, 1H), 2.13-2.09 (m, 1H), 1.62-1.49 (m, 3H), 1.00(t, *J* = 8.7 Hz, 3H), 0.91, (d, *J* = 6.9 Hz, 3H).

¹³C NMR (75MHz, CDCl₃): 96.6, 80.5, 72.7, 62.9, 55.6, 42.8, 35.8, 21.6, 14.1, 11.8.

HRMS (ES) *m/z* calcd for C₁₀H₂₂O₄Na (M+Na)⁺: 229.1416, found 229.1424.

(+)-23:

$[\alpha]_D^{25} = 14.2$ (*c* 0.70, CHCl₃).

IR (neat) 3497, 2933, 1711, 1221, 1045 cm⁻¹.

¹H NMR (300MHz, CDCl₃): δ 6.77 (d, *J* = 10.8 Hz, 1H), 4.61 (s, 2H), 4.19 (dq, *J* = 1.6Hz, 7.5Hz, 2H), 3.70-3.47 (m, 3H), 3.37 (s, 3H), 3.21 (d, *J* = 3 Hz, 1H), 2.50 -2.29 (m, 3H), 1.84 -1.38 (m, 3H), 1.29 (t, *J* = 6.9 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 0.92-0.083 (m, 6H).

¹³C NMR (75MHz, CDCl₃): 167.8, 141.1, 135.2, 96.7, 77.4, 72.5, 60.3, 55.5, 43.5, 36.4, 24.9, 20.6, 14.3, 14.1, 13.9, 12.1.

HRMS (ES) *m/z* calcd for C₁₆H₃₀O₅Na (M+Na)⁺: 325.1991, found 325.2001.

(+)-27:

$[\alpha]_D^{25} = 17.39$ (*c* 2.53, CHCl₃).

IR (neat) 3408, 2962, 2887, 1456, 1041 cm⁻¹.

^1H NMR (300MHz, CDCl_3): δ 7.70-7.67(m, 4H), 7.43-7.27 (m, 11H), 5.48 (d, J = 10.2 Hz, 1H), 4.70 [$d_{(1/2\text{AB})q}$, J = 11.1Hz, 1H], 4.57 [$d_{(1/2\text{AB})q}$ d, J = 11.1Hz, 1H], 4.14 (s, 2H), 3.73-3.62 (m, 2H), 3.38-3.34 (m, 1H), 2.73 (brs, 1H), 2.61-2.52 (m, 1H), 2.16-2.02 (m, 2H), 1.95-1.87 (m, 1H), 1.60-1.30 (m, 2H), 1.09-1.05 (m, 9H), 0.98-0.88 (m, 9H).
 ^{13}C NMR (75MHz, CDCl_3): 141.3, 138.3, 135.6, 135.5, 133.9, 129.5, 128.3, 127.6, 127.5, 124.5, 88.2, 75.1, 66.7, 66.3, 42.6, 37.6, 26.8, 25.4, 21.4, 19.2, 15.4, 13.1, 12.3.
 HRMS (ES) m/z calcd for $\text{C}_{35}\text{H}_{48}\text{O}_3\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 567.3270, found 567.3274.

(+)-31:

$[\alpha]_{\text{D}}^{25} = 26.2$ (c 2.06, CHCl_3).

IR (neat) 2961, 2930, 1725, 1110 cm^{-1} .

^1H NMR (300MHz, CDCl_3): δ 7.69-7.66 (m, 5H), 7.42-7.26 (m, 10H), 7.12 (dd, J = 8.4 Hz, 15.6 Hz, 1H), 5.80 (d, J = 15.6 Hz, 1H), 5.45 (d, J = 10.2 Hz, 1H), 4.60 ($d_{1/2\text{AB}q}$, J = 11.4 Hz, 1H), 4.50 ($d_{1/2\text{AB}q}$, J = 11.4 Hz, 1H), 4.13 (s, 2H), 3.72 (s, 3H), 3.26 – 3.22 (m, 1H), 2.64-2.44 (m, 2H), 2.13-1.99 (m, 2H), 1.07-1.04 (m, 12H), 0.93-0.82 (m, 8H).

^{13}C NMR (75MHz, CDCl_3): 167.2, 152.3, 141.2, 138.7, 135.5, 133.9, 129.5, 128.1, 127.6, 127.5, 127.3, 124.6, 120.4, 85.9, 74.3, 66.8, 51.3, 42.4, 40.0, 26.8, 25.2, 21.3, 19.3, 17.0, 13.0, 12.2.

LRMS (ES) m/z calcd for $\text{C}_{38}\text{H}_{50}\text{O}_4\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 621, found 621.

(+)-33:

$[\alpha]_{\text{D}}^{27} = 20.133$ (c 4.52, CHCl_3).

IR (neat) 2961, 2857, 1725, 1428, 1270 cm^{-1} .

^1H NMR (300MHz, CDCl_3): δ 9.45 (d, J = 8.1 Hz, 1H), 7.68-7.66 (m, 4H), 7.43-7.25 (m, 11H), 7.01 (dd, J = 7.8Hz, 15.6Hz, 1H), 6.09 (dd, J = 7.5Hz, 15.6 Hz, 1H), 5.46 (d, J = 10.2 Hz, 1H), 4.64 [$d_{(1/2\text{AB})q}$, J = 10.8 Hz, 1H], 4.48 [$d_{(1/2\text{AB})q}$, J = 11.1 Hz, 1H], 4.13 (s, 2H), 3.30 (t, J = 4.8Hz, 1H), 2.76-2.74 (m, 1H), 2.51-2.45 (m, 1H), 2.11-1.94 (m, 2H), 1.36-1.28 (m, 2H), 1.15-1.05(m, 12H) 0.92-0.83 (m, 6H).

^{13}C NMR (75MHz, CDCl_3): 194.3, 161.8, 141.5, 138.5, 135.5, 133.8, 132.2, 129.5, 128.2, 127.6, 127.5, 124.2, 86.0, 74.5, 66.6, 42.8, 40.3, 26.8, 25.0, 21.4, 19.2, 17.3, 13.0, 12.1.

HRMS (ES) m/z calcd for $\text{C}_{37}\text{H}_{48}\text{O}_3\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 591.3270, found 591.3268.

(+)-34:

$[\alpha]_{\text{D}}^{26} = 33.8$ (c 0.62, CHCl_3).

IR (neat) 2956, 2926, 1721, 1589, 1436, 1118 cm^{-1} .

^1H NMR (400MHz, CDCl_3): δ 7.67 (d, J = 7.8 Hz, 4H), 7.38-7.23 (m, 12H), 6.27-6.10 (m, 2H), 5.76 (d, J = 15.6 Hz, 1H), 5.45 (d, J = 10.4 Hz, 1H), 4.57 [$d_{(1/2\text{AB})q}$, J = 11.2 Hz, 1H], 4.48 [$d_{(1/2\text{AB})q}$, J = 11.2 Hz, 1H], 4.13 (s, 2H), 3.73 (s, 3H), 3.22 – 3.19 (m, 1H), 2.58-2.44 (m, 2H), 2.11-2.00 (m, 2H), 1.32-1.21 (m, 2H), 1.06-1.04 (m, 12H), 0.91 (t, J = 7.6 Hz, 3H), 0.84 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100MHz, CDCl_3): 167.7, 147.5, 145.5, 141.0, 138.9, 135.6, 135.5, 134.0, 133.9, 129.5, 128.2, 127.9, 127.6, 127.5, 127.3, 124.9, 118.9, 86.2, 74.3, 66.9, 51.4, 42.5, 40.5, 26.8, 25.1, 21.4, 19.3, 17.6, 13.0, 12.2.

HRMS (ES) m/z calcd for $\text{C}_{40}\text{H}_{52}\text{O}_4\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$: 647.3533, found 647.3543.

(-)-9:

$[\alpha]_D^{26} = -50$ (*c* 0.60, CHCl₃).

IR (neat) 2929, 2856, 1737, 1589 cm⁻¹

¹H NMR (400MHz, CDCl₃): δ 7.65-7.59 (m, 4H), 7.42-7.24 (m, 11H), 5.60 (dd, *J* = 2 Hz, 10Hz, 1H), 5.41 (ddd, *J* = 1.6Hz, 4.8Hz, 10Hz, 1H), 4.59 [d_{(1/2AB)q}, *J* = 11.6 Hz, 1H], 4.47 [d_{(1/2AB)q}, *J* = 11.6 Hz, 1H], 3.87-3.84 (m, 1H), 3.60 (s, 3H), 3.44 [d_{(1/2AB)q}, *J* = 10 Hz, 1H], 3.39 [d_{(1/2AB)q}, *J* = 10 Hz, 1H], 3.18 (d, *J* = 4.8Hz, 1H), 2.26-2.25 (m, 1H), 2.13 (t, *J* = 8.8 Hz, 1H), 2.00-1.90 (m, 2H), 1.67-1.62 (m, 2H), 1.46-1.40 (m, 2H), 1.07-1.00 (m, 12H), 0.90-0.81 (m, 6H).

¹³C NMR (100MHz, CDCl₃): 174.0, 139.7, 135.8, 133.8, 133.7, 133.1, 129.5, 128.1, 127.6, 127.5, 127.2, 127.1, 121.7, 83.4, 73.2, 66.8, 54.3, 45.6, 45.5, 43.9, 43.5, 43.1, 42.7, 27.0, 25.2, 24.4, 19.4, 14.3, 14.1, 8.1.

HRMS (ES) *m/z* calcd for C₄₀H₅₂O₄SiNa (M+Na)⁺: 647.3533, found 647.3564.

Current Data Parameters

NAME 0525-direc-13c

EXPNO 2

PROCNO 1

F2 - Acquisition Parameters

Date_ 20050529

Time 20.00

INSTRUM amx400

PROBHD 5 mm QNP 1H

PULPROG zgdc

TD 26624

SOLVENT cdcl3

NS 12257

DS 0

SWH 27777.777 Hz

FIDRES 1.043336 Hz

AQ 0.4792820 sec

RG 32768

DW 18.000 usec

DE 22.50 usec

TE 300.0 K

D11 0.03000000 sec

CPDPRG waltz16

P31 75.00 usec

S2 17 dB

HL1 17 dB

D1 6.00000000 sec

P1 5.00 usec

SFO1 100.6262588 MHz

NUCLEUS 13C

F2 - Processing parameters

S1 32768

SF 100.6138668 MHz

WDW EM

SSB 0

LB 0.00 Hz

GB 0

PC 0.20

^1H - ^1H NOE correlations in (-)-9

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Current Data Parameters
NAME      2997
EXPNO     3
PROCNO    1

F2 - Acquisition Parameters
Date_     20050602
Time      15.48
INSTRUM   av400
PROBHD    5 mm BBO BB-1H
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         80
DS         16
SWH        400.607 MHz
FIDRES     0.000103 Hz
AQ         0.256750 sec
RG          360
DW         122.400 nsec
DE         6.00 nsec
TE         298.2 K
D1         0.0010400 sec
D2         2.00000000 sec
DB         0.40000001 sec
D6         0.0000400 sec
MDREST     0.00000000 sec
MCWK       2.00000000 sec

----- CHANNEL f1 -----
NUC1       1H
P1         14.00 nsec
PL1        0.00 dB
SFO1       400.130449 MHz

F1 - Acquisition parameters
SFO1       400.130449 MHz
SFO2       101.625375 MHz
FIDRES     0.000103 Hz
AQ         0.256750 sec
RG          360
DW         122.400 nsec
DE         6.00 nsec
TE         298.2 K
D1         0.0010400 sec
D2         2.00000000 sec
DB         0.40000001 sec
D6         0.0000400 sec
MDREST     0.00000000 sec
MCWK       2.00000000 sec

F2 - Processing parameters
SI         32768
SF         400.130449 MHz
WDW         EM
SSB         0
LB          0.00 Hz
GB          0
PC          1.00

F1 - Processing parameters
SI         32768
SF         400.130449 MHz
WDW         EM
SSB         0
LB          0.00 Hz
GB          0
PC          1.00

3D NMR plot parameters
CX2        15.00 cm
CX1         15.00 cm
F2PLD0     6.000 ppm
F2LB        2401.67 Hz
F2PAC0     0.400 ppm
F2PAC1     199.65 Hz
F2PLD1     6.000 ppm
F2LB1       2401.68 Hz
F2PAC2     0.400 ppm
F2PAC3     199.65 Hz
F2PAC4     0.36689 ppm/c
F2HZCH     140.80251 MHz/c
F2PAC5     0.36689 ppm/c
F2HZCH     140.80251 MHz/c
  
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