Supplementary Material (ESI) for Chemical Communications

Zirconium mediated total synthesis of crinitol, 9-hydroxyfarnesoic acid, 9-hydroxyfarnesol, 9-hydroxysargaquinone and the selectively protected aglycone of moritoside and euplexide A

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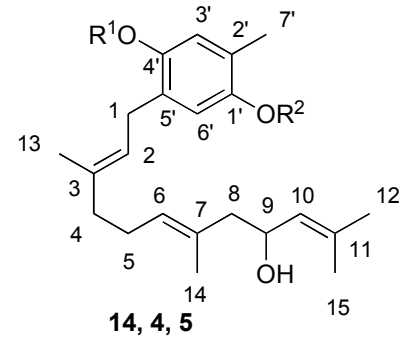
Comparison of the ^{13}C NMR data of compounds **2a**, **2b** and **3** synthesised in this work with data reported for the natural products.

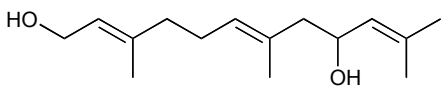
Comparison of ^{13}C NMR data of compound **14** with the aglycone portions of the natural products moritoside (**4**) and and Euplexide A (**5**).

Full data on 9-Hydroxyfarnesoic acid **1** and 9-hydroxyfarnesoic acid methyl ester.

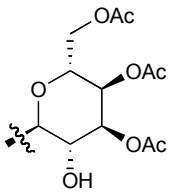
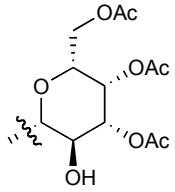
*Comparison of the ^{13}C NMR data of compounds **2a** and **14** synthesised in this work with that reported for the natural product 9-hydroxyfarnesol, and the aglycone portions of the natural products moritoside (**4**) and Euplexide A (**5**).*



14, 4, 5



2a, 9-hydroxyfarnesol

	R^1	R^2
14	H	Me
Moritoside, **4**		H
Euplexide A **5**		H

Moritoside **4**[1]	Euplexide A **5**[2]	**14**	9-Hydroxy-farnesol[3]	**2a**
δ_C ppm[a,b]	δ_C ppm[a,c]	δ_C ppm[d]	δ_C ppm[e]	δ_C ppm[d]
150.4 (C4')	150.4 (C1')	152.33	138.9	137.50
148.4 (C1')	148.4 (C4')	148.53	134.8	133.68
135.5 (C7)	135.6 (C3)	136.20	132.2	132.63
135.1 (C3)	135.2 (C11)	133.90	128.1	128.94
131.7 (C11)	131.8 (C7)	132.39	127.5	128.24
130.1 (C2')	130.1 (C5')	128.68	124.6	126.34
128.7 (C2)	128.8 (C6)	128.49	65.5	66.08
126.5 (C6)	126.4 (C10)	125.65	59.2	59.29
123.6 (C10)	123.5 (C2)	125.29	48.2	48.69
122.3 (C5')	122.4 (C2')	124.91	39.2	39.47
120.0 (C3')	120.0 (C3')	119.58	25.9	26.14
115.4 (C6')	115.3 (C6')	112.56	25.7	25.74
66.0 (C9)	65.6 (C9)	66.09	18.1	18.13
-	-	55.56 (OMe)	16.2	16.26
48.0 (C8)	48.1 (C8)	48.63	15.9	15.73
39.1 (C4)	39.1 (C4)	39.57		
28.0 (C1)	27.9 (C1)	30.09		
25.8 (C12)	25.8 (C12)	26.32		
25.3 (C5)	25.3 (C5)	25.76		
18.2 (C13)	18.2 (C15)	18.16		
16.2 (C7')	16.2 (C13)	16.18		
15.8 (C15)	15.8 (C7')	16.13		
15.6 (C14)	15.5 (C14)	15.89		

[a] Literature assignments for **4**[1] and **5**[2] are given, and only aglycone signals are shown. [b] recorded in $CDCl_3$ at 25 MHz. [c] recorded in $CDCl_3$ at 125 MHz.[d] recorded in C_6D_6 at 100.5 MHz.[e] recorded in $CDCl_3$ at unspecified field.

*Comparison of the ^{13}C NMR data of compounds **2b** and **3** synthesised in this work with data reported for the natural products crinitol and 9-hydroxysargaquinone.*

Crinitol[4]	**2b**	9-Hydroxy-sargaquinone (Rivera)[5]	9-Hydroxy-sargaquinone (Numata)[6]	**3**
δ_C ppm[a]	δ_C ppm[b]	δ_C ppm[c]	δ_C ppm[d]	δ_C ppm[b]
138.9	139.10	188.2	188.0	188.22
138.2	138.39	188.1	187.9	188.16
132.2	132.40	146.0	148.4	148.59
131.6	131.75	146.0	146.0	146.16
128.2	128.36	143.1		
127.0	127.19	139.5	139.6	139.78
124.6	124.76	138.2	138.1	138.30
123.9	124.12	133.3	133.1	133.33
65.4	65.57	132.5	132.3	132.48
59.2	59.36	132.0	132.1	131.97
48.1	48.26		131.6	131.79
39.5	39.66	127.8	127.9	128.10
39.2	39.34	127.5	127.4	127.50
26.4	26.56	124.2	124.0	124.22
25.8	26.01	118.6	118.5	118.62
25.6	25.79	66.0	65.9	66.06
17.7	17.81	48.3	48.1	48.34
16.6	16.73	39.7	39.6	40.37
16.1	16.30	39.7	39.4	39.74
15.9	16.03	27.5	27.6	27.79
		26.6	26.5	26.92
		26.6	26.4	26.64
		25.9	25.7	25.87
		17.9	17.7	17.88
		16.8	16.6	16.80
		16.4	16.3	16.63
		16.4	16.0	16.46
		16.2	16.0	16.23

[a] recorded in $CDCl_3$ at unspecified field.
[b] recorded in $CDCl_3$ at 100.5 MHz.
[c] recorded in $CDCl_3$ at 50 MHz.
[d] recorded in $CDCl_3$ at 75 MHz.

*9-Hydroxyfarnesoic acid **1** and 9-hydroxy-farnesoic acid methyl ester.*

Although the isolation of 9-hydroxyfarnesoic from a natural source has been reported, no physical data was given.[7] Proton NMR data (with unspecified field and solvent), IR, and MS data were give for 9-hydroxy-farnesoic acid methyl ester. We report below our data for these two compounds.

9-Hydroxyfarnesoic acid **1**:

^{1}H NMR (300 MHz, C_6D_6): ™ = 5.80 (1H, s(br)), 5.27 (1H, dseptet, J = 8.5, 1.1 Hz), 5.08 (1H, t, J = 5.9 Hz), 4.53 (1H, ddd, J = 8.5, 7.4, 5.6 Hz), 2.35 (1H, dd, J = 13.2, 7.4 Hz), 2.16 (1H, dd, J = 13.2, 5.5 Hz), 2.07 (3H, s(br)), 2.01-1.82 (4H, m), 1.58 (6H, s), 1.51 (3H, s(fine splitting)), 1.37 (1H, s, -OH).

^{13}C NMR (75 MHz, C_6D_6): ™ = 133.20 (s), 131.98 (s), 130.16 (d), 128.35 (d), 126.14 (d), 125.76 (s), 69.38 (d), 49.22 (t), 41.17 (t), 30.47 (t), 25.68 (q), 19.09 (q), 18.19 (q), 16.96 (q).

HRMS (EI): $C_{15}H_{22}O_2$ requires m/z = 234.1619. Found 234.1626.

(2*E*, 6*E*)-Methyl-9-hydroxy-3,7,11-trimethyldodeca-2,6,10-trienoate (9-hydroxy-farnesoic acid methyl ester):

^{1}H NMR (400 MHz, C_6D_6): ™ = 5.68 (1H, s), 5.13 (1H, d, J = 8.3 Hz), 4.94 (1H, t, J = 6.9 Hz), 4.29 (1H, apparent q, J = 5.5 Hz), 3.31 (3H, s), 2.09 (1H, dd, J = 13.3, 8.0 Hz), 2.03 (3H, s), 1.99 (1H, dd, J = 13.3, 5.0 Hz), 1.81 (2H, apparent q, J = 6.9 Hz), 1.71 (2H, t, J = 6.8 Hz), 1.47 (3H, s), 1.40 (3H, s), 1.37 (3H, s).

^{13}C NMR (100.5 MHz, C_6D_6): ™ = 166.59 (s), 159.23 (s), 133.31 (s), 132.99 (s), 129.02 (d), 126.51 (d), 115.79 (d), 66.43 (d), 50.24 (q), 48.36 (t), 40.49 (t), 25.94 (t), 25.50 (q), 18.50 (q), 17.90 (q), 16.16 (q).

IR (thin film) cm^{-1} = 1721.7, 1650.8 cm^{-1} (lit.[7] 1720, 1650 cm^{-1}).

LRMS (EI) m/z = 248 $(M-H_2O)^+$ (10%), 135 (78%), 93 (100%).

References

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