SUPPLEMENTARY MATERIAL

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8/29

**A Formal [3 + 3] Cycloaddition Approach to Chromenes and Chromanes.
Concise Total Syntheses of
(±)-Rhododaurichromanic Acid A and B and Methyl (±)-Daurichromenic Ester**

authored by

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Farnesal (8).

Farnesol (4.39 g, 0.0197 mmol) was dissolved in 80 mL of CH_2Cl_2 . The solution was cooled to 0°C , and DMSO (15.47 mL, 0.217 mol) and Et_3N (13.73 mL, 0.988 mol) were added in this order to the reaction mixture. SO_3 -pyridine (12.57 g, 0.079 mol) was added slowly over 10 min. After 50 min reaction was worked-up with 3% aq HCl, sat aq NaCl, and dried with NaSO_4 . The crude product was purified using flash silica gel column chromatography (gradient eluent: 0-10% EtOAc in hexane) to give 4.09 g of farnesal **8** (94%).

$R_f = 0.43$ (20% EtOAc in Hexane); clear oil; ^1H NMR (300MHz, CDCl_3) δ 1.60 (s, 3H), 1.61 (s, 3H), 1.68 (d, 3H, $J = 1.2$ Hz), 1.95-2.00 (m, 2H), 2.03-2.11 (m, 2H), 2.17 (d, 3H, $J = 1.2$ Hz), 2.21-2.28 (m, 4H), 5.06-5.10 (m, 2H), 5.88 (dd, 1H, $J = 1.2, 8.1$ Hz), 10.00 (d, 1H, $J = 8.4$ Hz); ^{13}C NMR (75MHz, CDCl_3) δ 16.1, 17.6, 17.7, 25.7, 25.8, 26.7, 39.7, 40.7, 122.5, 124.2, 127.5, 131.5, 136.6, 164.0, 191.3; IR (neat) cm^{-1} 2853s, 2767m, 1677s, 1632s, 1611s, 1443s, 1381s; mass spectrum (APCI): m/e (% relative intensity) 221 (50) ($\text{M} + \text{H}$) $^+$, 204 (20), 203 (100), 147 (10), 109 (10).

2-(4,8-Dimethyl-nona-3,7-dienyl)-2,7-dimethyl-2,6,7,8-tetrahydro-chromen-5 one (9).

Farnesal **8** (3.77 g, 0.0171 mol) was dissolved in a solution of piperidine (3.70 mL, 0.0374 mol) in EtOAc (30 mL). The solution was cooled to 0°C and stirred for 5 min. After which, acetic anhydride (3.7 mL, 0.0392 mol) was added dropwise. The flask was transferred into the 90°C oil bath and stirred for 1 h. The solution was then cooled down to room temperature and cannulated to a sealed tube that contained 5-methyl-cyclohexane-1,3-dione (3.23 g, 0.0256 mol) in toluene (70 mL). It was flushed with N_2 and heated at 90°C for 18 h. The crude product was purified using flash silica gel column chromatography (gradient eluent: 0-10% EtOAc in hexane) to give 3.91 g of **9** (70%).

$R_f = 0.29$ (20% EtOAc in Hexane); yellow oil; ^1H NMR (300MHz, CDCl_3) Two isomers δ 0.98 (s, 3H), 1.00 (s, 3H), 1.26 (s, 3H), 1.31 (s, 3H), 1.51 (s, 12H), 1.59 (s, 6H), 1.44-1.67 (m, 4H), 1.83-1.92 (m, 5H), 1.92-2.00 (m, 8H), 2.02-2.12 (m, 5H), 2.30-2.34 (m, 2H), 2.37 (m, 2H), 4.95-5.04 (m, 4H), 5.09 (d, 1H, $J = 10.2$ Hz), 5.11 (d, 1H, $J = 10.2$ Hz), 6.35 (d, 2H, $J = 10.2$ Hz); ^{13}C NMR (75MHz, CDCl_3) Two isomers δ 16.0, 17.7, 21.0, 21.1, 22.2, 22.6, 25.7, 26.6, 27.3, 27.6, 28.2, 28.4, 36.6, 36.8, 39.7, 41.7, 44.7, 44.8, 82.5, 82.6, 109.7, 109.8, 116.3, 116.5, 121.6, 121.6, 123.5, 123.5, 124.3, 131.3, 135.5, 171.7, 171.8, 194.8, 194.9; IR (neat) cm^{-1} 2962s, 2925s, 2873s, 1655s, 1594s, 1449m, 1420m, 1410m; mass spectrum (APCI): m/e (% relative intensity) 330 (20) ($\text{M} + 2\text{H}$) $^+$, 329 (100) M^+ , 273 (5), 193 (5).

2-(4,8-Dimethyl-nona-3,7-dienyl)-2,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-2H-chromene-6-carboxylic acid methyl ester (10).

$n\text{-BuLi}$ (0.0131 mol) was added dropwise to a solution of diisopropylamine (1.17 mL, 0.0160 mol) in THF (15 mL) at -78°C . The mixture was warmed to 0°C and stirred for 1 h. It was then cooled down to -78°C and compound **9** (3.90 mg, 0.0119 mol) was added dropwise. The reaction was stirred at -78°C for 1 h, and after which, it was transferred to a solution of methyl cyanofornate (1.70 mL, 0.0237

mol) in THF (15 ml) *via* cannula. After stirring for 10 min at -78°C and 10 min at 0°C the reaction was quenched with ice-cold water. The reaction mixture was worked-up with 3% HCl, sat aq NaCl, and dried over NaSO₄. The crude product was purified using flash silica gel column chromatography (gradient eluent: 0-5% EtOAc in hexane) to give 3.27 g of **10** (71%).

R_f = 0.35 (20% EtOAc in Hexane); pale-yellow oil; ¹H NMR (300MHz, CDCl₃) Mixture of major isomers δ 1.06 (s, 3H), 1.08 (s, 3H), 1.34 (s, 3H), 1.40 (s, 3H), 1.59 (s, 12H), 1.68 (s, 6H), 1.60-1.80 (m, 4H), 1.94-2.09 (m, 12H), 2.47-2.49 (m, 2H), 2.52-2.60 (m, 4H), 3.07 (d, 1H, J = 3.9 Hz), 3.11 (d, 1H, J = 4.2 Hz), 3.78 (s, 6H), 5.06-5.12 (m, 4H), 5.20 (d, 1H, J = 10.2 Hz), 5.21 (d, 1H, J = 10.2 Hz), 6.42 (d, 2H, J = 10.2); ¹³C NMR (75MHz, CDCl₃) Mixture of major isomers δ 16.0, 17.7, 19.8, 22.3, 22.6, 25.7, 26.7, 27.4, 27.7, 30.8, 31.0, 35.3, 35.5, 39.7, 41.8, 52.1, 60.2, 60.3, 83.0, 83.1, 109.2, 109.3, 116.2, 116.2, 122.0, 123.4, 123.5, 124.3, 131.4, 135.7, 135.7, 170.9, 171.0, 171.2, 189.4, 189.5, 193.2; IR (neat) cm⁻¹ 3054w, 2965s, 2252w, 1746s, 1650s, 1596s, 1416s; mass spectrum (APCI): m/e (% relative intensity) 388 (30) (M+2H)⁺, 387 (100) (M+H)⁺, 329 (20).

Methyl (±) daurichromenic ester (**11**).

A solution of **10** (0.89 g, 2.282 mmol) and DDQ (0.63g, 2.760 mmol) in toluene (50 ml) was refluxed overnight. The reaction mixture was filtered through the celite followed by a standard aqueous work-up. The crude product was purified using flash silica gel column chromatography (gradient eluent: 0-10% EtOAc in hexane) to give 0.39 g of **11** (44%).

R_f = 0.59 (20% EtOAc in Hexane); clear oil; ¹H NMR (300MHz, CDCl₃) δ 1.40 (s, 3H), 1.56 (s, 3H), 1.59 (s, 3H), 1.67 (s, 3H), 1.60-1.81 (m, 2H), 1.91-2.15 (m, 6H), 2.46 (s, 3H), 3.91 (s, 3H), 5.07 (t, 1H, J = 7.2 Hz), 5.10 (t, 1H, J = 6.9 Hz), 5.48 (d, 1H J = 10.2 Hz), 6.19 (s, 1H), 6.73 (d, 1H, J = 10.2 Hz), 12.00 (s, 1H); ¹³C NMR (75MHz, CDCl₃) δ 16.0, 17.8, 22.7, 24.5, 25.8, 26.7, 27.1, 39.8, 41.7, 51.9, 79.8, 105.0, 107.1, 111.7, 116.9, 123.9, 124.4, 126.3, 131.4, 135.5, 142.8, 158.0, 159.9, 172.5; IR (neat) cm⁻¹ 2968s, 2924s, 2856m, 1653s, 1620s, 1566s, 1441s, 1416m; mass spectrum (APCI): m/e (% relative intensity) 386 (30) (M+2H)⁺, 385 (100) (M+H)⁺, 354 (20), 353 (80), 327 (10), 235 (10); m/e calcd for C₂₄H₃₂O₄ 384.2301, found 384.2258.

Mixture of methyl (±)rhododaurichromanolic ester A and (±)rhododaurichromanolic ester B (**12a/b**).

Methyl (±) daurichromenic ester (**11**) (56.6 mg, 0.147 mmol) was transferred into a 100-mL size pyrex flask and dissolved in hexanes (30 ml). The reaction mixture was irradiated with medium-pressure mercury lamp for 65 h at room temperature while the lamp was placed 5 cm away from the flask. The UV lamp was situated in a standard photochemical emersion well and the well was cooled with chilled water. The crude product was purified using flash silica gel column chromatography (gradient eluent: 0-2% EtOAc in hexane) to give 44.6 mg of **12a/b** (79%).

R_f = 0.65 (20% EtOAc in Hexane); white powder; ¹H NMR (300MHz, CDCl₃) δ 0.75 (s, 3H), 1.10-1.21 (m, 2H), 1.35 (s, 3H), 1.38 (s, 3H), 1.40 (s, 3H), 1.51 (s, 3H), 1.60 (s, 3H), 1.58-1.74 (m, 8H), 1.64 (s, 3H), 1.71 (s, 3H), 1.82-1.94 (m, 4H), 1.97-2.08 (m, 2H), 2.40-2.51 (m, 2H), 2.46 (s, 6H), 2.54-

2.62 (m, 2H), 3.11 (d, 1H, $J = 9.3$ Hz), 3.19 (d, 1H, $J = 9.9$ Hz), 3.91 (s, 6H), 4.95 (t, 1H, $J = 7.2$ Hz), 5.18 (t, 1H, $J = 7.2$ Hz), 6.26 (s, 2H), 11.85 (s, 1H), 11.88 (s, 1H); ^{13}C NMR (75MHz, CDCl_3) δ 14.6, 17.4, 17.5, 22.6, 23.3, 24.0, 25.5, 25.6, 25.6, 26.0, 26.6, 27.3, 29.9, 30.6, 35.4, 35.7, 37.8, 38.4, 38.8, 40.2, 42.0, 42.2, 44.3, 46.1, 46.1, 51.6, 84.1, 84.2, 104.3, 104.4, 109.3, 109.4, 113.0, 125.0, 125.1, 130.4, 130.8, 139.9, 158.0, 158.1, 162.9, 163.1, 172.4; IR (film) cm^{-1} 2952s, 2864s, 1648s, 1621s, 1576s, 1452s, 1408s; mass spectrum (APCI): m/e (% relative intensity) 386 (20) ($\text{M}+2\text{H}$) $^+$, 385 (70) M^+ , 354 (25), 353 (100), 305 (5), 273 (15).

Compound 13.

A solution of **11** (126 mg, 0.326 mmol) in hexanes (350 ml) was irradiated by medium-pressure mercury lamp, using Vigor filter, as shown above for 6 h at -78°C . The crude product was purified using flash silica gel column chromatography (gradient eluent: 0-2% EtOAc in hexane) to give 15.6 g of **12a/b** (12%) and 7.2 g of **13** (5.7%).

$R_f = 0.15$ (2% EtOAc in Hexane); pale-yellow oil; ^1H NMR (500MHz, CDCl_3) δ 1.47 (s, 3H), 1.62 (s, 3H), 1.69 (s, 3H), 1.65-1.75 (m, 1H), 1.77-1.83 (m, 1H), 1.91-2.08 (m, 4H), 2.10-2.19 (m, 2H), 2.46 (s, 3H), 2.57 (dd, 1H, $J = 11.0, 20.5$ Hz), 2.89 (dd, 1H, $J = 9.5, 15.5$ Hz), 3.92 (s, 3H), 4.81 (s, 1H), 4.96 (s, 1H), 5.12 (m, 1H), 6.22 (s, 1H), 12.07 (s, 1H); ^{13}C NMR (75MHz, CDCl_3) δ 16.6, 17.6, 22.9, 24.0, 25.9, 26.5, 27.6, 29.6, 35.8, 36.7, 41.7, 46.0, 51.6, 85.1, 107.4, 110.1, 111.9, 123.9, 131.6, 139.7, 147.7, 157.8, 162.2, 172.5; IR (film) cm^{-1} 2962s, 2928s, 2362ws, 2341ws, 1648s, 1653s, 1585s, 1445s; mass spectrum (APCI): m/e (% relative intensity) 386 (20) ($\text{M}+2\text{H}$) $^+$, 385 (100) M^+ , 354 (10), 353 (30), 327 (5), 305 (5), 101 (5), 87 (25).

Mixture of ($\pm$)rhododaurichromanolic acid **A** and ($\pm$)rhododaurichromanolic acid **B** (**1a/b**).

To a solution of **12a/b** (40 mg, 0.104 mmol) in methanol (6 ml) and THF (6 ml) was added 6 M aq NaOH (3 ml). After stirring at room temperature for 48 h, the reaction was acidified with 2% aq acetic acid, followed by extraction with equal volumes of CH_2Cl_2 . The combined organic fractions were dried with sat aq NaCl and NaSO_4 . Flash chromatography (silica gel, elution with 70:30 hexanes/ethyl acetate) gave 27 mg of **1 a/b** (94%).

$R_f = 0.35$ (20% EtOAc in Hexane); white powder; ^1H NMR (500MHz, CDCl_3) δ 0.77 (s, 3H), 1.14-1.24 (m, 2H), 1.37 (s, 3H), 1.40 (s, 6H), 1.52 (s, 3H), 1.61 (s, 3H), 1.62-1.74 (m, 6H), 1.65 (s, 3H), 1.71 (s, 3H), 1.84-1.97 (m, 5H), 2.01-2.04 (m, 1H), 2.07-2.12 (m, 1H), 2.44-2.47 (m, 1H), 2.49-2.67 (m, 3H), 2.54 (s, 6H), 3.12 (d, 1H, $J = 9.5$ Hz), 3.20 (d, 1H, $J = 10$ Hz), 4.98 (t, 1H, $J = 7.0$ Hz), 5.19 (t, 1H, $J = 6.5$ Hz), 6.30 (s, 2H), 11.66 (s, 2H); ^{13}C NMR (75MHz, CDCl_3) δ 14.9, 17.7, 17.8, 22.9, 23.6, 24.3, 25.8, 25.9, 26.3, 26.9, 27.6, 30.1, 30.9, 35.6, 36.0, 38.0, 38.6, 39.2, 40.6, 42.3, 42.5, 44.6, 46.4, 84.7, 84.8, 103.4, 109.6, 109.8, 113.9, 125.3, 125.4, 130.8, 131.2, 141.9, 159.5, 164.2, 164.5, 176.6; IR (film) cm^{-1} 3406brs, 2962w, 2930w, 1621m, 1572w, 1455ms, 1366w; mass spectrum (APCI): m/e (% relative intensity) 372 ($\text{M}+2\text{H}$) $^+$ (5), 371 ($\text{M}+\text{H}$) $^+$ (80), 328 (20), 327 (100), 273 (10), 247 (10), 177 (5), 137 (10), 87 (10).

HPLC separation of 1a/b.

1a/b (16.2 mg) were separated by semi-preparative HPLC (pump: Agilent Technologies 1100 Series; column: Alltech Econosphere C18 10 μ 250x22; elution with [1% aqueous acetic acid] : CH₃CN with a ratio of 20 : 80 affording 5.5 mg of **1a** (34%) and 4.5 mg of **1b** (28%).

(±)Rhododaurichroman acid A (**1a**).

R_f = 0.36 (20% EtOAc in Hexane); white powder; mp 168-170 °C; ¹H NMR (500MHz, CDCl₃) δ 0.77 (s, 3H), 1.40 (s, 3H), 1.65 (s and m, 5H), 1.71 (s and m, 4H), 1.86 (ddd, 1H, J = 4.5, 12, 12 Hz), 1.90-1.96 (m, 3H), 2.06-2.13 (m, 1H), 2.50 (m, 1H), 2.53 (s, 3H), 2.58 (dd, 1H, J = 8.0, 10.0 Hz), 3.11 (d, 1H, J = 9.5 Hz), 5.18 (t, 1H, J = 7 Hz), 6.30 (s, 1H), 11.67 (s, 1H); ¹³C NMR (125MHz, CDCl₃) δ 14.9, 17.8, 22.8, 24.3, 25.8, 25.9, 27.6, 35.6, 38.6, 39.2, 42.5, 44.6, 46.4, 84.7, 103.3, 109.8, 113.8, 125.2, 130.2, 141.8, 159.4, 164.5, 176.3; IR (film) cm⁻¹ 3433brs, 2967w, 2929w, 1621m, 1572w, 1460ms, 1366w; mass spectrum (APCI): m/e (% relative intensity) 372 (M+2H)⁺ (5), 371 (M+H)⁺ (80), 328 (20), 327 (100), 273 (10), 247 (10), 177 (5), 137 (10), 87 (10); m/e calcd for C₂₃H₃₀O₄ 370.2144, found 370.2143.

(±)Rhododaurichroman acid B (**1b**).

R_f = 0.34 (20% EtOAc in Hexane); white powder; mp 159-161 °C; ¹H NMR (500MHz, CDCl₃) δ 1.14-1.24 (m, 2H), 1.37 (s, 3H), 1.40 (s, 3H), 1.52 (s, 3H), 1.61 (s, 3H), 1.64-1.73 (m, 4H), 1.83-1.91 (m, 1H), 2.00-2.05 (m, 1H), 2.45 (ddd, 1H, J = 3.5, 7.5, 7.5 Hz), 2.53 (s, 3H), 2.61 (m, 1H), 3.21 (d, 1H, J = 9.5 Hz), 4.96 (t, 1H, J = 7.0 Hz), 6.30 (s, 1H), 11.70 (s, 1H); ¹³C NMR (75MHz, CDCl₃) δ 17.7, 23.6, 24.3, 25.9, 26.3, 26.9, 30.1, 30.9, 36.0, 38.0, 40.5, 42.3, 46.4, 84.8, 103.4, 109.6, 113.8, 125.4, 130.8, 141.8, 159.5, 164.2, 176.2; IR (film) cm⁻¹ 3435brs, 2959w, 2927w, 1621m, 1571w, 1456ms, 1367w; mass spectrum (APCI): m/e (% relative intensity) 372 (M+2H)⁺ (5), 371 (M+H)⁺ (80), 328 (20), 327 (100), 273 (10), 247 (10), 177 (5), 137 (10), 87 (10); m/e calcd for C₂₃H₃₀O₄ 370.2144, found 370.2137.

¹H NMR Spectroscopic Comparisons:

Acid A		
Reported	Observed	$\Delta \delta$
0.76 (3H)	0.77 (3H)	+0.01
1.43 (3H)	1.40 (3H)	-0.03
1.63 (3H)	1.65 (3H)	+0.02
1.65 (1H)	1.65-1.71 (3H)	
1.70 (2H)		
1.71 (3H)	1.71 (3H)	0
1.85 (1H)	1.86 (1H)	+0.01
1.90 (2H)	1.90-1.96 (3H)	
1.95 (1H)		
2.10 (1H)	2.06-2.13 (1H)	
2.50 (1H)	2.50 (1H)	0
2.53 (3H)	2.53 (3H)	0
2.58 (1H)	2.58 (1H)	0
3.12 (1H)	3.11 (1H)	-0.01
5.18 (1H)	5.18 (1H)	0
6.30 (1H)	6.30 (1H)	0

Acid B		
Reported	Observed	$\Delta \delta$
1.20 (2H)	1.14-1.24 (2H)	
1.37 (3H)	1.37 (3H)	0
1.40 (3H)	1.40 (3H)	0
1.52 (3H)	1.52 (3H)	0
1.61 (3H)	1.61 (3H)	0
1.65 (2H)	1.64-1.73 (4H)	
1.67 (2H)		
1.86 (1H)	1.83-1.91 (1H)	
2.03 (1H)	2.00-2.05 (1H)	
2.50 (1H)	2.45 (1H)	-0.05
2.53 (3H)	2.53 (3H)	0
2.57 (1H)	2.61 (1H)	+0.04
3.20 (1H)	3.21 (1H)	+0.01
4.96 (1H)	4.96 (1H)	0
6.30 (1H)	6.30 (1H)	0
11.65 (1H)	11.70 (1H)	+0.05

¹³C NMR Spectroscopic Comparisons:

Acid A			Acid B		
Reported	Observed	$\Delta \delta$	Reported	Observed	$\Delta \delta$
175.93	176.25	+0.32	176.23	176.22	-0.01
164.34	164.48	+0.14	164.08	164.22	+0.14
159.34	159.42	+0.08	159.39	159.49	+0.10
141.64	141.81	+0.17	141.69	141.80	+0.11
131.00	131.18	+0.18	130.63	130.80	+0.17
125.15	125.24	+0.09	125.27	125.39	+0.12
113.72	113.82	+0.10	113.67	113.78	+0.11
109.64	109.75	+0.11	109.47	109.60	+0.13
103.11	103.27	+0.16	103.30	103.39	+0.09
84.53	84.65	+0.12	84.64	84.77	+0.13
46.25	46.37	+0.12	46.30	46.37	+0.07
44.54	44.60	+0.06	42.19	42.29	+0.10
42.38	42.45	+0.07	40.46	40.54	+0.08
39.16	39.21	+0.05	37.86	37.94	+0.08
38.54	38.60	+0.06	35.84	35.97	+0.13
35.49	35.64	+0.15	30.80	30.90	+0.10
27.45	27.59	+0.14	29.96	30.09	+0.13
25.75	25.91	+0.16	26.74	26.91	+0.17
25.70	25.83	+0.13	26.15	26.28	+0.13
24.11	24.30	+0.19	25.69	25.85	+0.16
22.76	22.84	+0.08	23.41	24.33	+0.92
17.64	17.79	+0.15	22.74	23.56	+0.82
14.78	14.87	+0.09	14.78	17.72	+2.94*

* There is likely a typo here in the reported literature value.

Revised ^{13}C NMR Data and Correspondence from Professor Yoshiki Kashiwada:

Dear Professor Hsung,

In response to your e-mail of 8/5/03, I have rechecked ^{13}C nmr data for rhododaurichromanin acid B. As you suggested, the ^{13}C resonance for the C-18 methyl was reported incorrectly, and its correct chemical shift is 17.56 ppm. In addition, the resonances for C-14 and 7-Me were also reported incorrectly, and should be revised to 23.41 and 24.16 ppm, respectively.

I am very sorry for your inconvenience. The data in that paper was prepared by my graduate student, but I was not aware those mistakes.

Unfortunately, we do not have enough amount of sample to send you.

I have attached the copies of ^{13}C -NMR spectra for rhododaurichromanin acids A and B. Since I could not find the spectrum for rhododaurichromanin acid identical with those reported, the chemical shifts in the attached file are slightly different from those reported. However, I hope that they would be helpful for you to identify your synthetic compounds.

I hope that your research work continues to go well.

With best regards.

Yoshiki Kashiwada, Ph.D.

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At 4:29 PM -0500 03.8.5, Richard P. Hsung wrote:

Dear Professor Kashiwada:

We have recently prepared rhododaurichromanin acids A and B that were isolated and reported by you and your colleagues [*Tetrahedron* **2001**, 57, 1559-1563.]. Our synthetic compounds matched your natural products in every aspect except one number. I have attached our comparisons here.

For the C-18 allylic methyl group in **rhododaurichromanin acid B**, our proton resonance matched yours at 1.52 ppm [3H], but our carbon resonance does not. Yours is at 14.78 ppm, and ours is at 17.72 ppm. Our number appears to make a little more sense by looking at your data as well as our own for the corresponding C-18 allylic methyl group in both **rhododaurichromanin acid A** and daurichromanin acid.

Our proton resonance for the C-18 Me in both **rhododaurichromanin acid A** and daurichromenic acid [ours is a corresponding methyl ester] matched exactly with pin-point precision, and carbon resonances are 17.79 ppm and 17.80 ppm, respectively, well within the range of your respective numbers of 17.64 ppm and 17.66 ppm.

May you check this issue for us, and also if possible, we wonder if you would be so kind as to provide us with NMR/MS quantities of rhododaurichromanin acid A and B. We would be very grateful for your help.

Thank you very much,

Respectfully yours,

Richard

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Attachment converted: G3 MT HD-2:Comparison.doc (WDBN/MSWD) (0000B944)

Revised ^{13}C NMR Spectroscopic Comparisons:

Acid A			Acid B		
Reported	Observed	$\Delta \delta$	Reported	Observed	$\Delta \delta$
175.93	176.25	+0.32	176.23	176.22	-0.01
164.34	164.48	+0.14	164.08	164.22	+0.14
159.34	159.42	+0.08	159.39	159.49	+0.10
141.64	141.81	+0.17	141.69	141.80	+0.11
131.00	131.18	+0.18	130.63	130.80	+0.17
125.15	125.24	+0.09	125.27	125.39	+0.12
113.72	113.82	+0.10	113.67	113.78	+0.11
109.64	109.75	+0.11	109.47	109.60	+0.13
103.11	103.27	+0.16	103.30	103.39	+0.09
84.53	84.65	+0.12	84.64	84.77	+0.13
46.25	46.37	+0.12	46.30	46.37	+0.07
44.54	44.60	+0.06	42.19	42.29	+0.10
42.38	42.45	+0.07	40.46	40.54	+0.08
39.16	39.21	+0.05	37.86	37.94	+0.08
38.54	38.60	+0.06	35.84	35.97	+0.13
35.49	35.64	+0.15	30.80	30.90	+0.10
27.45	27.59	+0.14	29.96	30.09	+0.13
25.75	25.91	+0.16	26.74	26.91	+0.17
25.70	25.83	+0.13	26.15	26.28	+0.13
24.11	24.30	+0.19	25.69	25.85	+0.16
22.76	22.84	+0.08	24.16	24.33	+0.17
17.64	17.79	+0.15	23.41	23.56	+0.15
14.78	14.87	+0.09	17.56	17.72	+0.16

SUPPLEMENTARY ¹H NMR SPECTRA

for the

communication

entitled

**A Formal [3 + 3] Cycloaddition Approach to Chromenes and Chromanes.
Concise Total Syntheses of
(±)-Rhododaurichromanic Acid A and B and Methyl (±)-Daurichromenic Ester.**

authored by

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avk_1_13

University of Minnesota
Department of Chemistry
VAC-300

Pulse Sequence: s2pu1

User: rhsavk

Date: Jan. 28, 2003

Solvent: CDCl₃

File: 030128v3_1302

Starting Time: 14:16:12

Completion Time: 14:24:06

Total acq. time 1 minute

UNITYplus-500 "spectrum"

Ambient temperature

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 90.0 degrees

Acq. time 2.000 sec

Width 5998.8 Hz

16 repetitions

OBSERVE H1, 299.9533563 MHz

DATA PROCESSING

Line broadening 0.1 Hz

FT size 65536

avk-1-17

University of Minnesota
Department of Chemistry
VAC-300

Pulse Sequence: s2pu1

User: rhasvk

Date: Mar. 2, 2003

Solvent: CDCl₃

File: 030302v3_0204

Starting Time: 12:57:14

Completion Time: 12:58:26

Total acq. time 1 minute

UNITYplus-500 "spectrum"

Ambient temperature

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 18.0 degrees

Acq. time 2.000 sec

Width 5998.8 Hz

16 repetitions

OBSERVE H1, 299.9533645 MHz

DATA PROCESSING

Line broadening 0.1 Hz

File size 65536

avk-1-21

University of Minnesota
Department of Chemistry
VAC-500

Pulse Sequence: s2pul

User: rnsavk

Date: Feb. 21, 2003

Solvent: CDCl₃

File: 030221V3-2002

Starting Time: 13:41:31

Completion Time: 13:50:42

Total acq. time 1 minute

UNITYplus-500 "spectrum"

Ambient temperature

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 90.0 degrees

Acq. time 2.000 sec

Width 5998.8 Hz

16 repetitions

OBSERVE H1, 299.9533649 MHz

DATA PROCESSING

Line broadening 0.1 Hz

FT size 65536

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avk-65

University of Minnesota
Department of Chemistry
VAC-300

Pulse Sequence: s2pul

User: rtsavk

Date: Apr. 7, 2003

Solvent: CDCl₃

File: 030407v3_2602

Starting Time: 20:31:11

Completion Time: 20:41:33

Total acq. time 1 minute

UNITYplus-500 "spectrum"

Ambient temperature

PULSE SEQUENCE

Relax. delay 1.500 sec

Pulse 90.0 degrees

Acq. time 2.000 sec

Width 5998.8 Hz

16 repetitions

OBSERVE H1, 299.9533660 MHz

DATA PROCESSING

Line broadening 0.1 Hz

FT size 65536

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STANDARD 1H OBSERVE

Pulse Sequence: szpu1
User: rnsavk
Date: Jun. 23, 2003
Solvent: CDCl3
File: awk-1-109.1b
Starting Time: 11:03:44
Completion Time: 11:04:48
Total acq. time 1 minute
UNITYplus-500 "spectrum"
Ambient temperature
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse: 90.0 degrees
Acq. time 1.999 sec
Width 6003.3 Hz
16 repetitions
OBSERVE H1, 300.1683397 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 131072

Univ of Minnesota, VI-500

Pulse Sequence: szpul
 User: rhasvk
 Date: Jul 7, 2003
 Solvent: CDCl₃
 File: qvk-1-109_side
 Starting Time: 18:17:25
 Total acq. time 1 minutes
 UNITYplus-500 "spectrum"
 Ambient temperature
 PULSE SEQUENCE
 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 32 repetitions
 OBSERVE H1, 499.8671219 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FT size 32768

13

Univ of Minnesota, VI-500

Pulse Sequence: szpul
User: rfsavk
Date: Jul 25, 2003
Solvent: CDCl3
File: avk-1-127_clean_mix
Starting Time: 19:17:24
Completion Time: 19:17:49
Total acq. time 1 minute
UNITYplus-500 "spectrum"
Ambient temperature
PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
4 repetitions
OBSERVE H1, 499.8671243 MHz
DATA PROCESSING
Line broadening 0.1 Hz
Ft size 32768

Univ of Minnesota, VI-500

Pulse Sequence: szpu1
 User: rhasvk
 Date: Jul 28, 2003
 Solvent: CDCl3
 File: avk-1-131_2_H
 Starting Time: 19:03:42
 Completion Time: 19:07:26
 Total acq. time 3 minutes
 UNITYplus-500 "Spectrum"
 Ambient temperature
 PULSE SEQUENCE
 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 64 repetitions
 OBSERVE H1 499.8671233 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FI size 32768

1a: rhododaurichromanic acid A

Univ of Minnesota, VI-500

Pulse Sequence: szpu1
 User: rhasvk
 Date: Jul 29, 2003
 Solvent: CDCl3
 File: f1a1-131_1.H
 Starting Time: 02:00:03
 Completion Time: 02:03:45
 Total acq. time 3 minutes
 UNITplus-500 "Spectrum"
 Ambient temperature
 PULSE SEQUENCE
 Relax. delay 1.500 sec
 Pulse 90.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 64 repetitions
 OBSERVE H1 499.8671233 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 Ft size 32768

1b: rhododaurichroman acid B

Acid A

Pulse Sequence: s2pul
 User: 1-14-87
 Date: Jul 28, 2003
 Solvent: CDCl3
 File: final-131-2-C
 Starting Time: 23:58:26
 Completion Time: 01:55:27
 Total acq. time 115 minutes
 UNITplus-500 "spectrum"
 Ambient temperature
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 67.5 degrees
 Acq. time 0.960 sec
 Width 32989.7 Hz
 1792 Repetitions
 OBSERVE C13, 125.681668 MHz
 DECOUPLE H1, 498.8686213 MHz
 Power 36 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 4.8 Hz
 FT size 65536

1a: rhododaurichromanic acid A

Acid B

Pulse Sequence: g2pu1
User: rhasvk
Date: Jul 28, 2003
Solvent: CDCl3
File: final-131-1c
Starting Time: 22:51:44
Completion Time: 01:58:21
Total acq. time 2.7 hours
UNITYplus-500 "spectrum"
Ambient temperature
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 67.5 degrees
Acq. time 0.801 sec
Width 18887.9 Hz
2640 repetitions
OBSERVE C13 75.3871144 MHz
DECOUPLE H1 289.850856 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 8.2 Hz
Ft size 65536

1b: rhododaurichromanic acid B