

Experimental

2,8,14,20-Tetraheptyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxycalix[4]arene (2)

Boron trifluoride etherate (1.14 g, 8.1 mmol) was added to a stirred solution of 3-methoxyphenol (**1**) (0.5 g, 4.0 mmol) and octanal (0.52 g, 4.0 mmol) in anhydrous dichloromethane (20 mL) and left to stand at room temperature (2 h). The reaction mixture was then washed with water (2 x 20 mL) and brine (1 x 20 mL), dried (MgSO₄) and the solvent removed under reduced pressure to give a dark red oil. This was dissolved in a minimum amount of hot ethanol that, upon cooling, afforded pale pink plates. Recrystallisation from methanol then gave pure **2** (0.75 g, 80%) as colourless plates, m.p. 160°. ¹H n.m.r. (CDCl₃) δ 0.90 (br t, 12 H, CH₂CH₃), 1.20-1.42 (m, 40 H, CH₂), 2.20 (m, 8 H, CH₂CH), 3.84 (s, 12 H, OCH₃), 4.28 (t, 4 H, J = 7.8 Hz, CHCH₂), 6.36, 7.23, (s, 2 x 4 H, Ar), 7.52 (s, 4 H, OH). ¹³C n.m.r. (CDCl₃) δ 14.7, 23.2, 28.7, 30.0, 30.3, 32.5, 34.6, 33.7, 56.5, 100.7, 124.4, 125.3, 125.4, 153.7, 154.4. Found: C, 76.8; H, 9.4; C₆₀H₈₈O₈; requires C, 76.9; H, 9.5%.

2,8,14,20-Tetraundecyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetramethoxycalix[4]arene (3)

The procedure for the preparation of **2** was repeated using 3-methoxyphenol (0.5 g, 4.0 mmol), dodecanal (0.74 g, 4.0 mmol) and BF₃.Et₂O (1.14 g, 8.1 mmol) to afford after normal workup and crystallisation **4** (0.86 g, 74%), m.p. 128-130° (MeOH). ¹H n.m.r. (CDCl₃) δ 0.88 (br t, 12 H, CH₂CH₃), 1.1-1.5 (m, 72 H, CH₂), 2.1-2.3 (m, 8 H, CH₂CH), 3.82 (s, 12 H, OCH₃), 4.26 (t, 4 H, J = 7.8 Hz, CHCH₂), 6.34, 7.21, (s, 2 x 4 H, Ar), 7.52 (s, 4 H, OH). ¹³C n.m.r. (CDCl₃) δ 14.7, 23.3, 28.7, 30.0, 30.3, 30.4, 32.6, 33.7, 34.6, 56.5, 100.7, 124.4, 125.3, 125.5, 153.7 and 154.4 (note – coincident alkyl signals at 30.4).

Fully characterised as the tetraacetate.

Acetic anhydride (2 mL) was added to a solution of calixarene **3** (200 mg, mmol) in pyridine (20 mL) and the solution heated at reflux overnight. The reaction mixture was cooled (r.t.) and diluted with water with vigorous stirring. The resulting solid was collected by vacuum filtration and washed thoroughly with dilute hydrochloric acid and then water. The off white solid was air dried and then recrystallised from methanol/chloroform to afford colourless crystals (180 mg, %), m.p. 181-182°. ¹H n.m.r. (CDCl₃) δ 0.87 (br t, 12 H, CH₂CH₃), 1.17-1.38 (m, 72H, CH₂), 1.78-1.92 (m, 8 H, CH₂CH), 2.14 (s, 12 H, CH₃CO), 3.62 (s, 12 H, OCH₃), 4.32 (t, 4 H, J= 7.4 Hz, CHCH₂), 6.42, 6.79 (s, 2 x 4 H, Ar). ¹³C n.m.r. (CDCl₃) δ 14.7, 21.3, 23.3, 28.4, 30.0, 30.3, 30.37, 30.45, 30.5, 32.6, 35.8, 35.9, 56.0, 105.7, 126.6, 128.6, 131.2, 148.0, 155.7, 170.0. Found: C, 75.9; H, 9.7; C₈₄H₁₂₈O₁₂; requires C, 75.9; H, 9.7%.

2,8,14,20-Tetraundecyl-4,10,16,22-tetrahydroxy-6,12,18,24-tetrapropoxycalix[4]arene (4)

The procedure for the preparation of **2** was repeated using 3-propoxyphenol (0.5 g, 3.3 mmol), dodecanal (0.61 g, 3.3 mmol) and BF₃.Et₂O (1.40 g, 9.9 mmol) to afford after

normal workup and crystallisation **4** (0.46 g, 44 %). ^1H n.m.r. (CDCl_3) δ 0.89 [t, 12 H, $J = 6.0$ Hz, $(\text{CH}_2)_{10}\text{CH}_3$], 1.07 [t, 12 H, $J = 7.3$ Hz, $(\text{CH}_2)_2\text{CH}_3$], 1.16-1.48 (m, 72H, CH_2), 1.8-2.0 (m, 8 H, $\text{CH}_2\text{CH}_2\text{O}$), 2.1-2.3 (br m, 8 H, CH_2CH), 3.80-4.08 (m, 8 H, OCH_2), 4.30 (t, 4 H, $J = 7.8$ Hz, CHCH_2), 6.34, 7.24 (s, 2 x 4 H, Ar), 7.56 (s, 4 H, OH). ^{13}C n.m.r. (CDCl_3) δ 11.0, 14.7, 22.8, 23.3, 28.7, 30.0, 30.3, 30.4, 32.6, 33.7, 34.7, 71.4, 101.7, 124.4, 125.5, 125.6, 153.7, 153.9. Found: C, 79.1; H, 10.7; $\text{C}_{84}\text{H}_{132}\text{O}_8$; requires C, 79.2; H, 10.8%.