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A short synthesis of (±)-furodisinine and (±)-furodisine

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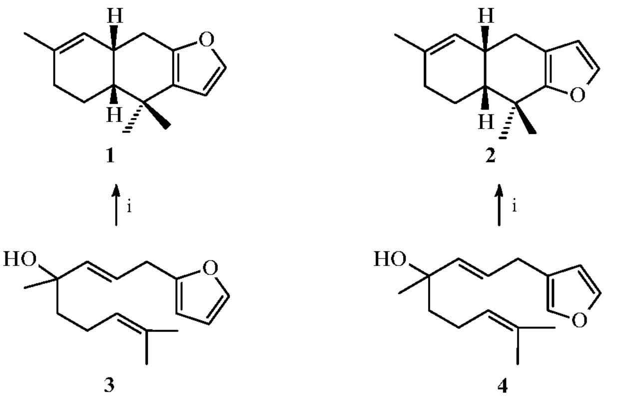
A simple synthesis of racemic forms of natural furanoterpenoids, furodisinine and furodisine, has been carried out by electrophilic cyclisation of readily accessible α- and β-furylmethyl derivatives of linalool.

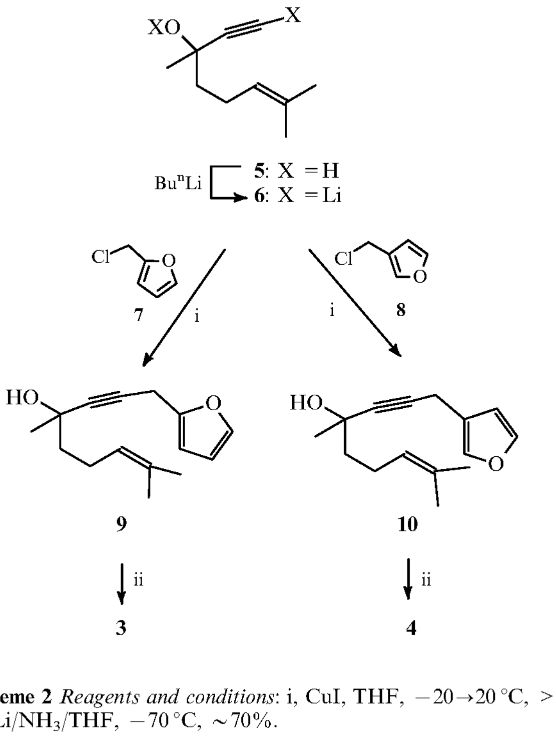
The structures of metabolites of certain types of sea sponges,[1] furodisinin **1** and furodisin **2**, has been confirmed by synthesising their racemic[2] and optically active forms.[3]



Scheme 1 *Reagents and conditions*: i, 0.2 equiv. 85% H_3PO_4, aq., PhMe, 100 °C, 20 min.

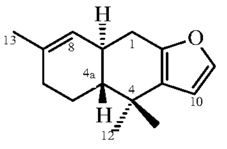
We proposed a new strategy for constructing these furanodecalins by cationic cyclisation of readily accessible derivatives of linalool **3** and **4** (Scheme 1). The latter were obtained from (±)-dehydrolinalool **5**, whose dilithium derivative **6** was subjected to CuI-catalysed condensation with chloride **7** (see ref. 4) or **8** (Scheme 2). The resulting alkynes **9** [4] and **10**, respectively, were then reduced into the corresponding dienes **3** [4] and **4** by treatment with Li in NH_3.

The subsequent search for conditions of efficient cationic cyclisation of isoprenoids **3**, **4** showed that this reaction should optimally be carried out in the presence of ~0.2 mol equiv. 85% H_3PO_4 in toluene at 100 °C. The target compounds **1** and **2** were isolated in ~40% yields from cyclisation products formed under these conditions by chromatography on SiO_2/10% $AgNO_3$. In both cases, the furanodecalins **1** and **2** were accompanied by their hitherto unknown *trans*-fused isomers, **11** and **12** (~10%), and by limonene derivatives, *cis-/trans-***13a,b** (<10%), respectively (Scheme 3). The latter probably resulted from deprotonation of the corresponding carbocationic intermediates **14a** and **14b** formed in the first step of cyclisation of the starting diolefins **3** and **4**.



Scheme 2 *Reagents and conditions*: i, CuI, THF, −20→20 °C, >50%; ii, Li/NH_3/THF, −70 °C, ~70%.

The spectral characteristics of the (±)-furodisinine **1**, (±)-furodisine **2** and limonene derivatives *cis*-**13a,b** almost coincide with those reported previously.[3] The hitherto unknown compounds **4** and **10**–**12** were identified by the combination of data from elemental and spectral[†] analyses.



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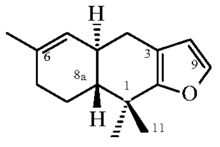

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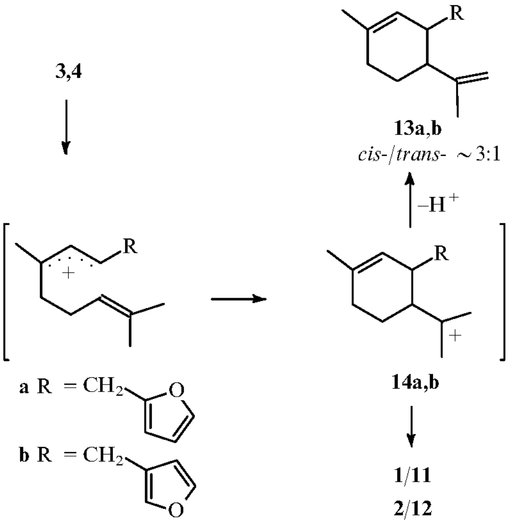

Scheme 3

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[†] **4**: ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 1.28 (s, 3H, 4-Me), 1.56 (m, 2H, 5-H), 1.60 and 1.68 (br. s, 6H, 8-Me), 2.2 (m, 2H, 6-H), 3.18 (br. d, 2H, 1-H, J = 6.0), 5.12 (br. t, 1H, 7-H, J = 7.1), 5.58 (dt, 1H, 3-H, J = 15.5 and 1.1), 5.76 (dt, 1H, 2-H, J = 15.5 and 5.9), 6.25 (m, 1H, 4′-H), 7.20 and 7.35 (m, 2H, 2′-H, 5′-H); m/z: 234 $[M]^+$. Found (%): C, 76.70; H, 9.41. $C_{15}H_{22}O_2$. Calc. (%): C, 76.88; H, 9.46.

10: ^{1}H NMR (200.13 MHz, $CDCl_3$) δ 1.50 (s, 3H, 4-Me), 1.62 and 1.70 (br. s, 6H, 8-Me), 1.65 (m, 2H, 5-H), 2.2 (m, 2H, 6-H), 3.38 (br. s, 2H, 1-H), 5.15 (br. t, 1H, 7-H, J = 7.0), 6.32 (m, 1H, 4′-H), 7.33 and 7.36 (m, 2H, 2′-H, 5′-H); m/z: 232 $[M]^+$. Found (%): C, 77.21; H, 8.95. $C_{15}H_{20}O_2$. Calc. (%): C, 77.55; H, 8.68.

11: mp 33–37 °C (hexane). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.02 (s, 3H, 11-H), 1.23 (s, 3H, 12-H), 1.30 (m, 1H, 4a-H), 1.37 (m, 1H, 5-H), 1.71 (br. s, 3H, 13-H), 1.90 (m, 1H, 5-H), 2.06 (m, 2H, 6-H), 2.22 (dd, 1H, 1-H, J = 15.6 and 11.7), 2.42 (m, 1H, 8a-H), 2.71 (dd, 1H, 1-H, J = 15.6 and 5.3), 5.30 (m, 1H, 8-H), 6.30 (br. s, 1H, 10-H), 7.25 (br. s, 1H, 9-H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 22.9 (C-5), 23.3 (C-13), 24.4 (C-11), 27.7 (C-12), 30.6 (C-1), 31.4 (C-6), 33.3 (C-4), 34.2 (C-8a), 46.8 (C-4a), 108.2 (C-10), 125.4 (C-8), 127.5 (C-3), 134.2 (C-7), 140.4 (C-9), 148.4 (C-2); HRMS m/z 216.15231 $[M]^+$, Calc. for $C_{15}H_{20}O$ 216.15131.

12: mp 32–35 °C (hexane). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 1.10 (s, 3H, 11-H), 1.30 (s, 3H, 12-H), 1.39 (m, 2H, 8-H, 8a-H), 1.70 (br. s, 3H, 13-H), 1.86 (m, 1H, 8-H), 2.04 (m, 2H, 7-H), 2.05 (dd, 1H, 4-H, J = 15.3 and 11.6), 2.30 (m, 1H, 4a-H), 2.50 (dd, 1H, 4-H, J = 15.3, 5.0) and 5.30 (m, 1H, 5-H), 6.15 (br. s, 1H, 10-H), 7.25 (br. s, 1H, 9-H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 22.1 (C-11), 22.6 (C-8), 23.2 (C-13), 25.2 (C-12), 29.7 (C-4), 31.1 (C-7), 34.6 (C-4a), 35.0 (C-1), 47.3 (C-8a), 109.8 (C-10), 114.4 (C-3), 125.6 (C-5), 133.6 (C-6), 140.2 (C-9), 158.0 (C-2); HRMS m/z 216.15211 $[M]^+$, Calc. for $C_{15}H_{20}O$ 216.15131.