

Electrochemical synthesis of euglobal-G1, -G2, -G3, -G4, -T1 and -IIc

Kazuhiro Chiba,* Takaaki Arakawa and Masahiro Tada

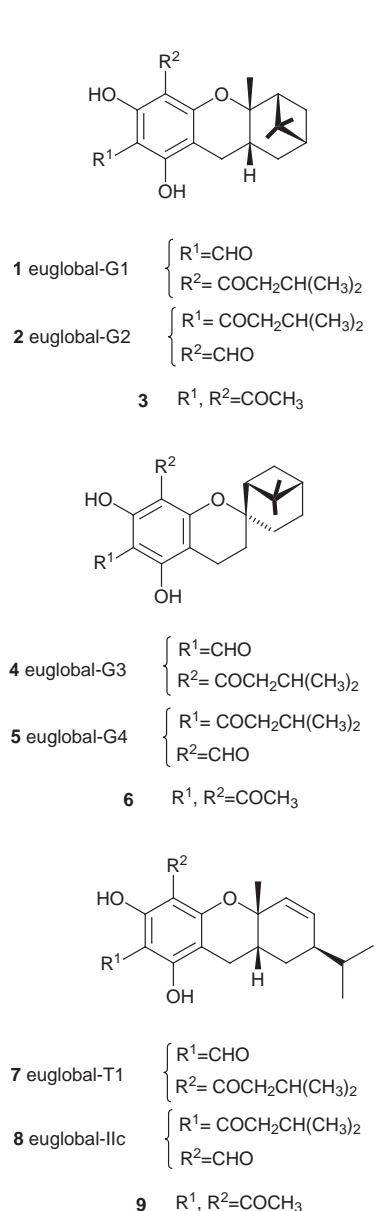
Laboratory of Bio-organic Chemistry, Tokyo University of Agriculture and Technology,
3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan

Six natural euglobals were synthesized by electrochemical methods. In a key step, cycloaddition between *in situ* generated quinomethanes and terpenes was performed on the surface of PTFE-fibre coated electrode to give natural products using 2,3-dichloro-5,6-dicyano-*p*-hydroquinone (DDQH₂) as a redox mediator. In this reaction system, biomimetic generation and cycloaddition of the unstable quinomethanes were efficiently completed by the selective oxidation of cresol derivatives.

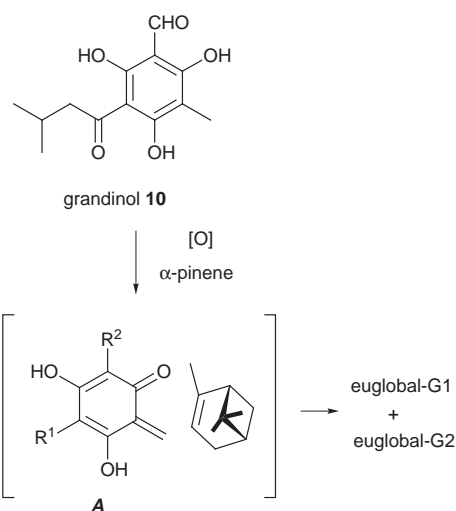
Introduction

Euglobals isolated from *Eucalyptus* spp. show potent inhibitory activity against Epstein-Barr virus activation.¹ These compounds have unique structures composed of acylalkylphloroglucinol and terpene moieties.² Although the biogenetic path-

way has not been established yet, it is most probable that a series of these compounds is biosynthesized by a hetero Diels-Alder reaction between the corresponding terpenes and a quinomethane generated by oxidative activation of grandinol **10** which has been also isolated from *Eucalyptus* (Scheme 1).³



Structures on natural euglobals and their analogues



Scheme 1 Proposed biogenetic pathway of euglobals

Initially we synthesized natural euglobal-G3 **4** and -G4 **5** *via* oxidation of **10** by excess 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (DDQ) in the presence of β -pinene in nitromethane.⁴ In this reaction, it was suggested that the *in situ* generated quinomethane was trapped by β -pinene. The DDQ oxidation, however, yields decomposition products of co-existing alkenes and/or generates toxic HCN gas, and electrochemical generation of quinones⁵ including DDQ⁶ has been extensively investigated using organic solvents. Presently we introduced a PTFE [poly-(tetrafluoroethylene)]-fibre coated electrode which performed efficient electron transfer and selective oxidation of phenolic substrates mediated by DDQH₂ in the presence of terpenes. By using the electrooxidation, the desired quinomethanes were successfully generated and trapped by terpenes on the PTFE fibres to form natural products.

Results and discussion

First, 2,6-diacetyl-4-methylphloroglucinol **11** was synthesized⁷ as a model compound for grandinol **10**. In the presence of 2 mol equiv. of β -pinene, compound **11** was oxidized by 2 mol equiv. of DDQ in nitromethane. After 30 min standing at ambient temperature, the desired cycloadduct **6** was obtained in 84.4% yield. Similarly, α -pinene and compound **11** gave **3**

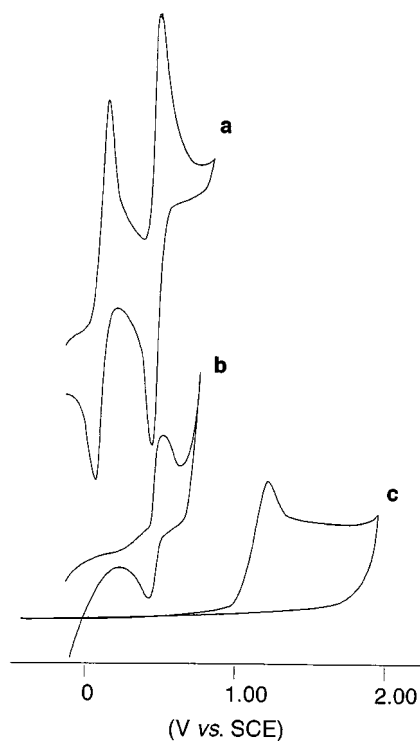
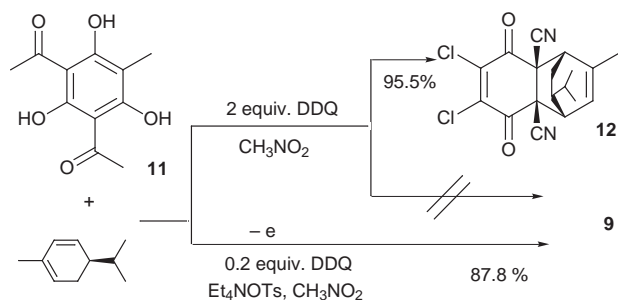


Fig. 1 Cyclic voltammograms of DDQ and phloroglucinol derivative **11**. **a**, DDQ, **b**, DDQ + **11**, **c**, **11**; samples (5.0 mm) were dissolved in 50 mM Et₄NOTs-CH₃NO₂



Scheme 2

in the presence of DDQ in 82.1% yield. The cycloaddition reaction was not successful in other solvents such as acetonitrile, methanol, DMSO, DMF nor diethyl ether. The results suggested that a quinomethane was generated by the DDQ oxidation, and was immediately trapped by terpenes in nitromethane. Nitromethane was suggested to play an important role in stabilizing the zwitterion intermediate to complete the cycloaddition. Under these reaction conditions, excess DDQ was required because it should be consumed by the oxidation of coexisting terpenes. In addition, *α*-phellandrene gave no desired cycloadducts by the oxidation of **11** with DDQ. Under these conditions, Diels–Alder adduct **12** between DDQ and *α*-phellandrene was obtained in 95.5% yield.

We therefore tried an electrochemical oxidation of **11** in the presence of non-stoichiometric amounts of DDQ as a redox mediator using the PTFE-fibre coated electrode. The electrode is expected to selectively oxidize polar substrates, which can pass through the hydrophobic fibres. The electrode was simply made by binding up a Pt plate with PTFE-fibres to form a hydrophobic reaction zone around the plate. Fig. 1 shows cyclic voltammograms of DDQ, **11** and a mixture of them in 50 mM Et₄NOTs-CH₃NO₂. The voltammogram of the mixture clearly showed redox peaks of DDQ, and DDQH₂ was expected to be oxidized at *ca.* 0.45–0.60 V vs. SCE. The electrochemical oxidation of **11** at 0.45 V vs. SCE in the presence of *α*-phellandrene and 0.2 mol equiv. of DDQ using the PTFE-fibre

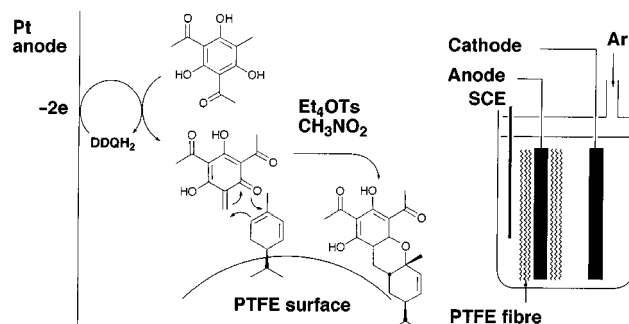
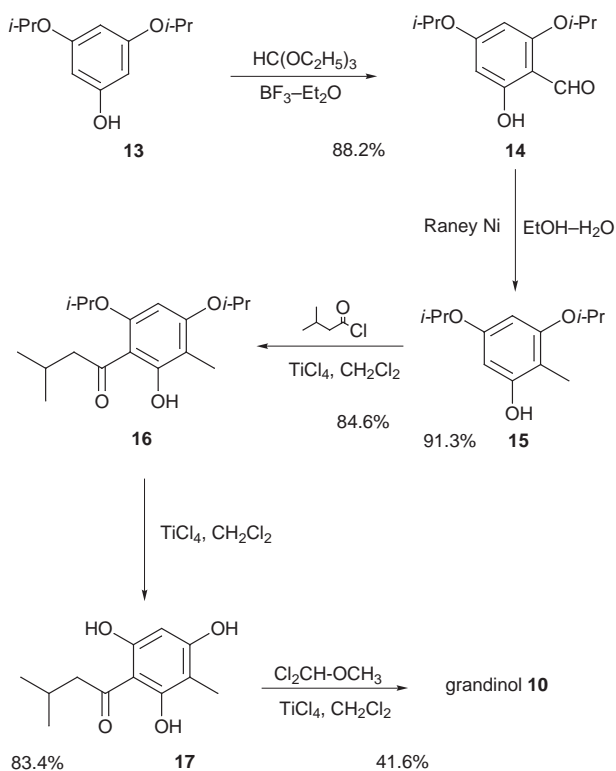


Fig. 2 Proposed reaction mechanism of *in situ* generated quinone methide using DDQ as the redox mediator on the PTFE-fibre coated electrode

coated electrode gave **9** in 87.8% yield without the formation of **12** (Scheme 2). In the absence of DDQ, no cycloadduct was obtained. These results imply that the electron transfer successfully occurred to give the quinomethanes in the redox cycle of DDQ on the Pt electrode. In this reaction solution, compound **11** dissolved to pass through the fibres, but most of the hydrophobic *α*-phellandrene around the electrode should be maintained on the fibres. It is suggested that the electrogeneration of the quinomethane was completed by efficient electron transfer from **11** to the redox mediator on the surface of the Pt plate, and the *in situ* generated quinomethane should be subsequently trapped by *α*-phellandrene on the fibres (Fig. 2). By using this reaction system, *α*- and *β*-pinene also gave the desired cycloadducts **3** and **6** with the corresponding quinomethane generated by the electrochemical oxidation of **11**, respectively (yield **3**: 88.2%, **6**: 76.4%).

In order to synthesize natural euglobals, it was planned that grandinol **10** should act as a precursor of the quinomethane intermediate in the key step (Scheme 3). First, the hydroxy



Scheme 3

groups of phloroglucinol monotosylate were protected by isopropyl bromide in K₂CO₃-DMF and the tosylate was hydrolyzed to give phloroglucinol diisopropyl ether **13**. A formyl group was introduced into compound **13** by HC(OEt)₃ in

BF₃–Et₂O to give **14**, and the formyl group was reduced to a methyl group by Raney Ni⁸ in aqueous ethanol to give **15**. After deprotection by TiCl₄,⁹ an isovaleryl group was introduced by Friedel–Crafts acylation. Compound **17** was then formylated to give **10**. Grandinol **10** was oxidized by the electrode mediated by 0.2 mol equiv. of DDQ in the presence of 2 mol equiv. of (+)-*a*-pinene to give euglobal-G1 **1** and -G2 **2** (6:5, yield 79.0%). In the presence of (+)-*β*-pinene, euglobal-G3 **4** and -G4 **5** were obtained (1:1, yield 89.3%). In addition, (–)-*a*-phellandrene was also subjected to the electrochemical reaction with grandinol **10**. In the presence of **10**, 0.2 mol equiv. of DDQ was added in 50 mM Et₄NOTs–CH₃NO₂, then 2 mol equiv. of (–)-*a*-phellandrene was added. The reaction mixture was oxidized at 0.45 V vs. SCE (2.5 F) at ambient temperature under Ar, and after work up, euglobal-T1 **7** and -IIC **8** were isolated in 50.5% and 28.1% yield, respectively. Spectral data and [α]_D-values of six euglobals were identical with those of natural products^{2,10} to establish their absolute configurations.

Experimental

NMR Spectra were measured on JEOL EX-270 and ALPHA-600 spectrometers at 270, 600 (¹H) and 67.9, 150 (¹³C) MHz for samples in CDCl₃ containing tetramethylsilane as internal standard; *J* values are given in Hz. IR and UV spectra were measured on a JASCO IR-810 IR spectrometer and a JASCO UVDEC-460 spectrophotometer, respectively. Mass spectra were recorded on a JEOL JMS-SX-102A spectrometer. Microanalyses were performed on a Perkin-Elmer 2400 II organic elemental microanalyzer. TLC was carried out on a Kieselgel GF₂₄₅ (0.25 mm thickness). Wakogel C-200 was used for column chromatography with hexane–ethyl acetate (EtOAc). HPLC was performed on a JASCO BIP-1 instrument (UV detector) with a column of LiChroprep Si 60 (40–63 μm, Merck). Optical rotations were measured on a JASCO DIP-360 digital polarimeter, and [α]_D-values are recorded in units of 10^{−1} deg cm g^{−1}. Redox potentials were measured by cyclic voltammetry (Yanagimoto P-900 cyclic polarograph) by using a Pt or a glassy carbon as anode and a Pt wire as cathode vs. SCE. The anode for the macro electrolysis was prepared by binding up a Pt plate (60 mm × 20 mm) with PTFE strings (composed of the PTFE-fibres 20 μm × 1 m, 2.0 g, Flon Industry) to completely cover the surface of the anode.

Electrochemical synthesis of model compounds **3**, **6** and **9**

Compound **11** (1.0 mmol) and *a*-pinene (2.0 mmol) were added to 50 mM Et₄NOTs–CH₃NO₂ (20 cm³). Into this solution was dissolved DDQ (0.2 mmol) and the solution was electrolysed by using the PTFE coated Pt anode (60 mm × 20 mm) and a Pt cathode (10 mm × 10 mm) at a constant potential (0.45 V vs. SCE) under Ar. After the reaction was completed (*ca.* 2.5 F), the reaction mixture was poured into AcOEt and the AcOEt solution was washed successively with 5% aq. NaHCO₃ and brine. The organic layer was dried over anhydrous MgSO₄. After filtration, and evaporation under reduced pressure, the residue was purified by silica gel column chromatography (hexane–AcOEt) to give a cycloadduct **3** (88.2%). By using this method, cycloadducts **6** and **9** were also obtained in the presence of *β*-pinene or *a*-phellandrene instead of *a*-pinene, respectively (yields: **6** 76.4%, **9** 87.8%).

1-(5-Acetyl-6,8-dihydroxy-2,14,14-trimethyl-3-oxatetra-cyclo[11.1.1.0^{2,11}.0^{4,9}]pentadeca-4,6,8-trien-7-yl)ethan-1-one **3.** An oil (Found: C, 70.2; H, 7.5; C₂₁H₂₆O₅ requires C, 70.37; H, 7.31%); *m/z* 358 (M⁺, 43%), 224 (68), 223 (100), 209 (43); *v*_{max}(NaCl)/cm^{−1} 2925, 1615, 1360; *δ*_H 16.10 (1H, s), 15.01 (1H, s), 2.77 (1H, dd, *J* 2.4, 15.6), 2.72 (3H, s), 2.69 (1H, m), 2.58 (3H, s), 2.41 (1H, dd, *J* 6.00, 15.6), 2.28 (1H, t, *J* 5.4), 2.12 (2H, m), 1.88 (1H, d, *J* 3.6), 1.50 (3H, s), 1.33 (1H, m), 1.30 (3H, s), 1.10 (3H, s), 0.82 (1H, d, *J* 11.4); *δ*_C 204.41, 203.34, 170.42, 169.12, 164.93, 104.45, 103.75, 100.80, 88.62, 55.35, 40.30,

33.80, 33.14, 32.90, 29.27, 28.09, 27.53, 27.46, 22.75, 22.38, 20.16; *λ*_{max}(EtOH)/nm 272 (log *ε*/dm^{−3} mol^{−1} cm^{−1} 4.57).

1-(6'-Acetyl-5',7'-dihydroxy-6,6-dimethylspiro[bicyclo[3.1.1]-heptane-2,2'-chromane]-8'-yl)ethan-1-one **6.** White crystals, mp 100–101 °C (Found: C, 70.1; H, 7.2; C₂₁H₂₆O₅ requires C, 70.37; H, 7.31%); *m/z* 358 (M⁺, 38%), 315 (37), 223 (100), 93 (23), 69 (33); *v*_{max}(KBr)/cm^{−1} 2911, 1640, 1590; *δ*_H 2.70 (3H, s), 2.66 (3H, s), 2.55 (2H, m), 2.28 (1H, m), 2.19 (1H, t, *J* 5.50), 2.05–2.00 (3H, m), 2.05–1.89 (2H, m), 1.99–1.90 (2H, m), 1.60 (1H, d, *J* 10.00), 1.29 (3H, s), 1.02 (3H, s); *δ*_C 204.3, 203.1, 170.3, 169.2, 162.1, 104.5, 104.0, 100.6, 86.9, 48.6, 40.4, 38.2, 33.0, 31.5, 29.7, 28.9, 27.5, 27.0, 24.7, 23.3, 15.7; *λ*_{max}(1,4-dioxane)/nm 276 (log *ε*/dm^{−3} mol^{−1} cm^{−1} 4.54), 342 (3.63).

1-[2-Acetyl-1,3-dihydroxy-10a-methyl-7-(methylethyl)-7,8,10a,8a-tetrahydro-9H-xanthen-4-yl]ethan-1-one **9.** An oil (Found: C, 70.2; H, 7.4; C₂₁H₂₆O₅ requires C, 70.37; H, 7.31%); *m/z* 358 (M⁺, 17%), 315 (31), 224 (52), 223 (100), 209 (23), 147 (24); *v*_{max}(NaCl)/cm^{−1} 2925, 1614, 1365; *δ*_H 16.08 (1H, s), 15.11 (1H, s), 5.75 (1H, dd, *J* 3.00, 10.20), 5.69 (1H, d, *J* 10.20), 2.70 (3H, s), 2.66 (3H, s), 2.63 (1H, m), 2.40 (1H, dd, *J* 7.80, 17.4), 2.13 (1H, m), 2.08 (1H, m), 1.73 (1H, m), 1.68 (2H, m), 1.25 (3H, s), 0.95 (3H, d, *J* 6.60), 0.93 (3H, d, *J* 6.60); *δ*_C 204.33, 203.35, 170.00, 169.22, 160.91, 133.14, 130.68, 104.20, 103.90, 100.03, 78.78, 38.62, 33.26, 33.02, 31.75, 29.68, 27.74, 27.40, 20.48, 20.00, 19.76; *λ*_{max}(EtOH)/nm 274 (log *ε*/dm^{−3} mol^{−1} cm^{−1} 4.73).

Synthesis of grandinol **10**

Phloroglucinol diisopropyl ether **13** was obtained as an oil (Found: C, 68.5; H, 8.5; C₁₂H₁₈O₃ requires C, 68.54; H, 8.63%); *m/z* 210 (M⁺, 52%), 168 (17), 126 (100); *v*_{max}(NaCl)/cm^{−1} 3410, 2991, 1602, 1489, 1150; *δ*_H 6.05 (1H, d, *J* 1.89), 6.01 (2H, d, *J* 1.89), 4.42 (2H, septet, *J* 5.94), 1.28 (12H, d, *J* 5.94); *δ*_C 159.6, 157.4, 96.7, 96.08, 70.2, 21.9.

Compound **13** was dissolved in 20 cm³ of BF₃–Et₂O and HC(OEt)₃ (1.8 g) was added to the solution at −10 °C under Ar. After 5 min, the reaction mixture was poured into 30 cm³ 5% aq. AcOK, and extracted with AcOEt 3 times. The combined AcOEt solution was dried over MgSO₄, filtered, and evaporated to dryness. The residue was separated on silica gel (hexane–AcOEt) to give **14** (yield 88.2%), an oil (Found: C, 65.3; H, 7.8; C₁₃H₁₈O₄ requires C, 65.53; H, 7.61%); *m/z* 238 (M⁺, 96%), 196 (23), 154 (100), 153 (53), 126 (15); *v*_{max}(KBr)/cm^{−1} 3500–3300, 2951, 1620, 1570, 1360, 1190; *δ*_H 12.47 (1H, s), 10.02 (1H, s), 5.90 (1H, d, *J* 1.89), 4.53 (2H, septet, *J* 5.94), 1.32 (6H, d, *J* 5.94), 1.30 (6H, d, *J* 5.90); *δ*_C 191.8, 166.4, 166.2, 162.0, 106.2, 93.5, 92.9, 70.8, 70.4, 21.7 (4C); *λ*_{max}(1,4-dioxane)/nm 270 (log *ε*/dm^{−3} mol^{−1} cm^{−1} 4.47), 336 (3.58).

Compound **14** was dissolved in EtOH–H₂O (1:1, 100 cm³) and refluxed for 6 h in the presence of Raney Ni (40 g). After cooling and filtration, the aqueous solution was extracted with AcOEt, and the organic layer was dried over MgSO₄. The AcOEt solution was then evaporated to dryness and the residue was separated by silica gel column chromatography to give **15** (yield 91.3%), a yellow oil (Found: C, 69.1; H, 8.9; C₁₃H₂₀O₃ requires C, 69.61; H, 8.99%); *m/z* 224 (M⁺, 67%), 140 (100), 139 (26), 126 (22), 111 (23); *v*_{max}(NaCl)/cm^{−1} 3200, 2981, 1619, 1588, 1510, 1101; *δ*_H 6.09 (1H, d, *J* 1.89), 6.01 (1H, d, *J* 1.89), 4.40 (1H, septet, *J* 5.94), 4.32 (1H, septet, *J* 6.21), 2.03 (3H, s), 1.29 (6H, d, *J* 6.21), 1.25 (6H, d, *J* 5.94); *δ*_C 157.4, 156.4, 155.1, 106.4, 96.1, 95.84, 70.8, 70.2, 22.1 (2C), 21.9 (2C), 7.89; *λ*_{max}(EtOH)/nm 208 (log *ε*/dm^{−3} mol^{−1} cm^{−1} 4.69), 272 (3.36).

To a solution of **15** (1.5 g) in 5 cm³ of dry CH₂Cl₂ were added 2.0 cm³ of TiCl₄ and 0.9 g of isovaleryl chloride at 0 °C under Ar. The reaction mixture was allowed to stand at ambient temperature for 30 min, and then 2 cm³ of MeOH was added dropwise to the solution. The solution was poured into water and extracted with AcOEt. Compound **16** was separated from AcOEt solution by silica gel column chromatography. Compound **16** was a yellow oil (Found: C, 70.1; H, 9.3;

$C_{18}H_{28}O_4$ requires C, 70.10; H, 9.15%; m/z 308 (M^+ , 37%), 251 (41), 209 (64), 167 (100); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 2980, 1621, 1579, 1420, 1130; δ_{H} 14.11 (1H, s), 5.95 (1H, s), 4.65 (1H, septet, J 5.94), 4.58 (1H, septet, J 6.21), 2.92 (2H, d, J 7.02), 2.23 (1H, septet, J 7.02), 2.00 (3H, s), 1.42 (6H, d, J 6.21), 1.36 (6H, d, J 5.94), 0.96 (6H, d, J 6.48); δ_{C} 205.8, 164.2, 161.7, 158.9, 106.3, 92.3, 89.3, 70.4, 70.2, 53.4, 25.2, 22.7 (2C), 22.1 (2C), 21.9 (2C), 7.4; $\lambda_{\max}(\text{EtOH})/\text{nm}$ 204 (log $\epsilon/\text{dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ 5.37), 294 (5.26).

Compound **16** was then allowed to stand at ambient temperature in a solution of TiCl_4 (2.0 cm^3) in CH_2Cl_2 (10 cm^3) for 48 h to give **17** (yield 83.4%), red crystals, mp 154–155 °C (Found: C, 64.1; H, 7.4; $C_{12}H_{16}O_4$ requires C, 64.27; H, 7.19%); m/z 224 (M^+ , 31%), 209 (18), 167 (100); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 3141, 2770, 1612, 1430; δ_{H} 5.83 (1H, s), 2.97 (2H, d, J 5.94), 2.23 (2H, septet, J 6.75), 2.04 (3H, s), 0.97 (6H, d, J 6.75); δ_{C} 206.0, 162.8, 159.7, 159.0, 105.0, 102.5, 94.8, 52.9, 25.3, 22.8 (2C), 7.0; $\lambda_{\max}(\text{EtOH})/\text{nm}$ 204 (log $\epsilon/\text{dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ 4.12), 292 (4.06).

To a solution of compound **17** in CH_2Cl_2 (5 cm^3), 1.0 cm^3 of TiCl_4 and 1.1 g of dichloromethyl methyl ether were added at -20 °C under Ar, and the mixture was allowed to stand at -20 °C for 2 h. The solution was then poured into crushed ice, and extracted with AcOEt to give **10** (41.6%), pink crystals, mp 113–114 °C (Found: C, 61.7; H, 6.6; $C_{13}H_{16}O_5$ requires C, 61.89; H, 6.39%); m/z 252 (M^+ , 18%), 237 (22), 185 (100), 167 (35), 69 (24); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 3359, 2968, 1630; δ_{H} 15.5 (1H, s), 14.32 (1H, s), 10.11 (1H, s), 3.00 (2H, d, J 6.75), 2.26 (1H, septet, J 6.48), 2.05 (3H, s), 0.99 (6H, d, J 6.48); δ_{C} 206.6, 191.9, 171.8, 167.8, 161.5, 104.3, 103.4, 100.0, 52.9, 25.1, 22.8, 6.4; $\lambda_{\max}(\text{EtOH})/\text{nm}$ 214 (log $\epsilon/\text{dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ 3.43), 246 (4.47).

Electrochemical synthesis of euglobal-G1 **1** and -G2 **2**

Grandinol **10** (504 mg) and (+)- α -pinene (816 mg) were dissolved in 10 cm^3 of 50 mM $\text{Et}_4\text{OTs}-\text{CH}_3\text{NO}_2$ at ambient temperature. To this solution was added DDQ and the mixture was electrolysed using a PTFE-fibre coated glassy carbon anode and a Pt cathode at a constant potential under Ar. After the reaction was complete (2.2 F), the reaction mixture was poured into AcOEt and the AcOEt solution was washed successively with 5% aq. NaHCO_3 and brine. The organic layer was washed and dried over anhydrous MgSO_4 . After filtration and evaporation under reduced pressure, the residue was purified by silica gel column chromatography (hexane–AcOEt) to give a mixture of euglobal-G1 **1** and -G2 **2** (6:5, yield 79.0%). The mixture was further separated by HPLC (hexane–AcOEt) to give purified **1** and **2**, respectively.

Euglobal-G1 **1**; white crystals, mp 112 °C, $[a]_{\text{D}} +129^\circ$ (c 0.01) (lit.,^{10a} +116°) (Found: C, 71.2; H, 8.0; $C_{23}H_{30}O_5$ requires C, 71.48; H, 7.82%); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 3650–3200, 1710, 1620, 1360; m/z 386 (M^+ , 85), 343 (22), 251 (100), 195 (33), 193 (31), 93 (64); δ_{H} 15.44 (1H, s), 13.15 (1H, s), 10.21 (1H, s), 3.01 (1H, dd, J 6.21, 15.39), 2.76 (1H, d, J 2.70), 2.71 (1H, m), 2.58 (1H, dd, J 7.56, 15.39), 2.43 (1H, m), 2.41 (1H, dd, J 12.45, 5.67), 2.23 (1H, m), 2.13 (1H, m), 1.91 (1H, m), 1.35 (1H, m), 1.51 (3H, s), 2.77 (1H, d, J 2.31), 1.31 (3H, s), 1.10 (3H, s), 0.99 (3H, d, J 6.59), 0.94 (3H, d, J 6.60), 0.80 (1H, d, J 10.56); δ_{C} 205.79, 192.48, 170.47, 166.93, 166.18, 104.67, 104.02, 100.59, 89.30, 55.38, 52.68, 40.42, 40.30, 33.74, 32.30, 29.16, 28.17, 27.60, 24.90, 23.05, 22.76, 22.44, 19.92; $\lambda_{\max}(\text{EtOH})/\text{nm}$ 278 (log $\epsilon/\text{dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ 4.56).

Euglobal-G2 **2**; an oil, $[a] +98.0^\circ$ (c 0.01) (lit.,^{10a} +103°) (Found: C, 71.2; H, 7.9; $C_{23}H_{30}O_5$ requires C, 71.48; H, 7.82%); m/z 368 (M^+ , 72%), 343 (22), 251 (100), 195 (35), 193 (28), 93 (60); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 3650–3200, 1625, 1300; δ_{H} 15.35 (1H, s), 14.36 (1H, s), 9.93 (1H, s), 2.99 (1H, d, J 6.48), 2.98 (1H, d, J 6.48), 2.68 (1H, m), 2.59 (1H, m), 2.45 (1H, dd, J 6.48, 16.2), 2.24 (1H, t, J 5.67), 2.14 (1H, t, J 5.28), 2.08 (2H, m), 1.88 (1H, m), 1.46 (3H, s), 1.30 (3H, s), 1.26 (1H, m), 1.10 (3H, s), 1.03 (3H, d, J 1.35), 0.98 (3H, d, J 1.35), 0.82 (1H, d, J 10.53); δ_{C} 206.32, 191.69, 171.30, 168.24, 164.41, 103.71, 103.52,

100.88, 87.60, 54.87, 52.75, 40.66, 40.28, 34.14, 28.78, 28.21, 27.90, 25.03, 22.78, 19.94; $\lambda_{\max}(\text{EtOH})/\text{nm}$ 278 (log $\epsilon/\text{dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ 4.57).

Electrochemical synthesis of euglobal-T1 **7** and -IIC **8**

Euglobal-T1 and -IIC were synthesized by the above method using α -phellandrene instead of α -pinene (yield 78.6%, **7**:**8** 9:5).

Euglobal-T1 **7**; an oil, $[a] -139^\circ$ (c 0.01) (lit.,^{10b} -143.7°) (Found: C, 71.6; H, 8.0; $C_{23}H_{30}O_5$ requires C, 71.48; H, 7.82%); m/z 386 (M^+ , 32%), 343 (36), 256 (64), 251 (75), 236 (61), 137 (100), 123 (49); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 2920, 1615, 1450; δ_{H} 15.40 (1H, s), 13.21 (1H, s), 10.19 (1H, s), 5.78 (1H, dd, J 10.2, 2.9), 5.71 (1H, br d, J 10.2), 2.96 (1H, dd, J 7.2, 14.4), 2.86 (1H, dd, J 7.2, 14.4), 2.69 (1H, dd, J 1.67, 6.3), 2.41 (1H, dd, J 16.7, 7.8), 2.20 (1H, m), 2.14 (1H, m), 2.08 (1H, m), 1.74 (1H, h, J 6.6), 1.71 (2H, m), 1.53 (3H, s), 0.98 (6H, d, J 6.6), 0.96 (3H, d, J 7.8), 0.93 (3H, d, J 7.8); δ_{C} 206.01, 192.42, 169.99, 167.08, 162.09, 133.47, 130.42, 104.46, 104.00, 99.66, 79.20, 53.19, 38.73, 32.65, 31.77, 27.62, 27.34, 25.46, 22.75, 22.68, 20.14, 20.06, 19.83; $\lambda_{\max}(\text{EtOH})/\text{nm}$ 280 (log $\epsilon/\text{dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ 4.30).

Euglobal-IIC **8**; an oil $[a] -135^\circ$ (c 0.01) (lit.,² -144°) (Found: C, 71.5; H, 7.6; $C_{23}H_{30}O_5$ requires C, 71.48; H, 7.82%); m/z 386 (M^+ , 16%), 355 (26), 256 (33), 167 (51), 149 (100); $\nu_{\max}(\text{NaCl})/\text{cm}^{-1}$ 2925, 1620, 1260; δ_{H} 15.40 (1H, s), 14.50 (1H, s), 10.04 (1H, s), 5.75 (1H, dd, J 2.4, 10.2), 5.69 (1H, d, J 10.2), 2.97 (2H, d, J 7.8), 2.66 (1H, dd, J 6.6, 16.2), 2.38 (1H, dd, J 7.2, 16.8), 2.25 (1H, h, J 6.6), 2.13 (1H, m), 2.05 (1H, m), 1.72 (1H, m), 1.68 (2H, m), 1.49 (3H, s), 0.98 (6H, d, J 6.6), 0.95 (3H, d, J 6.0), 0.94 (3H, d, J 6.6); δ_{C} 206.39, 191.88, 171.39, 168.11, 160.88, 133.19, 130.90, 103.73, 103.41, 100.49, 78.48, 52.68, 38.71, 33.22, 27.56, 27.48, 25.10, 22.77, 20.43, 20.05, 19.82; $\lambda_{\max}(\text{EtOH})/\text{nm}$ 278 (log $\epsilon/\text{dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ 4.51).

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