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A CONVENIENT SYNTHESIS OF TRIQUINACENE-2-CARBOXYLIC ACID AND A NEW APPROACH TOWARDS THE SYNTHESIS OF DODECAHEDRANE

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Abstract—A practical synthesis of triquinacene-2-carboxylic acid **1** from the readily available Thiele's acid **2** is reported. Optically active 2-formamidotriquinacene **20** derived from (+)-**1** was condensed with the acid chloride of (+)-**1** to give the secondary amide **23** *via* **22**. Compound **23** was then converted into the cyclic imidate salt **26** with the hope to eventually achieve the synthesis of the dodecahedrane nucleus (see **28**).

Since the first syntheses of triquinacene,[1-3] it was suggested that this compound or a derivative could yield dodecahedrane by a process equivalent to a dimerization.[a] One such derivative is triquinacene-2-carboxylic acid (**1**) which was first synthesized from triquinacene by Fukanaga.[b] The compound was more recently prepared *via* an interesting route which starts with the adduct of tetracyanoethylene and cycloöctatetraene iron tricarbonyl. This synthetic route, which was developed by Paquette and his collaborators,[8] was later used by Repic.[7]

We have recently completed a new synthesis of triquinacene-2-carboxylic acid by a convenient route which is based on our previous strategy developed during our synthesis of triquinacene[9,c] We wish to report this work. We report also a new approach toward dodecahedrane using triquinacene-2-carboxylic acid as starting material.

Synthesis of triquinacene-2-carboxylic acid

The synthesis of triquinacene-2-carboxylic acid (**1**) is illustrated in Scheme 1. The experimental details for the preparation of a 4:1 mixture of *exo* and *endo* ketone acetates **6** and **7** from Thiele's acid (**2**) *via* the intermediates **3**, **4**, and **5** have been previously reported.[9] A Grignard reaction on the mixture of **6** and **7** gave after chromatographic separation pure *trans*-diol **8** and pure *cis-endo*-diol **9** in 55 and 12% yield respectively. It is assumed that the Grignard reagent attacks the least hindered face of the carbonyl group in **6** and **7** yielding **8** and **9** respectively with the tertiary hydroxyl group in the *endo* orientation. The configuration of the *cis*-diol **9** was confirmed by the conversion of **9** into the corresponding carbonate derivative **10**. Interestingly, molecular models show that the *cis-exo* as well as the two possible *trans*-diol isomers of **9** cannot form a cyclic carbonate derivative.

Treatment of *trans*-diol **8** with methanesulfonyl chloride in the presence of triethylamine in benzene gave after column chromatography with florisil the pure diene mesylate **11**. When the same reaction was carried out on a large scale, 2-methyltriquinacene (**12**, 65%) was isolated instead of compound **11**. On the large scale experiment, the transformation of **11** into **12** occurred during the column chromatography.[10] 2-Methyltriquinacene (**12**) was also obtained (87%) from diene mesylate **11** by dehydromesylation with DBN.

Selenium dioxide oxidation of compound **12** gave triquinacene-2-carboxyldehyde (**13**) which was further oxidized (MnO_2 NaCN, CH_3OH, AcOH[11] to give methyl triquinacene-2-carboxylate (**14**, 81%). Finally, basic hydrolysis (KOH, H_2O, CH_3OH) of compound **14** gave (±)-triquinacene-2-carboxylic acid (**1**, 85%).

(+)-Triquinacene-carboxylic acid was then obtained by resolution of the racemic mixture with (−)-quinine by utilizing the experimental procedure described in reference 7.[b] Paquette and his collaborators[8] have reported that (−)-triquinacene-carboxylic acid (**15**) gives (+)-2,3-dihydrotriquinacen-2-one which was shown from appropriate chiroptical measurements to have the absolute configuration described by structure **16** (Scheme 2). (+)-Triquinacene-2-carboxylic acid corresponds therefore to the absolute configuration described by structure **1**.

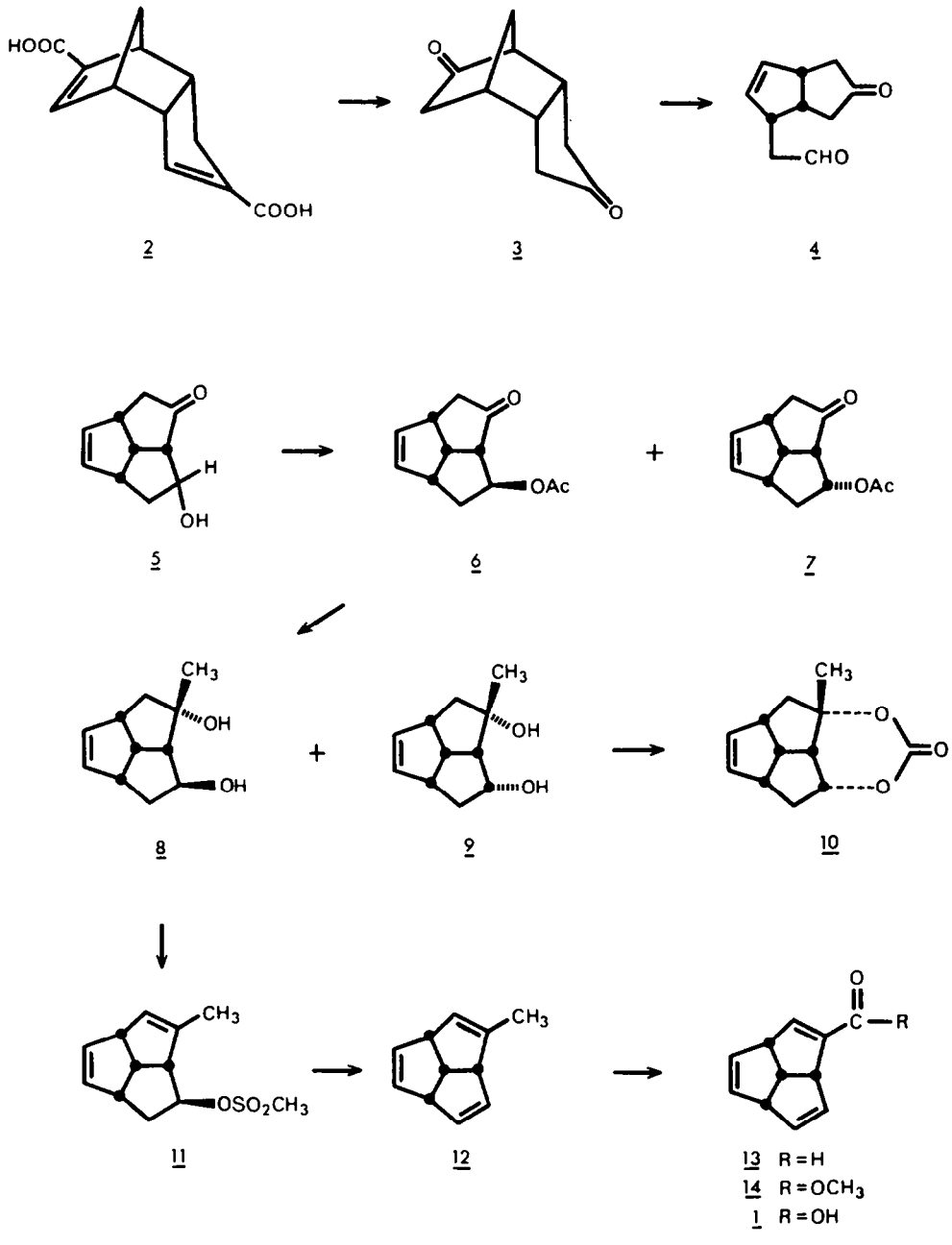
New approach towards the synthesis of dodecahedrane

(±)-Triquinacene-2-carboxylic acid was transformed into racemic triquinacene-2-isocyanate **19** (Scheme 3) *via* the intermediate formation of the acid chloride **17** (oxalyl chloride, benzene) and the acyl azide **18** (NaN_3, H_2O). Reduction of (±)-isocyanate **19** with sodium borohydride in tetrahydrofuran (12) yielded the crystalline (±)-2-formamidotriquinacene (**20**, 47% yield from **1**). Compound **20** was further characterized by methylation (NaH, THF, CH_3I) which gave the crystalline racemic N-methylformamide derivative **21**.

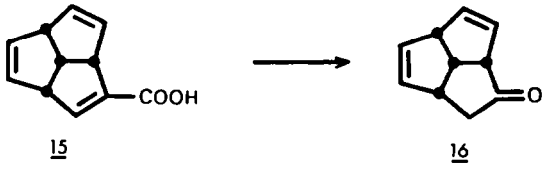
The optically active (+)-2-formamidotriquinacene (**20**) was then prepared from (+)-triquinacene-2-carboxylic acid (**1**) by following the above procedure. The sodium salt (NaH, THF) of dextrorotatory formamide **20** was then reacted with the optically active acid chloride **17** derived from (+)-triquinacene-2-carboxylic acid (**1**) to give N - formyl - N - (2 - triquinacenyl)triquinacene - 2 - carboxamide (**22**) in 80% yield. Compound **22** was then transformed (Na_2CO_3, CH_3OH) into the crystalline dextrorotatory N-(2-triquinacenyl)triquinacene - 2 - carboxamide (**23**, 65% from **20**).

Alkylation of the secondary carboxamide **23** (NaH, THF) with 1-bromopentane gave N-pentylcarboxamide **24**, while alkylation with 1-bromo-3chloropropane yielded the corresponding (+)-N-(3-chloropropyl) carboxamide **25**. Finally, compound **25** was converted into the

[a] For reviews on this subject, see Refs. 4 and 5.
[b] T. Fukanaga, unpublished work, see also Refs. 4–7.
[c] This work is summarized in chart 5 of Ref. 4.



Scheme 1.



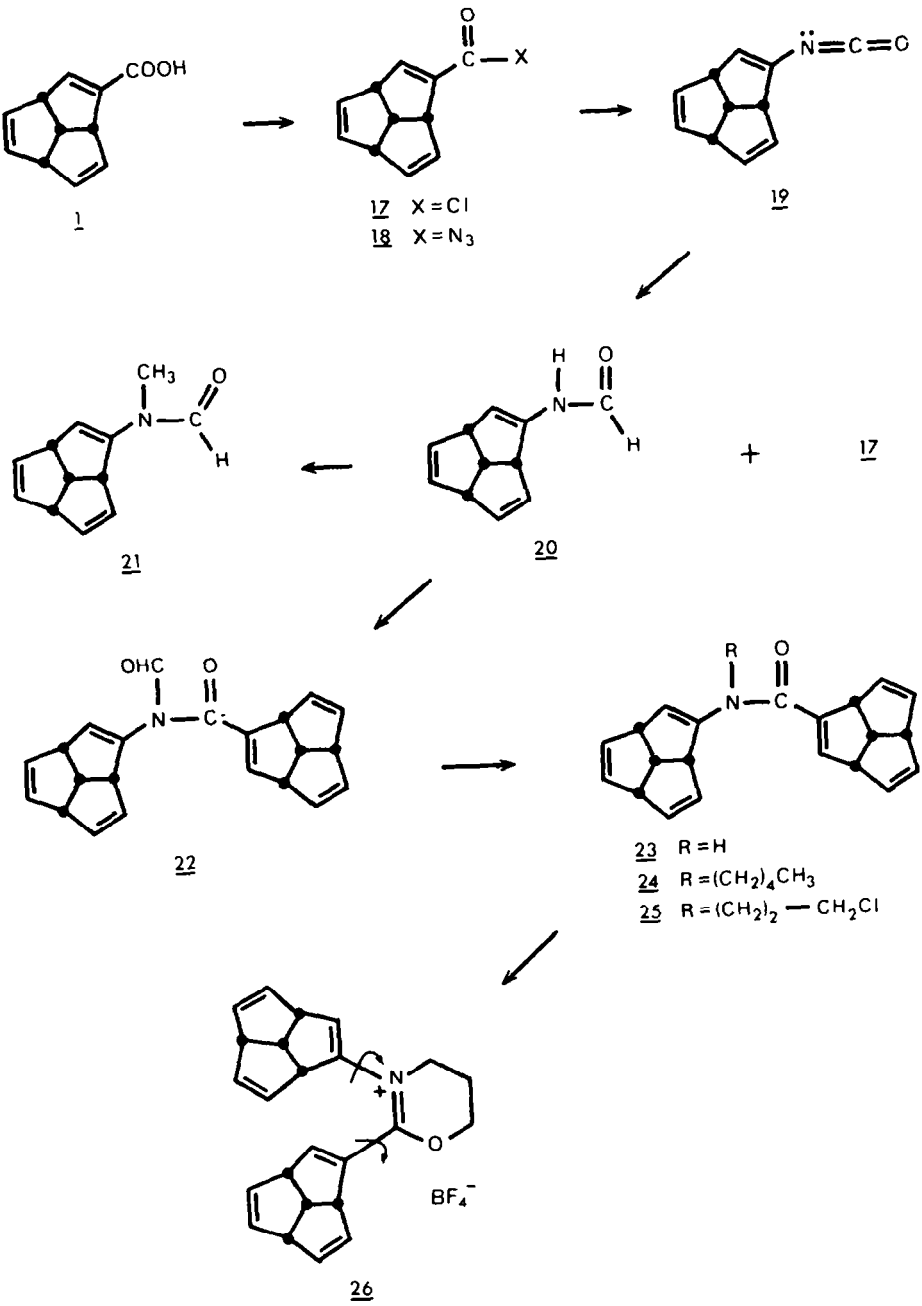
Scheme 2.

oily dextrorotatory imidate salt **26** ($AgBF_4$, CH_2Cl_2–benzene, 98%).

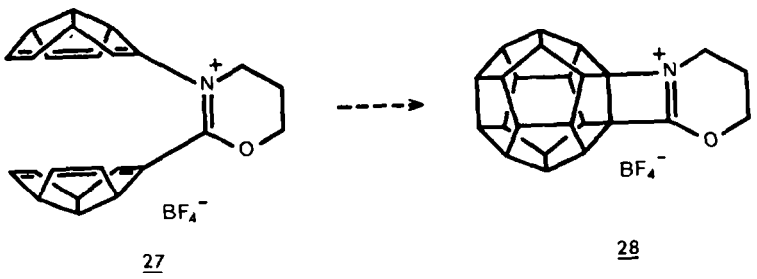
Our strategy to bring two triquinacene molecules into appropriate proximity is based on the cyclic imidate functional group. Although the two triquinacenyl groups can still rotate (see arrows in **26**), molecular models indicate that compound **26** can easily take conformation **27** (Scheme 4) which could allow a cyclization process on induction either thermally, photochemically, electrochemically or by other means, to render the hypothetical dodecahedrane imidate salt **28** or a close derivative thereof, a reality. However, all the experiments towards this end have failed so far.

EXPERIMENTAL

Infrared (IR) spectra were obtained on a Perkin-Elmer 257 spectrophotometer. Proton nuclear magnetic resonance were recorded on a Bruker WP-60 instrument with TMS as an internal standard. Mass spectra were obtained on Hitachi-Perkin-Elmer RMU-6-A and Micromass ZAB-2F machines. Magnesium sulfate was used to dry organic solvents. Ultraviolet (UV) spectra were registered on a Varian Techtron 635 spectrophotometer. Micro-



Scheme 3.



Scheme 4.

analyses were performed by C. Daesslé, Organic Microanalyses, Montreal and by Schwarzkopf Microanalytical Laboratory, New York.

Trans-*diol* **8** *and* cis-endo-*diol* **9**

An ethereal soln of MeMgI was prepared under N_2 by dropwise addition of a solution of MeI (59.5 ml, 0.97 mol) in anhydrous ether (500 ml) into a flask containing magnesium turnings (18.65 g, 0.776 mol) in ether (500 ml) over a period of 20 min. After the addition was completed, stirring was continued at room temperature for 30 min. A solution of a 4:1 mixture of ketone acetates **6** and **7** (20.0 g, 97 mmol) in ether (500 ml) was added dropwise to the Grignard reagent and the mixture was refluxed for 2 hr. The cooled reaction mixture was then poured into a saturated ammonium sulfate solution and the mixture extracted with ether (5 × 50 ml). The dried organic phase was evaporated and the crude product was purified by column chromatography with silica gel (20% acetone in CH_2Cl_2) to give *trans*-diol **8** (9.63 g, 55%) and *cis-endo*-diol **9** (2.0 g, 12%).

Trans-*diol* **8**. An analytical sample was prepared by recrystallization from ether–pentane; m.p. 70.5–71.0°C; IR (CH_2Cl_2): 3580 and 3420 cm^{-1}; NMR ($CDCl_3$) δ: 5.52 (2H, quadruplet, olefinic hydrogens), 4.20 (1H, multiplet, CHOH), 1.32 (3H, singlet, CH_3), 3.39–1.41 (10H, multiplet); MS *m/e*: 180 (M^+). Calc for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; found: C, 73.07; H, 9.22%.

Cis-endo-*diol* **9**. An analytical sample was prepared by recrystallization from dichloromethane–ether; m.p. 111.5–112.0°; IR (CH_2Cl_2): 3610 and 3400 cm^{-1}; NMR ($CDCl_3$) δ: 6.41–5.29 (3H, multiplet, olefinic hydrogens and CHOH), 1.39 (3H, singlet, CH_3), and 5.0–0.8 (10H, multiplet); MS *m/e*: 180 (M^+). Calc for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; found: C, 73.45; H, 8.71%.

Cyclic carbonate **10** of cis-endo-*diol* **9**

A solution of phosgene in dry benzene (4.46 ml, 3.2 g/50 ml, 2.86 mmol) was added to a solution of *cis-endo*-diol **9** (130 mg, 0.72 mmol) in benzene (15 ml) containing pyridine (0.225 ml, 2.89 mmol) during a period of 5 min. The reaction mixture was then stirred for 10 min at room temperature. Excess phosgene was destroyed by the slow addition of water and the mixture was extracted several times with dichloromethane. The extracts were combined, washed with hydrochloric acid (0.1 N), water and dried. The product obtained on removal of the solvent was recrystallized from ether–pentane (114 mg, 77%); m.p. 97–98°; IR (CH_2Cl_2): 1755 cm^{-1}; NMR ($CDCl_3$) δ: 6.13–5.66 (2H, multiplet, olefinic hydrogens), 4.25 (1H, multiplet, CHOCO), 3.12–1.04 (8H, multiplet), and 1.51 (3H, singlet, CH_3); MS *m/e*: 206 (M^+). Calc for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84; found: C, 69.70; H, 6.88%.

2-*Methyltriquinacene* (**12**)

(a) *From* trans-*diol* **8** (*large scale*). *Trans*-diol **8** (15.0 g, 0.083 mol) was dissolved in dry benzene (2 l) and cooled to 0°. Triethylamine (30.34 ml, 0.22 mol) and methanesulfonyl chloride (15.25 ml, 0.21 mol) were added. After 240 min and 12 hr additional triehylamine (12.84 ml, 0.093 mol) and methanesulfonyl chloride (6.42 ml, 0.09 mol) were added. The reaction was completed after 23 hr. The solvent was removed *in vacuo*. The residue was dissolved in water and extracted with ether (4 × 500 ml). The organic phase was washed with dilute hydrochloric acid, saturated sodium carbonate and water. The solvent was evaporated. Tlc analysis showed the presence of diene mesylate **11** as the major product. The residue was purified by column chromatography of Florisil (500 g) with dichloromethane to give 2-methyltriquinacene (**12**) (16.1 g, 65%) as an oil; IR (CH_2Cl_2): 3100, 3020, 2980, 1390 1370 and 1205 cm^{-1}; NMR ($CDCl_3$) δ: 5.70 (4H, quadruplet, olefinic hydrogens), 5.34–5.13 (1H, multiplet, olefinic hydrogens), 4.0–3.42 (4H, multiplet), and 1.72 (3H, doublet, CH_3) MS *m/e*: 144 (M^+).

(b) *From diene mesylate* **11**. Diene mesylate **11** (1.698 g, 7.07 mmol) was dissolved in 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (8.75 ml, 8.70 g, 70.1 mmol). The bath temperature was raised to 130–140° during 95 min under a nitrogen atmosphere. The mixture was then cooled and diluted with pentane (150 ml). The solution was washed with hydrochloric acid (3 N, 3 × 10 ml) and water. The organic extract was dried, the solvent was distilled to give crude 2-methyltriquinacene (TLC) which was purified by column chromatography with Florisil (pentane) 907 mg, 87%). The pure 2-methyltriquinacene (**12**) obtained was identical to the product of the preceding experiment.

Diene mesylate **11**

Trans-diol **8** (1.87 g, 12.3 mmol) dissolved in dry benzene (445 ml) and cooled at 0°. Triethylamine (3.78 ml, 27.0 mmol) and methanesulfonyl chloride (1.9 ml, 26 mmol) were added. After 4 hr, additional triethylamine (1.6 ml, 11.5 mmol) and methanesulfonyl chloride (0.8 ml, 10.9 mmol) were added. The reaction was left for 23 hr. Work-up as described above in procedure a gave a crude product which was purified by column chromatography with Florisil (100 g) to give pure diene mesylate **11** (2.02 g, 81%). The product was crystallized with ether–pentane (1.74 g, 70%). An analytical sample was prepared by recrystallization from ether–pentane; m.p. 69.5–72.0°; IR (CH_2Cl_2): 1155, 1320, and 1345 cm^{-1}; NMR ($CDCl_3$) δ: 5.63–4.85 (4H, multiplets, olefinic hydrogens and $CHOSO_2$), 3.79–2.91 (4H, multiplet), 3.01 (3H, singlet, CH_3SO_2), and 2.48–1.45 (5H, multiplet, methylene hydrogens, and CH_3); MS *m/e*: 240 (M^+). Calc. for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71; found: C, 59.74; H, 6.81%.

Triquinacene-2-carboxaldehyde (**13**)

Selenium dioxide (12.48 g, 0.11 mol) was added to a solution of 2-methyltriquinacene (**12**, 8.0 g, 55 mmol) in water (125 ml) and dioxane (2.37 ml). The reaction mixture was refluxed for 5 h, cooled and filtered through Celite. The soln was concentrated and diluted with CH_2Cl_2. The organic phase was washed with saturated aq NaCl, dried and evaporated to give the aldehyde **13** as an oil (8.18 g, 93%). This crude product was purified by filtration through a column of silica gel (160 g) with dichloromethane: IR (CH_2Cl_2): 1605, 1680, and 2690 cm^{-1}; NMR ($CDCl_3$) δ: 9.71 (1H, singlet, CHO), 6.67 (1H, singlet, HC=C–CHO), 5.72 (4H, multiplet, olefinic hydrogens), 4.11–3.67 (4H, multiplet); MS *m/e*: 158 (M^+).

Methyl triquinacene-2-carboxylate (**14**)

A solution of triquinacene-2-carboxaldehyde (**13**, 8.45 g, 0.05 mol) in anhydrous methanol (1 l) was added sodium cyanide (9.5 g, 0.19 mol), glacial acetic (3.59 g, 3.42 ml, 0.06 mol) and active manganese dioxide (75 g, 0.18 mol). The reaction mixture was stirred at room temperature for 16.5 h under nitrogen atmosphere. The mixture was filtered through Celite and concentrated. The mixture was diluted with water and extracted with ether (5 × 400 ml). The organic extract was dried and the solvent was evaporated to give methyl triquinacene-2-carboxylate (**14**) as an oil which was not purified further (15.8 g, 81%); IR (CH_2Cl_2): 1720 and 1640 cm^{-1}; NMR ($CDCl_3$) δ: 6.63 (1H, singlet, CH=C–$COOCH_3$), 5.71 (4H, multiplet, olefinic hydrogens), 3.73 (3H, singlet, $COOCH_3$), and 4.11–3.75 (4H, multiplet).

(±)-*Triquinacene-2-carboxylic acid* (**7**)

A solution of methyl triquinacene-2-carboxylate (**14**, 15.80 g, 0.084 mol) in methanol (1 l) was added to a solution of potassium hydroxide (56 g, 1.0 mol) in water (1 l) and the mixture was stirred at room temperature for 2.5 h. The solution was concentrated and water was added. The aqueous phase was acidified with hydrochloric acid (3.0 M) and extracted with dichloromethane (5 × 500 ml). Drying and evaporation of the organic phase gave triquinacene-2-carboxylic acid which was purified by sublimation (12.45 g, 85%); m.p. 127–129°C; IR (CH_2Cl_2): 3600, 2350, 1690, 1630, and 1608 cm^{-1}; NMR ($CDCl_3$) δ: 7.29 (1H, singlet, COOH), 6.77 (1H, singlet, olefinic hydrogen), 5.73 (4H, quintuplet, olefinic hydrogens), and 3.88 (4H, multiplet); MS *m/e*: 174 (M^+).

Resolution of (±)-*triquinacene-2-carboxylic acid* (**7**)

Following the procedure described in Ref. 7, quinine monohydrate (1.69 g, 4.95 mmol) was added to a solution of triquinacene-2-carboxylic acid (0.860 g, 4.95 mmol) in ethyl acetate (100 ml). The mixture was left at room temperature for two days. The solvent was evaporated and the product was crystallized from benzene; m.p. 220–222°; $[\alpha]_D$ −126.0° (c 0.425, CH_3OH).

Sulfuric acid (2N, 25 ml) was added to an ethereal solution

(50 ml) of the levorotatory quininium salt of triquinacene-2-carboxylic acid (1.29 g, 2.59 mmol). After 1 min, the reaction mixture was diluted with water and extracted with ether (3 × 50 ml). The ether extract was dried over sodium sulfate. Evaporation of the solvent left a crystalline product which was sublimed to give (+)-triquinacene-2-carboxylic acid (439 mg, 97%); m.p. 107–110°; $[\alpha]_D$ + 11.0° (c 0.544, CH_3OH).

(+)-2-Formamidotriquinacene (**20**)

Oxalyl chloride (3.95 g, 2.69 ml, 31.4 mmol) was slowly added to a solution of triquinacene-2-carboxylic acid (0.290 g, 1.67 mol) in anhydrous benzene (53 ml) under nitrogen. The mixture was left overnight at room temperature. It was then evaporated to dryness under vacuum. The last traces of oxalyl chloride were removed by repeated evaporation with benzene. The resulting acid chloride **17** (320.7 mg) was used immediately for IR spectroscopy (IRTRAN Cell, benzene): 1740 cm^{-1}.

A solution of acid chloride **17** (320.7 mg, 1.66 mmol) in acetone (0.7 ml) was added dropwise with stirring to a solution of sodium azide (117.8 mg, 1.81 mmol) in water (2.2 ml) at 0°. After the addition was completed, the reaction mixture was stirred for 30 min at 0°. Dichloromethane was then added to the reaction mixture and the organic layer was washed with aqueous sodium bicarbonate (5%, 2 × 25 ml) and water (2 × 15 ml). The dried organic layer was evaporated to dryness yielding crude acyl azide **18** (331 mg) which was used without further purification (IR (CH_2Cl_2): 2103, 1685, 1620, and 1610 cm^{-1}).

A solution of acyl azide **18** (331 mg, 1.66 mmol) was refluxed in anhydrous benzene (44 ml) during 2.5 h under nitrogen. The solution was then evaporated to dryness to give the crude triquinacene-2-isocyanate **19** (285 mg) which was used immediately for IR spectroscopy (CH_2Cl_2): 2240 and 1650 cm^{-1}.

Lithium borohydride (90.7 mg, 4.16 mmol) was added at 0°C and under nitrogen to a solution of triquinacene-2-isocyanate **19** (285 mg, 1.66 mmol) in anhydrous tetrahydrofuran (9 ml). The mixture was left at room temperature for 45 min. Water was added and the mixture was neutralized with carbon dioxide (pH = 7). The aqueous phase was extracted with ether (3 × 100 ml) and the dried organic phase was evaporated. The crude product was purified by filtration through a column of Florisil with ether to give crystalline 2-formamidotriquinacene **20** (140 mg, 49% from (+)-triquinacene-2-carboxylic acid). An analytical sample was prepared by recrystallization with ether–pentane; m.p. 121–123°; $[\alpha]_D$ +95.0° (c 0.587, CH_2Cl_2). Calc for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; found: C, 75.58; H, 6.40%. High resolution MS: calc for 173.0840; found: *m/e* 173.0837.

(±)-2-Formamidotriquinacene (**20**)

Following the above procedure, (±)-triquinacene carboxylic acid (66 mg, 0.38 mmol) gave racemic 2-formamidotriquinacene (31 mg, 47%). An analytical sample was prepared by recrystallization from ether–pentane; m.p. 91–93°; IR (CH_2Cl_2): 3400, 3390, 1700, and 1650 cm^{-1}; NMR ($CDCl_3$) δ: 8.59, 8.40 (1H, two singlets, CHO), 8.22–8.19 (1H, narrow doublet, NH), 5.71 (4H, quadruplet, olefinic hydrogens), 5.91 (1H, broad singlet, CH, broad singlet, CH=C–N), and 3.82 (4H, multiplet); MS: *m/e* 173 (M^+).

(±)-N-methylformamide **21**

Sodium hydride (50% in oil, 25.5 mg, 0.55 mmol) was washed with anhydrous tetrahydrofuran (2 × 10 ml) and tetrahydrofuran (10 ml) was added. A solution of (±)-2-formamidotriquinacene (**20**, 24 mg, 0.139 mmol) in tetrahydrofuran (3 ml) was added and the mixture was stirred at 0° for 10 min. Methyl iodide (196 mg, 1.39 mmol, 86 μl) was added to the mixture which was left at room temperature for 1.5 h. Saturated aq NH_4Cl was added and the mixture was extracted several times with ether. The dried organic phase was evaporated and the crude product was purified by column chromatography on Silica gel with ether to give pure (±)-N-methylformamide **21** (20 mg, 77%). An analytical sample was prepared by recrystallization from ether–pentane; m.p. 84–84.5°; IR (CH_2Cl_2): 1675 and 1633 cm^{-1}; NMR ($CDCl_3$) δ: 8.64 (1H, singlet, CHO), 6.6–5.59 (4H, multiplet, olefinic hydrogens), 5.04 (1H, broad singlet, CH=C–N), 4.27–3.61 (4H, multiplet), and 3.07 (3H, singlet, NCH_3). Calc for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; found: C, 76.89; H, 7.08; high resolution MS: calc for $C_{12}H_{13}NO$ *m/e* 187.0997; found: *m/e* 187.0995.

(+)-N-(2-triquinacenyl)triquinacene-2-carboxamide (**23**)

Sodium hydride (50% oil, 0.0532 g, 1.156 mmol) was washed with anhydrous tetrahydrofuran (3 × 15 ml). Tetrahydrofuran (15 ml) was then added under nitrogen and cooled at 0°. (+)-2-formamidotriquinacene (**20**, 100 mg, 0.58 mmol) in tetrahydrofuran (3 ml) was added to the suspension and the mixture was left at 0° for 10 min. A solution acid chloride **17** (122 mg, 0.64 mmol; derived from (+)-triquinacene-2-carboxylic acid) in tetrahydrofuran (3 ml) was then added to the reaction mixture which was then left at room temperature for 4 h. After filtration, the solvent was evaporated and the residue was purified on silica gel (10% ethyl acetate in pentane) to give the crude N-formylcarboxamide **22** (154 mg, 80%) (IR (CH_2Cl_2): 1715, 1675, 1620, and 1610 cm^{-1}; NMR ($CDCl_3$) δ: 6.27 (1H, broad singlet, CHO), 5.8–5.5 (10H, multiplet, olefin hydrogens), and 4.35–3.58 (8H, multiplets)).

Sodium carbonate (49.6 mg, 0.47 mmol) was then added to a solution of crude N-formylcarboxamide **22** (154 mg, 0.468 mmol) in methanol (12 ml). The reaction mixture was then stirred at room temperature for 30 min and filtered. The solvent was evaporated and the residue was dissolved in dichloromethane. The resulting solution was filtered and evaporated. The residue was purified by column chromatography with silica gel (9 g) (7% ethyl acetate in pentane) to give (+)-N-(2-triquinacenyl)triquinacene-2-carboxamide (**23**, 91.8 mg, 65%). An analytical sample was prepared by recrystallization with dichloromethane–ether; m.p. (under vacuum) 181.5–182.0°; $[\alpha]_D$ + 111.6° (c 0.506, CH_2Cl_2); IR (CH_2Cl_2): 3420, 1670, 1645, 1615, and 1500 cm^{-1}; NMR ($CDCl_3$) δ: 6.97 (1H, broad singlet, NHCO), 6.08 (1H, broad singlet, CH=C–CON), 5.51 (9H, multiplet, olefinic hydrogens), and 4.03–3.44 (8H multiplet); MS *m/e*: 300 (M^+); high resolution MS: calc for $C_{21}H_{19}NO$ *m/e* 301.1466; found: *m/e* 301.1465; UV (CH_3CN) λ_{max} 276 (ϵ 5465) and 234 mm (ϵ 4630); UV (CH_2Cl_2) λ_{max} 278 nm (ϵ 3940).

(+)-N-pentylcarboximide **24**

Sodium hydride (50% in oil, 9.56 mg, 0.20 mmol) was washed with anhydrous hexane (5 × 10 ml) and tetrahydrofuran was added (10 ml) under nitrogen. A solution of (+)-N-(2-triquinacenyl) triquinacene-2-carboxamide (**23**, 20 mg, 0.07 mmol) in dry tetrahydrofuran (4 ml) was added to the suspension and stirred for a few min. 1-Bromopentane (40.1 mg, 0.266 mmol, 32.8 μl) was added and the mixture was left at room temperature for 94 h. After filtration, the solvent was evaporated and the product was purified by column chromatography on Florisil (20% ethyl acetate in pentane) to give (+)-N-pentylcarboxamide **24** 12.2 mg, 50%). An analytical sample was prepared by crystallization from pentane; m.p. 68–70°; IR (CH_2Cl_2): 1640, 1605, and 1380 cm^{-1}; NMR ($CDCl_3$) δ: 5.8–5.4 (9H, multiplet, olefinic hydrogens), 5.14 (1H, broad singlet, CH=C–N), 4.32–3.3 (10H, multiplet), and 1.79–0.64 (9H, multiplet, $(CH_2)_3CH_3$: MS *m/e*: 371 (M^+); high resolution MS: calc for $C_{26}H_{29}NO$ *m/e* 371.2249; found: *m/e* 371.2252; UV (CH_2Cl_2) λ_{max} 258 (ϵ 4061) and 235 nm (ϵ 6310).

(+)-N-(3-chloropropyl)carboxamide **25**

Sodium hydride (50% suspension, 19.2 mg, 0.32 mmol) was washed with anhydrous tetrahydrofuran (3 × 10 ml) and was covered with tetrahydrofuran (10 ml) under nitrogen. A solution of (+)-N-(2-triquinacenyl)triquinacene-2-carboxamide (**23**, 40 mg, 0.133 mmol) in tetrahydrofuran (6 ml) was added and the mixture was stirred during 5 min. 1-Bromo-3-chloropropane (83.6 mg, 56.8 μl, 0.531 mmol) was then added. After 2 h, additional portions of sodium hydride (10 mg, 0.32 mmol) and 1-bromo-3-chloropropane (50 μl, 0.47 mmol, 75.8 mg) were added. After 5 h, another portion of 1-bromo-3-chloropropane (85 μl, 125 mg, 0.79 mmol) was added and the mixture was left at room temperature for 22 h. The mixture was then filtered and the solvent evaporated. The crude product was purified by column chromatography on Florisil (20% ethyl acetate in pentane) to give (+)-N-(3-chloropropyl)carboxamide **25** (47.2 mg, 94%). An analytical sample was prepared by recrystallization from ether–pentane; m.p. 97–100°; $[\alpha]_D$ + 271° (c 0.506, CH_2Cl_2); IR (CH_2Cl_2):

1740, 1600 and 1385 cm^{-1}; NMR ($CDCl_3$): δ 5.69 (1H, broad singlet, CH=C–CO), 5.46 (8H, quadruplet, olefinic hydrogens), 5.05 (1H, broad singlet, olefinic hydrogens), 5.05 (1H, broad singlet, olefinic hydrogen), 4.10–3.0 (12H, multiplet), and 1.86 (2H, quintet, CH_2–CH_2–Cl); MS: *m/e* 377 (M^+); high resolution MS: calc for $C_{24}H_{24}NOCl$ *m/e* 377.1546; found: *m/e* 377.1560. calc for $C_{24}H_{24}NOCl$: C, 76.28; H, 6.40; found: C, 75.94; H, 6.35%. UV (CH_3CN): λ_{max} 236 (ϵ 5860) and 260 nm (ϵ 3965).

Imidate salt **26**

A solution of silver tetrafluoroborate {7.9 mg, 0.04 mmol, i.e. 343 μl of a solution of $AgBF_4$ (1.141 g) in benzene (50 ml)} in CH_2Cl_2 (10 ml) was added to a solution of (+)-N-(3-chloropropyl)carboxamide **25** (15.2 mg, 0.04 mmol) in dry CH_2Cl_2 (1 ml). The mixture was left at room temperature for 22 h under N_2. Thin layer chromatography indicated the absence of starting product **25**. The mixture was filtered and the solvent was evaporated, the crude product was dissolved in dichloromethane, filtered and evaporated to give the imidate salt **26** (16.9 mg, 98%) which was not purified further; IR (CH_2Cl_2, IRTRAN Cell) 1595 and 1040 cm^{-1}; NMR ($CDCl_3$): δ 6.56 (1H, broad singlet, CH=C–CO), 5.9–4.5 (9H, multiplet, olefinic hydrogens), 4.66 (2H, triplet, CH_2–O), 4.18–3.71 (10H, multiplet), 2.25 (2H, quintet, CH_2–CH_2–O); $[\alpha]_D$ +271° (c 0.211, CH_2Cl_2); UV CH_3CN) λ_{max} 244 nm (ϵ 5600).

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