# Synthetic Approach to Novel Crinipellin Diterpenes. Construction of the Functionalised $C_{20}$-Tetraquinane Framework†

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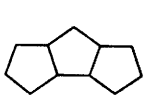
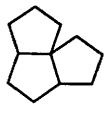
A synthetic approach towards novel tetraquinane diterpenes of the crinipellin group compounds (**4**–**8**) is delineated. The main theme of this approach centres around the use of readily available and adequately functionalised triquinane **10** as the key synthon to which an appropriately substituted five-membered ring can be annulated with concurrent generation of the spiro centre. Consequently, compound **10** was elaborated to the enone **22**, which was in turn subjected to cyclopentannulation employing three different intramolecular strategies, *viz.* photochemical cycloaddition (**22** ⟶ **23** ⟶ **24**), cationic enone–olefin cyclisation (**22** ⟶ **24** ⟶ **27**) and radical cyclisation (**22** ⟶ **32** ⟶ **27**). While five of the six stereogenic centres on the carbocyclic framework of tetraquinane **27** could be correctly set, the C(12)-isopropyl group was epimeric with respect to that in the natural products. Nevertheless, compound **27** was further elaborated to the $C_{20}$-tetraquinane **40** through chemical modifications in ring D, constituting the first synthesis of the complete skeleton of the criniepellins.

Among the natural products of current interest, oligoquinanes have come to occupy a position of pre-eminence and currently this fascinating and growing family comprises of over 80 compounds, isolated from diverse plant, marine and fungal sources.[1,2] Most of the oligoquinane natural products known so far are either based on the linear and angular triquinane frameworks **1** and **2**, respectively, or embody these moieties as part of a complex polycyclic framework.[1] However, natural products made up of four five-membered rings (tetraquinanes) have remained unknown until recently. In 1985, Anke *et al.* for the first time reported the isolation and structure determination of crinipellin diterpenoids, based on the tetraquinane framework **3**, from the culture broth of the basidiomycete *Crinipellis stipitaria* (Agaricales).[3] Five closely related and heavily functionalised $C_{20}$-diterpenes, crinipellin-A **4**, crinipellin-B **5**, *O*-acetylcrinipellin-A **6**, dihydrocrinipellin-B **7** and tetrahydrocrinipellin-A **8** were reported and three of them, compounds **4**, **5** and **6**, in which the electrophilic α-methylenecyclopentanone moiety remains intact, exhibit



**1**



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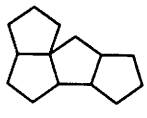
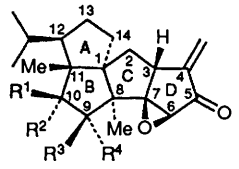


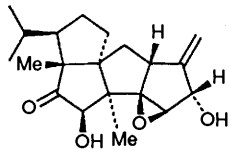
**3**

promising antibiotic activity. The structure elucidation of crinipellins rests secured on high-field $^1H$ and $^{13}C$ NMR data as well as an X-ray crystal-structure determination on crinipellin-B **5**.[3] From the biogenetic point of view, crinipellins are interesting creations of nature and probably arise through the intermediacy of a dolabellane cation.[4]

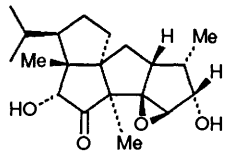
Crinipellins at once appealed to us as challenging and attractive targets for total synthesis for a variety of reasons, particularly in view of our ongoing interest in polyquinane natural product syntheses.[5] The tetracyclo[6.6.0.$0^{1,11}$.$0^{3,7}$]-tetradecane framework **3** present in crinipellins has not been synthesized previously[6] and encompasses both the linear and angular triquinane structures **1** and **2**. Also, there are present eight stereogenic centres, arranged next to one another, and three of them are contiguous quaternary carbon centres. In



**4** $R^1$ = H, $R^2$ = OH, $R^3$, $R^4$ = O
**5** $R^1$, $R^2$ = O, $R^3$ = OH, $R^4$ = H
**6** $R^1$ = H, $R^2$ = OAc, $R^3$, $R^4$ = O



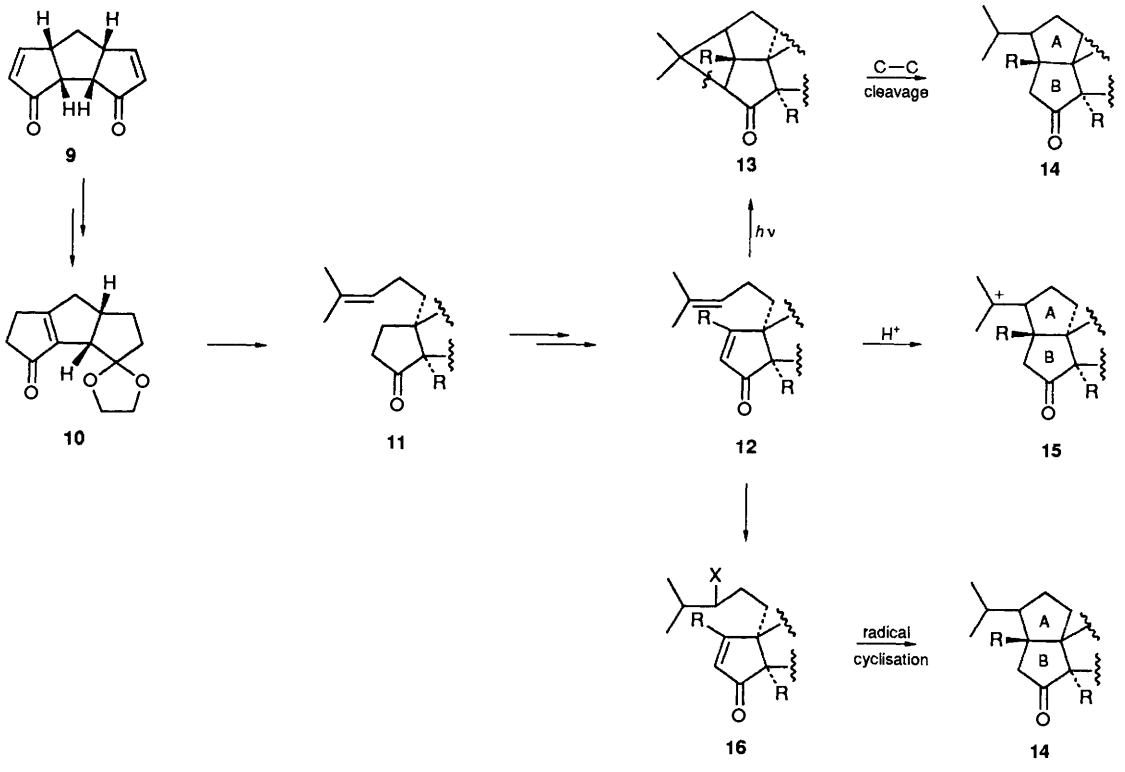
**7**



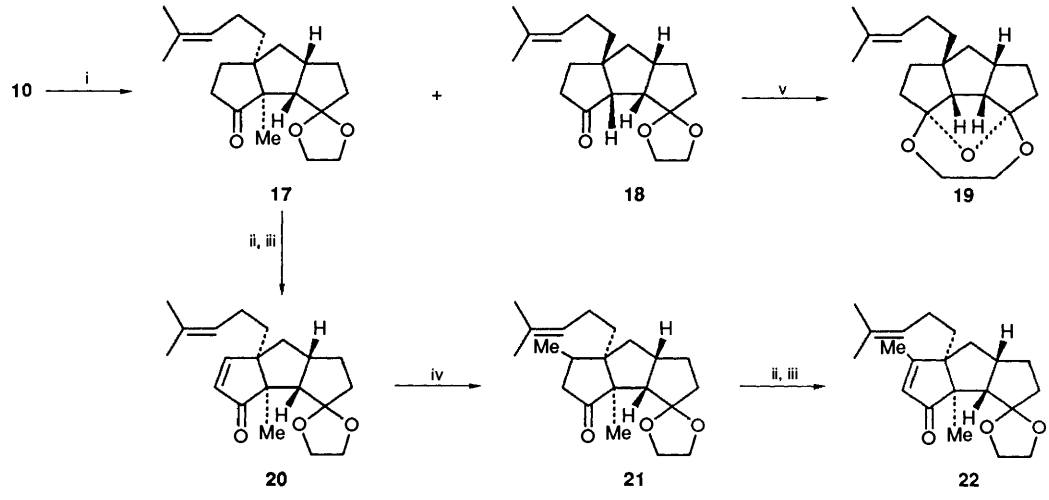
**8**

addition, crinipellins are embellished with a network of oxygen functionalities in the form of epoxide, hydroxy and carbonyl groups. In formulating a synthetic plan to crinipellins, the first concern was the development of a flexible methodology for the attainment of tetraquinane framework **3** with correct stereochemistry and adequate functionalisation. For the elaboration of framework **3**, functionalised triquinane precursors based on tricycles **1** and **2** and previously synthesized by us[7,8] appeared promising as either of them, through site-selective cyclopentannulation, could deliver the requisite framework. However, of the two options, we preferred the *cis,syn,cis*-triquinane bis-enone **9**, which had to be first desymmetrised and one of its enone moieties needed to be relocated and chemo-differentiated as in acetal **10**. Conjugate addition of an appropriate side-chain and capture of the resulting enolate by a carbon electrophile was expected to instal the two vicinal quaternary carbon centres (shown in structure **11**, Scheme 1). Further elaboration of compound **11** to enone **12** was expected to set up the stage for cyclopentannulation which we sought to effect through photochemical cycloaddition (**12** ⟶ **13** ⟶ **14**), cationic enone–olefin cyclisation (**12** ⟶ **15**) and radical cyclisation (**12** ⟶ **16** ⟶ **14**) processes, Scheme 1. The resulting tetraquinane system could then be elaborated to the targeted natural products. Realisation of Scheme 1 and construction of the functionalised $C_{20}$-framework of the novel diterpenes **4**–**8** is detailed here.[9]

† Submitted to mark the 150th anniversary of the Chemical Society/Royal Society of Chemistry.



Scheme 1

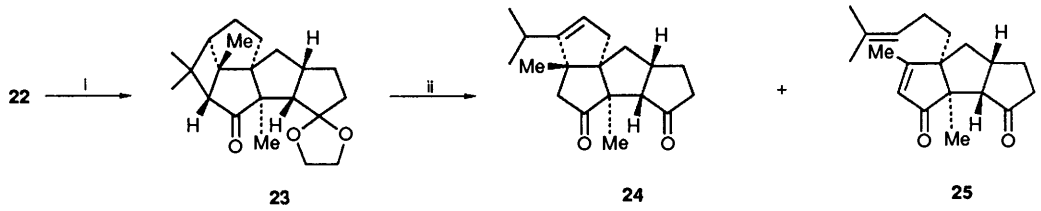


**Scheme 2** *Reagents, conditions and yields:* i, $Me_2C{=}CH[CH_2]_2MgBr$, $Me_2S{\cdot}CuBr$, THF, $Me_2S$, −78 °C, 2 h; MeI, HMPA, 16 h, 87%; ii, LHMDS, PhSeCl, THF, −78 °C to 25 °C, 10 h; iii, 30% $H_2O_2$, THF, 25 °C, 1 h, 75%; iv, MeLi, $Me_2S{\cdot}CuBr$, $Et_2O$, 20 °C, 90%; v, 10% HCl–THF, room temp. 1.5 h, 87%

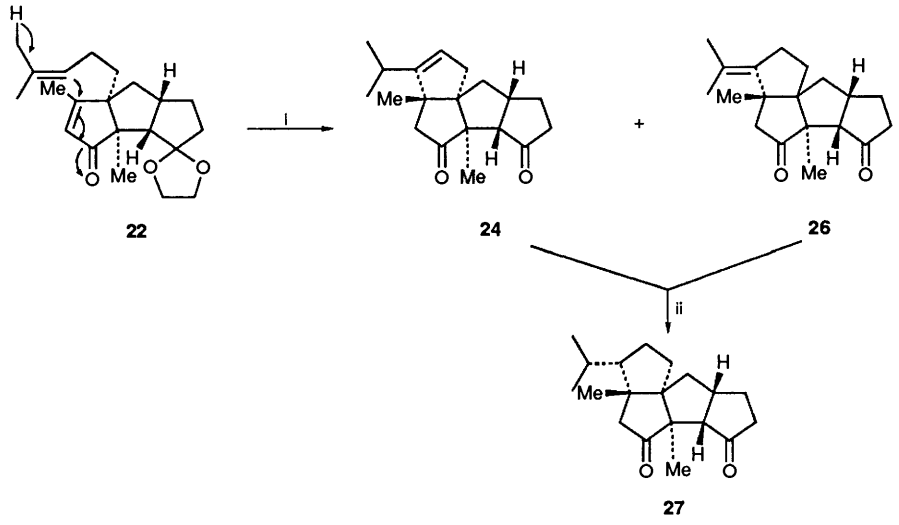
The previously described enone acetal **10**, available from bis-enone **9** in three steps,[7] on reaction with the Grignard reagent prepared from 5-bromo-2-methylpent-2-ene in the presence of $Me_2S{\cdot}CuBr$ complex and capture of the resultant enolate anion with methyl iodide furnished a 1.3:1 mixture of the required $C_{18}$-*cis,anti,cis*-product **17** and the nonmethylated $C_{17}$-*cis,syn*-, *cis*-product **18** in 87% yield. The stereochemistry of the *cis,syn,cis*-**18** product was readily recognised since attempted hydrolysis of its acetal moiety furnished the transannular acetal ether **19**.[10] Hydrolysis of the acetal moiety in *cis,anti,cis*-**17** product was uneventful and did not lead to a transannular acetalisation reaction. The somewhat fortuitous formation of the required product *cis,anti,cis*-**17** with two adjacent quaternary centres in position perhaps reflects the preferred capture of the enolate in the *cis,anti,cis*-series with methyl iodide compared with that in *cis-syn,cis*-isomer, Scheme 2.

The $C_{18}$-ketone **17** was now smoothly transformed to the α,β-unsaturated enone **20** *via* the phenylselenylation–selenoxide elimination sequence.[11] Addition of lithium dimethylcuprate to enone **20** proceeded as expected and the $C_{19}$-ketone **21** was realised satisfactorily. The $C_{19}$-ketone **21** was again converted into the corresponding α,β-unsaturated enone **22** following the phenylselenylation–selenoxide elimination sequence, Scheme 2. With the attainment of enone **22**, the stage was set for attempts on the photochemical, cationic and radical cyclisation strategies to form the fourth five-membered ring as contemplated in Scheme 1.

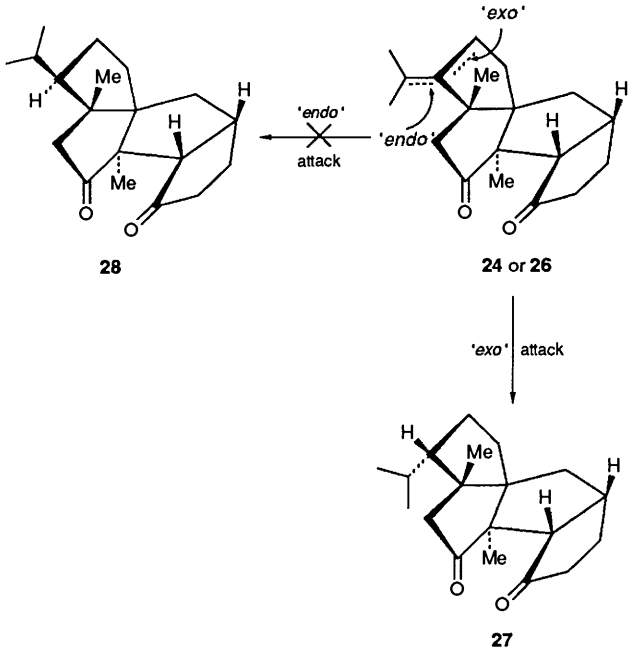
Irradiation of a cyclohexane solution of enone **22**, by a 450 W medium-pressure mercury vapour lamp, in a quartz vessel readily resulted in intramolecular 2 + 2-cycloaddition, and pentacyclic ketone **23** was obtained in 83% yield. Absence of unsaturation in the $^1H$ and $^{13}C$ NMR spectra and the presence




**Scheme 3** *Reagents, conditions and yields:* i, *hν*, cyclohexane, 40 min, 83%; ii, TMSCl–NaI, MeCN, 90 °C, 20 h, 81%




**Scheme 4** *Reagents, conditions and yields:* i, 70% $HClO_4$, EtOAc, 85 °C, 82%; ii, $H_2$, Pd/C (10%), EtOAc, 80%



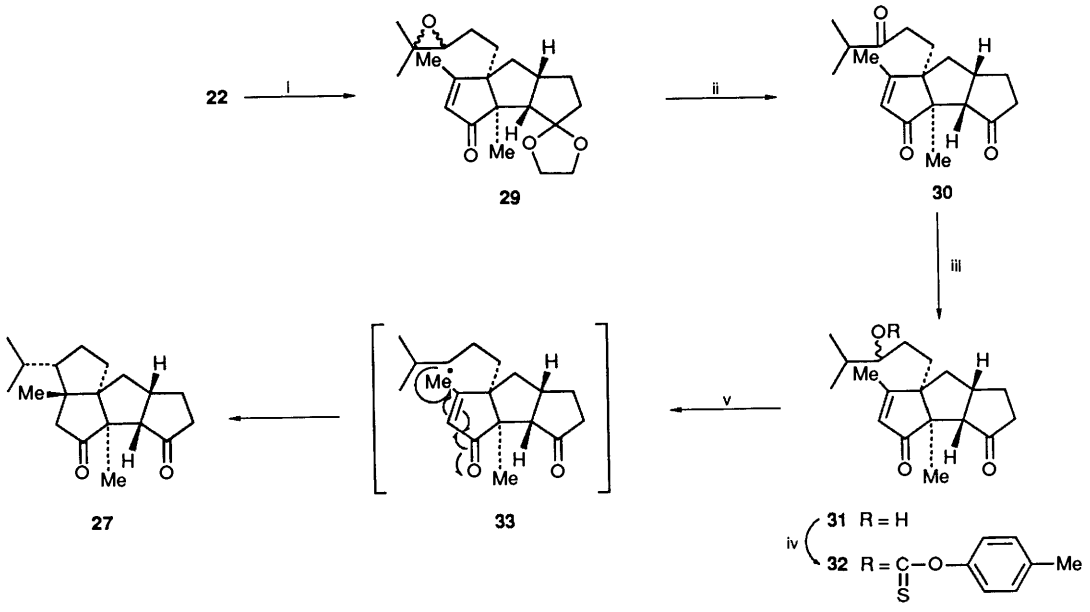

**Scheme 5**

of four quaternary methyl signals in the $^1H$ NMR spectrum was in full consonance with the assigned structure. The pentacyclic ketone **23** is a very desirable substrate with secure stereochemistry at seven contiguous stereogenic centres. Exposure of compound **23** to *in situ* generated trimethylsilyl iodide (TMSI) led to the regioselective cyclobutane C–C bond scission[12] and the tetracyclic ene dione **24** and the tricyclic diene dione **25** were obtained in the ratio 4:1 in 81% yield. The emergence of isopropyl doublets at $\delta_H$ 1.0 and 1.08 (*J* 7 Hz) besides other $^1H$ and $^{13}C$ NMR parameters fully supported the formation of the desired $C_{19}$-tetraquinane skeleton **24**, Scheme 3. Thus, five contiguous stereocentres, including three quaternary carbon centres, were correctly installed in a short manoeuvre.

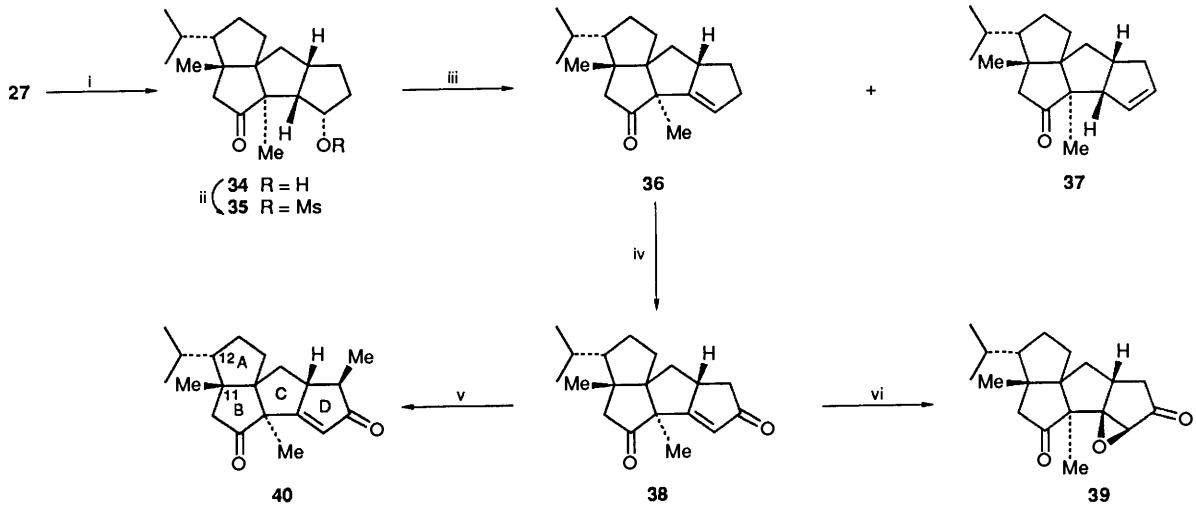
Enone **22** was next subjected to cationic enone–olefin cyclisation through exposure to catalytic amounts of perchloric acid. Two readily separable, crystalline, tetracyclic ene diones **24** and **26** were obtained in decent yield in 3:1 ratio, respectively. The structure of compound **24** was elucidated through the presence of an olefinic proton signal at $\delta_H$ 5.34 in the $^1H$ NMR spectrum and resonances at $\delta_C$ 156.1 and 121.5 in the $^{13}C$ NMR spectrum. The other ene dione **26** was devoid of any olefinic proton absorption in its $^1H$ NMR spectrum but had isopropylidene methyls at $\delta_H$ 1.56 and 1.72 and its $^{13}C$ NMR spectrum exhibited $sp^2$ carbon resonances at $\delta_C$ 142.7 and 123.1. However, both products **24** and **26** had two 3 H singlets in their $^1H$ NMR spectra, to confirm the establishment of two methyl-bearing quaternary centres and the tetraquinane skeleton. That products **24** and **26** were indeed double-bond isomers became apparent when either one of them on catalytic hydrogenation over Pd/C catalyst furnished a single, crystalline, saturated-dione **27**, Scheme 4.

A crucial point at this juncture, in the context of crinipellin synthesis, was the establishment of the stereochemistry at the newly established isopropyl-bearing carbon centre. It was our expectation that the neighbouring *exo*-Me group at C-11 will influence the stereochemistry of hydrogenation **24** or **26** ⟶ **27** and direct some *endo*-hydrogenation to give dione **28** of the required stereochemistry for crinipellins, Scheme 5. However, the formation of a single stereoisomer from both products **24** and **26** looked ominous and an X-ray crystal-structure determination* confirmed the exclusive formation of the sole stereoisomer **27** through *exo*-addition of hydrogen.

* X-ray crystal-structure determination was performed by Professor Vasantha Pattabhi, Department of Crystallography, Madras University, whom we thank for this information.



**Scheme 6** *Reagents, conditions and yields:* i, MCBPA, $Na_2CO_3$, $CHCl_3$, 0 °C, 45 min, 85%; ii, $BF_3$·$Et_2O$, $C_6H_6$, 0 °C to room temp., 3 h, 88%; iii, $NaBH_4$, MeOH, −15 to 5 °C, 45 min, 70%; iv, $MeC_6H_4OC(S)Cl$, pyridine–$CH_2Cl_2$, room temp., 2 h, 62%; v, $Bu_3SnH$, AIBN, $C_6H_6$, 90 °C, 2.5 h, 65%



**Scheme 7** *Reactions, conditions and yields:* i, $NaBH_4$, MeOH, 0–10 °C, 2 h, 75%; ii, MsCl, Py, 0–25 °C, 3 h, 93%; iii, NaI, HMPA, 80 °C, 2 h, 96%; iv, $Bu^tOOH$, PDC, Celite, benzene, 10–25 °C, 6 h, 43%; v, $LiNSiMe_2$ (LHMDS), tetrahydrofuran (THF), MeI, −78 °C, 2 h, 60%; vi, $NaHCO_3$, 30% $H_2O_2$, aq. THF, 0–25 °C, 0.5 h, 90%

The third variation for generating the tetraquinane framework, namely radical cyclisation starting from enone **22**, was now explored. Chemoselective epoxidation of enone **22** with *m*-chloroperbenzoic acid (MCBPA) furnished the epoxide **29**, which was rearranged with $BF_3$ diethyl ether to the trione **30**. Concurrently acetal hydrolysis could not be prevented during this step. Fortunately, compound **30** exhibited remarkable and desirable regio- and chemo-selectivity during controlled sodium borohydride reduction to furnish the alcohol **31** as a mixture of diastereoisomers in 70% yield. The hydroxy group in compound **31** was now activated for radical generation through conversion into its *p*-tolyl thionocarbonate derivative **32**.[13] When exposed to tributyltin hydride–azoisobutyronitrile (TBTH–AIBN), the ester **32** cyclised to furnish the tetracyclic dione **27** as the sole reaction product. Radical cyclisation in the intermediate **33** proceeds through a conformation that once again puts methyl and isopropyl group at $C_{12}$ and $C_{13}$, respectively, in *trans*-relationship, Scheme 6.

While the $C_{19}$-tetraquinane dione **27** was now readily accessible, it belonged to the 12-*epi*-crinipellin series. As we could not devise any protocol for the epimerisation of the C-12 isopropyl group, it was decided to proceed with compound **27** and complete the $C_{20}$-framework of the crinipellins. This required modification of functionality in the D-ring and installation of the last carbon atom in the form of the C-4 methyl group. Initially, a 1,2-carbonyl transposition of the C-6 carbonyl group in compound **27** was attempted so that the functionalisation pattern of crinipellin natural products, somewhat reminiscent of that of the coriolins,[5b,d] could be developed. However, several attempts towards the carbonyl tranposition protocol[14] remained unproductive and, therefore, an alternative methodology was devised. Regioselective and controlled reduction of the dione **27** furnished a hydroxy ketone **34**. The derived mesyl ester **35** on treatment with NaI in hexamethylphosphoric triamide (HMPA) underwent elimination to furnish a 1.2:1 mixture of olefinic ketones **36** and **37** in high yield, Scheme 7. The two olefinic ketones could be readily distinguished on the basis of their $^1H$ NMR spectra. The olefin **36** on allylic oxidation employing [$Bu^tOOH$–pyridinium dichromate (PDC)] reagent[15] furnished the enone **38**, which was eminently suited for the generation of ring D functionality. However, with only limited objectives in the 12-*epi*-series, two

reactions on ene dione **38** were attempted. First, compound **38** could be readily converted into the α,β-epoxy ketone **39** ($\delta_H$ 3.2, 1 H, s) on treatment with basic $H_2O_2$. Thus an important functional group moiety present in natural products could be generated. Secondly, kinetically controlled deprotonation and quenching with methyl iodide furnished the $C_{20}$-enone **40** representing the complete $C_{20}$-framework present in crinipellin diterpenes.

*Conclusions.*—In summary, we have devised and executed a strategy for the construction of the $C_{20}$-tetraquinane skeleton present among the antibiotically active crinipellin group of diterpenoids, starting from a readily available triquinane precursor. The methodologies deployed in the present work for the construction of ring A also has the potential for adaptation to the synthesis of other angular triquinane natural products.

## Experimental

M.p.s were recorded on a Buchi SMP-20 apparatus and are uncorrected. Liquid samples were bulb-to-bulb distilled using an oil bath. B.p.s refer to oil-bath temperatures. IR spectra were recorded on a Perkin-Elmer Model 1310 or 297 spectrometer. $^1H$ NMR spectra (100 MHz), and $^{13}C$ NMR spectra (25.0 MHz), were recorded on a JEOL FX-100 spectrometer. $^1H$ and $^{13}C$ samples were dissolved in $CDCl_3$ and chemical shifts are reported on the δ-scale with tetramethylsilane as internal standard. *J*-Values are given in Hz. Elemental analyses were performed on a 240C-CHN analyser. Mass measurements were carried out on an AEI MS-5076 mass spectrometer. Column chromatography was performed on ACME silica gel (100–200 mesh). All solvent extracts were washed with brine and dried over anhydrous $Na_2SO_4$. Light petroleum refers to the fraction boiling in the range 60–70 °C.

*1-Methyl-8-(4-methylpent-3-enyl)tricyclo*[6.3.0.0$^{2,6}$]*undecane-3,11-dione 3-Ethylene Acetal* **17**.—In a flame-dried, 100 $cm^3$, three-necked, RB flask fitted with a dry argon inlet, septum and mercury seal were placed $Me_2S$·CuBr complex (1 g, 4.8 mmol), dry dimethyl sulphide (5 $cm^3$) and dry THF (5 $cm^3$). The contents of the flask were cooled to −78 °C and a solution of the Grignard reagent [prepared separately from 5-bromo-2-methylpent-2-ene (20 mmol) in THF (20 $cm^3$)] was added slowly. The reaction mixture was stirred for 1 h and a solution of the enone **10**[7] (1 g, 4.4 mmol) in dry THF (5 $cm^3$) was added dropwise. After the mixture had been stirred for 2 h, the enolate was quenched with a solution of methyl iodide (0.6 $cm^3$) in HMPA (5 $cm^3$) by dropwise addition at the same temperature. The reaction mixture was then stirred for 16 h at room temperature and diluted with diethyl ether (50 $cm^3$). The ethereal layer was washed with basic ammonium chloride (3 × 30 $cm^3$), dried, and the solvent was removed to give an oily residue (1.5 g), which on TLC examination (10% ethyl acetate–light petroleum) showed the presence of two products. The material was charged on a silica gel (40 g) column. Careful elution with 5% ethyl acetate–light petroleum first furnished the cis,anti,cis-*product* **17** (700 mg, 50%); b.p. 140 °C/0.5 Torr; $\nu_{max}$(neat)/$cm^{-1}$ 2950 and 1730; $\delta_H$ 5.1 (1 H, t, $Me_2C$=C*H*), 4.0–3.7 (4 H, m, $OCH_2CH_2O$), 2.6–1.1 (16 H, series of m), 1.68 (3 H, br s, CH=C$Me_2$), 1.6 (3 H, br s, CH=C$Me_2$) and 1.08 (3 H, s, CMe); $\delta_C$ 223.1, 131.3, 124.8, 118.5, 64.7, 63.0, 60.9, 55.6, 55.3, 44.1, 39.6, 36.1, 35.4, 34.9, 28.7, 28.5, 25.5, 23.6, 17.4 and 11.6 (Found: C, 75.35; H, 9.5. $C_{20}H_{30}O_3$ requires C, 75.53; H, 9.43%).

Further elution with the same solvent gave the nonmethylated cis,syn,cis-1,4-*addition product* **18** (500 mg, 37.4%); b.p. 150 °C/0.3 Torr; $\nu_{max}$(neat)/$cm^{-1}$ 2950 and 1720; $\delta_H$ 5.2–4.9 (1 H, t, *J* 7, $Me_2C$=C*H*), 4.0–3.6 (4 H, m, $OCH_2CH_2O$), 3.3–1.1 (17 H, series of m), 1.68 (3 H, br s, CH=C$Me_2$) and 1.6 (3 H, br s, CH=C$Me_2$); $\delta_C$ 221.1, 131.6, 124.4, 117.6, 64.2, 64.1, 58.6, 56.1, 55.2, 43.6 (2C), 40.7, 39.4, 37.3, 31.7, 27.7, 25.6, 23.6 and 17.5 (Found: C, 75.05; H, 9.3. $C_{19}H_{28}O_3$ requires C, 74.96; H, 9.27%).

*Acid-catalysed Hydrolysis of the Keto Acetal* **18**. *Formation of the Acetal Ether* **19**.—To a solution of compound **18** (50 mg, 0.164 mmol) in THF (10 $cm^3$) was added 10% aq. HCl (0.5 $cm^3$) and the mixture was stirred at room temperature for 1.5 h. The THF was removed under reduced pressure and the residue was diluted with water (10 $cm^3$) and extracted with ethyl acetate (3 × 30 $cm^3$) The extract was washed with 10% aq. sodium hydrogen carbonate (2 × 5 $cm^3$) and dried. The residue obtained after removal of solvent was charged onto a silica gel (10 g) column. Elution with 15% ethyl acetate–light petroleum furnished compound **19** (33 mg, 87% based on the consumed starting material); $\nu_{max}$(neat)/$cm^{-1}$ 2950, 1290, 1200 and 1110; $\delta_H$ 5.04 (1 H, t), 4.08–3.6 (4 H, m), 3.0–1.26 (17 H, series of m), 1.68 (3 H, s) and 1.58 (3 H, s); $\delta_C$ 131.5, 124.6, 123.2, 67.6 (2C), 65.3, 58.5, 57.8, 45.7, 43.8, 42.2, 37.5, 36.6, 34.8, 30.5, 25.7, 24.3 and 17.6 (Found: $M^+$, 304.2052. $C_{19}H_{28}O_3$ requires M, 304.2031). Further elution of the column with the same solvent furnished the starting keto acetal **18** (13 mg).

*1-Methyl-8-(4-methylpent-3-enyl)tricyclo*[6.3.0.0$^{2,6}$]*undec-9-ene-3,11-dione 3-Ethylene Acetal* **20**.—In a 50 $cm^3$, three-necked, RB flask fitted with a dry $N_2$ inlet and septum and cooled to −78 °C was placed butyllithium (2 $cm^3$, 2 mmol in hexane). Hexamethyldisiliazane (HMDS) (0.46 $cm^3$, 2.2 mmol) was carefully injected and the resulting white slurry was stirred for 30 min. A solution of keto olefin **17** (500 mg, 1.57 mmol) in dry THF (10 $cm^3$) was then slowly added through a syringe. The resulting enolate solution was stirred for 40 min, quenched with a solution of benzeneselenenyl chloride (306 mg, 1.6 mmol) in dry THF (4 $cm^3$) and stirred for 10 h at room temp. The reaction mixture was diluted with water and extracted with diethyl ether (3 × 30 $cm^3$). The extract was washed, dried and concentrated to give the crude α-phenylselenated product (680 mg).

The crude product obtained above was dissolved in THF (10 $cm^3$), cooled to 0 °C, and 35% $H_2O_2$ (15 drops) was added. After being stirred for 1 h at room temperature, the reaction mixture was diluted with water (25 $cm^3$) and extracted with diethyl ether (50 $cm^3$). The extract was washed, dried and concentrated to give a UV-absorbing (TLC) residue (480 mg), which was charged on a silica gel (20 g) column. Elution of the column with 10% ethyl acetate–light petroleum furnished the *enone* **20** (385 mg, 77%); b.p. 170 °C/0.4 Torr; $\nu_{max}$(neat)/$cm^{-1}$ 2950, 1700, 1590 and 1020; $\delta_H$ 7.56 (1 H, d, *J* 6, C*H*=CHC=O), 6.04 (1 H, d, *J* 6, CH=C*H*C=O), 5.12 (1 H, t, $Me_2C$=C*H*), 4.2–3.8 (4 H, m, $OCH_2CH_2O$), 2.6–1.0 (12 H, series of m), 1.68 (3 H, br s, CH=C$Me_2$), 1.60 (3 H, br s, CH=C$Me_2$) and 1.08 (3 H, s, CMe); $\delta_C$ 216.0, 169.8, 131.8, 129.9, 124.9, 118.5, 64.0, 63.5, 59.6, 58.6, 55.6, 43.1, 37.1, 36.6, 35.1, 25.7, 24.8, 23.9, 17.7 and 13.5 (Found: C, 75.7; H, 9.0. $C_{20}H_{28}O_3$ requires C, 75.91; H, 8.92%).

*1,9-Dimethyl-8-(4-methylpent-3-enyl)tricyclo*[6.3.0.0$^{2,6}$]*undecane-3,11-dione 3-Ethylene Acetal* **21**.—In a flame-dried, 50 $cm^3$, three-necked, RB flask fitted with a dry argon inlet, septum and mercury seal were placed $Me_2S$·CuBr complex (200 mg, 0.96 mmol), in dry dimethyl sulphide (10 $cm^3$) and dry diethyl ether (1 $cm^3$). MeLi [1.9 mmol in THF (1.9 $cm^3$)] was added dropwise to the stirred mixture while the temperature was kept at 20 °C. After the mixture had been stirred for 5 min, a solution of the enone **20** (100 mg, 0.3 mmol) in dry diethyl ether (2 $cm^3$) was added dropwise. The mixture was stirred for 40 min, quenched with water, and extracted with diethyl ether (50 $cm^3$). The extract was washed with basic ammonium chloride (3 × 10 $cm^3$), dried and concentrated to give an oily residue (100 mg),

which was charged on a silica gel (10 g) column. Elution with 10% ethyl acetate–light petroleum furnished adduct **21** (78 mg, 75%); b.p. 140 °C/0.4 Torr; $\nu_{max}$(neat)/cm$^{-1}$ 2950 and 1720; $\delta_H$ 5.1 (1 H, t, $Me_2C{=}CH$), 4.0–3.8 (4 H, m, $OCH_2CH_2O$), 2.8–1.0 (15 H, series of m), 1.68 (3 H, br s, $CH{=}CMe_2$), 1.60 (3 H, br s, $HC{=}CMe_2$), 1.1 (3 H, d, *J* 7, HCMe) and 1.08 (3 H, s, CMe).

1,9-*Dimethyl*-8-(4-*methylpent*-3-*enyl*)*tricyclo*[6.3.0.0$^{2,6}$]-*undec*-9-*ene*-3,11-*dione* 3-*Ethylene Acetal* **22**.—In a 50 cm$^3$, three-necked, RB flask fitted with a dry $N_2$ inlet, septum mercury seal, and cooled to −78 °C was placed butyllithium (0.4 cm$^3$; 0.4 mmol in hexane). HMDS (0.1 cm$^3$, 0.5 mmol) was carefully injected and the resulting white slurry was stirred for 30 min. A solution of the ketone **21** (65 mg, 0.19 mmol) in dry THF (2 cm$^3$) was then added slowly through a syringe. The resulting enolate solution was stirred for 30 min, quenched with a solution of benzeneselenenyl chloride (40 mg, 0.2 mmol) in dry THF (1 cm$^3$) and stirred for 10 h at room temperature. The reaction mixture was diluted with water and extracted with diethyl ether (2 × 10 cm$^3$). The extract was washed, dried and concentrated to give the α-phenylselenated product (75 mg).

The crude product obtained above was dissolved in THF (2 cm$^3$) and 35% $H_2O_2$ (4 drops) was added. The reaction mixture was stirred for 2 h at room temperature, diluted with water, and extracted with diethyl ether (20 cm$^3$). The extract was washed, dried, and concentrated to give a UV-absorbing (TLC) product (65 mg), which was charged on a silica gel (10 g) column. Elution with 15% ethyl acetate–light petroleum furnished the *dimethyl enone* **22** (48 mg, 74%); b.p. 150 °C/0.3 Torr; $\nu_{max}$(neat)/cm$^{-1}$ 2950, 1680 and 1610; $\delta_H$ 5.92 (1 H, br s, $MeC{=}CHC{=}O$), 5.2–4.8 (1 H, t, $Me_2C{=}CH$), 4.2–3.7 (4 H, m, $OCH_2CH_2O$), 2.8–1.0 (12 H, series of m), 2.04 (3 H, d, *J* 1, $MeC{=}CHC{=}O$), 1.68 (3 H, br s, $CH{=}CMe_2$), 1.56 (3 H, br s, $CH{=}CMe_2$) and 1.2 (3 H, s, CMe); $\delta_C$ 214.2, 182.0, 131.6, 129.9, 124.7, 118.6, 63.9, 63.4, 62.3, 59.1, 55.8, 42.9, 37.3, 36.8, 33.4, 25.6, 24.6, 24.3, 17.7, 15.6 and 13.5 (Found: C, 76.3; H, 9.1. $C_{21}H_{30}O_3$ requires C, 76.36; H, 9.09%).

*Photoirradiation of Enone* **22**. *Formation of Pentacycle* **23**.—A solution of the enone **22** (20 mg, 0.056 mmol) in dry cyclohexane (100 cm$^3$) was degassed with a slow stream of $N_2$ for 10 min. This solution was irradiated in a quartz immersion well with a 450 W Hanovia medium-pressure mercury vapour lamp for 40 min. The residue obtained after removal of cyclohexane was charged on a silica gel (10 g) column. Elution with 15% ethyl acetate–hexane furnished the *pentacyclic compound* **23** (10 mg, 83% based on consumed starting material); $\nu_{max}$(neat)/cm$^{-1}$ 1720; $\delta_H$ 3.94–3.6 (4 H, m), 2.7–1.0 (14 H, series of m), 1.38 (3 H, s), 1.34 (3 H, s), 1.18 (3 H, s) and 0.82 (3 H, s); $\delta_C$ 228.1, 118.5, 66.3, 65.2, 63.1, 62.3, 58.3 (2C), 56.1, 47.1, 43.0, 40.2, 35.9, 35.2, 32.6, 29.7, 28.8, 25.9, 22.2, 21.2 and 11.5 (Found: C, 75.9; H, 9.0. $C_{21}H_{30}O_3$ requires C, 76.36; H, 9.09%). Further elution of the column with same solvent gave the unchanged starting material **22** (8 mg).

*TMSI-Mediated Clevage of Photoproduct* **23**.—In a 25 cm$^3$, RB flask equipped with $N_2$ inlet was placed freshly activated sodium iodide (90 mg, 0.6 mmol) and a solution of the pentacyclic compound **23** (10 mg, 0.03 mmol) in dry acetonitrile (5 cm$^3$) was injected. To this stirred solution was added freshly distilled trimethylsilyl chloride (50 mg, 0.45 mmol) through a syringe and the mixture was refluxed for 20 h. The reaction mixture was diluted with ethyl acetate (20 cm$^3$) and washed successively with saturated aq. sodium hydrogen carbonate (2 × 5 cm$^3$), 10% aq. sodium thiosulphate (2 × 5 cm$^3$) and water (2 × 5 cm$^3$). The residue obtained after removal of ethyl acetate was charged on a silica gel (10 g) column. Elution with 15% ethyl acetate–light petroleum solution furnished the *tetracyclic diketone* **24** (6 mg, 69%); m.p. 76–78 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 3040 and 1735; $\delta_H$ 5.34 (1 H, t, C=CH), 2.8–1.0 (13 H, series of m), 1.14 (3 H, s, CMe), 1.08 (3 H, d, HCC*Me*), 1.06 (3 H, s, CMe) and 1.0 (3 H, d, HC*Me*); $\delta_C$ 220.0, 219.5, 156.6, 121.5, 63.3, 63.1, 57.9, 54.1, 45.4, 40.2, 39.9, 39.7, 37.5, 26.5, 25.0, 24.6, 24.2, 22.5 and 15.3 (Found: C, 79.8; H, 9.1. $C_{19}H_{26}O_2$ requires C, 79.68; H, 9.15%).

Further elution with the same solvent furnished the *keto enone* **25** (1.5 mg, 17%); $\nu_{max}$ (neat)/cm$^{-1}$ 1735, 1695 and 1620; $\delta_H$ 5.92 (1 H, br s), 5.04–4.88 (1 H, m), 2.6–1.0 (12 H, series of m), 2.04 (3 H, d, *J* 1), 1.64 (3 H, s), 1.55 (3 H, s) and 1.22 (3 H, s); $\delta_C$ 218.6, 211.1, 180.1, 132.1, 129.8, 123.6, 62.3, 60.3, 58.2, 39.2, 38.0, 36.5, 33.6, 25.5, 24.2, 22.5, 17.6, 15.2 and 13.6 (Found: C: 79.7; H, 9.2. $C_{19}H_{26}O_2$ requires C, 79.67; H, 9.15%).

*Acid-catalysed Cyclisation of Enone* **22**. *Formation of Tetraquinanes* **24** *and* **26**.—A solution of enone **22** (45 mg, 0.13 mmol) in dry ethyl acetate (5 cm$^3$) was refluxed for 4 h in the presence of 70% perchloric acid (2 drops). The reaction mixture was quenched with 5% aq. $NaHCO_3$ and diluted with diethyl ether (20 cm$^3$). The extract was washed, dried, and concentrated to give an oily residue (40 mg), which on TLC examination (15% ethyl acetate–light petroleum) showed the presence of two products. This material was chromatographed on a silica gel (10 g) column. Careful elution with 8% ethyl acetate–light petroleum furnished the *exocyclic olefin* **26** (8 mg, 21%), which was crystallised from light petroleum; m.p. 126–128 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 2950 and 1720; $\delta_H$ 3.2–1.0 (14 H, series of m), 1.72 (3 H, br s, $CH{=}CMe_2$), 1.56 (3 H, br s, $CH{=}CMe_2$), 1.2 (3 H, s, CMe) and 1.06 (3 H, s, CMe); $\delta_C$ 220.7, 220.6, 142.7, 123.1, 65.2, 64.2, 56.6, 48.0, 47.8, 41.9, 38.6 (2C), 32.6, 31.3, 26.6, 23.8, 22.4, 20.5 and 14.6 (Found: C, 79.8; H, 9.1. $C_{19}H_{26}O_2$ requires C, 79.68; H, 9.15%).

Further elution of the column with the same solvent furnished the endocyclic olefin **24** (24 mg, 61%), identical with the sample obtained above.

*Catalytic Hydrogenation of Enones* **24** *and* **26**. 12-*Isopropyl*-8-11-*Dimethyltetracyclo*[6.6.0.0$^{1,11}$.0$^{3,7}$]*tetradecane*-6,9-*dione* **27**.—A solution of the olefin **24** (10 mg, 0.03 mmol) in dry ethyl acetate (1 cm$^3$) was hydrogenated (35 psi $H_2$ pressure) over 10% Pd/C (2 mg) for 20 h. The catalyst was filtered off and the solvent was removed to furnish the *saturated tetracyclic dione* **27** (8 mg, 80%), which was crystallised from light petroleum; m.p. 115 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 2950 and 1730; $\delta_H$ 2.8–1.0 (16 H, series of m), 1.18 (3 H, s, CMe), 1.12 (3 H, s, CMe), 0.96 (3 H, d, *J* 7, CH*Me*) and 0.86 (3 H, d, *J* 7, HC*Me*); $\delta_C$ 219.8, 219.7, 64.6, 61.4, 58.2, 57.5, 47.2, 45.0, 43.2, 40.2, 36.8, 34.6, 29.4 (2C), 25.8, 23.8, 23.5, 22.3 and 15.3 (Found: C, 79.0; H, 9.8. $C_{19}H_{28}O_2$ requires C, 79.12; H, 9.79%).

When either pure olefin **26** or a mixture of the olefins **24** and **26** was hydrogenated over Pd/C catalyst as described above, only compound **27** was obtained.

*Epoxidation of Enone* **22**.—Into a 25 cm$^3$, RB flask containing the olefinic enone **22** (55 mg, 0.166 mmol) in chloroform (10 cm$^3$) was suspended solid sodium carbonate (53 mg, 0.5 mmol) and the mixture was cooled to 0 °C. MCPBA (43 mg, 0.25 mmol) was added and the mixture was stirred for 45 min. The reaction mixture was diluted with chloroform (30 cm$^3$) and was washed with saturated aq. $Na_2CO_3$ (2 × 10 cm$^3$) and dried. Removal of solvent furnished a residue, which was charged on a silica gel (10 g) column. Elution with 30% ethyl acetate–light petroleum furnished the *epoxide* **29** (50 mg, 85%) as a diastereoisomeric mixture; b.p. 160 °C/0.3 Torr; $\nu_{max}$(neat)/cm$^{-1}$ 1685 and 1620; $\delta_H$ 5.92 (1 H, br s), 4.18–3.72 (4 H, m), 2.72–1.0 (13 H, series of m), 2.02 (3 H, d, *J* 1), 1.28 (3 H, s), 1.2 (3 H, s) and 1.16 (3 H, s); $\delta_C$ 214.0, 181.8, 181.4, 133.2, 130.1,

129.9, 128.2, 118.4, 64.6, 63.9, 62.3, 61.9, 61.6, 59.0, 58.6, 58.5, 54.6, 43.0, 42.6, 37.1, 36.6, 29.6, 24.7, 24.5, 24.2, 18.7, 15.6, 15.4, 13.6 and 13.4 (Found: $M^+$, 346.2164. $C_{21}H_{30}O_4$ requires *M* 346.2143).

$BF_3$-*Catalysed Rearrangement of Epoxide* **29** *to Trione* **30**.—To a solution of epoxide **29** (62 mg, 0.18 mmol) in benzene (5 $cm^3$) was added $BF_3$·diethyl ether (57 mg, 0.40 mmol) and the mixture was stirred for 3 h at room temperature. The reaction mixture was quenched with 10% aq. $NaHCO_3$ and extracted with ethyl acetate (3 × 15 $cm^3$). The extract was washed with brine (2 × 5 $cm^3$) and dried. Removal of solvent gave an oily residue, which was charged on a silica gel (10 g) column. Elution with 35% ethyl acetate–light petroleum furnished the *tricyclic trione* **30** (48 mg, 88%); b.p. 170 °C/0.2 Torr; $\delta_H$ 5.94 (1 H, br s), 2.64–1.0 (13 H, series of m), 2.0 (3 H, d, *J* 1), 1.18 (3 H, s) and 1.04 (6 H, d, *J* 6); $\delta_C$ 218.5, 213.6, 210.8, 179.6, 130.3, 61.9, 60.2, 58.1, 41.0, 39.3, 38.0, 36.5, 36.0, 26.3, 22.4, 18.2 (2C), 15.0 and 13.7 (Found: $M^+$, 302.1893. $C_{19}H_{26}O_3$ requires M, 302.1881).

*Sodium Borohydride Reduction of Trione* **30** *to Hydroxy Dione* **31**.—To a solution of trione **30** (48 mg, 0.158 mmol) in methanol (10 $cm^3$) cooled to −15 to −5 °C was added sodium borohydride (6 mg, 0.158 mmol) in four lots (5 min intervals). The reaction mixture was stirred at the same temperature for another 25 min and quenched with acetone (3 drops). The methanol was removed under reduced pressure and the residue was diluted with water (5 $cm^3$). Extraction with ethyl acetate (3 × 15 $cm^3$) and concentration gave an oily residue, which was charged on a silica gel (10 g) column. Elution with 45% ethyl acetate–light petroleum furnished a diastereoisomeric mixture of alcoholic products **31** (34 mg, 70%); b.p. 170 °C/0.2 Torr; $\nu_{max}$(neat)/$cm^{-1}$ 3600–3300br, 1735, 1695 and 1620; $\delta_H$ 5.94 (1 H, br s), 3.34–3.12 (1 H, br s), 2.6–1.1 (13 H, series of m), 2.08 (3 H, d, *J* 1), 1.22 (3 H, s) and 0.88 (6 H, d, *J* 7); $\delta_C$ 218.8, 211.3, 180.5, 125.8, 62.1, 60.5, 60.3, 58.2, 39.6, 39.2, 38.0, 36.5, 33.5, 33.3, 29.9, 29.6, 22.5, 18.8, 17.1, 15.2 and 13.7.

*Conversion of the Alcohol* **31** *into the* p-*Tolyl Thionocarbonate* **32**.—Hydroxy compound **31** (7 mg, 0.023 mmol) in methylene dichloride (5 $cm^3$) was placed in a 10 $cm^3$, RB flask fitted with nitrogen inlet. To this stirred solution at 0 °C was added pyridine (100 mg, 1.25 mmol) followed by *p*-tolylchlorothionoformate (8 mg, 0.04 mmol) and the mixture was stirred for 2 h at room temperature. Solvent was removed under reduced pressure and the residue was charged on a silica gel (5 g) column. Elution of the column with 20% ethyl acetate–light petroleum furnished the *thionocarbonate* **32** (6.5 mg, 62%); $\nu_{max}$(neat)/$cm^{-1}$ 1735, 1695 and 1620; $\delta_H$ 7.2–6.88 (4 H, ABq), 5.96 (1 H, br s), 5.1 (1 H, m), 2.34 (3 H, s), 2.02 (3 H, d, *J* 1), 2.0–1.0 (13 H, series of m), 1.24 (3 H, s) and 0.92 (6 H, d, *J* 7) (Found: $M^+$, 454.2334. $C_{27}H_{34}O_4S$ requires M, 454.2347).

*Radical Cyclisation of Intermediate* **33** *to Tetraquinane Dione* **27**.—A solution of the *p*-tolyl thionocarbonate **32** (6 mg, 0.013 mmol) in dry benzene (10 $cm^3$) was placed in a RB flask equipped with septum, reflux condenser, and nitrogen inlet. To this were added TBTH (10 mg, 0.034 mmol) and AIBN (1 mg). The reaction mixture was refluxed for 2.5 h and was diluted with benzene (20 $cm^3$). The diluted reaction mixture was washed successively with 10% aq. potassium fluoride (2 × 5 $cm^3$), water (2 × 5 $cm^3$) and brine (2 × 5 $cm^3$), and was dried. The crude product obtained after removal of the solvent was charged on a neutral alumina (5 g) column. Elution with 15% ethyl acetate–light petroleum furnished the tetracyclic diketone **27** (2.5 mg, 65%). The IR and $^1H$ NMR spectra of this material were identical with the same compound obtained in earlier experiments.

*Sodium Borohydride Reduction of Dione* **27**.—A solution of the diketone **27** (45 mg, 0.156 mmol) in dry methanol (10 $cm^3$) was placed in a 25 $cm^3$, RB flask equipped with nitrogen inlet. To this solution was added sodium borohydride (6 mg, 0.158 mmol) during 10 min. The reaction mixture was stirred for 2 h at 0–10 °C and then quenched by addition of a few drops of acetone. The residue obtained after removal of solvent under reduced pressure was diluted with water (5 $cm^3$) and extracted with ethyl acetate (3 × 10 $cm^3$). The extract was washed successively with water (2 × 5 $cm^3$) and brine (2 × 5 $cm^3$) and dried. Removal of solvent gave crude material, which was charged on a silica gel (10 g) column. Elution with 20% ethyl acetate–light petroleum furnished the pure *hydroxy ketone* **34** (34 mg, 75%); m.p. 152–153 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 3500 and 1720; $\delta_H$ 4.26 (1 H, m), 3.78–1.0 (16 H, series of m), 1.3 (3 H, s), 1.14 (3 H, s), 1.0 (3 H, d, *J* 7) and 0.94 (3 H, d, *J* 7) (Found: $M^+$, 290.2246. $C_{19}H_{30}O_2$ requires M, 290.2247).

*Conversion of Hydroxy Compound* **34** *into Mesyl Ester* **35**.—A solution of the hydroxy ketone **34** (20 mg, 0.069 mmol) in pyridine (0.5 $cm^3$) was placed in a 5 $cm^3$, RB flask. To this stirred solution at 0 °C was added methanesulphonyl chloride (10 mg, 0.087 mmol) under $N_2$ and the mixture was allowed to come to room temperature. After being stirred for 2 h the mixture was diluted with water (5 $cm^3$) and extracted with ethyl acetate (3 × 10 $cm^3$). The organic phase was washed successively with 10% HCl (2 × 5 $cm^3$) and 10% aq. sodium hydrogen carbonate (2 × 5 $cm^3$) and was dried. The crude mesyl derivative obtained after removal of solvent was purified by passage through a short silica gel column to furnish pure *ester* **35** (23.5 mg, 93%), m.p. 105–107 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1725, 1340 and 1160; $\delta_H$ 5.14 (1 H, br s), 3.04 (3 H, s), 2.82–1.0 (16 H, series of m), 1.24 (3 H, s), 1.12 (3 H, s), 1.0 (3 H, d, *J* 7) and 0.92 (3 H, d, *J* 7) (Found: C, 65.4; H, 8.2. $C_{20}H_{32}O_4S$ requires C, 65.22; H, 8.70%).

*Conversion of Keto Mesyl Ester* **35** *into Isomeric Enones* **36** *and* **37**.—A solution of the keto mesyl ester **35** (23 mg, 0.0625 mmol) in dry HMPA (10 $cm^3$) was introduced into a 25 $cm^3$, two necked, RB flask fitted with a reflux condenser and containing sodium iodide (40 mg, 0.275 mmol). The reaction mixture was heated at 80 °C for 2 h, cooled, poured into ice-cold water (10 $cm^3$), and extracted with diethyl ether (3 × 10 $cm^3$). The extract was washed and dried. The residue obtained after removal of solvent was charged on a silica gel (10 g) column. Elution with 1% ethyl acetate–light petroleum gave, first, the *trisubstituted olefin* **36** (9 mg, 53%); m.p. 59–61 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1725; $\delta_H$ 5.42 (1 H, m), 2.96–1.0 (15 H, series of m), 1.28 (3 H, s), 1.12 (3 H, s), 0.94 (3 H, d, *J* 7) and 0.90 (3 H, d, *J* 7); $\delta_C$ 217.1, 158.1, 121.1, 69.7, 58.8, 57.0, 49.2, 47.4, 46.9, 40.4, 37.1, 34.3, 32.8, 30.4, 29.5, 26.9, 23.1, 22.3 and 17.0 (Found: $M^+$, 272.2136. $C_{19}H_{28}O$ requires M, 272.2141).

Further elution of the column with same solvent furnished the *disubstituted olefin* **37** (7.5 mg, 44%); m.p. 63–64 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1725; $\delta_H$ 5.76 (2 H, br s), 3.16–1.0 (14 H, series of m), 1.22 (3 H, s), 1.0 (3 H, d, *J* 7), 0.92 (3 H, s) and 0.88 (3 H, d, *J* 7); $\delta_C$ 215.4, 130.6, 129.8, 65.6, 61.8, 58.8, 58.1, 46.4, 45.9, 43.5, 40.0, 38.6, 33.7, 29.8, 28.5, 26.3, 23.2, 22.2 and 15.3 (Found: $M^+$, 272.2141).

*Allylic Oxidation of Ene* **36** *to Enone* **38**.—A solution of the olefin **36** (10 mg, 0.03 mmol) in dry benzene (5 $cm^3$) was placed in a 10 $cm^3$, RB flask containing Celite (45 mg) and PDC (54 mg, 0.144 mmol). To this stirred solution at 10 °C was added 70% t-butyl hydroperoxide (13 mg, 0.144 mmol). The reaction mixture was stirred for 6 h at room temperature. The contents were then filtered through a small Celite pad, which was washed with diethyl ether (5 $cm^3$). The filtrate and washings were evaporated

and the residue was charged on a silica gel (5 g) column. Elution with 20% ethyl acetate–light petroleum furnished the *keto enone* **38** (4.5 mg, 43%) as a solid; m.p. 114–116 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 1735, 1705 and 1610; $\delta_H$ 5.94 (1 H, d, *J* 2), 3.2–1.0 (13 H, series of m), 1.32 (3 H, s), 1.26 (3 H, s), 1.0 (3 H, d, *J* 7) and 0.92 (3 H, d, *J* 7); $\delta_C$ 214.3, 209.4, 191.4, 125.8, 67.1, 60.6, 58.3, 47.7, 47.6, 43.7, 43.1, 40.0, 34.5, 30.3, 29.5, 26.3, 23.1, 22.3 and 17.0 (Found: M$^+$, 286.1933. $C_{19}H_{26}O_2$ requires M, 286.1933).

*Epoxidation of Enone* **38**.—A solution of the keto enone **38** (2 mg, 0.007 mmol) in THF (0.5 cm$^3$) was placed in a 5 cm$^3$, RB flask containing water (0.5 cm$^3$) and sodium hydrogen carbonate (10 mg). To this stirred solution at 0–5 °C was added 30% $H_2O_2$ (0.01 cm$^3$) and the mixture was stirred for 30 min. The reaction mixture was diluted with ethyl acetate (15 cm$^3$) and washed and dried. The solid residue obtained after removal of ethyl acetate was charged on a silica gel (3 g) column. Elution with 20% ethyl acetate–light petroleum furnished the *epoxy ketone* **39** (1.9 mg, 90%); m.p. 171–172 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 1730; $\delta_H$ 3.26 (1 H, s), 2.8–1.2 (13 H, series of m), 1.32 (3 H, s), 1.0 (3 H, d, *J* 7), 0.96 (3 H, s) and 0.90 (3 H, d, *J* 7) (Found: M$^+$, 302.1882. $C_{19}H_{26}O_3$ requires M, 302.1882).

*Methylation of Compound* **38**.—Into a 25 cm$^3$, two-neck, RB flask equipped with nitrogen inlet and septum was introduced butyllithium (0.25 cm$^3$, 0.3 mmol) in hexane solution and the contents were cooled to −78 °C. HMDS (76.5 mg, 0.47 mmol) was carefully injected and the resulting slurry was stirred for 25 min. A solution of enone **38** (7 mg, 0.024 mmol) in THF (3 cm$^3$) was injected. The resulting enolate solution was stirred for 30 min at the same temperature and was then quenched with a solution of methyl iodide (17 mg, 0.12 mmol) in THF (2 cm$^3$). The mixture was stirred for another 2 h, the reaction was quenched by addition of water, and the product was extracted with ethyl acetate (3 × 5 cm$^3$). The extract was washed and dried. The residue obtained after removal of the solvent was charged on a silica gel (5 g) column. Elution with 15% ethyl acetate–light petroleum furnished the enone **40** (2.5 mg, 60% based on the consumed starting material) and the starting enone **38** (3 mg recovery). The enone **40** was characterised as follows: $\nu_{max}$(neat)/cm$^{-1}$ 1735, 1700 and 1615; $\delta_H$ 5.86 (1 H, d, *J* 2), 3.2–1.0 (12 H, series of m), 1.32 (3 H, s), 1.28 (3 H, s), 1.04 (3 H, d, *J* 7), 0.96 (3 H, d, *J* 7) and 0.90 (3 H, d, *J* 7); *m/z* 300.

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## References

1 L. A. Paquette, *Top. Curr. Chem.*, 1979, **79**, 43; 1984, **119**, 1; L. A. Paquette and A. M. Doherty, *Polyquinane Chemistry. Reactivity and Structure Concepts in Organic Chemistry*, Springer-Verlag, Berlin, 1987, vol. 26.
2 For a compilation of triquinane natural products, see, K. Srinivasa Rao, Ph.D. Thesis, University of Hyderabad, 1988; see also, T. Hudlicky, G. S. Zingde, M. G. Natehus, B. C. Ranu and P. Papadopolous, *Tetrahedron*, 1987, **43**, 5685.
3 T. Anke, J. Heim, F. Knoch, U. Mocek, B. Stetfan and W. Steglich, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 709.
4 B. F. Bowden, J. C. Brackman, J. C. Coll and S. J. Mitchell, *Aust. J. Chem.*, 1980, **33**, 927.
5 (*a*) G. Mehta and A. V. Reddy, *J. Chem. Soc., Chem. Commun.*, 1981, 756; (*b*) G. Mehta, A. V. Reddy and A. N. Murthy, *J. Chem. Soc., Chem. Commun.*, 1982, 540; (*c*) G. Mehta, D. S. K. Reddy and A. N. Murthy, *J. Chem. Soc., Chem. Commun.*, 1983, 824; (*d*) G. Mehta, A. N. Murthy, D. S. K. Reddy and A. V. Reddy, *J. Am. Chem. Soc.*, 1986, **108**, 3443; (*e*) G. Mehta and K. S. Rao, *J. Chem. Soc., Chem. Commun.*, 1985, 1464; (*f*) G. Mehta and K. S. Rao, *J. Am. Chem. Soc.*, 1986, **108**, 8015.
6 For recent reports, see G. Mehta and K. S. Rao, *J. Chem. Soc., Chem. Commun.*, 1987, 1578; A. G. Griesbeck, *Chem. Ber.*, 1990, **123**, 549.
7 G. Mehta, A. Srikrishna, A. V. Reddy and M. S. Nair, *Tetrahedron*, 1981, **37**, 4543.
8 G. Mehta and K. S. Rao, *Tetrahedron Lett.*, 1984, **25**, 3481.
9 Portions of this work have appeared in a preliminary communication, G. Mehta, K. S. Rao and M. S. Reddy, *Tetrahedron Lett.*, 1988, **29**, 5025.
10 For related examples, see G. Mehta, K. S. Rao, N. Krishnamurthy, V. Srinivas and D. Balasubramanian, *Tetrahedron*, 1989, **45**, 2743.
11 H. J. Reich, J. M. Renga and I. L. Reich, *J. Am. Chem. Soc.*, 1975, **97**, 5434.
12 M. T. Crimmins and S. W. Mascarella, *J. Am. Chem. Soc.*, 1986, **108**, 3435.
13 M. J. Robins, J. S. Wilson and F. Hansske, *J. Am. Chem. Soc.*, 1983, **105**, 4059.
14 V. V. Kane, V. K. Singh, A. Martini and D. L. Doyle, *Tetrahedron*, 1983, **39**, 345.
15 N. Chidambaram and S. Chandrasekhar, *J. Org. Chem.*, 1987, **52**, 5048.

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