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# A cytotoxic triketone–phloroglucinol–bullatenone hybrid from *Lophomyrtus bullata*

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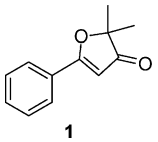
***Received 28th June 2005, Accepted 19th July 2005***
***First published as an Advance Article on the web 3rd August 2005***

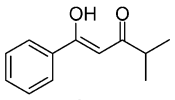
Cytotoxic activity against the P388 cell line was seen in a crude extract of the New Zealand shrub *Lophomyrtus bullata* (Myrtaceae). Bioactivity-guided isolation led to a compound with NMR spectra complicated by the presence of two isomers. These crystallised together and an X-ray structure showed them to be stereoisomeric hybrids of triketone, phloroglucinol and bullatenone units. NMR measurements on the mixed isomers, as well as a cyclic ether produced from them by acid catalysed dehydration, were consistent with these structures. The natural products, named bullataketals A and B, have cytotoxic activity against the P388 cell line ($IC_{50}$ 1 μg $ml^{-1}$), and antimicrobial activity against *Bacillus subtilis*.

## Introduction

While screening New Zealand plants for selected biological activities[1] we discovered that ethanol extracts of the foliage of *Lophomyrtus bullata* (Sol. ex A. Cunn.) Burret (Myrtaceae)[2] exhibited significant cytotoxic and antimicrobial properties. A shrub or small tree, *L. bullata* has an ethnopharmacologic history: with the Maori name ramarama, it was used to treat cuts and bruises.[3,4] The first chemical investigations, of steam distillates of the leaves, resulted in the isolation of a compound named bullatenone[5] whose structure was later shown to be **1**.[6] *L. bullata* is still the only known natural source of bullatenone **1**, which has potential uses as an insect repellent,[7] against ulcers,[8] and in sunscreens[9] and fragrances.[10] Subsequent studies of the essential oil identified as additional constituents α- and β-pinene, (−)-alloaromadendrene, 1-hydroxy-4-methyl-1-phenyl-1-penten-3-one **2** and 2-isopropylchromone.[11] We now report the compounds responsible for the cytotoxic and antimicrobial properties of the plant extracts.




**1**




**2**

## Results and discussion

An extract of *L. bullata* foliage was fractionated over silica gel, eluting with dichloromethane, to give a sample containing the main cytotoxic activity against the P388 cell line, plus a fraction containing bullatenone **1**. The main cytotoxic fraction was subjected to reversed-phase HPLC to give a substance **3**, at a purified yield of about 0.1% w/w of dry foliage.

Compound **3** was an orange coloured oil whose $^1H$ NMR spectrum (Table 1) showed low field signals for six strongly hydrogen-bonded hydroxyls between 10 and 17 ppm. Although this material was homogeneous on RP HPLC and on a variety of TLC systems, both the $^1H$ and $^{13}C$ NMR spectra appeared to correspond to a *ca.* 2 : 3 mixture of two closely related, probably isomeric compounds. The IR spectrum was dominated by a broad carbonyl signal (1605 $cm^{-1}$) and the $^{13}C$ NMR spectrum (Table 1) showed three pairs of ketone signals (203–213 ppm). These features recalled the cyclic β-triketones, *e.g.* **4**, an unusual group of natural products[12] found mainly in plants of the family Myrtaceae, together with acyl phloroglucinols, *e.g.* **5**, their putative precursors. These compounds have been shown to possess a variety of biological activities, including plant growth regulation[12] and antibacterial activity.[13] They are also found as building blocks in more complex bioactive natural products. Examples include: insecticidal triketone–flavonoid compounds;[14] anti-inflammatory phloroglucinol–flavonoids;[15] phloroglucinol–monoterpenes inhibiting Epstein Barr virus activation;[16] and phloroglucinol–sesquiterpenes with antibacterial activity.[12] Triketone–phloroglucinol combinations are also found, such as the antibacterial myrtucommulone A **6**[17] and semimyrtucommulone **7**[18] from the European myrtle. Comparison of the $^{13}C$ NMR data showed close matches for most of the signals of semimyrtucommulone **7** in the spectrum of compound **3**. The $^1H$ NMR spectra of **7** and **3** also showed signals in common, but the spectrum of **3** lacked the aromatic methyl signal of **7**.

The positive ion EI-MS of compound **3** showed a possible molecular ion at 604 Da consistent with a molecular formula of $C_{36}H_{44}O_8$. This interpretation was supported by an ion at 422 Da, which could be due to loss of syncarpic acid **8** from a triketone moiety.[17] Another ion at 543 Da could correspond to dehydration and α-cleavage of the isobutyryl group of the phloroglucinol moiety, as found for myrtucommulone A **6**.[17]

This proposed molecular formula for the *L. bullata* compound **3**, together with the assignment of triketone and phloroglucinol moieties as in **7**, left a $C_{12}H_{14}O$ moiety to be identified. The NMR spectra (Table 1) showed a mono-substituted phenyl group, two more methyl singlets and a $CH_2$–CH ABX system still unaccounted for. However, because of overlaps in the methyl region, exacerbated by the signal doubling, we were unable to determine the full structure of **3** from NMR experiments. Fortunately, re-isolation on a larger scale yielded crystals, and we were able to "shoot the fox" and determine the structure of the substance by X-ray crystallography.

The crystal structure (Fig. 1) revealed that it consisted of near 1 : 1 mixture of isomers **3A** and **3B**, differing in the relative configurations of the chiral centres (C7′ and the linked C7″ + C9″ of the bicyclic ketal). The co-crystallisation of configurational isomers is interesting, but not uncommon. An especially relevant example is the co-crystallisation of the triketone–flavanone compounds, kunzeanones A and B **9**.[19] Another feature of the crystals of **3** is that, despite the presence of chiral centres, they were centrosymmetric, *i.e.* both isomers **3A** and **3B** were present

DOI: 10.1039/b509076h

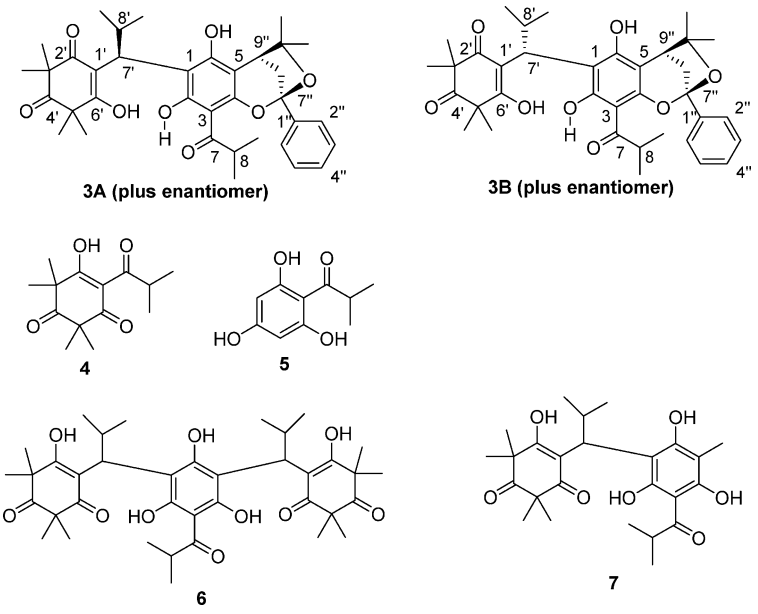



**Table 1** $^{13}C$ and $^{1}H$ NMR data for bullataketals **3A** (minor) and **3B** (major) and cyclisation product **11**[a]

| Atom | **3A** (minor) | | **3B** (major) | | **11** | |
|---|---|---|---|---|---|---|
| | $^{13}C$ | $^{1}H$ | $^{13}C$ | $^{1}H$ | $^{13}C$ | $^{1}H$ |
| 4′ | 212.85 | — | 212.35 | — | 212.1 | — |
| 7 | 211.73 | — | 211.22 | — | 209.4 | — |
| 2′ | 203.62 | — | 203.05 | — | 197.3 | — |
| 6′ | 176.60 | — | 178.59 | — | 167.3 | — |
| 2 | 161.92 | — | 161.77 | — | 157.7 | — |
| 6 | 160.43 | — | 159.92 | — | 151.8 | — |
| 4 | 154.72 | — | 154.89 | — | 160.5 | — |
| 1″ | 139.17 | — | 139.29 | — | 138.7 | — |
| 4″ | 128.82 | 7.38 (m) | 128.75 | 7.38 (m) | 128.8 | 7.42 (m) |
| 3″ + 5″[b] | 128.26 | 7.38 (m) | 128.24 | 7.38 (m) | 128.3 | 7.42 (m) |
| 2″ + 6″[b] | 125.63 | 7.62 (m) | 125.60 | 7.62 (m) | 125.9 | 7.66 (br d, 7) |
| 1′[b] | 114.22 | — | 114.17 | — | 108.1 | — |
| 1/5/7″[b] | 108.42 | — | 108.42 | — | 111.8[c] | — |
| 1/5/7″[b] | 108.35 | — | 108.35 | — | 108.1[c] | — |
| 1/5/7″[b] | 108.27 | — | 108.18 | — | 103.1[c] | — |
| 3 | 103.24 | — | 103.15 | — | 104.1 | — |
| 10″[b] | 91.37 | — | 91.36 | — | 90.9 | — |
| 3′ | 54.31 | — | 54.89 | — | 56.1 | — |
| 5′ | 49.00 | — | 48.80 | — | 47.2 | — |
| 7′ | 40.84 | 3.81 (d, 10) | 39.36 | 3.78 (d, 10) | 35.1 | 4.32 (d, 3) |
| 9″ | 40.23 | 3.64 (d, 4) | 40.17 | 3.62 (d, 4) | 39.83 | 3.61 (d, 4) |
| 8[b] | 38.84 | 3.79 (m) | 38.80 | 3.79 (m) | 39.77 | 3.94 (hpt, 7) |
| 8″[b] | 37.94 | 2.35 (d, 12) | 37.49 | 2.38 (d, 12) | 38.3 | 2.81 (dd, 4, 12) |
| — | — | 2.68 (dd, 4, 12) | — | 2.68 (dd, 4, 12) | — | 2.25 (d, 12) |
| 3′Me[b] | 26.69 | 1.42 (s) | 26.26 | 1.43 (s) | 26.7[c] | 1.60 (s) |
| 8′ | 26.67 | 3.11 (m) | 26.06 | 3.04 (m) | 31.4 | 1.87 (d hpt, 3, 7) |
| 5′Me[b] | 25.86 | 1.35 (s) | 25.53 | 1.36 (s) | 25.2[c] | 1.44 (s) |
| 5′Me[b] | 25.53 | 1.41 (s) | 25.49 | 1.41 (s) | 25.0[c] | 1.40 (s) |
| 10″Me[b] | 24.86 | 1.48 (s) | 24.86 | 1.48 (s) | 25.0[c] | 1.36 (s) |
| 10″Me[b] | 24.82 | 1.26 (s) | 24.79 | 1.14 (s) | 24.6[c] | 1.23 (s) |
| 3′Me | 24.17 | 1.33 (s) | 23.88 | 1.30 (s) | 24.4[c] | 1.47 (s) |
| 8′Me | 22.03 | 0.89 (d, 6.5) | 21.98 | 0.78 (d, 6.5) | 21.0 | 0.78 (d, 7) |
| 8′Me | 21.98 | 0.85 (d, 6.5) | 21.81 | 0.77 (d, 6.5) | 19.3 | 0.75 (d, 7) |
| 8Me | 19.76 | 1.07 (d, 6.5) | 19.57 | 1.05 (d, 6.5) | 18.7 | 1.27 (d, 7) |
| 8Me | 19.04 | 1.03 (d, 6.5) | 19.33 | 1.03 (d, 6.5) | 17.4 | 1.25 (d, 7) |
| 2OH | — | 16.76 (s) | — | 16.50 (s) | — | 13.68 (s) |
| 6′OH | — | 11.33 (s) | — | 10.48 (s) | — | — |
| 6OH | — | 10.64 (s) | — | 11.49 (s) | — | — |

[a] In $CDCl_3$: shift in ppm (multiplicity {hpt = heptuplet}, coupling in Hz). [b] Assignments within or between **3A** and **3B** uncertain. [c] Assignments interchangeable within column.

as pairs of enantiomers. The residual oil had $[\alpha]_D = 0.04°$, optically inactive within experimental error. Since the $^1H$ and $^{13}C$ NMR spectra of this residual oil were indistinguishable from those of the crystals, we conclude that the ketals were racemic, *i.e.* that the crystals did not represent the selective separation of a racemate from a scalemic mixture of enantiomers. While such a finding is unusual among natural products, another triketone–phloroglucinol compound, the antibiotic rhodomyrtone **10** has been found to be racemic,[20] and optical activities of myrtucommulone A **6** and semimyrtucommulone **7** do not seem to have been reported. Compounds **3A** and **3B** contained the predicted triketone–phloroglucinol grouping, plus a bicyclic ketal moiety, so we propose the names bullataketal A and B.

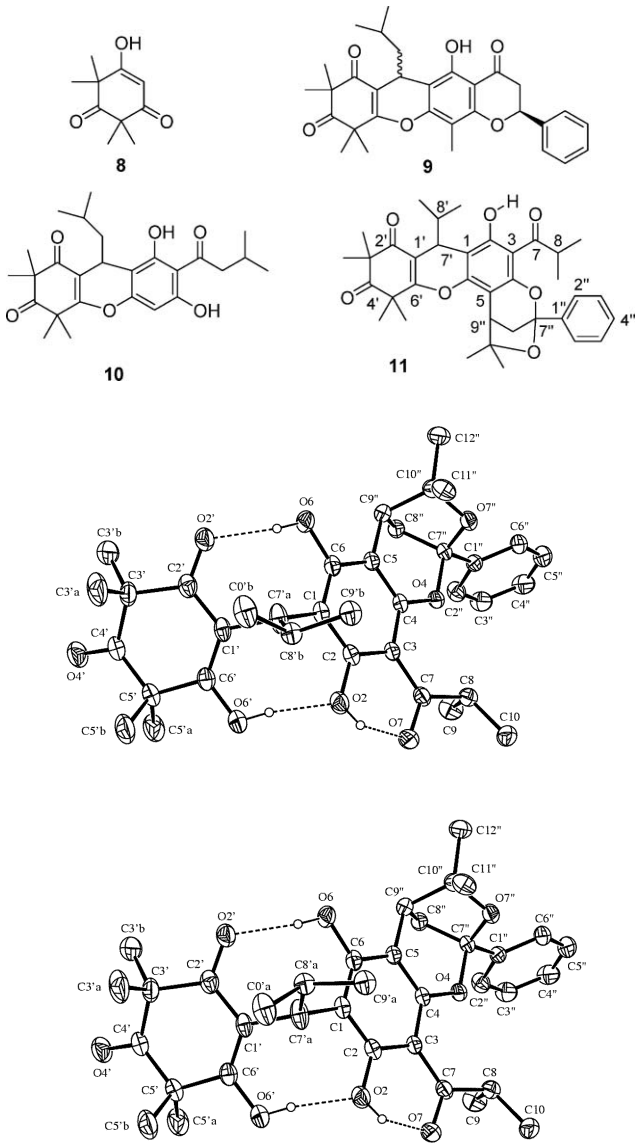


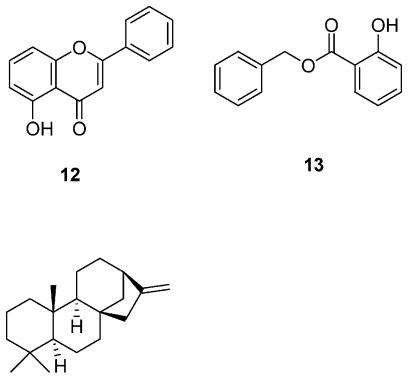

**Fig. 1** Structures of bullataketals **3A** (minor, top) and **3B** (major, bottom) in crystal form (only one enantiomer of each is shown).

Re-examination of the NMR spectra (Table 1) in light of these findings confirmed our earlier assignments made by comparing the spectra of the bullataketals and semimyrtucommulone, and also resulted in assignments for the bicyclic ketal moiety. H9″ showed only one measurable vicinal coupling (Table 1), because of an almost 90° dihedral angle with one H8″. The CIGAR correlations, based on 2- and 3-bond $^1H$–$^{13}C$ couplings, suggested that the two C7″ acetal signals from the bicyclic ketal moiety overlapped the C1 and C5 signals at 108.2–108.4 ppm. We could only find one previous natural example of this bicyclic ketal moiety, in castavinol from Bordeaux red wines,[21] which had an acetal signal at 109.7 ppm: in reasonable accord with that proposed for C7″ of the bullataketals (Table 1).

Our assignments of the OH NMR signals of **3A** and **3B**, based on 2D NMR correlations, are generally in agreement with a proposed relationship of chemical shift and hydrogen bond strength. Bertolasi *et al.* have shown that the strongest intramolecular hydrogen bonds, with donor–acceptor oxygen atom distances of 2.41–2.55 Å from X-ray structures, have OH NMR chemical shifts of 14.9–19.0 ppm.[22] The O2–O7 distance is 2.402 Å in the crystal structure of **3A** and **3B**, and the chemical shifts assigned for O2–H are 16.76 and 16.50 ppm (Table 1). The strength of this hydrogen bond is also reflected by coupling between O2–H and C7, shown by a CIGAR correlation, as we have found in similar systems.[23,24] Signals at 16.30–16.70 ppm were also reported for myrtucommulone A **6**,[17] but surprisingly not for semimyrtucommulone **7**.[18] Weaker hydrogen bonds, with donor–acceptor distances of 2.59–2.64 Å are expected to have OH proton chemical shifts of 8.6–10.1 ppm.[22] The crystal structure (Fig. 1) showed 2.619 Å for O6′–O2, and 2.676 Å for O6–O2′ in bullataketals **3A** and **3B**, but our NMR assignments (Table 1) showed corresponding shifts of 11.33 and 10.48 ppm for O6′–H, and 10.64 and 11.49 ppm for O6–H, a little above this range.

Before the crystal structure was obtained, we tried to simplify the NMR spectra of the bullataketals by acid-catalysed cyclization and dehydration, as carried out on myrtucommulone A **6**[17] and other triketone–phloroglucinols.[25] Warming a solution of the bullataketals **3A** and **3B** in $CDCl_3$ with Nafion(H) resulted in the loss of the hydrogen-bonded resonances at $\delta_H$ 16.76 and 16.5 ppm and the appearance of new resonances around $\delta_H$ 13.6 ppm. Upon work-up of the product mixture, one compound was obtained pure by PTLC. This exhibited a highest $m/z$ ion at 543 Da, shown by HREIMS to have the composition $C_{33}H_{35}O_7$, as required for M-43 (loss of $C_3H_7$) from a compound formed from **3A** or **3B** by dehydrative cyclisation. The NMR spectra of this compound were in accord with expectations for structure **11**, based on comparisons with the NMR data for kunzeanone A **9**,[19] but with a stronger intramolecular hydrogen bond than in **9** (Table 1). After the establishment of structures **3A** and **3B** for the bullataketals, we did not investigate the other products of the reaction, which were at least two apparently isomeric compounds.

In addition to bullatenone **1** and the bullataketals **3A** and **3B**, the previously reported 1-hydroxy-4-methyl-1-phenyl-1-penten-3-one **2** was present in the *L. bullata* extract. Other known compounds, but new from *L. bullata*, were identified by GC-MS and NMR as 5-hydroxyflavone **12**, benzyl salicylate **13**, and the diterpene phyllocladene **14**.




The bullataketals **3A** and **3B** were the main cytotoxic compounds in the extract of *L. bullata*, with the mixture showing an $IC_{50}$ of 1 μg ml$^{-1}$ (1.7 μM) against the P388 mouse leukaemia cell line. This is over twenty times more active than the component building blocks: triketone **4** and phloroglucinol **5** both had P388 $IC_{50}$s >25 μg ml$^{-1}$;[13] and we found that bullatenone **1** had a P388 $IC_{50}$ of 22 μg ml$^{-1}$. The bullataketals **3A** and **3B** also showed antibacterial activity against *Bacillus subtilis*, with a

minimum inhibitory dose of around 30 μg per disk. We suggest that the increased biological activity of the bullataketals **3A** and **3B**, compared to the simpler building blocks, is due to the increased lipophilicity. We have discussed this idea in more detail for a series of synthetic triketones, which showed maximum activity at a calculated log*P* (Clog*P*) of around 6,[13] where *P* is the octan-1-ol/water partition coefficient.[26] The Clog*P* for the bullataketals **3A** and **3B** is 6.6, so these compounds can pass through cell membranes more easily than triketone **4** (Clog*P* 2.0), phloroglucinol **5** (Clog*P* 1.6) and bullatenone **1** (Clog*P* 2.4). Although we do not know the function of the bullataketals **3A** and **3B** in *L. bullata*, they seem to represent another case of natural product hybrids in which the generation of chemical diversity and enhanced biological activity is at relatively low cost to the producing organism, in accord with the hypotheses of Tietze *et al.*,[27] and Firn and Jones.[28]

Therefore we propose a biosynthesis of bullataketals **3A** and **3B** which involves a minimum of enzymes and building blocks (Fig. 2). Phloroglucinol **5** can be derived from isobutyryl-CoA **15** by a polyketide synthase (PKS) adding three malonyl-CoA **16** units, as in the biosynthesis of hyperforin.[29] Methylation of **5** with *S*-adenosyl methionine (SAM) would give **4**, as shown by Birch for a similar triketone, tasmanone.[30] The biosyntheses of bullatenone **1** and 1-hydroxy-4-methyl-1-phenyl-1-penten-3-one **2** have not been studied, but for **2** we propose a mechanism similar to the "biological Claisen condensation" demonstrated for the biosynthesis of [6]-gingerol.[31] In *L. bullata*, **2** may be obtained *via* a biological Claisen condensation of benzoyl-CoA **17** with the first PKS intermediate **18**. Formation of bullatenone **1** from **2** could involve either dehydrative cyclisation after preliminary hydroxylation at C4, or intramolecular oxidative cyclisation of a dienol form of **6** (Fig. 2). Aldol-like coupling of **4** and **5**, followed by loss of water and reduction, would give the hypothetical intermediate **19** as a mixture of stereoisomers. Compound **19** is not known, and we did not see it in our *L. bullata* extracts, but it is closely related to semimyrtucommulone **7**. Another aldol-like coupling, this time of **19** and bullatenone **1**, followed as before by elimination of water and reduction, would yield **20** (also not known). Acid-catalysed cyclisation of **20** would give the bullataketals **3A** and **3B** (Fig. 2).

## Experimental

### General procedures

All solvents were distilled before use, and were removed by rotary evaporation at temperatures up to 35 °C. Octadecyl functionalised silica gel (C18) was used for reversed-phase (RP) flash chromatography, and Merck silica gel 60, 200–400 mesh, 40–63 μm, was used for silica gel flash chromatography. TLC was carried out using Merck DC-plastikfolien Kieselgel 60 $F_{254}$, first visualised with a UV lamp, and then by dipping in a vanillin solution (1% vanillin, 1% $H_2SO_4$ in EtOH), and heating. PTLC was performed on Merck silica gel 60 F-254 on glass plates (Merck 5715). Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Mass, UV, and IR spectra were recorded

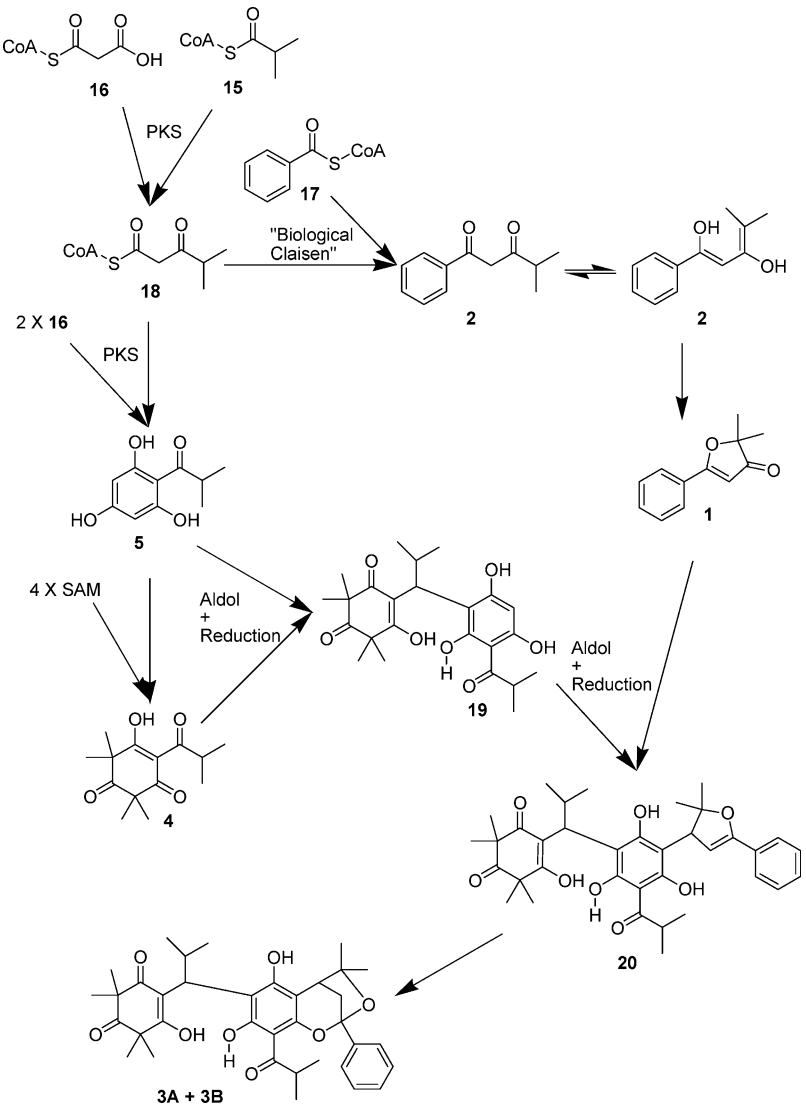



**Fig. 2** Proposed biosynthesis of unique *Lophomyrtus bullata* compounds: bullatenone **1** and bullataketals **3A** and **3B**.

on Kratos MS-80, Shimadzu UV 240, and Perkin-Elmer 1600 FTIR instruments, respectively. NMR spectra, at 25 °C, were recorded at 500 MHz for $^1$H and 125 MHz for $^{13}$C on a Varian INOVA-500 spectrometer, and at 400 and 100 MHz on a Bruker AMX-400 spectrometer. Chemical shifts are given in ppm on the $\delta$ scale referenced to the solvent peaks $CHCl_3$ at 7.25 and $CDCl_3$ at 77.0. HPLC equipment consisted of a Waters 717 autosampler, 600 pump and controller, and a 2487 UV detector controlled by Omega software. Preparative HPLC used a RP-18 column (Phenomenex Luna 5 µm C18, 250 × 10 mm) fitted with a guard column (Phenomenex SecurityGuard 5 µm C18, 4 × 3 mm,) at 30 °C, using a mobile phase flow rate of 5.0 mL min$^{-1}$, with UV detection at 280 nm. Details of the P388 cytotoxicity and antimicrobial assays are given elsewhere.[32]

### Collections

The first collection of *L. bullata* was from Whangarae Bay on the 13th March 2000, voucher code 000313–04. The second collection was from Dunedin Botanical Gardens on the 27th January 2003.

### Isolation

Dried, ground *L. bullata* leaf and twig (54 g) from the first collection was extracted by shaking overnight in chloroform (500 ml), the extract filtered and evaporated *in vacuo*, to give a green gum (8.8 g). Column chromatography over silica gel (20 g) of the extract eluting with dichloromethane gave, after recombination based on TLC behaviour, the cytotoxic triketone-rich fraction (0.53 g, P80-35-2). Reverse phase HPLC of this fraction (0.10 g) eluting with 5% water in methanol for 10 min, then a gradient up to 100% methanol over 5 min, then 100% methanol for 5 min gave the bullataketal **8** in one peak collected between 11.60 and 12.80 min (6 mg).

In a large-scale isolation from the second *L. bullata* collection, the triketone-rich fraction (894 mg) was subjected to further flash chromatography on a column (21 × 1.8 cm) of silica gel 60. Hexanes (550 mL) eluted only traces of material after which $Et_2O$–hexanes (1 : 9 v/v) eluted an orange band. The individual fractions (8 × 20 mL) were evaporated (total weight of orange oil *ca.* 780 mg) and analysed by TLC and $^1$H NMR spectroscopy. All contained triketones, with the centre-cut of the fractions homogeneous by TLC, and the earlier and later fractions containing small amounts of other constituents. PTLC of the early fractions (hexane–$Et_2O$, 9 : 1 v/v) followed by GCMS and NMR resulted in the identification of the minor constituents as 1-hydroxy-4-methyl-1-phenyl-1-penten-3-one **2**,[11] benzyl salicylate **13**[33] and phyllocladene **14** (enantiomer not determined, $^1$H NMR spectrum identical to an authentic sample[34]). Bullatenone **1**[11] and 5-hydroxyflavone **12**[35] were similarly isolated from the later fractions and identified by NMR, MS and melting points. From the centre-cut fractions crystals slowly separated. These were re-crystallised from hexane containing a few drops of $Et_2O$ to provide the bullataketals **3A** and **3B** as pale yellow tablets (*ca.* 20 mg): mp 156–159 °C; $[\alpha]_D$ +0.04° (*c* 1.1 in $CHCl_3$, run on residual oil from crystallisation); UV (MeOH)/nm $\lambda_{max}$ (log $\varepsilon$) 288 (3.85) and 237 (3.92); IR (dry film)/cm$^{-1}$ $\nu_{max}$ 1605; $^1$H and $^{13}$C NR data in Table 1; +EIMS (70 eV) *m/z* 604.3025 ($M^+$, 0.1%, $C_{36}H_{44}O_8$ requires 604.3023), 543 (10), 422 (8), 368 (33), 325 (93), 205 (88), 105 (100).

### Crystal structure determination of compounds 3A and 3B

**Crystal data.** $C_{36}H_{44}O_8$, $m$ = 602.70, $T$ = 173(2) K, monoclinic, space group $P2_1/n$, $a$ = 16.999(5) Å, $b$ = 11.735(8) Å, $\beta$ = 112.405(17)°, $c$ = 17.495(10) Å, volume = 3227(3) Å$^3$, $Z$ = 4, $\mu$ = 0.087 mm$^{-1}$, reflections collected = 19841, independent reflections = 5648 [$R$(int) = 0.074], final $R$ indices [$I > 2\sigma(I)$] $R$ = 0.061, $wR$ = 0.145.†

### Acid catalysed cyclisation of the bullataketals 3A and 3B

To a sample of the oily bullataketals **3A** and **3B** (9 mg) dissolved in $CDCl_3$ (*ca.* 0.8 mL) in a NMR tube were added two pellets (*ca.* 6 × 1.5 mm) of 10–20% Nafion SAC on silica gel (Aldrich 47,454-1) and the lower part of the stoppered tube was immersed in an oil bath maintained at 65 °C. The tube was periodically removed and the contents examined by $^1$H NMR spectroscopy. Within a few hours there were clear indications of changes in the H-bonded OH resonances and after 24 h a group of signals around $\delta_H$ 13.6 was dominant. The supernatant was decanted from the Nafion pellets which were then rinsed with $CHCl_3$ (*ca.* 2 × 0.5 mL). The combined supernatant and washings were evaporated to a pale yellow oil (9 mg) which was subjected to PTLC (petroleum ether 40–60 °C–$Et_2O$, 9 : 1 v/v). A major product **11** was obtained, by elution ($CHCl_3$–MeOH, 9 : 1 v/v) of a 0.38 $R_F$ band followed by removal of the solvent, as a pale yellow oil (*ca.* 2 mg): UV (MeOH)/nm $\lambda_{max}$ (log $\varepsilon$) 214 sh (4.17), 297 (3.98) and 328 sh (3.37); IR (dry film)/cm$^{-1}$ $\nu_{max}$ 1651; $^1$H and $^{13}$C NMR data in Table 1; +EIMS (70 eV) *m/z* 543.2384 ($M^+$–$C_3H_7$, 100%, $C_{33}H_{35}O_7$ requires 543.2383), 105 (40), 69 (40).

## Acknowledgements

Thanks to G. Burge, N. Pile and S. Stewart for collections; G. Ellis for biological assays; M. Thomas, W. Redmond, R. Yamdagni and Q. Wu for NMR spectra; and B. Stewart and D. Fox for mass spectra. This research was supported by the New Zealand Foundation for Research, Science and Technology, the Natural Sciences and Engineering Research Council of Canada (grant-in-aid to MHB) and the University of Calgary.

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