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A biomimetic type expedient approach to the tricyclic core of xyloketals. Application to a short, stereocontrolled synthesis of alboatrin and a remarkable *epi* to natural isomerisation

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ABSTRACT

An expedient synthesis of the linear tetrahydrofurano benzopyran ring system of xyloketals is described involving an ortho ester Claisen rearrangement and an intramolecular cationic cyclisation. This strategy was applied for a short, stereocontrolled and high yield synthesis of the phytotoxic metabolite alboatrin.
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Xyloketals are a group of novel, structurally unique, closely related natural products originating from a mangrove fungus of the xylaria species which enclose a highly labile internal ketal in the form of a tetrahydrofurano benzopyran in their structural inlay.[1] Xyloketal A **1**, a representative compound belonging to this group possesses a distinctive C_3-symmmetric molecular structure. This is also a potent inhibitor of acetyl choline esterase and considered a lead compound in the treatment of Alzheimer's disease.[2] Xyloketal D **2** is a simpler structural sibling of **1** incorporating a single linear tricyclic network. In view of their unusual structural features and associated biological properties, xyloketals have emerged as attractive targets for synthesis.[3] We have initiated a comprehensive programme towards their synthesis and have looked at developing a convenient method for the linear tricyclic ring system embedded in these compounds. The core structural motif as in **2** along with an identical stereochemical disposition of the three contiguous stereogenic centres is also present in alboatrin **3**, a phytotoxic metabolite isolated from the culture filtrate of Verticillium alboatrum[4] This inhibits the root growth of the host plant (Maris Kabul) and causes vascular-wilt disease in alfalfa. The originally assigned structure was later corrected to **3** involving inversion of the configuration of the secondary methyl group at C-3.[5a] Representative syntheses of **3** have also been reported.[4,5] We had previously disclosed a synthesis of **3** in which an intra-molecular ketene–alkene cycloaddition followed by an oxidative ring expansion served as the key steps for the development of the tricyclic ring system.[6] Low yields in crucial steps and the need to separate the mixture of products in the initial aromatic Claisen rearrangement step affected the overall yield profile in the synthesis. Prompted by our interest to develop an expeditious synthetic route to the xyloketals, we now present a convenient synthesis of the central tricyclic ring system, and demonstrate the efficacy of the strategy by application to a short, stereocontrolled and high yield synthesis of alboatrin. In the course of the synthesis, we have also observed a remarkable case of isomerisation of the *epi*- to the natural isomer, which enabled a further improvement in the total overall yield.

Retrosynthetically, we envisaged the generation of the tricyclic ring system of xyloketals through a cationic intramolecular cyclisation of a properly hydroxyethyl substituted benzopyran **4**, the annulation providing the thermodynamically more stable cis ring junction in a hydrindane-like system. This alcohol **4** was to be available from a Johnson orthoester Claisen rearrangement of the chromenol **5**, which was to be accessed from the chromone carboxylate **6**, obtainable from the *o*-hydroxyacetophenone **7** by a standard procedure (Scheme 1). Initially we decided to test the efficacy of this hypothesis by applying it to the synthesis of a linear unsubstituted tricyclic model compound. Reduction of the known ethyl chromone-2-carboxylate **8**[7] employing a combination of sodium cyanoborohydride and boron trifluoride etherate[8] furnished the chromene carboxylate **9** through a chemoselective deoxygen-

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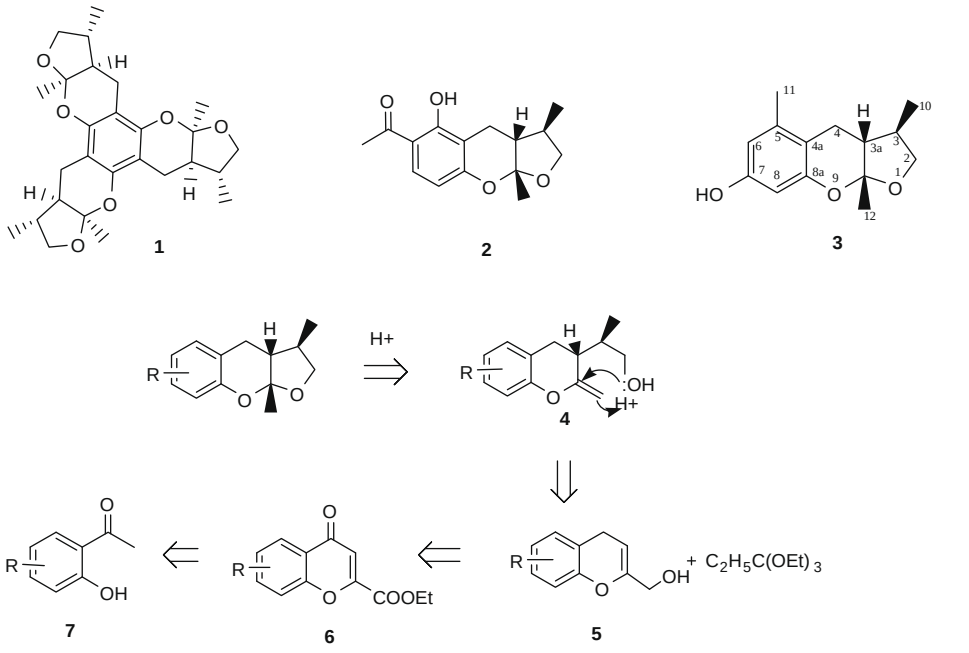
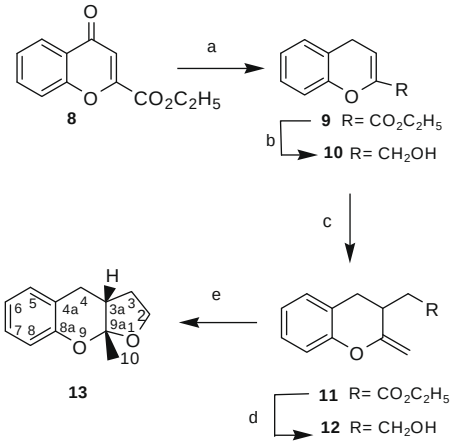


Scheme 1.

ation in about 74% yield. The absence of the benzylic ketone in the IR and the appearance of a doublet at δ 3.53 in the ^{1}H NMR for the benzylic methylene group alongwith the expected splitting of the olefinic proton into a triplet attested to the formation of the desired chromene carboxylate.

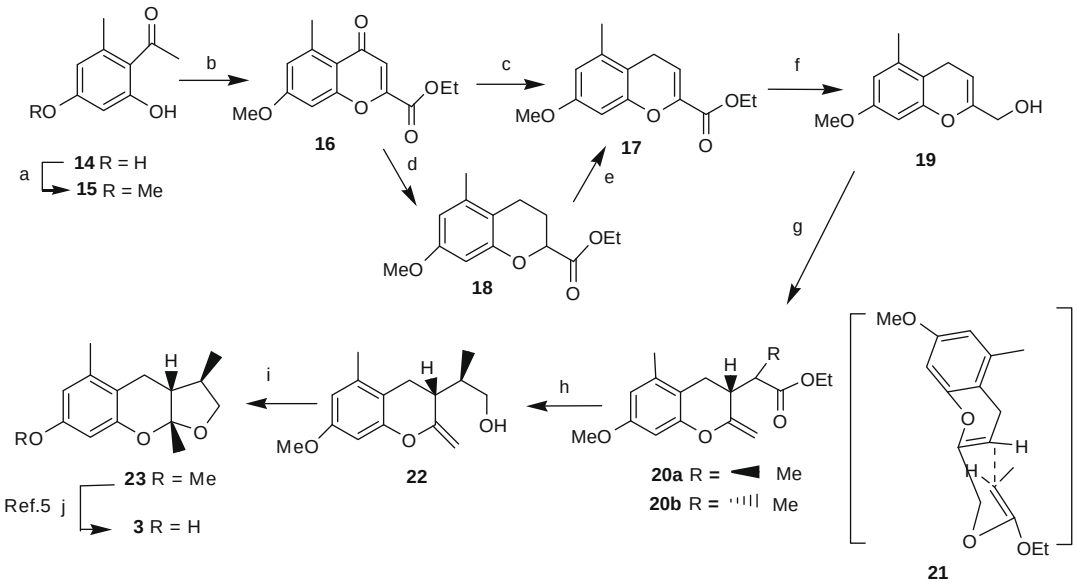
The interaction of this ester with LAH in ether delivered the allylic alcohol **10** in excellent yield. Refluxing a homogenous mixture of this alcohol and triethyl orthoacetate in xylene in the presence of a catalytic amount of propionic acid resulted in the expected ortho ester Claisen rearrangement[9] to furnish the rearranged ester **11** in 96% yield. The structure of this product was duly attested by the appropriate features in the ^{1}H NMR spectrum, particularly the two broad singlets at δ 4.27 and 4.60 for the exo-methylene protons.[10] The reaction of ester **11** with LAH achieved the reduction of the ester function to the corresponding alcohol **12** in excellent yields properly set up for the proposed intramolecular cyclisation. In the event, the mild acid treatment of a THF solution of this alcohol ensured the expected cationic cyclisation to furnish the tricyclic ketal **13** incorporating the basic structural network of the xyloketals (Scheme 2). The structure was amply supported by the appropriate features in the ^{1}H NMR spectrum showing a strong singlet at δ 1.58 for the angular methyl group and appropriate features for the methylene protons.[10] The cis ring juncture to this product has been assigned based on previous precedents in the synthesis[3] of xyloketals and was further supported from nuclear Overhauser enhancement (NOE) studies which showed a strong connection between the angular methyl group and the angular hydrogen at C-3a.



Scheme 2. Reagents and conditions: (a) $BF_3{\cdot}Et_2O$, $NaCNBH_3$, THF, reflux, 3 h,74%; (b) LAH, THF, −40 °C to 0 °C, 1 h, 92%; (c) $CH_3C(OEt)_3$, C_2H_5COOH(Cat.), xylene, 140 °C, 6 h, 96%; (d) LAH, THF, 0 °C, 1 h, 97%; (e) H_2SO_4(Cat.), THF, 0 °C–rt, 2 h, 96%.

With the demonstrated success of our projected approach to the xyloketal core through a synthesis of the model compound, we decided to first apply the methodology to a synthesis of alboatrin. The point of departure was the known resacetophenone **14**.[11] The interaction of this with methyl iodide in refluxing acetone with added potassium carbonate achieved the selective methylation of the less encumbered phenolic group to provide the methyl ether **15**. An intra-molecular hydrogen bonding between the carbonyl oxygen and the adjacently placed phenolic group in **14** renders the distal phenolic function more reactive resulting in this selectivity. Condensation of the methyl ether **15** with diethyl oxalate followed by dehydration of the resultant 2-hydroxy chromanone furnished the desired chromone carboxylate **16** in an overall 90% yield.[10] Exposure of this keto-ester to the previously tried combination of sodium cyanoborohydride and boron trifluoride etherate accomplished the chemoselective removal of the carbonyl oxygen and afforded the chromene carboxylate **17**, but in a low yield (25%).[10] In an effort to improve the yield of this product, **16** was subjected to total hydrogenation to the chromane carboxylate **18** in 95% yield. The double bond was then reinstated taking advantage of the ester functionality through phenyl selenylation followed by oxidative elimination, which ensured the smooth re-introduction of the double bond to furnish the unsaturated ester **17** in very good overall yield (83%) (Scheme 3).

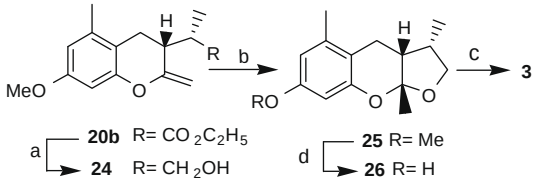
Proceeding with the synthesis, the chromene carboxylate **17** was reduced with LAH and furnished the allylic alcohol **19** in 93% yield, which was subjected to the Johnson orthoester Claisen rearrangement employing triethyl orthopropionate to obtain a rearranged product incorporating the desired secondary methyl



Scheme 3. Reagents and conditions: (a) K_2CO_3, acetone, MeI, reflux, 3 h, 92%; (b) (i) NaH, $(CO_2C_2H_5)_2$, THF, 0 °C–rt, 8 h; (ii) PTSA, C_6H_6, reflux, overall yield 90%; (c) $BF_3{\cdot}Et_2O$, $NaCNBH_3$, THF, reflux, 4 h, 25%; (d) Pd/C, H_2, C_2H_5OH, 3 h, 95%; (e) (i) LDA, PhSeBr, THF, −78 °C, 92%; (ii) H_2O_2, CH_2Cl_2/THF (2:1), 0 °C–rt, 90%; (f) LAH, THF, −40 °C to 0 °C, 1 h, 93%; (g) $C_2H_5C(OEt)_3$, C_2H_5COOH(Cat.), xylene, 140 °C, 6 h, 97%; (h) LAH, THF, 0 °C, 1 h, 90%; (i) H_2SO_4(Cat.), THF, 0 °C–rt, 2 h, 96%; (j) BBr_3, CH_2Cl_2, −78 °C, 1 h, 80%.

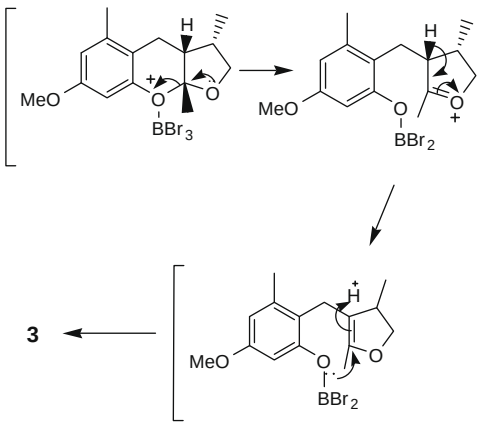
group also. Thus, refluxing a homogenous mixture of the alcohol and triethyl orthopropionate in xylene in the presence of a catalytic amount of propionic acid delivered the rearranged γ,δ unsaturated ester(s) **20** as a mixture of two diastereomers in 9:1 ratio in 97% total yield (Scheme 3). These were separated by column chromatography, and the structure of the major isomer was assigned as **20a**[10] considering the chair-like conformation for the intermediate allyl enol ether **21** involving very few interactions.[9] The final confirmation of the assignment, however, depended on its conversion to alboatrin itself. Reduction of the ester **20a** with LAH furnished the alcohol **22** in 90% yield. When this alcohol was subjected to mild acid treatment, it underwent an intramolecular cationic cyclisation as before to afford the methyl ether **23** of alboatrin as the only isolated product in 96% yield. The melting point and spectral features (^1H and ^{13}C NMR) of this material were identical with our previously synthesised sample.[5] Demethylation of this to alboatrin **3** having already been reported,[5,12] this concluded a short, high yield synthesis of the metabolite (Scheme 3). The synthesis further substantiated the structural and stereochemical assignment to the Claisen rearrangement product **20a**.

Murphy and co-workers, in their synthesis of alboatrin, had obtained *epi*-alboatrin **26** as the major product.[5] *epi*-Alboatrin differed from its natural counterpart chiefly in its spectral features. In the ^1H NMR spectrum, the C-3 secondary methyl protons displayed an upfield shift, appearing as a doublet at δ 0.88 arising from the shielding by the aromatic ring in the convex conformation of the molecule. We had obtained the diasteromer **20b**[10] as a minor component in the orthoester Claisen rearrangement, and decided to utilize this for a synthesis of *epi*-alboatrin **26** employing the same sequence of reactions as detailed above for the synthesis of alboatrin. LAH reduction of the ester **20b** furnished the alcohol **24** in 90% yield. When this was subjected to mild acid treatment it afforded *O*-methyl-*epi*-alboatrin **25** in near quantitative yields. As anticipated, in the ^1H NMR spectrum of **25**[10], the C-3 secondary methyl protons appeared as a doublet at δ 0.84. When **25** was subjected to demethylation with BBr_3, the only product isolated in 80% yield was not *epi-alboatrin* **26**, but *alboatrin* **3** (Scheme 4). The identity was established from spectral comparison with an authentic sample. This was indeed an unusual and unique case of isomerisation and is thought to proceed through a remarkable tandem ring



Scheme 4. Reagents and conditions: (a) LAH, THF, 0 °C, 1 h, 90%; (b) H_2SO_4(Cat.), THF, 0 °C–rt, 2 h, 96%; (c) BBr_3, CH_2Cl_2, −78 °C, 1 h, 80%; (d) EtSNa, DMF, 6 h, 86%.

opening and re-cyclisation process. We suggest that the primary process is the cleavage of the internal ketal to furnish a dihydrofuran phenol intermediate which undergoes a protonation with concomitant anti-addition of the phenolic moiety to finally deliver **3** (Scheme 5). Interestingly the protonation takes place *syn* to the secondary methyl group at C-3. Ichihara et al., in their synthesis of **3**[4], had implicated a similar dihydrofuran intermediate. However, based on the subsequent revision of the configuration of the methyl group at C-3, their conclusion relating to protonation anti to this methyl group also needs revision. Support for this proposal accrued from aborting the demethylation of **25** midway. A



Scheme 5.

work-up of the reaction furnished a mixture of alboatrin **3** and *o-methyl alboatrin* **23**, indicating a primary ring cleavage followed by re-cyclisation prior to demethylation. Another aspect of great interest and encouragement that emerged from these observations was that the stereochemistry of the Claisen rearrangement product **20** was irrelevant for the final outcome of the synthesis. Indeed, when a mixture of both the isomers **20a** and **20b** was subjected to the sequence of reactions involving LAH reduction, acid treatment and demethylation, alboatrin **3** was the sole product isolated in an excellent overall yield. To circumvent the problem of epimerisation under Lewis acid conditions, demethylation of **25** was tried with sodium ethyl mercaptide. This afforded the expected *epi*-alboatrin **26**[10] in 86% yield as the only product. ^{1}H NMR spectral data which matched with the reported[5a] values attested to the identity of the product. *epi*-Alboatrin also when treated with BBr_3 under previously stated demethylation conditions fully isomerised to alboatrin.

In summary, we have developed a very efficient and stereocontrolled route to the linear tricyclic network of the xyloketals by employing a diastereoselective Claisen rearrangement and an intramolecular cationic cyclisation as the key steps, and demonstrated their efficacy by applying the methodology to a short, high yield synthesis of the phytotoxic metabolite alboatrin. The synthesis affords the final product in nine steps from the resacetophenone **14** in an overall yield of 44%. A unique case of isomerisation of the *epi* to the natural isomer under Lewis acid conditions has also been observed. It is anticipated that with appropriate modifications in the substitution pattern in the aromatic ring, this route will serve as a convenient access to the xyloketals.

Acknowledgements

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10. All new compounds reported here gave analytical and spectral data consistent with assigned structures. *Selected spectral data:* For **11**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, J = 6.9 Hz, 3H); 2.4 (dd, J = 8.0, 15.6 Hz, 1H); 2.59 (dd, J = 6.6, 15.6 Hz, 1H), 2.65 (dd, J = 6.6, 15.6 Hz, 1H); 2.99 (dd, J = 4.8, 15.6 Hz, 1H); 3.18–3.11 (m, 1H); 4.17 (q, J = 6.9 Hz, 2H); 4.27 (s, 1H); 4.60 (s, 1H); 6.90 (t, J = 7.8 Hz, 2H); 7.04 (d, J = 7.2 Hz, 1H); 7.15 (t, J = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 30.6, 32.7, 37.0, 60.7, 89.8, 115.8, 120.7, 121.5, 127.9, 129.2, 152.4, 157.8, 171.7. For **13**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.58 (s, 3H); 1.73–1.80 (m, 1H); 2.02–2.07 (m, 1H); 2.42–2.48 (m, 1H); 2.79 (d, J = 16.6 Hz, 1H); 3.06 (dd, J = 5.7, 16.6 Hz, 1H); 3.88–4.02 (m, 2H); 6.83–6.89 (m, 2H); 7.06–7.14 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.2, 26.3, 28.8, 41.1, 66.8, 107.1, 117.0, 119.4, 120.7, 127.7, 129.3, 153.4. For **16**: mp 132–134 °C; IR (KBr) ν^{max} 1645 cm^{-1}, 1737 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (t, J = 6.9 Hz, 3H); 2.72 (s, 3H);3.80 (s, 3H); 4.37 (q, J = 6.9 Hz, 2H); 6.66 (s, 1H), 6.77 (s, 1H); 6.88 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 22.9, 55.8, 62.8, 98.8, 116.36, 117.2, 117.4, 142.8, 150.4, 159.5, 160.8, 163.4, 179.4. HRMS (EI) Found: MH$^+$, 263.0928; $C_{14}H_{14}O_5$ requires; MH$^+$ 263.0921. For **17**: IR (Neat) ν^{max} 1732 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H); 2.09 (s, 3H); 3.29 (d, J = 4.2 Hz, 2H); 3.66 (s, 3H); 4.23 (q, J = 7.2 Hz, 2H); 6.13 (t, J = 4.2 Hz, 1H); 6.37 (s, 1H); 6.38 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 19.6, 22.8, 55.7, 61.8, 99.7, 109.4, 110.6, 112.4, 138.3, 141.8, 152.1, 159.2, 162.1. HRMS (ESI) Found: M+Na$^+$, 271.0946; $C_{14}H_{16}O_4$ requires; M+Na$^+$, 271.0946. For **20a**: IR (Neat) ν^{max} 1732 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, J = 6.9 Hz, 3H); 1.26 (t, J = 7.2 Hz, 3H); 2.2 (s, 3H); 2.52–2.57 (m, 1H); 2.70 (d, J = 4.8 Hz, 2H); 2.86–2.89 (m, 1H); 3.74 (s, 3H); 4.10 (q, J = 6.9 Hz, 2H); 4.17 (s, 1H); 4.56 (s, 1H); 6.33 (s, 1H); 6.38 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.5, 15.2, 19.6, 24.1, 39.2, 41.0, 55.6, 60.8, 90.9, 99.1, 110.1, 111.3, 137.8, 153.7 157.3, 159.3, 175.8. HRMS (EI) Found: MH$^+$, 291.1589; $C_{17}H_{22}O_4$ requires; MH$^+$ 291.1598. For **20b**: IR (Neat) 1732 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, J = 6.9 Hz, 3H); 1.24 (t, J = 7.2 Hz, 3H); 2.14 (s, 3H); 2.43–2.47 (m, 1H); 2.61 (dd, J = 2.4, 16.2 Hz, 1H); 2.73 (dd, J = 5.1, 16.2 Hz, 1H); 2.82–2.87 (m, 1H); 3.74 (s, 3H); 4.13 (q, J = 7.2 Hz, 2H); 4.25 (s, 1H); 4.66 (s, 1H); 6.30 (s, 1H); 6.38 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 16.4, 19.4, 26.3, 39.7, 39.8, 55.3, 60.6, 92.7, 98.7, 109.9, 111.1, 138.1, 153.3, 155.4, 158.8, 176.0. For **25**: Colourless solid. Mp 54–55 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (d, J = 6.9 Hz, 3H), 1.51 (s, 3H), 2.21 (s, 3H), 2.43–2.53 (m, 2H); 2.68–2.70 (m, 2H); 3.58 (t, J = 8.1 Hz, 1H), 3.71 (s, 3H), 4.12 (t, J = 8.1 Hz, 1H), 6.29 (d, J = 2.4 Hz, 1H), 6.35 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 19.4, 20.8, 24.3, 35.5, 43.8, 55.2, 74.8, 100.1, 107.9, 109.4, 113.1, 136.8, 155.2, 158.7; HRMS (EI) Found: MH$^+$, 249.1484, $C_{15}H_{20}O_3$ requires 249.1485. For **26**: colourless solid. Mp 145–148 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (d, J = 6.8 Hz, 3H); 1.53 (s, 3H); 2.19 (s, 3H); 2.44–2.55 (m, 2H); 2.68–2.69 (m, 2H); 3.57 (t, J = 6.7 Hz, 1H); 4.12 (t, J = 7.9 Hz, 1H); 5.9 (br s, 1H); 6.32 (s, 1H); 6.35 (d, J = 2.1, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 19.2, 20.6, 24.4, 35.5, 44.0, 74.80, 102.2, 108.1, 110.3, 112.8, 136.8, 155.0, 155.2.
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12. In our paper (Ref. 5), the ^{1} H NMR value for the C-3 secondary methyl protons in (**3**) was mistakenly given as δ 0.89, instead of δ 1.04. See correction, *Tetrahedron* **2008**, *64*, 6809.