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A novel group of allenic hydrocarbons from five Australian (Melolonthine) beetles†

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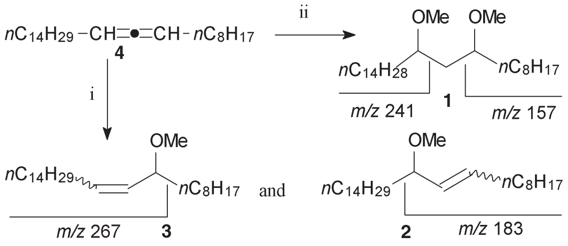
Allenic hydrocarbons, previously unknown as a molecular class from insects, are represented by $CH_3(CH_2)_n$-CH=•=CH-$(CH_2)_7CH_3$ (n = 11–15, 17, 19) in several Australian melolonthine scarab beetles and with demonstrated (R)-chirality when n = 11 and 13.

Melolonthine scarabs are pests of field crops and pastures,[1] and we have undertaken studies of the chemistry of certain sugarcane scarabs from north-eastern Australia. Cuticular hydrocarbons[2] from female adults were of surprisingly limited constitutional variation. In *Antitrogus consanguineus*, one component represents (GC analysis) *ca.* 50% of the cuticular hydrocarbons and this appeared to be a C-25 hydrocarbon with a molecular ion m/z 348 ($C_{25}H_{48}$), confirmed by GCMS-CI analysis. A minor component was the bis-homologue $C_{27}H_{52}$ (M^+, 376). On this basis, both incorporated two degrees of unsaturation.

A methoxymercuration–reductive demercuration ($NaBH_4$) protocol was conducted to locate the sites of unsaturation, with the resulting methyl ether groups guiding the mass spectral fragmentations.[3] This reaction provided a mixture of several mono- and bis-methyl ethers with the two most abundant bis-methyl ethers exhibiting identical mass spectra. These were deduced to be stereoisomers of 9,11-dimethoxypentacosane **1** on the basis of their fragmentations (Scheme 1). Two further components were similarly deduced to be mixtures of stereoisomers of 11-methoxypentacos-9-ene **2** and 9-methoxypentacos-10-ene **3**, resulting from initial mono-methoxymercuration and then reduction. This indicated that the C-25 hydrocarbon was $\Delta^{9,10}$-pentacosadiene **4** (Scheme 1). GC-MS analyses of the methyl ethers resulting from $NaBD_4$ reduction support these conclusions. In the case of bis-ethers **1**, two deuterium atoms were incorporated (*e.g.* M-15 at m/z 399 from m/z 397) but the ions at m/z 241 and 157 were unchanged. This confirms that both Hg atoms became attached to the central carbon of the allene (*i.e.* C-10), so that on reduction 10-$^2H_2$-**1** was formed.



Scheme 1 *Reagents and conditions*: i, $Hg(OAc)_2$–MeOH then $NaBH_4$; ii, as for i (double addition/reduction).

Similarly the minor C-27 component was concluded to be $\Delta^{9,10}$-heptacosadiene **5**, based on the formation of two isomers of 9,11-dimethoxyheptacosane, and also 9-methoxyheptacos-10-ene and 11-methoxyheptacos-9-ene. A more varied mixture of regioisomeric mono- and bis-methyl ethers would be anticipated from both conjugated and non-conjugated dienic hydrocarbons.

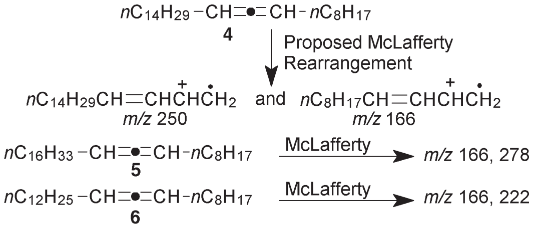
These conclusions were supported by diagnostic ions at m/z 166 and m/z 250 (for the C-25 compound) and m/z 166 and m/z 278 (for the C-27 compound), attributable to McLafferty rearrangement ions, known to appear in the mass spectra of acyclic allenes[4] (Scheme 2).

The major component was partially purified (HPLC:silica–hexane, *ca.* 0.3 mg). The ^1H NMR signal at δ 5.04 (br, m) correlated (HSQC) with the ^{13}C NMR signal at 90.8 ppm, (representing both sp^2-carbons), both signals being consistent with the allene structure. The signal for the central carbon of the allene group (expected ~200 ppm) was not discernible from this dilute sample.[5]

GCMS comparisons established that the C-25 allene **4** was also a minor cuticular component in two other sugarcane beetles, *Lepidiota negatoria* and *Dermolepida albohirtum*. Extracts from *D. albohirtum* and *L. picticollis* contained as a major component an allene with M^+ 320 ($C_{23}H_{44}$) and diagnostic ions at m/z 166 and m/z 222, again indicating 9,10-di-unsaturation. The $\Delta^{9,10}$-tricosadiene structure **6** was proposed for this constituent. When co-injected with a set of standard alkanes, the allenes **4**, **5** and **6** eluted just prior to the corresponding alkane and have equivalent chain lengths of 24.9, 26.9 and 22.9, respectively.

To confirm the identity of these three components, syntheses of **4**, **5** and **6** were then undertaken and a route was developed for delivery of both racemic and enantiomerically enriched systems. Key steps utilised were the 'acetylene zipper' reaction,[6] regioselective addition of $^nBu_3SnH$ to a propargylic alcohol, and *anti* elimination of $^nBu_3SnOMs$ (or $^nBu_3SnOAc$)[7] to install the propa-1,2-diene unit. This approach is shown in Scheme 3 for $\Delta^{9,10}$-pentacosadiene **4**.

Similar approaches furnished the racemic $\Delta^{9,10}$-tricosadiene **6** and $\Delta^{9,10}$-heptacosadiene **5**. GC-MS comparisons, including co-elution studies, established that the natural components were



Scheme 2

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† Electronic supplementary information (ESI) available: analytical data for **4**, **5**, **6** and **9**, and proposed McLafferty rearrangements for **4**. See http://www.rsc.org/suppdata/cc/b1/b101801i/

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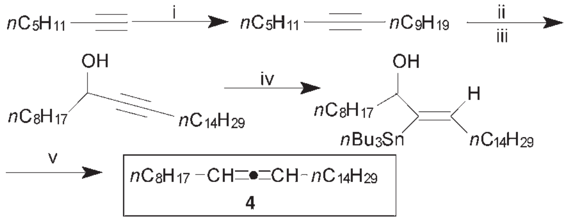
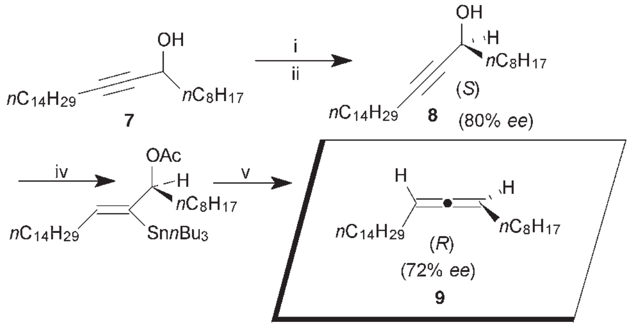


Scheme 3 *Reagents and conditions*: i, *n*BuLi, THF −78 °C/−40 °C then $n\text{C}_9\text{H}_{19}\text{Br}$, HMPA (97%); ii, KH, DAP (79%); iii, *n*BuLi, THF −78 °C/ −40 °C then $n\text{C}_8\text{H}_{17}\text{CHO}$ (51%); iv, $n\text{Bu}_3\text{SnH}$, AIBN 90 °C; v, MsCl, Et_3N (60% from alkynol).

6, **4** and **5**. In the case of the synthesised $\Delta^{9,10}$-pentacosadiene **4**, its ^{1}H and ^{13}C NMR spectra matched precisely the spectra of the natural component.

The chirality of the natural allenes was then addressed. The enantiomers of (±)-$\Delta^{9,10}$-tricosadiene **6** and (±)-$\Delta^{9,10}$-pentacosadiene **4** were base-line separated on a heptakis(6-*O*-*tert*-butyldimethylsilyl-2,3-di-*O*-methyl) β-cyclodextrin column, after *ca*. 160 min at 155 °C and *ca*. 200 min at 165 °C respectively. The natural $\Delta^{9,10}$-pentacosadiene (from *A. consanguineus*) was of high ee, and co-eluted with the first eluting enantiomer of the racemate. This applied also to $\Delta^{9,10}$-tricosadiene from *D. albohirtum*. The present allenes provide remarkable examples of the separation efficacy of these modified cyclodextrin phases.[8]

Nonracemic allenes of known predominating chirality were required next. The C-25 propargylic alcohol **7** (Scheme 4) was first oxidised to the ketone, and reduction with Me-CBS[9] afforded the (*S*)-alcohol **8** (80% ee, Mosher's ester analyses).[10] The predominant configuration was confirmed by converting the alcohol into decane-1,2-diol, whose rotation ($[\alpha]_\text{D}$ −7°; *c*, 0.12, MeOH) may be compared with that for the authentic (*S*)-isomer, ($[\alpha]_\text{D}$ −11.9°; *c*, 0.43, MeOH).[11] The (*S*)-propargylic alcohol **8** was then hydrostannylated, acetylated and treated with TBAF in DMSO to effect *anti*-elimination of $^n\text{Bu}_3\text{SnOAc}$[12] and give the (*R*)-enantiomer, **9** ($[\alpha]_\text{D}$ −17° (*c*, 0.54, CHCl_3)[13] in 72% ee (enantioselective gas chromatography). Co-injection studies established that natural $\Delta^{9,10}$-pentacosadiene in *A. consanguineus* was predominantly the (*R*)-enantiomer (89% ee).



Scheme 4 *Reagents and conditions*: i, TPAP, NMO (82%); ii, (*S*)-MeCBS (2.5 equiv.) $\text{BH}_3{\cdot}\text{SMe}_2$ (5 equiv.) −30 °C 1 h (70%); iii, $n\text{Bu}_3\text{SnH}$ AIBN 90 °C neat; iv, Ac_2O, pyridine (14% from alkynol); v, TBAF, DMSO reflux (77%).

An analogous approach with (*S*)-tricosa-10-yn-9-ol (80% ee) provided predominantly (*R*)-$\Delta^{9,10}$-tricosadiene (77% ee, 36% from the alcohol). Natural $\Delta^{9,10}$-tricosadiene was then shown to be (*R*)-configured with 86% ee. Given the consistency of the location of the $\Delta^{9,10}$-propadiene unit, a predominating (*R*)-chirality is likely for $\Delta^{9,10}$-heptacosadiene, as well.

Examination of males of a further cane beetle species, *L. crinita* has revealed the presence of the higher allene, $\Delta^{9,10}$-hentriacontane, $\text{C}_{31}\text{H}_{60}$ (M^+ = 432 and McLafferty ions at *m*/*z* 334 and 166). A lower level component is $\Delta^{9,10}$-nonacosadiene, the C-29 allene (M^+ = 404, *m*/*z* 306 and 166). Co-occurring with the dominant C-25 allene in *A. consanguineus*, are much lower levels of the *even carbon numbered* $\Delta^{9,10}$-tetracosadiene (M^+ 334, *m*/*z* 246, 166) and $\Delta^{9,10}$-hexacosadiene (M^+ 362, *m*/*z* 264, 166), in the former case confirmed by synthesis.

All allenes identified have $\Delta^{9,10}$-unsaturation, and those odd numbered in carbon are considerably favoured. Administration of labelled potential precursors is being conducted to reveal possible routes to these hydrocarbons. As far as we are aware, allenic hydrocarbons were previously unknown from insects, although the male-produced pheromone of the dried bean beetle (*Acanthoscelides obtectus*) incorporates an allene moiety.[14] The biological role of these compounds is being investigated.

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Notes and references

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