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Absolute Configuration of Sordidin and 7-Episordidin Emitted by the Banana Weevil, *Cosmopolites sordidus*

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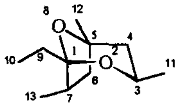
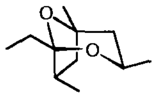
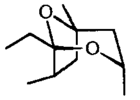
Abstract: Male-specific volatile components released by the banana weevil, *Cosmopolites sordidus* Germar, from Australia have been identified as (1*S*,3*R*,5*R*,7*S*)-1-ethyl-3,5,7-trimethyl-2,8-dioxabicyclo[3.2.1]octane and the 7*R*-epimer (as a minor component) by synthesis and enantioselective gas chromatography.

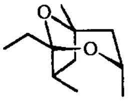
The banana weevil, *Cosmopolites sordidus* Germar is a world-wide pest of banana trees. In 1993, Budenberg[1] reported evidence for a male-produced aggregation pheromone for this species from Africa. The major male-specific volatile component was subsequently isolated by Ducrot[2] in 1995 and identified by spectroscopic evidence and synthesis as (1*S**, 3*R**,5*R**,7*S**)2,8-dioxa-1-ethyl-3,5,7-trimethylbicyclo[3.2.1.]octane **1** with the trivial name 'sordidin'. GC/EAD confirmed the biological activity of **1** and five minor male volatiles, one of which was the C-7 epimer **2**. A synthesis of the racemates of **1** - **4** and the results of some field tests utilising this mixture have also been described.[3] Mori[4] has recently reported a synthesis of (±), (+) and (-)-**1** and determined the absolute stereochemistry of the natural sordidin to be (1*S*,3*R*,5*R*,7*S*).



(1*S*,3*R*,5*R*,7*S*)-**1**


(1*S*,3*R*,5*R*,7*R*)-**2**

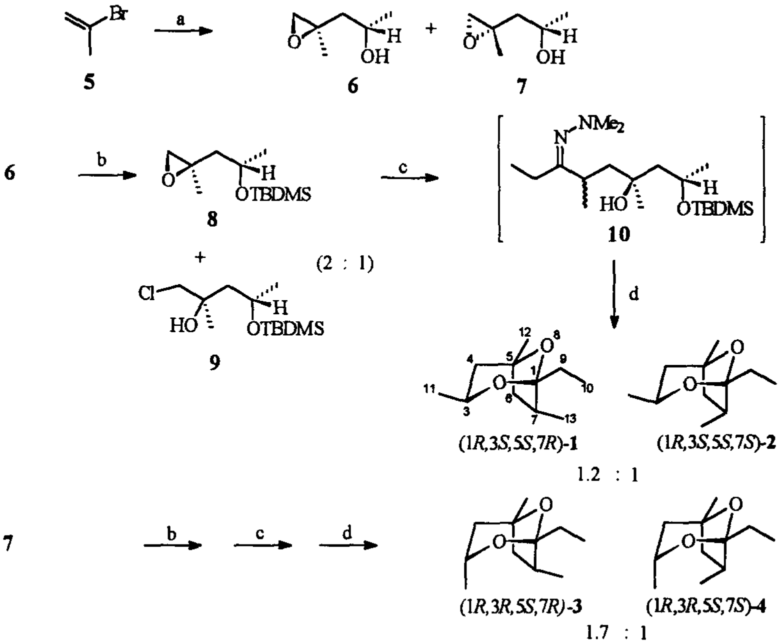

(1*S*,3*S*,5*R*,7*S*)-**3**


(1*S*,3*S*,5*R*,7*R*)-**4**

In this letter we report that male *Cosmopolites sordidus* from Australia also release sordidin but apparently at a substantially lower level than that reported for their African counterparts. We also report a synthesis of (1*R*, 3*S*,5*S*,7*R*)- **1** and its C-7 epimer (1*R*,3*S*,5*S*,7*S*)-**2** which on comparison with insect volatiles confirm Mori's assignment[4] of the absolute stereochemistry for sordidin. The minor stereoisomer-**2** was also detected in the insect volatiles and now shown for the first time to have absolute stereochemistry (1*S*,3*R*,5*R*,7*R*) i.e.7-episordidin.

Volatiles were collected from separated male and female insects using Super Q and Tenax as adsorbent[5] and GCMS analysis showed only low levels of **1** in male volatiles with trace levels of compound **2**. These compounds were not observed in female volatiles. The levels of sordidin were somewhat variable but were always significantly lower than those reported by Ducrot[2] from African weevils. Volatiles collected from male weevils from Alstonville, NSW (subtropical) and from a mixed sex sample from Tully in north Queensland (tropical) showed similar levels of sordidin **1** and also 7-episordidin **2**.

Scheme 1 summarises our synthesis of (1*R*,3*S*,5*S*,7*R*)-**1** and (1*R*,3*S*, 5*S*, 7*S*)-**2**. The Grignard reagent from propenyl bromide **5** was reacted with (*S*)-(-)-propenyl oxide to give (*S*)-pent-1-en-4-ol which was epoxidised with *m*-chloroperbenzoic acid to afford a mixture of epoxyalcohols **6** and **7** (*ca.* 40:60 by ^{13}C NMR). These were separated (HPLC, silica, hexane/ethyl acetate (1:1)) and epoxy alcohol **6** was protected as the corresponding *t*-butyldimethylsilyl ether **8**. Compound **8** partially ring opened during work-up to **9**, from which it was readily separated by silica gel chromatography. Alkylation of 3-pentanone-N',N'-dimethylhydrazone with **8** afforded intermediate **10** which on treatment with *t*-butyl ammonium fluoride induced deprotection and cyclisation to afford a mixture of acetals (1.2:1). These acetals were separated by preparative GC to give (1*R*,3*S*,5*S*,7*R*)-**1** and (1*R*, 3*S*, 5*S*,7*S*)-**2**.[6] The overall yield of the acetal mixture was quite good as indicated by GCMS analysis of the product mixture, but volatility of both the reagents and the products led to significant losses during isolation.



(a)1) 1 eq Mg; 2) 0.1 eq CuI, 0.8 eq (*S*)-(-)-propylene oxide; 3) 1 eq MCPBA (60%). (b) 2.3 eq imidazole, 2.5 eq TBDMSCl, CH_2Cl_2 (ca 50%); (c) 6 eq 3-pentanone N'N'-dimethylhydrazone,n-BuLi, THF (ca 50% by GCMS); (d) TBAF, silica.

Scheme 1

The enantiomeric purity of (1*R*,3*S*,5*S*,7*R*)-**1** (97%ee) and of (1*R*,3*S*,5*S*,7*S*)-**2** (87% ee) were determined by GC analysis using a permethylated β-cyclodextrin column. Comparison with insect volatiles, showed the natural components were (1*S*,3R,5*R*,7*S*)-**1** (>81% ee) and (1*S*,3*R*,5*R*,7*R*)-**2** (>85% ee). Estimates of ee for the natural components were hampered by low levels. Best estimates were obtained from a mixed sex sample of 200 weevils from Tully.

Treatment of epoxyalcohol **7** in a manner similar to that described above for **6**, afforded (1*R*,3*R*,5*S*,7*R*)-**3** and (1*R*,3*R*,5*S*,7*S*)-**4** (1.7:1). The enantiomeric purity of (1*R*,3*R*,5*S*,7*R*)-**3** was estimated to be 98% ee, but the enantiomers of **4** were not resolved on the permethylated β-cyclodextrin column. Compound **3** was tentatively identified as a very minor component in volatiles collected from the mixed sex sample from Tully. Isomer **4** was not observed in any extracts.

Acknowledgements: Banana weevils were kindly provided by Dr Neil Trevorrow, NSW Dept. of Agriculture, Alstonville and Richard Piper, Scientific Advising, Tully. Dr Trevorrow also kindly provided a mixture of racemic acetals (**1**-**4**) for comparison purposes in chiral analysis.

REFERENCES and NOTES

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2. Beauhaire, J.; Ducrot, P.-H.; Malosse, C.; Rochat, D.; Ndiege, I.O.; Otieno, D.O. *Tetrahedron Lett.* **1995**, *36*, 1043-1046. See also, Beauhaire, J.; Ducrot, P.-H. *Bioorganic and Medicinal Chem.* **1996**, *4*, 413. Numbering on our structure **1** differs from that shown in ref 2,3,4 where O-8 was overlooked.
3. Ndiege, I.O.; Jarayaman, S.; Oehlschlager, A.C.; Gonzalez, L.; Albizar, D.; Fallas, M. *Naturwissenschaften*. **1996**, *83*, 280-282.
4. (a) Mori, K.; Nakayama, T.; Takikawa, H. *Tetrahedron Lett.* **1996**, *37*, 3741-3744. (b) Mori, K. *Biosci. Biotech. Biochem.* **1996**, *60*, 1925-1932.
5. Volatiles were collected overnight from 20 - 200 weevil batches at 23 ± 2°C on 200mg Super Q with 60ml/min airflow and eluted with 2ml CH_2Cl_2. Volatiles were similarly collected on 200mg TenaxTA and thermally desorbed directly into a GCMS.
6. Compounds **1** and **2** had MS and ^{13}C and ^1H NMR spectra in agreement with those previously reported.[4] **1** had $[\alpha]_D^{25}$ = -27° (c = 0.013, $CDCl_3$), in good agreement with that (-26°) reported.[4] Compounds **6** - **9** had MS and ^{13}C and ^1H NMR spectra consistent with their structures. **8** $[\alpha]_D^{25}$ = +0.6 (c = 1.6, $CHCl_3$).

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