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SHORT COMMUNICATION

# Synthesis of corn rootworm pheromones from commercial diols

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A mixture of stereoisomers of the corn rootworm pheromones was synthesised via the Grignard coupling of protected bromohydrins with alkylcuprate as a key step. The synthesis of 8-methyldec-2-yl propanoate (*I*), the northern corn rootworm *Diabrotica longicornis* Say pheromone, was achieved from pentane-1,5-diol in four steps with an overall yield of 35.1 % and 10-methyltridecan-2-one (*II*), the southern corn rootworm *Diabrotica undecimpunctata howardi* Barber pheromone, was synthesised from octane-1,8-diol as commercially available starting material in five steps with an overall yield of 28.7 %.

**Keywords:** *Diabrotica longicornis* Say, *Diabrotica undecimpunctata howardi* Barber, Grignard coupling, pheromone, bromohydrin, diol

The northern corn rootworm, *D. longicornis* Say and the southern corn rootworm, *D. undecimpunctata howardi* Barber are widely distributed polyphagous insects found on maize, peanuts, legumes and corns in the North American and Asian continents. Their pheromones are shown in Fig. 1. The sex pheromone of *D. longicornis* Say was isolated and identified by Krysan et al. (1986) as 8-methyldec-2-yl propanoate, with two chiral centres at C-2 and C-8. The (2*S*,8*R*) isomer has proved strongly attractive to males of the insect over the other isomers. Meanwhile, 10-methyltridecan-2-one (*II*) with a chiral centre at C-10 was identified as the sex pheromone of *D. undecimpunctata howardi* Barber by Guss et al. (1983). Males of the beetle exhibited a strong preference for the *R* over the *S* enantiomer.

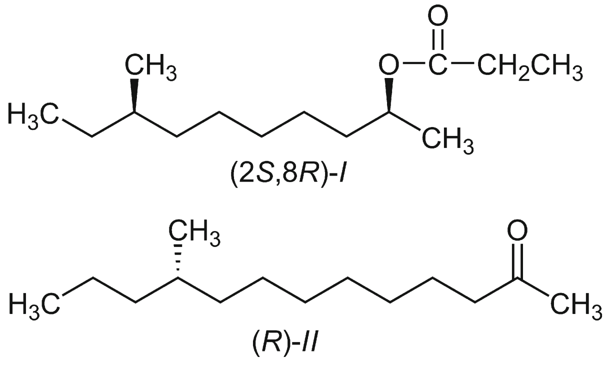

**Fig. 1.** Structures of northern corn rootworm *Diabrotica longicornis* Say (*I*) and southern corn rootworm *Diabrotica undecimpunctata howardi* Barber (*II*) pheromones.

The synthesis of racemic 8-methyldec-2-yl propanoate was first reported from methyl cyclopropyl ketone via seven steps (Guss et al., 1983, 1988) or from nona-1,8-diene (Chow & Kitching, 2001) as the starting material. Mori (2010) introduced four different ways from three to nine steps for the synthesis of racemic 8-methyldec-2-yl propanoate with 19 % to 40 % overall yields. All four isomers of this propanoate system were synthesised by exploiting the selectivity of an alcohol dehydrogenase (TBADH) catalyst in the reduction of nonane-2,8-dione (Keinan et al., 1992). Another enantiomer (2*R*,8*R*) was synthesised by transformations

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*Corresponding author, e-mail: danh5463bd@yahoo.com; dangchihien@gmail.com of the bisepoxides and epoxydiols (Chow & Kitching, 2002).

With the aid of the pheromones, effective and cost-efficient control of the insect populations can be foreseen, hence several total syntheses of the 10-methyltridecan-2-one enantiomer have been published (Rossi et al., 1985; Senda & Mori, 1983; Nguyen et al., 1987). Most recently, (*R*)-*II* was synthesised by an asymmetric Michael addition using enantiomerically pure (4*S*)-benzylthiazolidinethione as a chiral auxiliary (Lu et al., 2009). Shikichi and Mori (2012) employed Grubbs' catalyst efficiently in the synthesis of (*R*)-*II* from (*S*)-3-hydroxy-2-methyl propanoate. The synthesis of racemic 10-ethyltridecan-2-one has been also carried out from methyl cyclopropyl ketone (Guss et al., 1984) or from furan-2-carbaldehyde (Kovalev et al., 1994).

A low-cost method of synthesis is particularly necessary in the practical use of the pheromones. In addition, the data of synergism or inhibition were insufficiently scrutinised when various mixtures of the stereoisomers of the pheromones were tested. Accordingly, it was decided to synthesise a racemic mixture of 8-methyldec-2-yl propanoate and 10-ethyltridecan-2-one for monitoring the population of the insects in Asia, including Vietnam. Herein, an efficient procedure for synthesising two pheromones from commercial diols is reported, using Grignard coupling of the protected bromohydrins as a key step.

All manipulations were performed under a dry nitrogen atmosphere using Schlenk techniques. The starting pentane-1,5-diol and octane-1,8-diol were purchased from Merck (Germany) and other reagents were purchased from Aldrich. THF was dried with Na/benzophenone and freshly distilled prior to use. The other solvents were purchased from Fluka and used without further purification. Column chromatography was performed with Merck Kieselgel 60. IR spectra were recorded on a BRUKER EQUINOX 55 IR spectrophotometer. $^{1}$H (500 MHz) and $^{13}$C (125 MHz) NMR were recorded on a BRUKER AVANCE 500 NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in $\delta$ relative to TMS. GC-MS analyses were carried out using an Agilent Technologies 6890N (USA). Refractive indices ($n_D$) were measured with an ABBE refractometer Way-2S.

2-((5-Bromopentyl)oxy)tetrahydro-2*H*-pyran (*IVa*) (IUPAC name: 2-((5-bromopentyl)oxy)oxan) was prepared following the method reported previously, with a slight modification, as follows: a mixture of pentane-1,5-diol (*IIIa*, 6.76 g, 65 mmol), acetone (40 mL) and HBr (40 %, 11.45 mL, 78 mmol) in petroleum ether (100 mL) was heated under reflux for 4 h using Dean-Stark equipment. The organic layer was separated, hexane (100 mL) was added and the mixture was refluxed continuously for a further 4 h (monitored by GC). This process was repeated four times. The combined organic layers were washed successively with a 5 % aqueous solution of $NaHCO_3$, water and brine and dried with $MgSO_4$. The solvents were evaporated under diminished pressure to afford 8.0 g of the crude product. A mixture of the crude product (6.0 g, 36 mmol), 3,4-dihydro-2*H*-pyran (7.0 g, 70 mmol) and pyridinium *p*-toluenesulphonate (PPTS) (105 mg) in dry dichloromethane (DCM) (21 mL) was stirred overnight. Next, the solution was diluted with ether and washed once with half-saturated brine to remove the catalyst. The ethereal solution was dried, concentrated and the product was distilled under reduced pressure (b.p. 120 ℃/0.8 kPa) to afford a colourless liquid (9.28 g, 64.9 % yield in two steps); $n_D^{28} = 1.4402$.

2-((8-Bromooctyl)oxy)tetrahydro-2*H*-pyran (*IVb*) (IUPAC name: 2-((8-bromooctyl)oxy)oxan was synthesised in the manner reported for *IVa*, using octane-1,8-diol as a starting material (yield 62.5 %; b.p. 158 ℃/0.267 kPa; $n_D^{28} = 1.4420$. The physical and spectral data of *IVa* and *IVb* were in accordance with those already published for authentic samples.

7-Methylnonan-1-ol (*Va*) was synthesised as follows: the Grignard reagent solution obtained from 1-bromo-2-methylbutane (15.1 g, 0.1 mol) and magnesium (2.0 g, 0.1 mol) in anhydrous THF (30 mL) was slowly added drop-wise using a syringe to a solution of (*IVa*) (12.55 g, 50 mmol) in THF (30 mL) containing a catalytic amount of $Li_2CuCl_4$ (0.2 M solution in THF, 10 mL, 2 mmol) at 20 ℃. After stirring overnight at ambient temperature, the mixture was poured into an aqueous solution of $NH_4Cl$ and extracted with diethyl ether. The organic layer was washed with an aqueous solution of $NaHCO_3$, water and brine, then dried with anhydrous $MgSO_4$ and concentrated under reduced pressure to afford 11.0 g of the crude product. A mixture of the crude product (10 g, 41 mmol), *p*-toluenesulphonic acid (PTSA) (300 mg) and methanol (200 mL) was stirred at 50 ℃ for 2 h. The mixture was then concentrated to half-volume, poured into the $NaHCO_3$ solution and the product was extracted with diethyl ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and the solvent was evaporated to afford 7-methylnonan-1-ol (5.83 g, 81.8 % yield in two steps) which was purified by distillation under reduced pressure (b.p. 89 ℃/1.33 kPa; $n_D^{28} = 1.4292$).

9-Methyldodecan-1-ol (*Vb*) was prepared in a similar manner to that reported for *Va*, using *IVb* and 2-bromopentane as a starting material (yield 80.9 %; b.p. 115 ℃/0.533 kPa; $n_D^{29} = 1.4280$).

7-Methylnonanal (*VIa*) was synthesised using a method reported previously (Kovalev et al., 1993), with a slight modification, as follows: a solution of (*Va*) (5.05 g, 32 mmol) in DCM (25 mL) was added to a suspension of pyridinium chlorochromate (PCC) (10.5 g, 48.75 mmol) in anhydrous DCM (50 mL) and

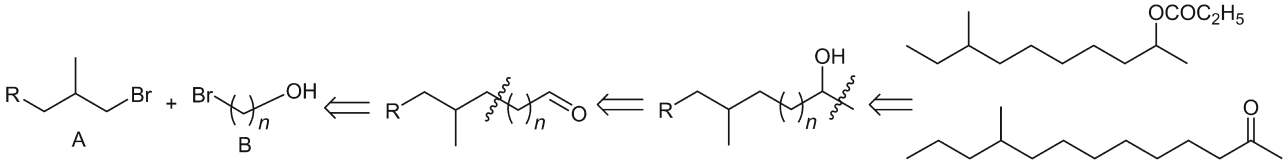

**Fig. 2.** Synthetic strategy of pheromones.

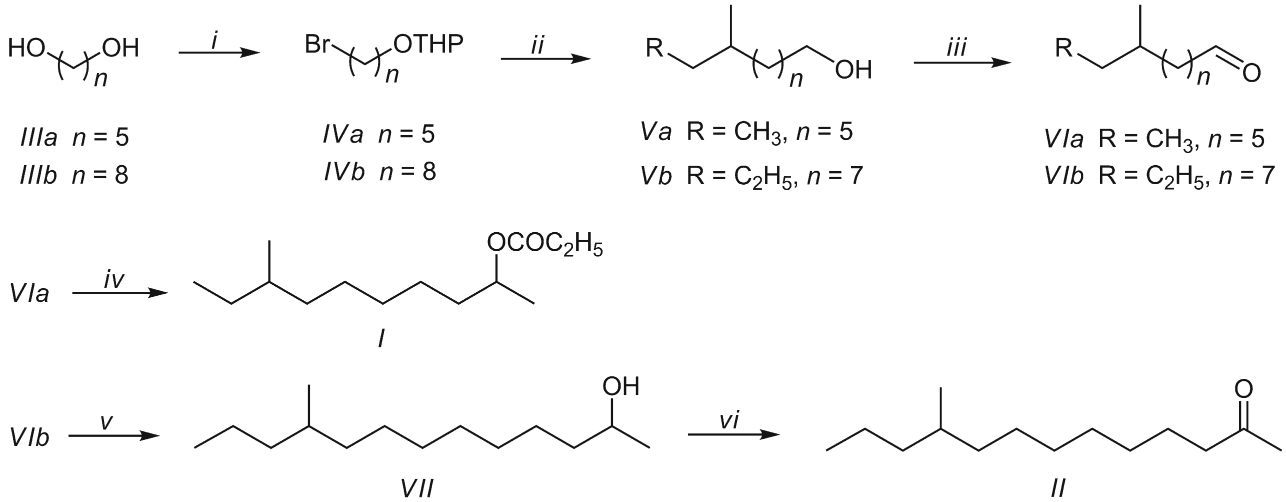

**Fig. 3.** Synthesis of pheromones *I* and *II*. Reaction conditions: *i*) 1. HBr/petroleum ether/acetone, 2. 3,4-dihydro-2*H*-pyran, DCM, PPTS, 4 h; *ii*) 1. Mg, $Li_2CuCl_4$/THF, 0–5 ℃, 1-bromo-2-methylbutane or 2-bromopentane, 2. PTSA, MeOH, 50 ℃; *iii*) PCC, DCM, r.t.; *iv*) 1. $CH_3MgI$/THF, 0 ℃, 2. $(EtCO)_2O$/THF, r.t.; *v*) $CH_3MgI/Et_2O$, 0 ℃; *vi*) Jones reagent.

the mixture was stirred at ambient temperature for 2.5 h (monitored by GC) followed by dilution with hexane (100 mL) and filtration through a short column of silica gel (15 g), using hexane/diethyl ether ($\varphi_r$ = 9 : 1) as eluent. The combined filtrate and eluents were concentrated and the crude product was purified by distillation under reduced pressure to afford *VIa* (4.1 g, 82.1 %; b.p. 88 ℃/1.6 kPa; $n_D^{29} = 1.4218$).

9-Methyldodecanal (*VIb*) was prepared in a similar manner to that reported for *VIa*, using *Vb* as a starting material (yield 81.7 %; b.p. 101 ℃/133.3 Pa; $n_D^{28}$ = 1.4241).

8-Methyldecan-2-yl propanoate (*I*) was synthesised using a method reported previously (Kovalev et al., 1993), with modification follows: a solution of (*VIa*) (3.9 g, 25 mmol) in anhydrous THF (30 mL) cooled to 0 ℃ was slowly added drop-wise using a syringe to the Grignard reagent prepared from methyl iodide (7.1 g, 50 mmol) and magnesium (1.2 g, 50 mmol) in anhydrous THF (30 mL), then the mixture was stirred at ambient temperature for 6 h (monitored by GC). After cooling to 0–5 ℃, propionic anhydride (3.25 g, 25 mmol) in THF (10 mL) was added drop-wise and the mixture was stirred overnight at ambient temperature. The reaction mixture was poured into an aqueous solution of $NH_4Cl$ and the product was extracted with diethyl ether. The combined organic layers were washed with an aqueous solution of $NaHCO_3$, water and brine, dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified on a column of silica gel using hexane/EtOAc ($\varphi_r$ = 5 : 1) to afford *I* (4.6 g, 80.7 %; $n_D^{30} = 1.4230$).

10-Methyltridecan-2-ol (*VII*) was prepared in a similar manner to that reported for *I*, except for the addition of propionic anhydride into the reaction mixture. The yield was 87.9 %; b.p. 84 ℃/66.7 Pa; $n_D^{29.5}$ = 1.4317.

10-Methyltridecan-2-one (*II*) was prepared (79.3 % yield) in the manner reported by Senda and Mori (1983).

The synthetic strategy used is shown by the retrosynthetic analysis outlined in Fig. 2. The important key intermediates of both pheromones are the respective alcohols which have a similar structure. These alcohols can be formed by the Grignard reaction between the respective aldehydes and the Grignard reagent obtained from iodomethane. The aldehydes can be divided into two fragments, fragment A, containing a branched alkyl, and fragment B, containing a functional group. Fragment B can be prepared from commercial diols, pentane-1,5-diol (for the synthesis of *I*) and nonane-1,9-diol (for the synthesis of *II*). However, for the synthesis of *VII*, an economical way was selected designed from octane-1,8-diol and 2-bromopentane.

The synthetic pathway is shown in Fig. 3. The diols were converted to bromohydrins by treating

**Table 1.** Spectral data of prepared compounds

| Compound | Spectral data |
|---|---|
| *I* | IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 726, 772, 807, 878, 922, 1006, 1082, 1126, 1193 (s, C—O), 1274, 1337, 1377, 1462, 1737 (s, C═O), 2858, 2930, 2961<br>$^1$H NMR (500 MHz, $CDCl_3$), $\delta$: 0.79–0.88 (6H, m), 1.13 (3H, t, $J$ = 7.8 Hz), 1.20 (3H, d, $J$ = 6.0 Hz), 1.26–1.65 (13H, m), 2.29 (2H, q, $J$ = 7.5 Hz), 4.87–4.93 (1H, m)<br>$^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$: 9.22, 11.37, 19.19, 19.99, 25.44, 26.98, 27.97, 29.48, 29.81, 34.38, 35.99, 36.52, 70.80, 174.14<br>MS, $m/z$: 228 ($M^+$) |
| *II* | IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 1162, 1359, 1462, 1718, 2855, 2926, 2956<br>$^1$H NMR (500 MHz, $CDCl_3$), $\delta$: 0.84 (3H, d, $J$ = 7.0 Hz), 0.88 (3H, t, $J$ = 7.0 Hz), 1.06–1.40 (17H, m), 2,13 (3H, s), 2.39–2.42 (2H, t, $J$ = 7.5 Hz)<br>$^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$: 14.38, 19.65, 20.13, 23.91, 27.00, 29.20, 29.43, 29.79, 29.81, 32.47, 37.05, 39.42, 43.83, 209.26<br>MS, $m/z$: 212 ($M^+$) |
| *Va* | IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 724, 770, 896, 1057 (s, C—O), 1125, 1205, 1377, 1461, 2856, 2927, 3339 (br, OH)<br>$^1$H NMR (500 MHz, $CDCl_3$), $\delta$: 0.84–0.88 (6H, m), 1.06–1.38 (11H, m), 1.54–1.59 (2H, quint, $J$ = 7.0 Hz), 1.84 (1H, s), 3,63 (2H, t, $J$ = 6.7 Hz)<br>$^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$: 11.36, 19.19, 25.79, 27.05, 29.48, 29.79, 32.80, 34.39, 36.56, 62.98<br>MS, $m/z$: 158 ($M^+$) |
| *Vb* | IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 722, 1056, 1125, 1377, 1463, 2854, 2925, 3338<br>$^1$H NMR (500 MHz, $CDCl_3$), $\delta$: 0.83 (3H, m), 0.88 (3H, d, $J$ = 7.0 Hz), 1.26–1.68 (19H, m), 3.63 (2H, t, $J$ = 7.0 Hz)<br>$^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$: 14.39, 19.66, 20.14, 25.77, 27.05, 29.46, 29.95, 32.49, 32.82, 37.07, 39.44, 63.05<br>MS, $m/z$: 200 ($M^+$) |
| *VIa* | IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 727, 771, 856, 968, 1132, 1378, 1462, 1728 (s, C═O), 2715, 2857, 2929, 2960<br>$^1$H NMR (500 MHz, $CDCl_3$), $\delta$: 0.86–0.9 (6H, m), 1.06–1.67 (11H, m), 2.40–2.43 (2H, dt, $J$ = 1.8 Hz, $J$ = 7.3 Hz), 9.76 (1H, t, $J$ = 1.8 Hz)<br>$^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$: 11.37, 19.17, 22.15, 26.82, 29.47, 29.53, 34.35, 36.37, 43.93, 202.93<br>MS, $m/z$: 156 ($M^+$) |
| *VIb* | IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 723, 1027, 1235, 1389, 1461, 1724, 2854, 2929<br>$^1$H NMR (500 MHz, $CDCl_3$), $\delta$: 0.89 (3H, m), 0.96 (3H, d, $J$ = 7.0 Hz), 1.26–1.68 (17H, m), 2.42 (2H, m), 9.76 (1H, t, $J$ = 1.8 Hz)<br>$^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$: 14.39, 19.65, 20.13, 25.52, 26.97, 29.39, 29.51, 29.77, 32.47, 37.03, 39.41, 43.92, 202.93<br>MS, $m/z$: 198 ($M^+$) |
| *VII* | IR, $\nu_{\text{max}}/\text{cm}^{-1}$: 1118, 1375, 1462, 2854, 2926, 2959, 3356<br>$^1$H NMR (500 MHz, $CDCl_3$), $\delta$: 0.83–0.89 (6H, m), 1.10 (2H, m), 1.18–1.21 (17H, m), 1.41–1.45 (3H, m), 4.05 (1H, m)<br>$^{13}$C NMR (125 MHz, $CDCl_3$), $\delta$: 14.38, 19.64, 20.12, 23.43, 25.78, 27.04, 29.66, 29.94, 29.93, 32.47, 37.06, 39.37, 39.42, 68.14<br>MS, $m/z$: 214 ($M^+$) |

with hydrobromic acid in a mixture of petroleum ether/acetone (Trivedi et al., 1999). These bromohydrins were treated with 3,4-dihydro-2*H*-pyran in DCM to give the corresponding *O*-tetrahydropyranyl-protected alkyl bromides *IVa* or *IVb* with yields of over 60 % in two steps. Next, a coupling between the Grignard reagent prepared from 1-bromo-2-methylbutane or 2-bromopentane with *IVa* or *IVb* was performed as a crucial step. The Grignard coupling reaction was carried out at ambient temperature in the presence of dilithium tetrachlorocuprate followed by detetrahydropyranylation with PTSA in methanol at 50 ℃ to give the corresponding alcohols with yields of over 80 % in two steps. Oxidation of *Va* and *Vb* with PCC afforded the aldehydes *VIa* (82.1 % yield) and *VIb* (81.7 % yield), respectively. Next, a reaction of the Grignard reagent (prepared from iodomethane) with aldehyde *VIb* gave alcohol *VII* with a yield of 87.9 %. Finally, alcohol *VII* was treated with the Jones chromic acid reagent to afford ketone *II* with a yield of 79.3 % while ester *I* was prepared with a yield of 80.7 % following the method devised by Iwamoto et al. (1983) by the reaction of methylmagnesium iodide with aldehyde *VIa* and propionic anhydride in THF.

All products were characterised by IR and NMR spectra (Table 1) which were in accordance with those reported previously (Mori, 2010; Lu et al., 2009).

In conclusion, this work demonstrates a short, simple and efficient synthetic route to a stereoisomer mixture of the sex pheromones. Compounds *I* and *II*, the sex pheromones of *D. longicornis* Say and *D. undecimpunctata howardi* Barber, were synthesised with overall yields of 35.1 % (four steps) and 28.7 % (five steps) calculated on starting pentan-1,5-diol and octan-1,8-diol, respectively. These results contribute to the methodology to further advance the practical use of pheromones as environmentally benign tools for pest control.

## Supplementary data

Supplementary data ($^1$H and $^{13}$C NMR spectra) associated with this article can be found in the online version of this paper (DOI: 10.1515/chempap-2015-0027).

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