

## SYNTHESIS OF SOME ALKENOIC PLANT VOLATILES

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**Abstract.** Synthesis of  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated *trans*-hexenols and *trans*-octenols has been accomplished by the condensation reaction of malonic acid with butyric and capronic aldehydes, respectively, and subsequent reduction of corresponding unsaturated acids by lithium aluminium hydride in diethyl ether. The reactions performed in the polar basic solvent, pyridine, were oriented to producing  $\alpha,\beta$ -unsaturated acids in good yields. In a nonpolar solvent, *p*-xylene, the condensation reaction produced  $\beta,\gamma$ -unsaturated acids in good yield. The synthesized compounds are useful as pest insect attractants in vegetable crops.

**Key words:** green leaf volatiles, hexenols, octenols, condensation reaction, insect attractants, kairomones.

### INTRODUCTION

As part of our research on plant–insect relationships we are interested in the synthesis and field testing of some green leaf volatile components supplemented with kairomone compounds. A variety of 6-carbon alcohols and aldehydes – hexanol, hexanal, (E)-2-hexenol, (Z)-3-hexenol, and (E)-2-hexenal – are formed by oxidative degradation of leaf lipids and referred to as “green leaf volatiles” [1, 2].

These volatile compounds are the major contributors to the characteristic green odour for various plant taxa. It seems reasonable to assume that such volatile compounds are important odour cues to the insect pests of these plants. Some volatile plant kairomones have a practical use as lures to attract insects to traps for monitoring or controlling pest insect populations [3–5].

We made an attempt to elucidate the role of green leaf volatiles in chemical communication and to determine the spectrum of insect species attracted to these compounds. The amount of kairomones released from the traps must be big in order for them to be effective baits for vegetable pests. This means that green leaf volatiles should be synthesized in large quantities. Although the green leaf volatile components have rather simple

and closely related structures, the samples used to determine the attractivity must be of high degree of purity. The procedures utilized in the synthesis of green leaf volatiles must meet strict requirements of high regio- and stereospecificity, they must be simple and efficient in producing good yields of optimally pure compounds.

In this paper we report a general and versatile method for the preparation of *trans*-2- and *trans*-3-alkenols, in which the condensation reaction is the key element. The synthesis of *trans*-alkenols can be accomplished with a simple two-step procedure of good yield. The synthetic route reported here involves the preparation of *trans*-alkenic acids followed by lithium aluminium hydride reduction to the desired alcohols. It has the advantage of being a simple reaction of commercially available inexpensive reagents, such as saturated aldehydes and malonic acid.

The condensation reaction is widely used for carbon-carbon double bond formation. The amine-catalyzed Knoevenagel condensation reactions of aldehydes and active methylene compounds such as malonic acid can be oriented to synthesize  $\alpha,\beta$ - or  $\beta,\gamma$ -unsaturated compounds in a predictable way by modifying the base strength, the catalyst present, and the polarity of the medium [6, 7]. As a result, the condensation of an aldehyde with malonic acid may be dramatically changed by changing the solvent [8]. Therefore, we investigated the reaction of *n*-butyric and capronic aldehydes with malonic acid in polar (Method A) and nonpolar (Method B) basic solvents to synthesize both positional isomers.

The condensation of aldehydes with malonic acid in polar basic solvents such as piperidine and pyridine produces  $\alpha,\beta$ -unsaturated acids [9]. The widely applicable Doebner modification of Knoevenagel condensation in pyridine-piperidine solution using about equal amounts of aldehyde and malonic acid gives products of high stereochemical purity (95–100%) in good yields [9].

Of the numerous synthetic approaches to the  $\beta,\gamma$ -unsaturated acids described in literature we found the Ragoussis' modification [8] for the condensation reaction the most efficient. The reaction of aldehydes with a three-fold molar excess of malonic acid and a catalytic amount of piperidinium acetate in nonpolar solvents, such as xylene, yields  $\beta,\gamma$ -unsaturated acids. The presence of an excess of malonic acid is needed to overbalance the amount of acid, which is self-decomposed when the temperature exceeds 100°C.

## EXPERIMENTAL

### Materials and analysis

**Synthones and solvents.** All aldehydes and solvents were used after distillation. Commercial malonic acid (former SU grade "pure for analysis"),  $\text{LiAlH}_4$ , and inorganic salts were used without further purification.

**Analysis.** All condensation products were analysed after their reduction with lithium aluminium hydride in diethyl ether and distillation in accordance with the standard procedure. The resultant alkenic alcohols were analysed in a gas chromatograph equipped with an FID detector and 2.5 m × 2.5 mm column packed with 5% polyethylene glycol adipate on Inerton Super. The retention times were compared with those for standard compounds (hexanol, E-2-hexanol, E-3-hexanol, and E-2-octenol). The IR spectra showed 3020 cm<sup>-1</sup> (olefinic C—H) and 970–980 cm<sup>-1</sup> (*trans*-olefinic) bonds.

### Condensation reactions. Method A

**E-2-hexenoic acid.** Malonic acid (0.6 mol, 63 g) was dissolved in pyridine (90 ml). After the lightly exothermic reaction completed, *n*-butyric aldehyde (0.5 mol, 36 g) and piperidine (0.05 mol, 4.3 g) were added and the reaction mixture was heated in a water bath until the evolution of CO<sub>2</sub> had stopped (4 h). Then it was cooled and poured into a mixture of ice and concd. HCl to remove pyridine and piperidine. The condensation products were extracted into benzene, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was concentrated in rotary evaporation. The remaining product was purified by distillation to yield 44 g (77%) of E-2-hexenoic acid, b.p. 92–97°C/10 mmHg.

**E-2-octenoic acid.** E-2-octenoic acid was prepared in the manner described above but using *n*-capronic aldehyde (0.5 mol, 50 g) instead of *n*-butyric aldehyde. This condensation yielded 52.6 g (74%) of E-2-octenoic acid, b.p. 156–160°C/20 mmHg.

### Method B

**E-3-hexenoic acid.** Piperidinium acetate (0.04 g) was generated from equimolecular quantities of piperidine and acetic acid. *n*-Butyric aldehyde (0.5 mol, 36 g) was added to a solution of malonic acid (1.5 mol, 156 g) and piperidinium acetate (0.04 g) in *p*-xylene (400 ml) in the reaction apparatus equipped with a Dean-Stark device and with a device to observe the CO<sub>2</sub> evolution. The reaction mixture was heated until the evolution of CO<sub>2</sub> and water had stopped (5 h). The mixture was washed with a saturated aq. NaCl (50 ml), dried with (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was concentrated *in vacuo*. The residue was purified by distillation under reduced pressure to give 20.7 g (36%, lit. 30% [8]) of E-3-hexenoic acid, b.p. 107–108°C/15 mmHg. A repetition of the experiment yielded 23.2 g (41%) of the desired acid.

**E-3-octenoic acid.** E-3-octenoic acid was prepared according to the method described above using *n*-capronic aldehyde (0.5 mol, 50 g) instead

of *n*-butyric aldehyde. This condensation yielded 53.1 g (75%, lit. 70% [8]) of E-3-octenoic acid after distillation, b.p. 136–140°C/10 mmHg. The results of condensation reactions are summarized in Table 1.

Table 1

Condensation reactions of aldehydes with malonic acid

Carbonyl compound	Method	Product	Yield, % <sup>a</sup>	Purity, % <sup>b</sup>	B.p. acid, °C/mmHg	B.p. alc, °C/mmHg
<i>n</i> -Butanal	A	E-2-hexenoic acid	77	91	92–97/10	157–161/760
<i>n</i> -Butanal	B	E-3-hexenoic acid	36–41	88	107–108/15	57–60/10
<i>n</i> -Hexanal	A	E-2-octenoic acid	74	93	156–160/20	77–80/10
<i>n</i> -Hexanal	B	E-3-octenoic acid	75	95	136–140/10	82–85/15

<sup>a</sup> yield of distilled products;

<sup>b</sup> isomeric purity determined in the form of alcohols produced by reducing the acids with LiAlH<sub>4</sub>.

The desired alcohols were obtained by a general lithium aluminium hydride reduction procedure in nearly quantitative yields and purified by distillation. The results of the analysis are presented in Table 2.

Table 2

Isomeric purity of synthesized alcohols

Compound	α,β-unsaturated		β,γ-unsaturated		Saturated
	E-	Z-	E-	Z-	
E-2-hexenol	91	2	4	–	3
E-3-hexenol	7	–	88	3	2
E-2-octenol	93	1	5	–	1
E-3-octenol	3	–	95	1	1

Field experiments

The field experiments were carried out between 25 May and 8 August 1995 in the fields of vegetable crops. Some alkylisothiocyanates, β-phenylethanol, and *n*-valeric acid were also tested. All compounds (0.8 ml) were impregnated into a material called “Wettex” and sealed into plastic bags

before placing them into sticky traps (Atrakon A). The field tests demonstrated that some of the tested baits were attractants or had a synergistic effect for some insect species. The results of the field tests are published elsewhere [10].

## RESULTS AND DISCUSSION

First we investigated the reaction of malonic acid with aldehydes to find out about the effect of different condensation conditions on the distribution of position isomers with the aim of preparing  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated compounds in the purest possible state. The reactions performed in a polar basic solvent, pyridine, were oriented to producing  $\alpha,\beta$ -unsaturated acids in good yields. The condensation of butyric and capronic aldehydes yielded 77% of E-2-hexenoic acid and 74% of E-2-octenoic acid, respectively.

In a nonpolar solvent, *p*-xylene, the condensation reaction produced  $\beta,\gamma$ -unsaturated acids in good yield, e.g. 75% for E-3-octenoic acid. The yield of E-3-hexenoic acid was moderate (36–41%). This result compares well with literature data. The corresponding alcohols were formed in nearly quantitative yields by lithium aluminium hydride reduction of unsaturated acids.

The results of the synthesis of hexenols and octenols suggest that the two condensation modifications used can also be applied to unsaturated compounds of longer C-chains.

The data of the gas-chromatographic analysis of products indicated 88–95% stereo- and positional isomeric purity.

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## MÕNEDE ROHELISE LEHE ALKEENSETE LÖHNAKOMPONENTIDE SÜNTEES

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$\alpha,\beta$ - ja  $\beta,\gamma$ -mitteküllastatud heksenoolid ja oktenoolid valmistati või- ja kapronaldehüüdi kondensatsioonil maloonhappega ning saadud produktide järgneval taandamisel liitiumalumiiniumhüdriidiga dietüületris. Polaarse aluselises solvendis (püridiin) toimunud reaktsiooni puhul saadi  $\alpha,\beta$ -mitteküllastatud ühendid, mittepolaarse solvendi (*p*-ksüleen) korral on kondensatsiooniproduktiks  $\beta,\gamma$ -mitteküllastatud ühendid. Heksenooli ja oktenooli nimetatud isomeerid on ebastabiilsed, seismisel moodustuvad nii kondensatsiooniproduktid kui ka vastasisomeerid. Seetõttu on kirjeldatud lihtne ning mugav sünteesimeetod hädavajalik, kui ühendeid kasutatakse kairomoonidena putuka ja taime kommunikatsiooni uurimisel või praktilises taimekaitstes kahjurputukate indikatsiooniks.