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A facile synthesis of (*E*)-2-hexenyl (*E*)-2- hexenoate and (*E*)-2-hexenyl (*Z*)-3-hexenoate, pheromone components of *Riptortus pedestris*

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Abstract We investigated optimal condition for synthesis of (*E*)-2-hexenyl (*E*)-2-hexenoate (**1**) and (*E*)-2-hexenyl (*Z*)-3-hexenoate (**2**), the pheromone components of *Riptortus pedestris*, by Steglich esterification. The reaction with 1.1-1.5 equivalent of dicyclohexylcarbodiimide (DCC), 1.5-2.0 equivalent of (*E*)-2-hexenol, and 0.1 equivalent 4-dimethylaminopyrinde (DMAP) to (*E*)-2-hexenoic acid in toluene or (*Z*)-3-hexenoic acid in dichloromethane led **1** and **2** in 76-78% and 87-91% yield, respectively.

Key words (*E*)-2-hexenyl (*E*)-2-hexenoate, (*E*)-2-hexenyl (*Z*)-3-hexenoate, Steglich esterification, Pheromone, *Riptortus pedestris*

Introduction

The bean bug, *Riptortus pedestris* (= *R. clavatus*) (Hemiptera: Alydidae) is one of the most important pests of soybean in Korea and Japan and sweet persimmon in Korea (Chung *et al.*, 1995; Wada *et al.*, 2006). Since its aggregation pheromones, (*E*)-2-hexenyl (*E*)-2-hexenoate (**1**), (*E*)-2-hexenyl (*Z*)-3-hexenoate (**2**), tetradecyl isobutyrate, and octadecyl isobutyrate have been identified (Leal *et al.*, 1995; Yasuda *et al.*, 2007), the pheromone mixture is applied to 'attract and kill' method for managing the pest.

The ester **1** is also used as an attractant to pest *Piezodorus hybneri* (Hemiptera: Pentatomidae) (Endo *et al.*, 2006; Huh *et al.*, 2006) and the ester **2** acts as a pheromone of *R. serripes* (Aldrich *et al.*, 1993) and for a kairomone of *Ooencyrtus nezarae* (Hymenoptera: Encyrtidae) (Mizutani *et al.*, 1997; Son *et al.*, 2009), which is an egg parasitoid of *R. pedestris*. Therefore, utilization of the esters **1** and **2** for pest management is expected to be very high.

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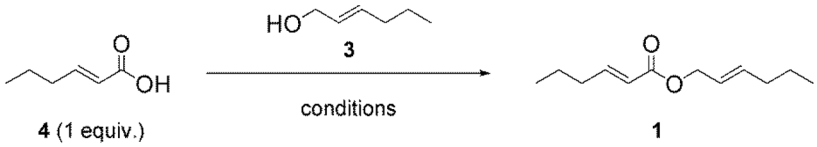
The previously reported syntheses of ester **1** and **2** were mainly based on the esterification of (*E*)-2-hexenol (**3**) with the corresponding acyl chlorides which were derived from (*E*)-2-hexenoic acid (**4**) and (*Z*)-3-hexenoic acid (**5**) with oxalyl chloride, respectively (Leal *et al.*, 1995; Huh *et al.*, 2005). The one-pot preparation by Mitsunobu reaction in the presence of triphenylphospine and diethyl azodicarboxylate (DEAD) was also reported (Muto, 2011). Although these synthetic procedures gave good yield, esterification via acyl chloride was needed 2 steps preparation which carcinogenic benzene was used as a solvent, and Mitsunobu esterification was needed relative expensive reagent-e.g., DEAD. Therefore, a much simpler and cost-saving method, of greater efficiency, for the synthesis of **1** and **2** has been required for mass production.

We have searched for a new synthetic strategy with high yield, short preparation time, and cost-saving preparation. Steglich esterification is one of good candidate for such a condition, since it prepares ester with cheap reagent in one step with efficiency (Neises and Steglich, 1978). However, it has not yet applied to synthesis of **1** and **2**.

In the present work, we report the one-pot synthesis of (*E*)-2-hexenyl (*E*)-2-hexenoate (**1**) and (*E*)-2-hexenyl (*Z*)-3-

Table 1. Reaction conditions for one-pot synthesis of (*E*)-2-hexenyl (*E*)-2-hexenoate (**1**)



Entry	Pyridine (equiv.)	DCC (equiv.)	DMAP (equiv.)	**3** (equiv.)	Solvent	Time	Temp.	Purity[1] (%)	Yield (%)
1	0	1.1	1.0	2.0	CH_2Cl_2	3 h	rt	95.6	54
2	0	1.1	0.1	2.0	CH_2Cl_2	3 h	rt	95.6	67
3	0	1.5	0.1	2.0	CH_2Cl_2	3 h	rt	96.0	71
4	0	1.1	0.1	1.5	CH_2Cl_2	3 h	rt	94.7	66
5	0	1.5	0.1	1.5	CH_2Cl_2	3 h	rt	95.3	74
6	1.0	1.1	0.1	2.0	CH_2Cl_2	3 h	rt	94.6	70
7	1.0	1.5	0.1	2.0	CH_2Cl_2	3 h	rt	96.1	65
8	1.0	1.1	0.1	1.5	CH_2Cl_2	3 h	rt	95.9	60
9	1.0	1.5	0.1	1.5	CH_2Cl_2	3 h	rt	92.7	67
10	1.0	1.1	0.1	2.0	CH_2Cl_2	18 h	rt	95.2	75
11	0.0	1.1	0.1	2.0	CH_2Cl_2	18 h	rt	95.2	78
12	1.0	1.1	0.1	1.0	CH_2Cl_2	3 h	rt	89.2	59
13	1.0	1.1	0.1	2.0	CH_2Cl_2	3 h	reflux	87.4	62
14	0	1.1	0.1	2.0	diethyl ether	3 h	rt	93.5	58
15	0	1.5	0.1	2.0	diethyl ether	3 h	rt	96.6	58
16	0	1.1	0.1	1.5	diethyl ether	3 h	rt	95.3	56
17	0	1.5	0.1	1.5	diethyl ether	3 h	rt	96.1	56
18	0	1.1	0.1	2.0	toluene	3 h	rt	96.2	78
19	0	1.5	0.1	2.0	toluene	3 h	rt	95.7	76
20	0	1.1	0.1	1.5	toluene	3 h	rt	97.0	77
21	0	1.5	0.1	1.5	toluene	3 h	rt	95.7	77

[1]Purity was determined by GC-FID.

hexenoate (**2**) in the various conditions to explore optimal reaction condition of using 4-dimethylaminopyrinde (DMAP), dicyclohexylcarbodiimide (DCC), and alcohol **3** (Table 1).

When 1.0 equiv. of DMAP was used, the reaction gave 54% yield (entry 1). The yields were improved to 67% by reducing the proportion of DMAP to 0.1 equiv. (entry 2). Therefore, 0.1 equiv. of DMAP was applied for investigation of optimal condition. Under this condition, we have studied the influence of various parameters, as shown in Table 1. The reaction condition with 1.5 equiv. of DCC and 1.5 or 2.0 equiv. of alcohol gave moderate yield (65-74%), regardless the presence of pyridine (entries 2-11). These suggested that pyridine did not participate in the reaction. Whereas the reaction condition with 1.1 equiv. DCC and 1.5 equiv. of alcohol gave relatively lower yield (entries 4 and 8). Longer reaction time little bit increased the yield (entries 10 and 11). Heating or low amount of alcohol **3** (1.0 equiv.) led to lower yield and purities (entries 12 and 13). To investigate the solvent effect, diethyl ether and toluene were also used as solvent. In case of diethyl ether, the yields were 56-58% (entries 14-17). Whereas toluene was used, it was shown 76-78% yield (entries 18-21). To prepare the ester **1** in convenience, the anhydrous solvent was not used in these experiments. The lower yield used diethyl ether as a solvent seems to be result from the content of water in diethyl ether.

The ester **2** could be prepared at a high yield of 87-91% using 1.1-1.5 equiv. of DCC and 1.5-2.0 equiv. of alcohol **3** in dichloromethane (same conditions to entry 2-5).

In conclusion, esters **1** and **2** were satisfactorily prepared by Steglich esterification with 1 equiv. of acid, 1.1-1.5 equiv. of DCC, 1.5-2.0 equiv of alcohol and 0.1 equiv. of DMAP in toluene or CH_2Cl_2. By using cheap reagent, DCC, and

shortening the reaction procedure, this method can provide cost-saving preparation of **1** and **2**.

Synthesis

To mixture of hexenoic acid 1.14 g (**4** or **5**; 10 mmol) and alcohol **3** in a solvent (40 mL), DMAP was added at 0°C. Dropwise addition of DCC in CH_2Cl_2 (15 mL) was followed. The mixture was stirred for 1 h at 0°C while gradually white precipitate was formed. The temperature was raised to room temperature and the reaction mixture was stirred for further 3 h at the temperature. The formed dicyclohexylurea was removed by filtration and the filtrate was diluted with 150 mL of diethyl ether. After usual workup, the ester was purified by column chromatography on silica gel (eluent – ether/hexane = 1/50). Spectral data were coincided with previous report (Huh *et al.*, 2005).

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톱다리개미허리노린재 페로몬, (*E*)-2-hexenyl (*E*)-2-hexenoate과 (*E*)-2-hexenyl (*Z*)-3-hexenoate의 합성

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요 약 톱다리개미허리노린재의 페로몬 성분인 (*E*)-2-hexenyl (*E*)-2-hexenoate (**1**) 과 (*E*)-2-hexenyl (*Z*)-3-hexenoate (**2**)의 합성에 있어 Steglich 에스테르화 반응의 최적 조건을 검토하였다. (*E*)-2-헥센산 또는 (*Z*)-3-헥센산에 대하여 1-1.5 당량의 디사이클로카보다이이미드 (DCC), 1.5-2.0 당량의 (*E*)-2-헥센놀과 0.1 당량의 4-디메틸아미노피리딘(DMAP)과 반응하였을 때, 각각 76-78% 와 87-91%의 수율로 **1**과 **2**를 얻었다.

색인어 (*E*)-2-hexenyl (*E*)-2-hexenoate, (*E*)-2-hexenyl (*Z*)-3-hexenoate, Steglich esterification, Pheromone, 톱다리개미허리노린재