of R_M is likely to reflect qualitatively the relative strength of the interaction between cation and ClO_4^- ion rather than an average number of ClO_4^- ion around the metal ion in the resin phase, since a part of the metal ion absorption is expected to associate with the sulfonate group, which is caused by resin shrinkage and dehydration of the metal ion. In fact, there is appreciable difference between the absorption spectra of either Nd^{3+} or U^{4+} in the resin phase in contact with concentrated $HClO_4$ and the spectra of those ions in resin in dilute $HClO_4$, the latter spectra being the same as those of the ions in the aqueous phase at either high a low acidity[4]. The difference in the absorption spectra additionally supports the conclusion that ClO_4^- ion associates with metal ions in the resin phase. The results observed in this work, however, would not allow for the differentiation whether the association results in a simple ion-pair[1] as $M(H_2O)_x^{n+}$-ClO_4^- and/or complex of diffent kind.

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A Convergent Synthesis of (Z)-13-Octadecen-l-yl acetate, the Pheromone Mimic of the Rice Leaf Folder Moth and Its Biological Activity Test

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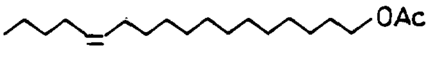
(Z)-13-Octadecen-l-yl acetate, the pheromone mimic of the Rice Leaf Folder Moth, Cnaphalocrosis medinalis, was synthesized from 1,13-tridecanediol in three steps. Monoacetylation of 1,13-tridecanediol followed by PCC oxidation gave 13-acetoxytridecan-l-al. Wittig olefination of the 13-acetoxytridecan-l-al with pentylidenetriphenylphosphonium ylide afforded (Z)-13-octadecen-l-yl acetate, the pheromone mimic of the Rice Leaf Folder.

Introduction

Rice Leaf Folder, Cnaphalocrosis medinalis, is an economic pest of the rice in Korea and China. In 1979, Arida[1] reported that (Z)-octadecen-l-yl actate (1) (Figure 1) is a component of the pheromone mimic of the Rice Leaf Folder, Cnaphalocrosis medinalis.

Generally, since pheromonal activity is sensitive to insect species, place, and climate, Department Entomology, Institute of Agricultural Sceience in Suwon, Korea needed a fair amount of the pheromone mimic of the Rice Leaf Folder Moth to conduct biological activity test.

Here we wish to report a convergent synthesis of (Z)-13-octadecen-l-yl acetate (1), the pheromone mimiç of the Rice Leaf Folder and biological activity test as attractants for males of the Rice Leaf Folder Foth.



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(Z)-13-Octadecen-1-yl acetate

Figure 1. (Z)-13-Octadecen-1-yl acetate.

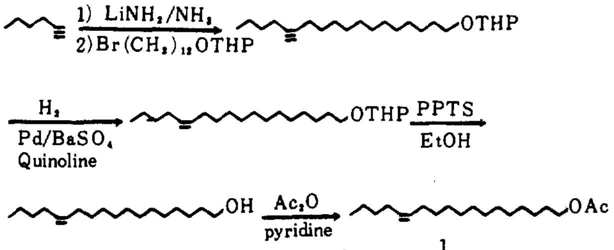
Results and Discussion

The component of the pheromone mimic (1) was synthesized by the conventional actylenic route[2] starting from l-hexyne (Scheme 1).

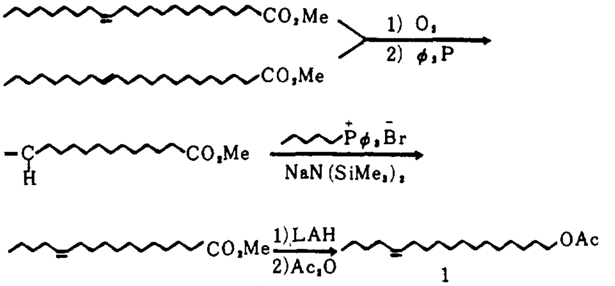
In 1979, Bestmann *et al*[3] reported that a synthesis of (Z)-13-octadecen-l-yl acetate (1) by Wittig olefination of methyl 13-oxotridecanoate with pentylidenetriphenylphosphonium ylide and the subsequent conversion of the resulting methyl (Z)-13-octadecenoate into the compound (1) (Scheme 2).

We have developed the following convergent and cost-effective synthetic method for the synthesis of (Z)-13-octadecen-l-yl acetate (1) from 13-tridecanediol in three steps.

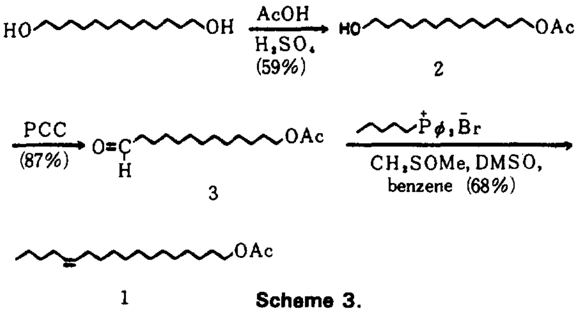
Monoacetylation of 1,13-tridecanediol[4] was effected by heating with acetic acid and sulfuric acid in cyclohexane as two phase system afforded 13-acetoxytridecan-l-ol (2) without any diacetate formed or starting diol remained. PCC oxidation[5] of the monoacetate (2) gave 13-acetoxytridecan-l-al (3) in 87% yield. Wittig olefination reaction[6] of 13-acetoxytridecan-l-al (3) with pentylidenetriphenylphosphonium ylide generated in situ by dimsyl sodium in the presence of DMSO and benzene afforded (Z)-13-octadecen-l-yl acetate (1) (Scheme 3).



Scheme 1.



Scheme 2.



Scheme 3.

Biological Activity Test

Field test was conducted in Haenam-gun, Chun-nam in Korea to establish that the synthetic pheromone mimic was attractive to males of the Rice Leaf Folder Moth. Pheromone vials of A and B traps at a concentration of 50μg per polyethlene capsule were tested from June 10 to Sept 30, 1983 using water traps with covers.

From the above results (Table 1), 3 peaks were observed in the pheromone trap throughout crop growing season of 1983. The first peak was in mid June, the second in late July, and the third from late August to early September. The male moths were first entrapped by the pheromone on the 11th, June and the last one was captured on the 30th, September. However, the amount of the male moth caught in pheromone traps was low.

Those data on each trap catches provide effective informations on the timely application of agricultural chemicals to eradicate these species.

Experimental

Infrared spectra were recorded with Shimadzu IR-440 spectrophotometer. Proton NMR were taken on a BRUKER WP 80 SY 80MH$_z$ NMR spectrophotometer, using tetramethylsilane as an internal reference. All solvents and liquids were distilled before use.

13-Acetoxytridecan-l-ol (2). To 1,13-Tridecanediol (0.71g) in cyclohexane (30m*l*) was added acetic acid (15m*l*), water (20m*l*), sulfuric acid (0.05m*l*). The reaction mixture was heated to 50-55°C for 5hr. After cooling, the cyclohexane layer was washed with water and 5% sodium hydrogen carbonate solution and again water. The organic layer was dried over anhydrous potassium carbonate, and concentrated in vacuo to give pure 13-acetoxytridecan-l-ol (2) (0.50g, 59%). IR cm^{-1}: 3300, 2900, 1730. NMR δ: 1.30-1.80 (22H, m), 2.05(3H, *s*), 3.65(2H, *t*), 4.10(2H, *t*).

13-Acetoxytridecan-l-al (3). To a solution of pyridinum chlorochromate (0.45g) in dichlorometane (5m*l*) was added 13-acetoxytridecan-l-ol (0.44g). The reaction mixture was stirred at room temperature for 2hr. The organic layer was extracted

TABLE 1: The Attracted Numbers of the Males of the Rice Leaf Folder Moth for the Synthetic Pheromone

Date	A	B	Date	A	B
6.5-6.10	3	1	8.6-8.10	1	0
6.11-6.15	3	2	8.11-8.15	1	0
6.16-6.20	1	0	8.16-8.20	0	0
6.21-6.25	0	1	8.21-8.25	0	0
6.26-6.30	0	0	8.26-8.31	3	4
7.1-7.5	0	0	9.1-9.5	2	1
7.6-7.10	0	0	9.6-9.10	3	2
7.11-7.15	0	0	9.11-9.15	1	1
7.16-7.20	3	1	9.16-9.20	0	0
7.21-7.25	2	2	9.21-9.25	0	0
7.26-7.31	3	2	9.26-9.30	2	1
8.1-8.5	0	0	Total	28	18

with ether, and filtered through alumina bed. The filtrate was washed with saturated sodium chloride, and dried over anhydrous sodium sulfate, and concentrated in vacuo to give 13-acetoxytridecan-l-al (3) (0.38g, 87%). IR cm^{-1}: 2900, 2750, 1730, 1220. NMR δ: 1.30-1.75 (20H, m), 2.05 (3H, s), 2.40 (2H, *t*), 4.10 (2H, *t*), 9.80 (1H, *t*).

(Z)-13-Octadecen-l-yl acetate (1). To sodium hydride (free of oil : 0.03g) was added dimethyl sulfoxide (3 m*l*), and slowly heated for 1 hr under nitrogen atomosphere. After cooling, to the reaction mixture was added pentylidenetriphenylphosphonium bromide (0.51g) in DMSO (2m*l*) at room temperature. To the reaction mixture was added 13-acetoxytridecan-l-al (3, 0.10g) in DMSO (1 m*l*) and diluted with dry benzene (5 m*l*). The reaction mixture was stirred at room temperature for 3hr and added to water (20m*l*) and extracted with ether: n-hexane (1:1). The organic layer was separated and washed with water and dried over anhydrous magnesium sulfate, and concentrated in vacno, and separated by flash column chromatography using ether: petroleum ether (1:1) as eluent to give (Z)-13-octadecen-l-yl acetate (1) (0.08g, 68%). IR cm^{-1}: 2900, 1750, 1460, 1240, 1040. NMR δ: 0.90 (3H, s), 1.30-1.70 (28, *m*), 2.05 (3H, *s*), 4.05 (2H, *t*), 5.35(2H, *t*).

Field Test. Pheromone vials at a concentration of 50 μg of (Z)-13-octadecen-l-yl acetate (l) per polyethylene capsule were tested in the paddy field of Haenam area. The traps used in these tests were circular water pan (30D × 27H) with 2 rectangular windows (4 × 20cm). Polyethylene vials were held 4-6cm above the water surface of the trap. The traps consisted of trap cover to shade the bait. Water in the traps was treated with dilute detergent solution to increase the trap catch. The insects caught in these traps were counted and checked every 5 days. Blank test has been done with traps without pheromone vials.

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Kinetics of the Zn(II)-Catalyzed Hydrolysis of 2-Acetylpyridineketoximyl Diphenyl Phosphate

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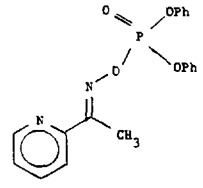
Kinetic data of the Zn(II) ion-catalyzed hydrolysis of 2-acetylpyridineketoximyl acetate (*S*) are measured. The reaction proceeds through the accumulation of an intermediate (*I*). 2-Acetylpyridineketoxime (Ox) is released in the breakdown step of *I*. Phenol is not formed as a part of the products, and, therefore, diphenyl phosphate and *Ox* are produced by the breakdown of *I*. Based on the dependence of the rates for the formation and the breakdown of *I* on [Zn(II)] and pH, and considering the UV spectral properties of *I*, the structure of *I* is tentatively assigned as the penta-covalent intermediate formed by the addition of a water molecule to *S*.

Studies on the metal ion-catalyzed reactions of organic compounds have revealed many important catalytic principles.[1,2] In addition, these systems serve as models for metalloenzymes and have proposed catalytic roles of the active-site metal ions. For example, our studies on the Zn(II) or Cu(II)-catalyzed hydrolysis of esters derived from pyridyl oximes disclosed several new catalytic features.[3-7] Moreover, mechanistic data obtained previously for the action of carboxypeptidase A, a metallo-exopeptidase, have been reinterpreted in terms of the catalytic roles disclosed by the model study with the oxime esters.[4,5].

Hydrolysis of phosphate esters is a biologically important reaction.[8-10] We have extended our study to the metal ion-catalyzed hydrolysis of 2-acetylpyridineketoximyl diphenyl phosphate (*S*) in an attempt to understand the catalytic roles of metal ions in both enzymatic and nonenzymatic phosphate hydrolysis. A typical metallo-phosphatase is alkaline phosphatase.[11]



(*S*)