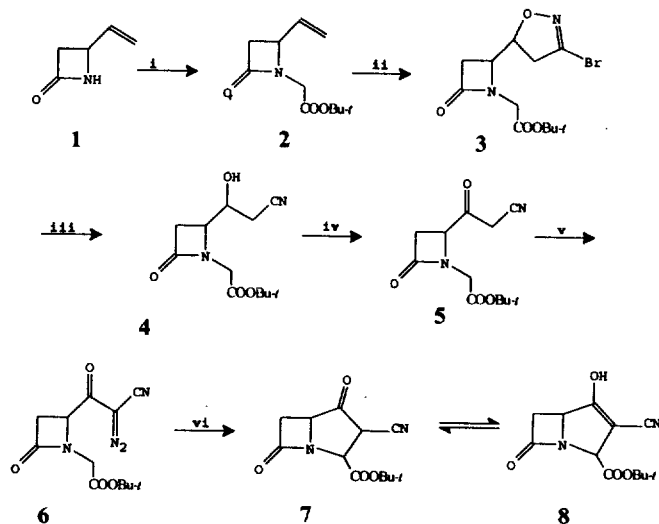


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 6. Spectral data of **5a**: ^1H NMR (200 MHz, CDCl_3) δ 0.15 (s, 9H), 1.84 (d, $J=1.6$ Hz, 3H), 2.75 (bs, 2H), 3.50 (dd, $J=1.6, 3.5$ Hz, 1H), 5.17 (m, 1H), 6.85-7.95 (m, 4H); Ms (m/z): M^+ 272 (92), $M^+ + 1$ (65), $M^+ + 2$ (22), 257 (96), 183 (78).
 Spectral data of **5b**: ^1H NMR (200 MHz, CDCl_3) δ 1.81 (t, 3H), 2.65 (dd, 2H), 2.90 (dd, 2H), 4.55 (m, 1H), 7.01-7.84 (m, 4H); Ms (m/z): M^+ 200 (75), $M^+ + 1$ (48), $M^+ + 2$ (50), 185 (62), 72 (83).
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i) LiHMDS, THF, -78°C ; $\text{BrCH}_2\text{COOtBu}$, rt; ii) $\text{Br}_2\text{C}=\text{NOH}$, NaHCO_3 , EtOAc , rt; iii) EtSnA , MeOH , 0°C ; iv) Jones reagent, acetone, 0°C ; v) Et_3N , TsN_3 , acetonitrile, rt; vi) $\text{Rh}_2(\text{OAc})_4$, benzene, reflux.

Scheme 1.

chromatography.

A β -hydroxy nitrile **4**, 1-[(*t*-butoxycarbonyl)methyl]-4-(2-cyano-1-hydroxyethyl)-2-azetidinone, was obtained in 68% yield from compound **3** by treatment of sodium ethanethiolate (1.1 eq.) in methanol. Compound **4** showed bands for a hydroxy group and a cyano group at 3450 and 2250 cm^{-1} , respectively. Compound **4** was oxidized to 1-[(*t*-butoxycarbonyl)methyl]-4-(2-cyano-1-oxoethyl)-2-azetidinone (**5**) with Jones reagent in acetone in 74% yield. The oxidized product showed no hydroxy band in its ir spectrum but two strong carbonyl (a β -lactam carbonyl and an ester carbonyl) bands around 1700 - 1750 cm^{-1} were observed. Diazotization of this compound by following the Regitz method⁴ ($\text{TsN}_3/\text{Et}_3\text{N}$, acetonitrile, 25 - 35°C) gave 1-[(*t*-butoxycarbonyl)methyl]-4-(2-cyano-2-diazo-1-oxoethyl)-2-azetidinone (**6**) in 84% yield. The diazo compound **6** showed bands at 2250 and 2140 cm^{-1} for the cyano group and the diazo group, respectively. Refluxing of the benzene solution of compound **6** with rhodium acetate (cat. amount) for 12 hours gave 1-oxocarbapenam **7**, *t*-butyl 2-cyano-1-oxocarbapenam-3-carboxylate, in 52% yield. The 1-oxocarbapenam was unstable and decomposed slowly at room temperature.⁵ It showed a band at 1775 cm^{-1} for a β -lactam carbonyl group and at 1720 cm^{-1} for an ester carbonyl group. In the ir spectrum, it showed a hydroxy group band at 3400 cm^{-1} , which might imply the existence of an enol tautomer (**8**).

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Synthesis of 2-Cyano-1-oxocarbapenam-3-carboxylate

Min Hyo Seo, Youn Young Lee*, and Yang Mo Goo[†]

Department of Chemistry, Seoul National University,
Seoul 151-742, Korea

[†]Department of Pharmacy, Seoul National University,
Seoul 151-742, Korea

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Recently we found that when 3-bromo-2-isoxazolines were treated with sodium ethanethiolate, they could be converted effectively to β -hydroxy nitriles.¹ 3-Bromo-2-isoxazolines can be obtained easily from alkenes by treatment of bromonitrile oxide.² We adapted this reaction for the synthesis of an 1-oxocarbapenam derivative. Thus, we wish to report here the conversion of 4-vinyl-2-azetidinone to 1-oxocarbapenam.

4-Vinyl-2-azetidinone (**1**) was synthesized from 1,3-butadiene by reaction with chlorosulfonyl isocyanate.³ 1-[(*t*-Butoxycarbonyl)methyl]-4-vinyl-2-azetidinone (**2**) was obtained from 4-vinyl-2-azetidinone (**1**) by reaction with *t*-butyl bromoacetate in the presence of LiHMDS in THF at -78°C (yield: 83%). It was converted to 4-(3-bromo-2-isoxazolin-5-yl)-1-[(*t*-butoxycarbonyl)methyl]-2-azetidinone (**3**) in the yield of 86% by reaction with dibromoaldoxime in ethyl acetate in the presence of sodium bicarbonate (1.5 eq.) and a small amount of water. The intensities of two doublets at 3.23 and 4.03 ppm ($J=18.0$ Hz) and two doublets at 3.72 and 4.12 ppm ($J=18.0$ Hz) in the ^1H NMR spectrum of compound **3** implies that it is a mixture of two diastereomers (6:4). The two isomers could not be separated by column

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5. The 1-oxocarbapenam should be purified rapidly. It can be stored in refrigerator under nitrogen atmosphere for a week.
6. ² ¹H NMR (CDCl₃) δ 1.48 (s, 9H, *t*-Bu), 2.72 (dd, 1H, *J*=14.6, 2.3 Hz, H-3), 3.26 (dd, 1H, *J*=14.6, 5.1 Hz, H-3), 3.50 (d, 1H, *J*=18.4 Hz, NCH₂CO₂), 4.08 (d, 1H, *J*=18.4 Hz, NCH₂CO₂), 4.14-4.33 (m, 1H, H-4), 5.19-5.45 (m, 2H, =CH₂), 5.85 (m, 1H, CH=); IR (neat) 1760, 1735, 1150 cm⁻¹. ³ ¹H NMR (CDCl₃) δ 1.47 (s, 9H, *t*-Bu), 2.62 (dd, 1H, *J*=15.0, 2.7 Hz, β-lactam H-3), 2.80-3.50 (m, 2H, CH₂-C=N), 3.14 (dd, 1H, *J*=15.0, 5.3 Hz, β-lactam H-3), 3.23 (d, 0.6H, *J*=18.0 Hz, NCH₂CO₂), 3.72 (d, 0.4H, *J*=18.0 Hz, NCH₂CO₂), 3.84-3.99 (m, 0.4H, β-lactam H-4), 4.03 (d, 0.6H, *J*=18.0 Hz, NCH₂CO₂), 4.12 (d, 0.4H, *J*=18.0 Hz, NCH₂CO₂), 4.20 (m, 0.6H, β-lactam, H-4), 4.76-4.92 (m, 0.4H, CH-O), 4.96 (dt, 0.6H, *J*=9.6, 3.2 Hz, CH-O); IR (neat) 2980, 1755, 1735, 1580, 1150, 835 cm⁻¹. ⁴ mp 89-93 °C; ¹H NMR (CDCl₃) δ 1.48 (s, 9H, *t*-Bu), 2.44-2.59 (m, 2H, CH₂CN), 2.60-3.40 (m, 2H, H-3), 3.48 (d, 0.4H, *J*=18.0 Hz, NCH₂CO₂), 3.68 (d, 0.6H, *J*=18.0 Hz, NCH₂CO₂), 3.77 (m, 1H, H-4), 4.16 (m, 1H OCH), 4.34 (d, 0.4H, *J*=18.0 Hz, NCH₂CO₂), 4.42 (d, 0.6H, *J*=18.0 Hz, NCH₂CO₂); IR (neat), 3400, 2980, 2250, 1755, 1735, 1240, 1150 cm⁻¹. ⁵ ¹H NMR δ 1.47 (s, 9H, *t*-Bu), 2.60-3.40 (m, 2H, H-3), 3.41 (s, 2H, CH₂CN), 3.72 (dd, 2H, *J*=16.8, 6.8 Hz, NCH₂CO₂), 4.53 (m, 1H, H-4); IR (neat), 2980, 2250, 1755, 1725, 1420, 1240, 1150 cm⁻¹. ⁶ ¹H NMR (CDCl₃) δ 1.47 (s, 9H, *t*-Bu), 2.49-3.38 (m, 2H, H-3), 3.76 (dd, 2H, *J*=16.8, 7.0 Hz, NCH₂CO₂), 4.50 (m, 1H, H-4); IR (neat) 2980, 2250, 2140, 1755, 1730, 1410, 1100 cm⁻¹. ⁷ ¹H NMR (CDCl₃) δ 1.47 (s, 9H, *t*-Bu), 2.86-3.35 (m, 2H, H-6), 3.52 (d, 0.4H, *J*=7.8 Hz, H-3), 3.64-3.92 (m, 1H, H-2, H-3), 4.15-4.56 (m, 1H, H-5), 10.92 (s, 0.6H, =C-OH); IR (neat) 3400, 2980, 2250, 1755, 1730, 1430, 1200, 1150 cm⁻¹.

Sex Pheromone of the Perilla Leaf Pyralid Moth: Isolation and Identification

Suk-Ku Kang* and Kwang-Youl Seol†

Department of Chemistry, Sung Kyun Kwan University,
Natural Science Campus,
Suwon 440-746, Korea

†Sericultural Experiment Station,
Rural Development Administration,
Suwon 440-100, Korea

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Recently, the perilla leaf pyralid moth, *Pyrausta niopealis* Walker, is a major of perilla in Korea and possibly in some

Table 1. Number of males of the perilla leaf pyralid attracted to the abdominal tip extract of virgin females in the laboratory cage

Replications	Number of males attracted					Mean ± SE*
	1	2	3	4	5	
Treatments						
Experiment 1						
0.1 female equivalent	2	3	5	2	1	2.6 ± 0.7
Control (only solvent)	0	0	0	0	0	0.0
Experiment 2						
0.5 F.E.	4	8	6	5	4	5.5 ± 0.7
Control	0	0	0	0	0	0.0
Experiment 3						
1 F.E.	5	9	8	8	6	7.2 ± 0.7
Control	0	0	0	0	0	0.0
Experiment 4						
2 F.E.	15	20	14	12	12	14.6 ± 1.5
Control	0	0	0	0	0	0.0
Experiment 5						
5 F.E.	12	18	14	8	7	11.8 ± 2.0
Control	0	0	0	0	0	0.0

*Means that the same letters are not significant at 5% level with DUNCAN's multiple-range test.

parts of China. This pest occurs four times in a year. Usually Korean eat perilla leaves freshly with roasted beef or raw fish, therefore it is desirable that application of insecticides should be kept to a minimum. When larvae become the third instar, they scatter and larvae make the short breakoffs and roll leaves and eat mesophyll. Therefore it is very difficult to apply insecticides on this pest. Thus, the use of sex pheromone in the direct control or forecasting of this insect would be valuable. Here we wish to report the chemical structure of the two components of the sex pheromones of the perilla leaf pyralid moth.

Insects were reared on an artificial diet developed by Seol.¹ Laboratory bioassay of attractiveness for the abdominal tip extracts of virgin females was performed. We have counted the number of male response due to the quick and strong response to female extract. As shown in Table 1, strong responses of males to the crude extracts were observed throughout the range of doses tested, 0.1 to 0.5 female equivalent (F.E.). On the whole, the numbers of males attracted to the extracts increased as the doses were increased.

Florisil (60-10 mesh) was used as an adsorbent for partial purification of the sex pheromone in the crude extracts according to a class-separating method for lipids.² Hexanes, 5% ether in hexane, and ether were used in this order as eluting solvents. Only the fraction eluted by 5% ether in hexane was potent with respect to EAG response.³ The active fraction was concentrated and examined by gas chromatography (Shimadzu GC 14A) equipped with an effluent splitter and a hydrogen flame ionization detector. Column (OV-101 column) effluents trapped which had retention time 10.0 min to 13.5 min at 150→300 °C of 4 °C/min showed EAG activity (Figure 1).

The active fractions were examined by a gas chromatography-mass spectrometer (GC-MS) (JEOL DX 300) by the