

n-hexane: ether = 7:3, SiO₂; IR (NaCl, neat) 2950, 2850, 2750, 1700, 1690, 1620 cm⁻¹; ¹H-NMR (80MHz, CDCl₃) 0.90-1.40 (m, 17H), 2.70 (t, 2H), 6.78 (dd, 1H), 6.88 (dd, 1H), 9.80 (d, 1H). 4-oxotridecan-1-ol; TLC; R_f = 0.25, n-hexane: ether = 7:3, SiO₂; IR (NaCl, neat) 3100-3400, 2955, 2850, 1720 cm⁻¹; ¹H-NMR (80MHz, CDCl₃)

0.88-1.80 (m, 17H), 2.50-3.00 (m, 6H), 3.80 (t, 4H). (Z)-13-eicosen-10-one (**1**); IR (NaCl, neat) 2960, 1715, 1620, 1450 cm⁻¹; ¹H-NMR (80MHz, CDCl₃) 0.90 (t, 6H), 1.15-1.50 (m, 22H), 1.80-2.50 (m, 8H), 5.30 (m, 2H).
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A Short Synthesis of (±)-Callosobruchusic Acid, the Copulation Release Pheromone(Erectin) of the Azuki Bean Weevil

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In 1981, Yamamoto *et al.*¹ isolated and identified the copulation release pheromone of the azuki bean weevil, *Callosobruchus chinensis* L., as (E)-3,7-dimethyl-2-octene-1,8-dioic acid(**1**) (Callosobruchusic acid) (Figure 1). In 1983, Mori *et al.*² synthesized two enantiomers. Both were biologically active² as the copulation release pheromone of *Callosobruchus chinensis* L.. This pheromone induces the male to extrude his genital organ and to attempt copulation.

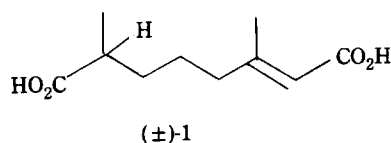
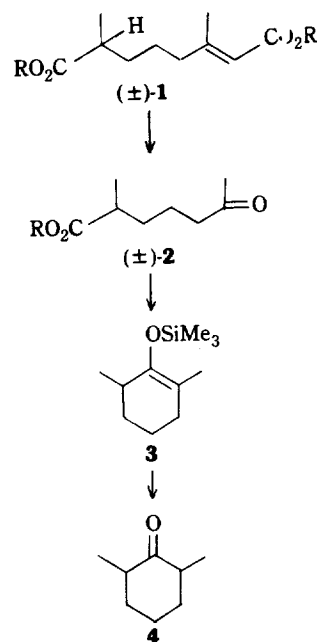


Figure 1

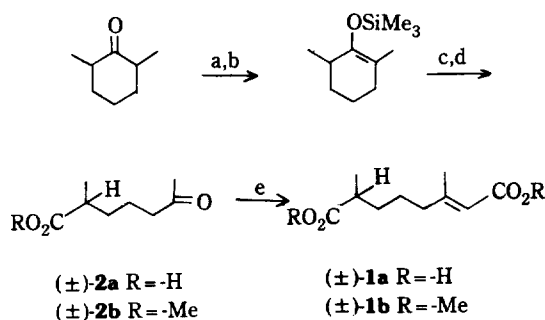
The azuki bean weevil is a persistent pest insect of the azuki bean, cowpea and other important beans. The Institute of Agricultural Sciences in Suwon Korea needed a fair amount of this pheromone to conduct field test experiments, therefore we undertook to synthesize (±)-callosobruchusic acid, (±)-**1**, (±)-(2E)-3,7-dimethyl-2-octene-1,8-dioic acid.

It has been well known that the Emmons olefination reaction of the ketone **2** with the anion of dimethylmethoxycarbonylmethylphosphonate gives predominantly (E)-olefin ester stereoselectively³. A simple retrosynthetic analysis(Scheme 1) reveals that methyl 2-methyl-6-oxo-heptanoate **2** is the key intermediate. The ketone **2** can be easily prepared from silyloxyalkene **3** by ozonization reaction⁴. Silyloxyalkene **3** can be obtained by silylation⁵ of the enolate of commercially available 2,6-dimethylcyclohexanone, **4**.

2,6-Dimethylcyclohexanone(**4**) was silylated by treating with LDA followed by addition of Me₃SiCl to give silyloxyalkene **3**⁷ in 95% yield. Ozonolysis of **3** in methanol followed by Me₂S work up afforded (±)-2-methyl-6-oxo-heptanoic acid **2a** in 60% yield. Esterification of the acid **2a** with diazomethane⁶ gave the methyl ester **2b**⁷ in 95% yield. Emmons olefination reaction of the ketone **2b**⁷ with the anion of dimethylmethoxycarbonylmethylphosphonate furnished the unsaturated ester (±)-**1b**⁷ in 80% yield. The diester **1b** was treat-



Scheme 1



Scheme 2. Synthesis of (±)-**1a**^a

^a(a) LDA, THF, -78°C (b) Me₃SiCl (c) O₃, MeOH, -78°C (d) Me₂S, -78°C→rt (e) (MeO)₂POCH₂CO₂Me, NaH, DME, 50-60°C.

ed with 1N HCl to afford the diacid **1a**⁷ in 85% yield (Scheme 2). The compound synthesized was identical in all respects (TLC, IR, NMR) with the compound reported in the literature.

References

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7. Satisfactory physical properties and spectroscopic data (¹H-NMR, IR) were obtained for the compounds: Sily-

loxyalkene (3): TLC; R_f =0.74, hexane:CH₂Cl₂=5:5, SiO₂; IR(NaCl, neat) 2900, 1670 cm⁻¹; ¹H-NMR (80MHz, CDCl₃) 0.15(9H, s, 3CH₃), 1.05(3H, d, CH₃), 1.32(4H, m, CH₂CH₂), 1.55(3H, s, CH₃), 1.95(3H, m, HCH₂); bp 40°C/15 mmHg. 2-Methyl-6-oxo-heptanoic acid(2b): TLC; R_f =0.47, CH₂Cl₂, SiO₂; IR (NaCl, neat) 2950, 1720 cm⁻¹; ¹H-NMR(80MHz, CDCl₃) 1.17(3H, d, CH₃), 1.56(4H, m, CH₂CH₂), 2.14(3H, s, CH₃), 2.43(3H, m, HCH₂), 3.68(3H, s, CH₃). 3,7-Dimethyl-2-octene-1,8-dioate(1b): TLC; R_f =0.82, CH₂Cl₂, SiO₂; IR(NaCl, neat) 2930, 1715, 1640 cm⁻¹; ¹H-NMR(80MHz, CDCl₃) 1.16(3H, d, CH₃), 1.55(4H, m, CH₂CH₂), 2.14(3H, s, CH₃), 2.43(3H, m, HCH₂), 3.68(6H, s, CH₃CH₃), 5.67(1H, s, H). 3,7-Dimethyl-2-octene-1,8-dioic acid(1a): TLC; R_f =0.14, CH₂CH₂, SiO₂; IR(NaCl, neat) 3600, 3000, 2950, 1700, 1650 cm⁻¹; ¹H-NMR(80MHz, CDCl₃) 1.20(3H, d, CH₃), 1.62(4H, m, CH₂CH₂), 2.16(3H, s, CH₃), 2.46(3H, m, HCH₂), 5.79(3H, brs, HC=, CO₂H, CO₂H).

t-Butyl 2-Pyridon-1-yl Carbonate and Benzyl 2-Pyridon-1-yl Carbonate. New Amino Protective Reagents for t-Butoxycarbonylation and Benzyloxy- carbonylation of Amines and Amino Acids

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The t-butoxycarbonyl (Boc) group is one of the most important amino protective groups along with benzyloxycarbonyl (Cbz) group because of the resistance to racemization during peptide synthesis and facile cleavage of Boc group.¹ The Boc group was originally introduced with t-butyl chloroformate but its use has been limited due to its instability.² In the case of benzyloxycarbonylation of amino acids, benzyl chloroformate has been widely used, but it is thermally unstable and decomposes to yield carbon dioxide and benzyl chloride when it is stored over a long period of time. Thus, considerable efforts have been devoted to the development of a variety of useful and reliable reagents for the protection of amino acids during last 30 years.^{1,3} Recently, we have introduced several efficient amino protective reagents for t-butoxycarbonylation and benzyloxycarbonylation of amino acids.^{4,5} We now wish to report that new amino protective reagents, t-butyl 2-pyridon-1-yl carbonate and benzyl 2-pyridon-1-yl carbonate, are very effective for t-butoxycarbonyla-

tion and benzyloxycarbonylation of amines and amino acids.

t-Butyl 2-pyridon-1-yl carbonate was conveniently prepared in 70% yield by the reaction of 2-pyridon-1-yl chloroformate, generated from phosgene and 1-hydroxy-2(1H)-pyridone⁶ in the presence of pyridine, with equimolar amounts of t-butyl alcohol in methylene chloride at room temperature (Eq. 1).⁷ Benzyl 2-pyridon-1-yl carbonate was easily prepared in 90% yield by treatment of benzyl chloroformate with equimolar amounts of 1-hydroxy-2(1H)-pyridone and triethylamine in methylene chloride at room temperature (Eq. 2).⁸ t-Butyl 2-pyridon-1-yl carbonate and benzyl 2-pyridon-1-yl carbonate were obtained as stable crystalline compounds, showing no sign of decomposition when kept at room temperature for one month.

As shown in Table 1, simple amines were cleanly t-butoxycarbonylated to give the corresponding t-butyl carbamates within 10 min at room temperature and sterically hindered amines such as 2,6-dimethylpiperidine and diisopropylamine worked well, although they required longer reaction times. Similarly, benzyloxycarbonylation of amines proceeded well with benzyl 2-pyridon-1-yl carbonate. When t-butoxycarbonylation of amino acids were carried out in aqueous N,N'-dimethylformamide, the N-Boc amino acids were obtained in relatively low yields because t-butyl 2-pyridon-1-yl carbonate was decomposed to some extent in aqueous N,N'-dimethylformamide. It was found that t-butoxycarbonylation of amino acids proceeded cleanly in p-dioxane, even

