

SYNTHESIS OF THE TWO ISOMERS OF THE POTENTIAL SEX PHEROMONE
OF *THAUMETOPOEA PITYOCAMPA* (LEPIDOPTERA, NOTODONTIDAE) AND
RELATED MODEL COMPOUNDS

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The synthesis of the major component of the sex pheromone secretion of the processionary moth, *Thaumetopoea pityocampa* (Denis and Schiff.) (Lepidoptera, Notodontidae), (Z)-13-hexadecen-11-ynyl acetate (1), the corresponding (E)-isomer (2) and the four structurally related model compounds (Z/E,Z,Z)-5,9,13-hexadecatrienyl acetate (3), (Z/E,Z,Z)-3,7,11-hexadecatrienyl acetate (4), (Z/E,E,Z)-7,9,13-hexadecatrienyl acetate (5) and (Z)-7-hexadecen-5-ynyl acetate (6) is described.

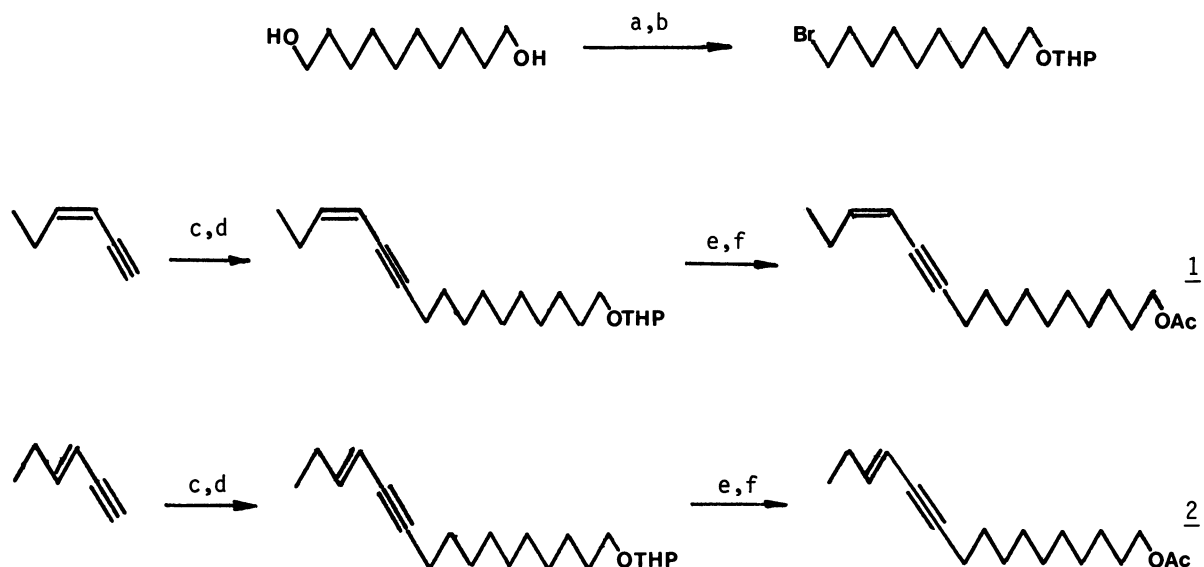
As we have mentioned in a previous communication,¹ preliminary mass spectral data suggested a linear triunsaturated C₁₆ acetate structure for the major component of the sex pheromone secretion of the processionary moth, *Thaumetopoea pityocampa*. To obtain gas chromatographic and mass spectral information about the nature of these unsaturations, we undertook the synthesis of several model compounds, previously unknown in the literature.

(Z/E,Z,Z)-5,9,13-hexadecatrienyl acetate (3) and (Z/E,Z,Z)-3,7,11-hexadecatrienyl acetate (4) were prepared by the sequence depicted in Scheme 1. Wittig condensation of ethyl (Z)-8-oxo-4-octenoate with *n*-propyl and *n*-pentyl triphenylphosphonium bromides (K-tBuO/THF, 30 min., 250°C) afforded, respectively, the corresponding dienic esters in a 94:6 Z:E isomer ratio.² Reduction of these esters with LAH, followed by Collins oxidation of the resulting alcohols yielded the expected aldehydes which were condensed with the corresponding 5-hydroxypentyl and 3-hydroxypropyl triphenylphosphonium bromides to give, after acetylation, the desired 3 and 4 in a 1:1 Z:E isomer ratio at the new formed double bond^{3,4} (δ_{CDCl_3} 5.35, t, HC=C).

The GC retention times of the triunsaturated acetates 3 and 4 on polar and apolar columns were shorter than that exhibited by the natural product. Since it is known that conjugated dienes show longer retention times than unconjugated isomers⁵, some kind of interaction between the double bonds in the active compound was inferred. Therefore, (Z/E,E,Z)-7,9,13-hexadecatrienyl acetate (5) and (Z)-7-hexadecen-5-ynyl acetate (6) were synthesized as outlined in Scheme 2.

product, that of 6 was very similar, suggesting the presence on an enyne functionality in the active compound. In fact, when enough amount of natural pheromone secretion was available for FT-NMR analysis, the structure of (Z)-13-hexadecen-11-ynyl acetate (1) could be assigned to the putative pheromone.¹ The structure elucidation was confirmed by comparison with authentic samples of 1 prepared by two independent routes. We describe herein one of them, the short and efficient sequence depicted in Scheme 3,^{7,8} and the other one will be described elsewhere.⁹

Scheme 3



a: HBr 48%/C₇H₁₆ 70%; b: DHP/H⁺ 75%; c: BuLi/THF/HMPT; d: Br(CH₂)₁₀OTHP 98%; e: *p*-TsOH/MeOH 94%; f: Ac₂O/Py 83%.

The required 3-hexen-1-yne¹⁰ was obtained as a 60:40 Z:E isomer mixture by dehydration of hex-1-yn-4-ol through the corresponding tosylate.^{11,12} Separation of this mixture into the corresponding pure Z and E isomers was easily accomplished by spinning band distillation at atmospheric pressure. Condensation of the lithium salt of the Z isomer with 10-tetrahydropyranyloxy-1-bromodecane¹³ in HMPT at room temperature gave the expected tetrahydropyranyl derivative of (Z)-13-hexadecen-11-ynol in nearly quantitative yield (98%). Acid hydrolysis of the crude, followed by acetylation, afforded the desired (Z)-13-hexadecen-11-ynyl acetate (1) in 83% yield. (δ_{CDCl_3} 5.45, d J=10,5 Hz, C=CH-C $\equiv$ C; 5.85, dt J=10,5 Hz and J'=7,5 Hz, CH₂CH=C; 4.1, t J=7 Hz, CH₂OAc; 2.35, t J=7 Hz, C $\equiv$ C-CH₂; 2.3, q J=7,5 Hz, CH₂C=C; 2.1, s, CH₃CO; 1.3, complex absorption, CH₂ sat.; 1.0, t J=7,5 Hz, CH₃CH₂).⁴

The E isomer 2 was obtained from the E enyne in comparable yields for each step.

(δ_{CDCl_3} 5.5, d J=16 Hz, C=CH-C $\equiv$ C; 6.1, dt J=16 Hz and J'=6,5 Hz, CH₂CH=C; 4.1, t J=7 Hz, CH₂OAc; 2.3, t J=7 Hz, C $\equiv$ C-CH₂; 2.1, q J=7,5 Hz, CH₂C=C; 2.1, s, CH₃CO; 1.3, complex absorption, CH₂ sat.; 1.0, t J=7,5 Hz, CH₃CH₂)⁴.

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