

Studies on Pheromones of Female Eri-Silk Moth, II. Preparation of Some Conjugated C₁₆-C₁₇ Alkadienals and Comparison of Them with the Pheromone by GLC

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Some conjugated C₁₆-C₁₇ alkadienals **6** were prepared by conventional method : 2-alkenyl phosphonium bromides **2** were condensed with aldehydes **3** by the Wittig reaction using the silazide method⁸⁾ to give conjugated dienes **4** (a mixture of geometric isomers), which were then converted *via* the alcohols **5** to the aldehydes **6**. Of these products, C₁₆-alkadienals gave more similar behavior to the pheromone from Eri-silk moth than C₁₇-compounds. None of these synthetic products, **5** and **6**, however, exhibited pheromonal activity toward male Eri-silk moths.

We have previously¹⁾ investigated the structure of pheromone from Eri-silk moth, *Philosamia cynthia ricini*, and had assumed from the functional group tests performed in comparison with the pheromone from the silk-moth, bombykol, that it should be an unsaturated carbonyl compound. Further, we have observed that the dinitrophenylhydrazone derivatives of Eri-silk moth pheromone was located in the position corresponding to C₁₆-C₁₈ normal saturated aldehydes in TLC.²⁾

W.L. Roelofs and his co-workers³⁾ have studied the chemical structure of the pheromone from a related species, *Antheraea polyphemus*, and have shown that it consists of a mixture of two components, (6*E*,11*Z*)-6,11-hexadecadienyl acetate (HDDAc) and (6*E*,11*Z*)-6,11-hexadecadienal (HDDal) (9:1). The latter is similar to the Eri-silk moth pheromone in chemical structure and we have assumed that it would be identical or at least very closely related to this aldehyde compound.

H. J. Bestmann and his co-workers (Erlangen University) have investigated the pheromonal activity of many related synthetic compounds toward the male Eri-silk moth using electroantennography (EAG) technique. According to a private communication from him^{4a)}, among the geometric isomers of 6,11-hexadecadienol (HDDol),

-hexadecadienal (HDDal) and -hexadecadienyl acetate (HDDAc), (6*E*,11*Z*)-6,11-HDDal has exhibited conspicuously high activity. Therefore it was once postulated that the Eri-silk moth pheromone would be identical to (6*E*,11*Z*)-6,11-HDDal. However, from results obtained from the GLC-EAG method using an extract from female Eri-silk moth, it was apparent that there were clear discrepancies in t_R -values between the postulated compound and the naturally occurring pheromonal substance.^{4b)*}

We then re-investigated the Eri-silk moth pheromone by means of functional group tests and observed that the pheromonal activity of the extract was diminished on the treatment with tetracyanoethylene or maleic anhydride. From this observation we have assumed that the pheromone should very probably contain a *E*, *E*-conjugated system in its structure.^{2)**}

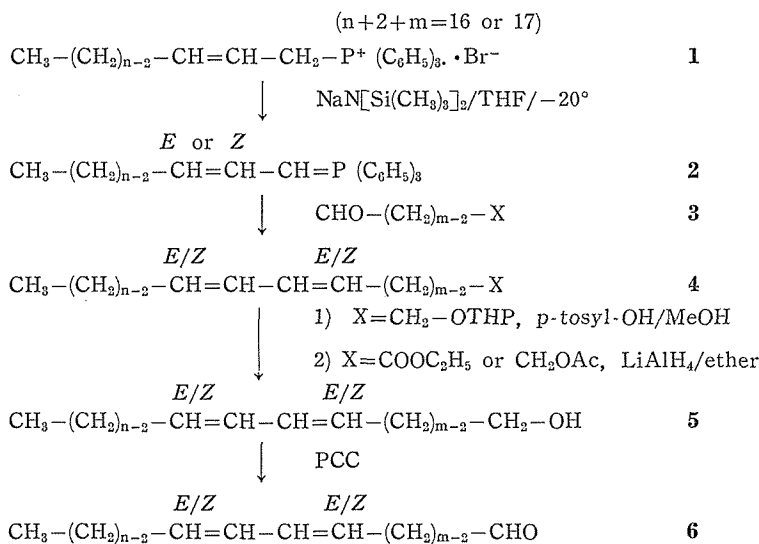
The results obtained above have prompted us to search for simple and practical syntheses dealing with C₁₆-C₁₇ conjugated dienols or dienals in order to determine the structure of the real pheromone of Eri-silk moth. The starting materials were selected from the viewpoint of cost and availability. Well known synthetic methods were employed to reach the target compounds fast and easily, except that the synthetic compounds would be mixtures of geometric isomers.

The syntheses of the titled compounds **6** were carried out in the following way (Fig. 1)^{5,6)}: (*Z*)- or (*E*)-alkadienylidene triphenylphosphorane (C_{n+2}-component) which were prepared from the corresponding phosphonium bromide **1**⁷⁾ using silazide⁸⁾ and ω -substituted alkanal **3** were condensed by the Wittig reaction to give a ω -substituted conjugated alkadiene derivative **4**. In this situation both *Z*- and *E*-configurations can result with respect to the newly formed double bond, thus the diene system obtained must be a mixture of *Z*,*Z*- and *Z*,*E*- or of *E*,*Z*- and *E*,*E*-geometric isomers, depending on the *Z*- or *E*-configuration of the alkadienyl phosphonium bromide **1**. Further, the original double bond in **1** was shown to be unstable under these reaction conditions and underwent isomerization to some extents.^{***} These are, however, of no concern in the case where it is desired to detect whether any one of the possible 4 geometric isomers has pheromonal activity or not. As the aldehyde compounds, C_m-components, in the Wittig reaction were used the following com-

* According to his private communication^{4b)}, t_R : *E*,*Z*-HDDal=4.5min, *E*,*Z*-HDDAc=8.8min (FI-detector), and the active zone from the extract=6.6min (EAG-detector) in GLC (2m, SE-30, 180°).

** Direct isolation of the pheromone from the extract was also attempted, however, no peak observed in the active zone in GLC.

*** In this text, however, the compounds obtained by using (*Z*)-alkenylidene phosphorane are conveniently designated as (*Z*/*E*,*Z*)- and that obtained by using (*E*)-alkenylidene phosphorane as (*Z*/*E*,*E*)-compounds, respectively, that is, a designation of (*Z*/*E*) was used for the position of newly formed double bond and the original configuration of alkadienyl triphenyl phosphonium bromide was conserved. Thus, **4a** (*z*), for example, means that it was prepared from **2a** (*z*) and **3**.

Fig.1 General Scheme for Syntheses of C₁₆-C₁₇ Conjugated Alkadienals

1, 2	n	3	m	X	4, 5, 6	n	m	X in 4	
a	4	c	5	CH ₂ OTHP	C ₁₆ {	a	4	10	COOC ₂ H ₅
b	5	d	6	"		b	5	9	CH ₂ OAc
c	6	e	7	"		c	6	8	CH ₂ OTHP
d	7	f	8	"		d	7	7	"
e	8	g	9	CH ₂ OAc		e	8	6	"
f	9	h	10	COOC ₂ H ₅		f	9	5	"
g	10				C ₁₇ {	g	5	10	COOC ₂ H ₅
h	11					h	9	6	CH ₂ OTHP

pounds: as C₅-component was taken 5-hydroxy pentanal, as C₆₋₈ components 1-(2'-tetrahydropyranyloxy)-hexanal, -heptanal and -octanal, as C₉-component 9-acetoxy-nonanal and as C₁₀ component 9-ethoxycarbonyl-nonanal in each reaction. At any rate, ω -substituted C₁₆-C₁₇ conjugated alkadiene compound **4** prepared in these ways were then converted *via* the alcoholic compound **5** to the corresponding aldehyde **6**.

Each final product **6** was analyzed by GLC using a capillary column, Z-45 (nonpolar, 45m). Some of them showed four peaks and some others three ones, although the separation of these peaks was fairly poor. The fourth peak (the latest one) in **5a**, for example, was elucidated to be *E,E*-geometric isomer due to the diminution or disappearance after treatment with tetracyanoethylene.²⁾ The other peaks could not directly be assigned to the expecting isomers, but assumed that there were no unexpected or unusual substances in these peaks based on the presence of the same parent peaks in GC/MS. Such situation was found to be true

also in other products **5**. Table II shows rough ratios of these peak areas in each product. From these observation it is very probable that each product **6** consists of four or at least both geometric isomers expected from the starting material.^{cf13)}

Table 1. Rough Distribution of the Partially Separated Peak Areas of Products **6** in GLC*

Compound 6	First Peak	Second P.	Third P.	Fouth P.
a(Z)	2	3	2	3-4
a(E)** 1)	2	1.5	0.5	6
2)	1.5-2	1-1.5	0.5	6
b(Z)	0.5	4	3	2.5
b(E)	1	3-4	2-3	3
e(Z)	0.5	4.5	2	3
e(E)	0.5	4	0.5	6
g(Z)	0.5	4.5	3	2
g(E)	1	4	2	3
h(Z)	0.5	4	1	4
h(E)	0.5	4	1-2	4
	First P.	Second P.	Third P.	
f(Z)	4.5	2	4	
f(E)	5	1	4	

* Capillary column Z-45 (nonpolar, 45m×0.5mm) at 180° /N₂ 0.37kg at Inlet, t_R ca. 16-20 min, standard C₁₆-hydrocarbon=13.9 and C₁₇-hydrocarbon=19.1 min.

** In the Wittig reaction, 1) by using NaN [Si (CH₃)₃]₂ and 2) by using LiN [Si (CH₃)₃]₂.

In each synthesized compound the GLC patterns in the packed column were examined using several columns, in which the straight chain saturated hydrocarbons were used as the internal standard to get the structural relationship between the synthesized compounds and the pheromone of Eri-silk moth. As the results, it should be realized that the t_R-value of the pheromone is much closer to that of a C₁₆-compound in the nonpolar column provided the pheromone contains a set of conjugated double bonds, and, however, that a C₁₆-compound does not always show the coincident value to the pheromone in the polar column.

In addition, pheromonal activity tests were carried out using the above synthesized compounds. At all concentrations, however, they exhibited no pheromonal activity toward male Eri-silk moths.

A possibility can be here not absolutely excluded that a pheromonally active substance, even if formed and presented in the synthetic product, has not exhibited its activity owing to the masking effect with the other geometric isomers. We have attempted to detect the activity of the separated eluate from the GLC at the outlet using male Eri-silk moths. In the similar experiment using the natural extract

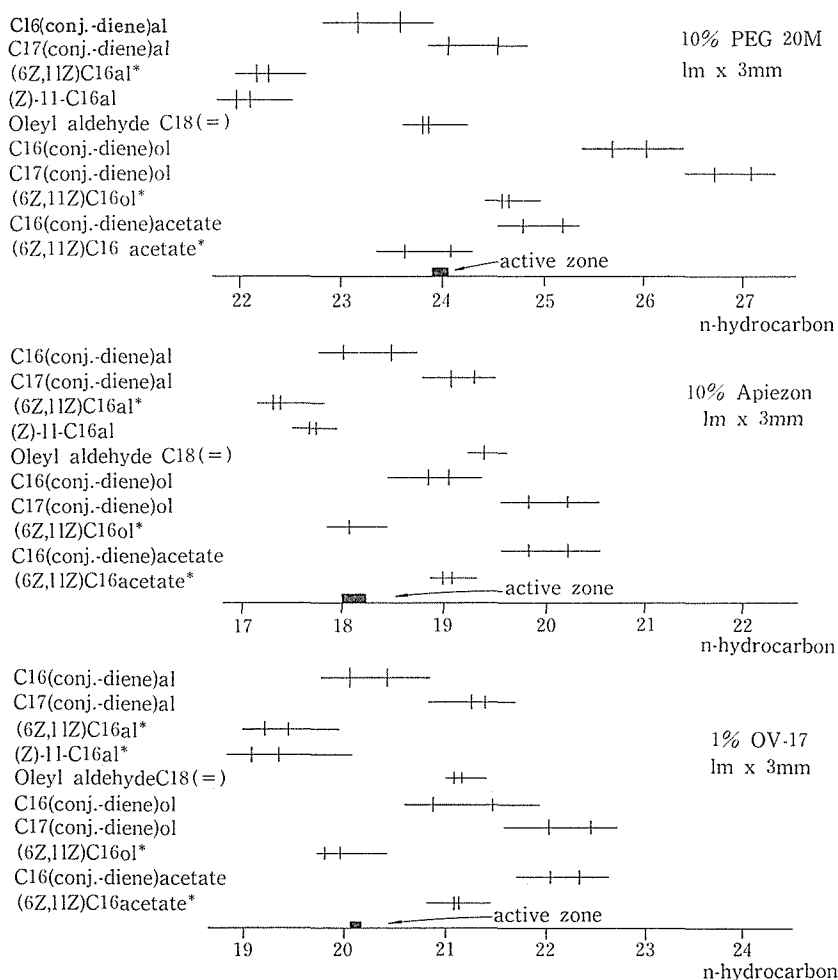


Fig. 2 Comparison of t_R -Values of Synthesized Compounds with That of the Active Zone of the Extract from Female Eri-Silk Moths on Different Packed Columns in GLC (The horizontal line shows a range between the earliest beginning and the latest end of peaks and the distance between the both vertical lines a range between the earliest peak and the latest one in each compound group or in repeated experiments on a compound).
* Synthesized in our laboratory.

from female Eri-silk moth the activity of the eluate can be detected clearly. We have, however, not found any response of the animal for the eluate of these aldehyde products.

We have also observed that the activity of the natural extract can be depressed to some extent by admixing with the synthetic product **6**, and that the extent is

increased when several products of **6** are added multiply. This means that these synthetic products **6** can act competitively on the active site of the membrane of antenna, that is, they have some similarity in the molecular structure with the real pheromone. However, it can be also concluded that in the product **6** real pheromone is not formed and contained: If the real pheromone were formed and presented in the product of **6**, the activity of the natural extract should be vanished completely after admixing with the product **6**, for each product **6** is by itself non-active and this fact means that the possibly contained real pheromone can not exhibit its activity owing to the masking effect with the other substances. In this situation the pheromone amount in the added natural extract will not be able to be free from the masking effect and to exhibit the activity.

The conclusion to be drawn from these results is that the naturally occurring pheromone of Eri-silk moth differs in structure from the synthesized compounds dealt with in the present paper, and also that there is no any active compound in the above synthesized products.

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EXPERIMENTAL PROCEDURES

NMR-spectra: Hitachi R-24 (60MHz), TMS as standard in CDCl₃. — Mass spectra: Shimadzu GCMS-7000 (70eV). — IR-spectra: spectrometer Hitachi EPI 52. — GLC: Hitachi K-63 and K-53, FI-detector, stainless packed column, 1m×3mm ID, 1) PEG 20M (10%), 2) Apiezon (10%) and 3) OV-17 (1%); Capillary column, Z-45 (45m). — TLC: Hexane/ethyl-methyl ketone (4 : 1) was thoroughly used as developing solvent. — Mps and bps were not corrected.

I. Preparation of Starting Components

- 1) *2-Alkenyl triphenylphosphonium bromide (1a-f)*: s. in the previous paper.⁷⁾
- 2) *5-Hydroxypentanal (3c)*: From 2,3-dihydropyran by treating with HCl.⁹⁾
- 3) *ω-(2'-Tetrahydropyran-2-yl)alkan-1-ol (-hexan-, -heptan- and -octan-1-ol)*: Each corresponding diol and 2,3-dihydropyran (1eq) were dissolved in ether or dioxane and to this solution were added a few drops of conc. HCl under stirring

and ice cooling. After 2–12 h stirring the dioxane was removed *in vacuo*. The residue was dissolved in ether and washed to the neutral and after drying over Na_2SO_4 fractionally and repeatedly distilled. *THPO*-(CH_2)₆-*OH*: bp_{1.6} 136° (42%), TLC/Rf=0.31, IR (cm^{-1}): 3380, NMR (δ): 3.4–4.2 (m, O- CH_2 in ring, 2H) 3.5 (t, $J=5\text{Hz}$, $-\text{CH}_2\text{-O}\times 2$, 4H) 4.5 (br-t, methine-H, 1H). *THP-O*-(CH_2)₇-*OH*: bp_{0.5} 130° (46%), TLC/Rf=0.47, IR: 3400, NMR: 3.5 (m, $-\text{CH}_2\text{-O}\times 2/\text{O-CH}_2$ in ring, 6H) 4.5 (br-t, methine-H, 1H). *THPO*-(CH_2)₈-*OH*: bp_{0.2} 148° (55%), TLC/Rf=0.36, IR: 3380, NMR: 3.5 ($-\text{CH}_2\text{-O}\times 2/\text{O-CH}_2$ in ring, 6H) 4.5 (br-t, methin-H, 1H).

4) ω -(2'-*Tetrahydropyran*loxy)-*alkanal* (*-hexanal* (**3d**), *-heptanal* (**3e**) and *-octanal* (**3f**)): For example, **3f**; According to the procedure in Lit.¹⁰, to the solution of pyridinium chlorochromate (PPC) (17.04g, 0.079 mole) in CH_2Cl_2 (110 ml) was added the solution of 8-(2'-*tetrahydropyran*loxy)-*octanol*-(*I*) (12.12g, 0.053 mole) in CH_2Cl_2 (22 ml) and stirred for 3h at room temperature. After the usual post-treatment and purification by means of florisil-column and SiO_2 -column chromatograph, the product was fractionally distilled. An oil, **3f**. bp_{0.2} 96°* (Lit.¹¹) bp_{0.05} 75–110°, 4.77g (40%). TLC/RF=0.67, IR (cm^{-1}): 2700, 1725; NMR (δ): 2.3 (m, $-\text{CH}_2\text{-CHO}$, 2H) 2.9–4.0 (m, $-\text{CH}_2\text{-O}/\text{O-CH}_2$ in ring, 4H) 4.5 (br-t, methine-H, 1H) 9.5 (t, $J=1.5\text{Hz}$, CHO, 1H). **3d**: bp _{0.9} 111–113°* (22%), TLC/Rf=0.60, IR: 2710, 1735; NMR: 2.35 (d-t, $J=1.5$ and 6Hz, $-\text{CH}_2\text{-CHO}$, 2H) 3.0–4.2 (m, $-\text{CH}_2\text{-O}/\text{O-CH}_2$ in ring, 4H) 4.45 (br-t, methine-H, 1H) 9.65 (t, $J=1.5\text{Hz}$, CHO, 1H) **3e**: An oil (33%), TLC/Rf=0.62, IR: 2710, 1735, NMR: 2.3 (m, $-\text{CH}_2\text{-CHO}$, 2H) 3.0–4.0 (m, $-\text{CH}_2\text{-O}/\text{O-CH}_2$ in ring, 4H) 4.5 (br-s, methine-H, 1H) 9.65 (t, $J=1.5\text{Hz}$, CHO, 1H).

5) 9-*Acetoxy-nonanal* (*I*) (**3g**): According to the Lit.¹², oleyl acetate (bp_{0.25} 164°, TLC/Rf=0.87) was ozonolyzed in CH_2Cl_2 at ca. -20° . An oil, bp₄ 144° (75%) (Lit.¹²) bp₁₄ 162°, 75%). TLC/Rf=0.59. NMR CCl_4 , (δ): 1.1–1.9 (m, $-\text{CH}_2$ -, 12H) 1.9–2.1 (s, CO- CH_3 , 3H) 2.1–2.6 (d-t, $-\text{CH}_2\text{-CHO}$, 2H) 3.8–4.1 (t, $-\text{CH}_2\text{-O}$, 2H) 9.5–9.7 (t, CHO, 1H). IR(cm^{-1}): 2920 2840 (CH) 2700 (CHO) 1740 1700 (C=O).

6) 9-*Ethoxycarbonyl-nonanal*-(*I*) (**3h**): Prepared from ethyl undecenate by ozonolysis (in CH_2Cl_2 at -20° , 15h) according to the Lit.¹²) and in analogous method with **3g** An oil, bp₅ 124–5° (63.5%). TLC /Rf=0.63. NMR (CDCl_3 , δ): 3.4–4.3 (q, $-\text{O-CH}_2\text{-CH}_3$, 2H) 9.6–9.7 (t, CHO, 1H). IR (cm^{-1}): 2700(CHO) 1740 (C=O).

II. Condensation of the Components by Means of Wittig Reaction and the Following Conversion to Aldehyde Compounds

1) *Alkadiene derivatives* (**4a-h**(*Z*) and **4a-h**(*E*)): For example, 1-(2'-*tetrahydropyran*loxy)-8(*Z/E*, 10*Z*)-8,10-hexadecadiene (**4c**(*Z*)); According to the Lit.⁸), sodium bis-trimethylsilyl amide (1.77g, 1.1 eq) was dissolved in abs. THF (20 ml) and to

* They are considerably decomposed at the boiling point.

this solution was added (*Z*)-2-octenyl triphenylphosphonium bromide (**1c**(*Z*)) (3.97g, 8.76m mole) in argon under stirring. The reaction mixture colored deep red. After stirring for 1/4h in argon the reaction solution was cooled by using a mixture of ice and salt (ca. -15°) and the solution of 8-(2'-tetrahydropyranyloxy)-octanal (**3f**) (2.00g, 1.0 eq) in abs. THF (10 ml) was added dropwise under stirring in argon. The red colour of the reaction solution diminished gradually and it was clean-colored. After stirring overnight in argon, the solvent was removed by evaporation and the residue dissolved in hexane. The insoluble matter was filtered off and the hexane extract concentrated *in vacuo* to dryness. The residue was purified by means of the preparative TLC (solvent, hexane/ethyl-methyl ketone (4:1), zones were visualized by using UV-lamp and the upper part over R_f 0.64 was extracted.). An oil, **4c**(*Z*), 1.41g. The other compounds were also prepared analogously. Yield: 18-60%; TLC (R_f): 0.82-0.90; IR (cm^{-1}): =CH 2925-3020, C=O 1740 in **a**(*Z*), **a**(*E*), **b**(*Z*) and **b**(*E*), C=C 980-990 and 720-730; NMR (δ): 4.6-6.5 (CH=CH) 3.95-4.05 ($\text{CH}_2\text{-O}$ in **a**, **b**, **g**(*Z*) and **a**, **b**, **g**(*E*)) 2.9-4.0 ($\text{CH}_2\text{-O}$ in **c**, **d**, **e**, **h**(*Z*) and **c**, **d**, **e**, **h**(*E*)) 1.8-2.5 ($\text{CH}_2\text{-CO}/=\text{CH-CH}_2$).

2) *Alkadienol*-(*I*), i) **5a**, **b**, **g**(*Z*) and **5a**, **b**, **g**(*E*): For example, (*9Z/E*, *11Z*)-9, 11-hexadecadienol-(*I*) (**5b**(*E*)); To the solution of anhydrous ether (20 ml) of LiAlH_4 (0.04g, 1.4 eq) was added the solution of **4b**(*E*) (0.21g, 0.75 m mole) in ether (10 ml) under stirring in nitrogen dropwise. After the further stirring for 1.5h at room temperature, AcOEt was added under cooling in ice-water and filtered by suction. The filtrate was washed successively with 2N HCl aq, NaHCO_3 aq and sat. NaCl aq, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to dryness. The residue was separated and purified by means of preparative TLC in the same manner as described in 1) to give an oil, 0.14g. The other compounds in this term were also analogously obtained. Yield: 44-83%; TLC (R_f): 0.49-0.59; IR (cm^{-1}): OH 3300-3350, =CH 3000-3010, CH=CH 980-990 and 720; NMR (δ): 4.8-6.6 (m, CH=CH) 3.5-3.6 (t, $J=6\text{Hz}$, $\text{CH}_2\text{-C}$) 1.8-2.6 (m, =CH- CH_2).

ii) **5c-f**, **h**(*Z*) and **5c-f**, **h**(*E*): For example, (*8Z/E*, *10E*)-8, 10-hexadecadienol-(*I*) (**5c**(*Z*)); The above (at 1)) obtained product **4c**(*Z*) (1.27g, 3.94 m mole) was dissolved in the methanol solution (25ml) of *p*-toluene sulfonic acid (0.83g) overnight. After removal of methanol *in vacuo*, the residue was dissolved in ether and washed to the neutral. It was evaporated *in vacuo* and the residue was purified by means of the preparative TLC as described at 1). An oil, 0.38g. The other compounds in this term were also analogously obtained. Yield: 38-59%; TLC (R_f): 0.51-0.58; IR (cm^{-1}): OH 3330-3380, =CH 3000-3020, CH=CH 980-990 and 720-730; NMR (δ): 4.6-6.5 (m, CH=CH) 3.5 (t, $J=6\text{Hz}$, $\text{CH}_2\text{-O}$) 1.8-2.8 (m, =CH- CH_2).

3) *Alkadienal* (**6a-h**(*Z*) and **6a-h**(*E*)): For example, (*8Z/E*, *10Z*)-8, 10-hexadecadienal **6c**(*Z*); According to the Lit.¹⁰⁾ to the solution of pyridinium chlorochromate

(0.06g, 0.28m mole) in CH_2Cl_2 (1 ml) was added the solution of the above obtained **5c(Z)** (0.04g, 0.17m mole) in CH_2Cl_2 (1 ml) under stirring at room temperature. The stirring was continued for 3h. The post-treating and the purification by passing through the florisil-column were performed as in the Lit.¹⁰⁾ The product was then purified by means of preparative TLC in the same manner as described above to give an oil, 0.02g. The other compounds **6** were analogously prepared. Yield : 26–78%; TLC (Rf): 0.79–0.89; IR (cm^{-1}): =CH 3000–3010, CHO 2700–2720 and 1725–1735, CH=CH 960–995 and 720–730; NMR (δ): 9.55–9.65 (t, $J=1.5\text{Hz}$, CHO) 4.6–6.5 (m, CH=CH) 1.8–2.8 (m, =CH- $\underline{\text{CH}_2}$ -/ $\underline{\text{CH}_2}$ -CHO); M^+ 236 for **a-f(Z)** and **a-f(E)**, 250 for **g,h(Z)** and **g,h(E)**.

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摘 要

エリ蚕雌フェロモンに関する研究 II

数種の C_{16} ~ C_{17} の共役二重結合含有アルカジエナールの調製と
それらのエリ蚕フェロモンとのGLCにおける比較

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数種の C_{16} ~ C_{17} の共役二重結合含有アルカジエナールを従来の方法で調製した。すなわち、2-アルケニルホスホニウムブロマイドからシラジド法で得られるイリドに、アルデヒド化合物をウイテヒ反応で縮合して、共役二重結合含有化合物とし、これらは各々アルコールを経てアルデヒドに導いた。得られたアルカジエナールは各々理論的に4乃至少なくとも2幾何異性体の混合物であるが、キャピラリカラムのGLCでは多くのものが3~4ピークを与えた。各種の充填カラムを用いて真実のエリ蚕からのフェロモンと t_R について比較したところ、無極性カラムでは C_{17} よりも C_{16} の方がより似た値を示した。しかし、極性カラムでは C_{16} も必ずしも一致した結果は示さなかった。一方、ここで合成された C_{16} ~ C_{17} のアルコール及びアルデヒドの何れも、エリ蚕の雄に対しては、羽搏きテストに関する限り、全く活性を示さなかった。