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STEREOSELECTIVE AND VERSATILE APPROACH FOR THE SYNTHESIS OF GOSSYPLURE AND ITS COMPONENTS[1]

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Abstract—Efficient synthetic routes to gossyplure and its components (**1a** and **1b**) were formulated. The three key units *viz* the alkynol **3**, the bromide **5**, and the alkanal **13** were derived from easily accessible starting materials. Alkylation of **3** with **5**, and subsequent semihydrogenation followed by oxidation, provided the C_{11}-alkenal **8** which was subjected to a stereocontrolled Wittig reaction with a C_5-phosphonium salt, to yield directly the desired pheromone (**1a** + **1b**). The synthesis of its individual components involved the manipulation *via* an acetylenic intermediate, *viz* the alkynol **14** which was obtained through alkylation of **3**. A sequence of well-established reactions on **14**, then provided the corresponding (*E*)- and (*Z*)-alkenylphosphonium salts which upon a (*Z*)-specific Wittig olefination with the C_7-aldehyde (**13**), led to the stereoselective synthesis of **1a** and **1b**.

In recent years, considerable attention has been focussed on finding alternative approaches to the use of conventional pesticides in the control of insect pests. One of the important developments in this direction has been the evaluation of pheromones in the integrated pestmanagement.[2] A large number of pheromones have been investigated, but of these, the ones that pertain to agricultural pests have received greater attention. One of these, is the pink bollworm moth *Pectinophora gossypiella* (Saunders), a destructive pest of cotton. The sex pheromone of this moth, was identified as a mixture of (7*Z*, 11*Z*)- and (7*Z*, 11*E*) – 7,11-hexadecadienyl acetates (**1a** and **1b**), and given the trivial name "gossyplure".[3] It was also found that neither component is active alone but a synergistic combination of **1a** and **1b** (*ca* 1:1 ratio) serves as the pheromone.[4] The (7*Z*, 11*E*)-isomer has also been identified as the sex pheromone of Angoumois grain moth, *Sitotroga cerealella*.[5]

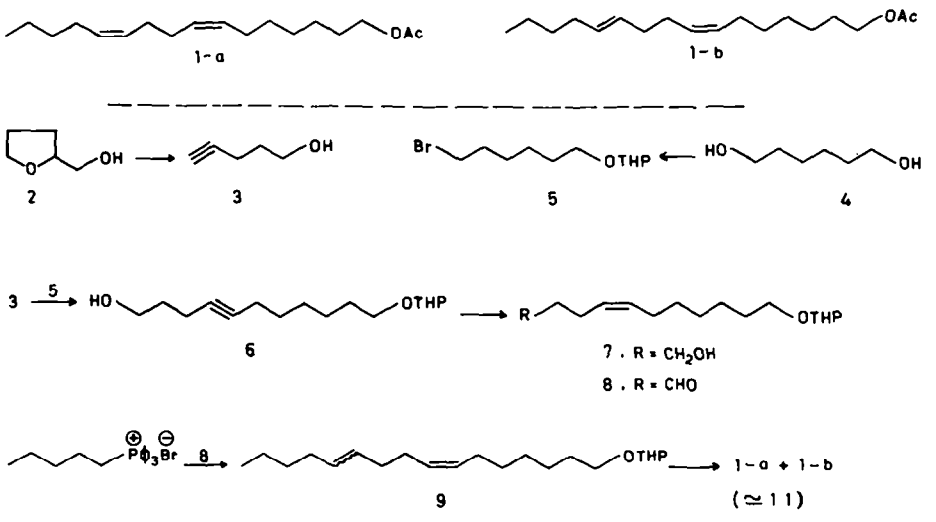
Extensive field trials have been carried out to exploit gossyplure (**1a** + **1b**) for monitoring, as well as for controlling pink bollworm moth.[6] In fact, of all the attempts directed at pest management with pheromones, probably the most impressive results and economic justification has been obtained with gossyplure. Although several syntheses of this pheromone have been reported,[7] there is still a need for an approach that is stereoselective, and also practical. In connection with our work on some pheromones of agricultural importance, the synthesis of gossyplure (Scheme 1) and its components (Scheme 2) was undertaken.[1] As evident from the schemes, the approach involved essentially three key units which were linked with the concomitant formation of C-7 and C-11 olefinic bonds. The geometry of these linkages was either controlled *via* stereoselective Wittig reaction, or predetermined through the use of acetylenic intermediates. One of the prime considerations was the utilisation of easily available starting materials such as tetrahydrofurfuryl alcohol, hexamethylene glycol and aleuritic acid. Amongst these, the alcohol (2) was the main raw material, since its cleavage[8] provides a bifunctional C_5-unit, *viz* the alkynol **3** which appeared to be an ideal intermediate for the synthesis of 1,5-dienes such as **1a** and **1b**.

Direct synthesis of gossyplure (Scheme 1)

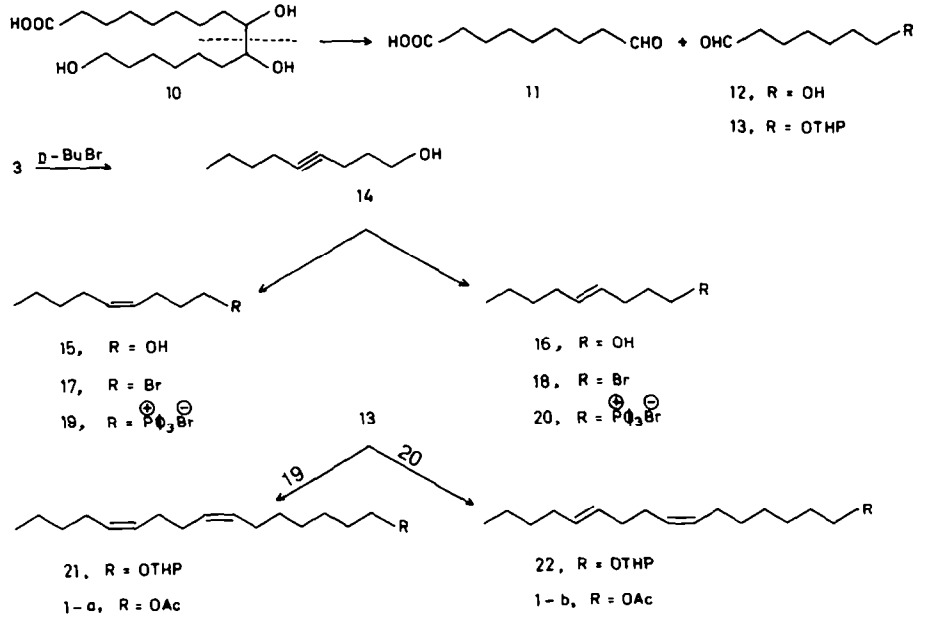
This route was based on a $(C_5 + C_6) + C_5$ – type "block-building" approach, and it directly provided the title pheromone (as a *ca* 1:1 mixture of **1a** and **1b**). Partial bromination of the diol **4** followed by pyranylation (DHP, PPTS/CH_2Cl_2)[9] of the resulting bromohydrin, provided the C_6-bromide **5**. Alkylation of **3** with **5** yielded the alkynol **6** which on semihydrogenation in the presence of P-2 Ni catalyst,[10] afforded the corresponding (*Z*)-alkenol **7**. Oxidation of **7** with Collins reagent[11] gave the alkynal **8**, a suitably functionalised C_{11}-unit. The key step in the synthesis was based on the report of Anderson and Henrick, who have shown[12] that equilibration (with EtOH at −40° for 10 min) of the intermediate *threo*- and *erythro*- "betains" leads to an approximately 1:1 mixture of (*E*)- and (*Z*)-alkenes. In the present work, this stereocontrolled Wittig reaction was employed for the olefination of the alkynal **8** with (n-pentyl)triphenylphosphonium bromide.[13] The resulting product on acetolysis,[14] yielded a compound which exhibited the physiochemical properties identical with that reported[12] for gossyplure. GLC-analysis of the product (as its epoxide) revealed that its two components (**1a** and **1b**) were present in *ca* 1:1 ratio.

Synthesis of the individual components (Scheme 2)

This route was devised in order to obtain the individual components (**1a** and **1b**) of the pheromone, and was based on a $(C_5 + C_4) + C_7$ approach. The primary goal was to acquire a C_9-unit which was done by the alkylation of **3** with n-butyl bromide. Partial reduction of the resulting alkynol **14** with H_2 and with Na/NH_3, provided the (*Z*)-alkenol **15** and (*E*)-alkenol **16** respectively, which were reacted with triphenylphosphonium dibromide to obtain the corresponding bromides (**17** and **18**) in 80–85% yield. Although, similar in sequence, the earlier preparation[15] of these bromides proceeded in only



Scheme 1.



Scheme 2.

moderate (40–45%) yields. The bromides (**17** and **18**) were then converted to the corresponding phosphonium salts (**19** and **20**).

Having fixed the C-11 olefinic linkages of **1a** and **1b** in the above salts, the next task was to generate the C-7 double bond. The desired C_7-unit for this purpose, was derived from aleuritic acid (**10**). Periodate oxidation of this acid has been reported for the preparation of the carboxy aldehyde **11**[16] and also the hydroxy aldehyde **12**.[17] However, neither of the two methods is suitable for the preparation of both the fragments. Since these compounds are valuable intermediates, it was decided to standardise the optimal conditions for the cleavage of **10**. By using a biphasic ($CHCl_3/H_2O$) reaction - medium, and controlling the reaction - conditions (pH 6–7, temp 35–40°), the two aldehyde fragments were obtained in 90–95% (crude) yield, reproducibly. The hydroxy aldehyde **12** was protected as its THP-ether **13**, and purified by "flash chromatography".[18] The two suitably functionalised units *viz* the C_9-salt (**19** or **20**) and the C_7-aldehyde **13** were then linked *via* a (*Z*)-selective Wittig olefination reaction. For this purpose, NaH was used as the base, and THF–DMSO (2:1) as the solvent system. The resulting 1,5-dienes (**21** and **22**) upon acetolysis,[14] furnished the two gossyplure-components (**1a** and **1b**) which exhibited the physico-chemical properties, identical with those reported.[19]

In terms of brevity and flexibility, the present approach is an attractive alternate to the existing syntheses of gossyplure (and its components). Furthermore, with proper manipulation of the starting units, this scheme can be employed for the synthesis of a broad spectrum of 1,5-dienes.

EXPERIMENTAL

All the bps are uncorrected. The IR spectra (ν_{max}, cm^{-1}) were recorded on a Perkin–Elmer Infracord 137–B spectrophotometer. The PMR spectra (δ scale, ppm) were determined on a Varian A–60A spectrometer, using TMS as an internal reference. Unless otherwise mentioned, the compounds were taken as thin films for IR, and as CCl_4 solns for the recording of PMR spectra. Mass spectra were recorded on a VG Micromass 7070F instrument. Purity of the products was checked by TLC/GLC. The GLC-analysis was carried out on a 5% OV-17 column, unless mentioned otherwise.

All the reactions involving organometallic reagents were conducted under argon, and the transfer of solvents/reagents was carried out with syringes. Anhyd CH_2Cl_2 (dried over P_2O_5) and and DMSO (dried over CaH_2), were stored on molecular sieves (type 4A). Ether and THF were freshly distilled (over sodium benzophenone ketyl) prior to use.

4-Pentyn-1-ol (**3**). Following the known procedure,[8] this intermediate was derived from tetrahydrofurfuryl alcohol.

1-Bromo-6-(2'-tetrahydropyranyloxy)hexane (**5**). Partial bromination of **4** (23.6 g, 0.2 M) was carried out by stirring with 40% aqueous HBr (100 ml) under reflux for 24 hr, while the mixture was continuously extracted with benzene. The extract was washed with brine, dried over Na_2SO_4, and concentrated. The residue was distilled under reduced pressure to obtain the corresponding bromohydrin (29.3 g, 81%); b.p. 114–116°/10 torr (lit.[20] 105–106°/5 torr).

To a stirred and cooled (0–5°) soln of the above bromo alcohol (26.5, 0.1 M) and PPTS (500 mg) in CH_2Cl_2 (100 ml), dihydropyran (10.1 g, 0.12 M) was added. The mixture was continued to stir at the same temp for 0.5 hr and then at the ambient temp for further 4 hr. Thereafter, it was diluted with ether (200 ml), washed with 1 N Na_2CO_3 followed by brine, dried over K_2CO_3, and worked up as usual, to provide **5** (23.1 g, 87%); b.p. 135–140°/5 torr (lit.[21] 102–105°/0.1 torr); GLC: 3% SE–30, 120°, 14 lb/in.^{2}-N_2, R_t = 11.5 min; IR: 2950, 1445, 1355, 1205, 1140, 1120, 1080, 1035, 985, 910, 875 and 815; PMR: 1.4–2.0 (m, 14H, $(-CH_2-)_7$), 3.3–3.9 (m, 6H, $-CH_2Br$ & $(-CH_2O-)_2$), and 4.50 (br. s, 1H, $-\overset{|}{O}CHO-$).

11-(2'-Tetrahydropyranyloxy) undec-4-yn-1-ol (**6**). To a suspension of $LiNH_2$ (0.2 M, from 1.4 g Li) in anhyd NH_3 (150 ml), a soln of **3** (8.4 g, 0.1 M) in THF (10 ml) was added over a period of 15 min. To the resulting dark grey soln, **5** (26.5 g, 0.1 M) dissolved in anhyd THF (20 ml), was introduced over a period of 1 hr, and the mixture was continued to stir for further 5 hr. The reaction was then quenched with NH_4Cl (10 g), and allowed to stand overnight for the evaporation of ammonia. The residue was dissolved in cold water, extracted with ether, and the extract was washed with a sat NH_4Cl *aq*. After drying over K_2CO_3, the extract was concentrated, and the residue was subjected to "flash chromatography"[18] (silica gel column, 10% EtOAc in petroleum ether). As expected, the crude product separated into three fractions *viz* an O-alkylated product (5–6%), a dialkylated product (8–9%), and the desired **6** (20.5 g, 76%); TLC: silica gel, 30% EtOAc in benzene, R_f = 0.44; IR: 3510, 2970, 1450, 1360, 1145, 1125, 1075, 1030, 910, 870 and 815; PMR ($CDCl_3$): 1.3–1.9 (m, 16H, $(-CH_2-)_8$), 2.0–2.4 (m, 4H, $-CH_2C{\equiv}CCH_2-$), 2.55 (br. s, D_2O-exchangeable, OH), 3.3–4.0 (m, 6H, $(-CH_2O-)_3$), and 4.60 (br. s, $-\overset{|}{O}CHO-$); MS: m/e = 250 ($M-H_2O$), 223 and 167.

Attempt to purify **6** by distillation failed, since it underwent depyranylation on heating.

(Z)-11-(2'-Tetrahydropyranyloxy)undec-4-en-1-ol (**7**). To a stirred soln of Ni $(OAc)_2 \cdot 4H_2O$ (1.24 g, 5 mM) in 95% EtOH, a soln of $NaBH_4$ (285 mg, 7.5 mM) in 95% EtOH was added dropwise. To the resulting suspension of P-2 Ni catalyst,[10] ethylene diamine (0.9 g) and **6** (13.4 g, 50 mM) were added. The mixture was shaken under a slight positive pressure of H_2. After the absorption of H_2 had ceased, the mixture was filtered through a short pad of celite. The filtrate was concentrated, diluted with water, and extracted with ether. Evaporation of the solvent, provided **7** (13.4 g, almost quantitative) which showed a single spot on TLC. An analytical sample was obtained by preparative TLC on silica gel (pH 7–8, buffered with NaOAc) plates. Elution with 30% EtOAc in benzene, gave the compound at R_f = 0.45; IR: 3490, 2965, 1440, 1350, 1140, 1120, 1075, 1030, 905, 865 and 810; PMR($CDCl_3$): 1.4–1.8 (m, 16H, $(-CH_2-)_8$), 1.9–2.3 (m, 4H, $-CH_2CH{=}CHCH_2-$), 2.98 (s, D_2O-exchangeable, OH), 3.4–3.9 (m, 6H, $(-CH_2O-)_3$), 4.46 (br. s, 1H, $-\overset{|}{O}CHO-$) and 5.33 (m, 2H, $-CH{=}CH-$); (Found: C, 71.32; H, 10.90; Calc. for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18%).

(Z)-11-(2'-Tetrahydropyranyloxy)undec-4-en-1-al (**8**). To a stirred and cooled (20–25°) soln of anhyd pyridine (25.5 ml, 0.32 M) in anhyd CH_2Cl_2 (400 ml), CrO_3 (16 g, 0.16 M) was added in a few portions, and the stirring continued for 30 min. To the resulting burgandy coloured soln of Collins reagent,[11] **7** (5.4 g, 0.02 M) dissolved in CH_2Cl_2 (20 ml), was added in one lot. After stirring for 15 min, the reaction was quenched with water (4 ml), the supernatant liquid decanted off from the black gummy masss, and passed through a short column of florosil. The filtrate was washed successively with ice-cold 1 N HCl, water, 5% soln of Na_2CO_3, brine, and dried over Na_2SO_4. Solvent removal yielded **8** (4.82 g, 90%); IR: 2965, 2740, 1735, 1450, 1360, 1145, 1125, 1080, 1035, 910, 870 and 815; PMR: 1.35–1.90 (m, 4H, $(-CH_2-)_2$), 1.9–2.5 (m, 6H, $OHCCH_2CH_2CH{=}CHCH_2-$), 4.52 (br. s, 1H, $-\overset{|}{O}CHO-$), 5.37 (m, 2H, $-CH{=}CH-$), and 9.84 (t, J = 1.5 Hz, 1H, $-CHO$). Since the product was sufficiently pure (judged by TLC), it was used as such for the next step.

Gossyplure (**1a + 1b**). To a stirred suspension of (n-pentyl) triphonylphosphonium bromdie[13] (5 g, 12 mM) in anhyd ether (30 ml), n–BuLi (6.7 ml of 1.8 M in hexane, 12 mM) was added dropwise. After stirring for 1 hr at the ambient temp, the resulting reddish orange coloured ylide soln was cooled to −40°, treated with a soln of **8** (2.7 g crude, 10 mM) in ether (5 ml), and stirred for 80 min. To the resulting pale yellow suspension, EtOH (20 ml) was added dropwise which led to the formation of a gummy mass. After stirring at the same temp (−40°) for 10 min, the cooling bath was removed, and the mixture was continued to stir for further 2 hr. Thereafter, it was treated with brine, filtered, the organic layer separated, and the aqueous portion was extracted with ether. The combined extract was dried over $MgSO_4$, and evaporated. The residue was thoroughly extracted with hexane, and filtered through a short pad of neutral alumina (act. I). Solvent removal left a pale yellow coloured oily liquid which was dissolved in AcOH (5 ml) containing AcCl (1 ml). The mixture was stirred in an ice-bath for 3 hr, and then overnight at the ambient temp. Thereafter, it was diluted with ice-cold water, and extracted with ether–pentane (2:1). The product obtained following the usual work up, was purified by column chromatography and subsequent "short path" distillation to furnish (1.51 g, 54% from (**8**) the expected pheromone, *viz* gossyplure (**1a + 1b**); b.p. 130–132°/1 torr (lit.[12] 80°/0.02 torr); IR: 2950, 1745, 1460, 1370, 1240, 1030 and 970; PMR: 0.93 (dist. t, 3H, $-CH_3$), 1.10–1.67 (m, 12 H, $(-CH_2-)_6$), 1.80–2.33 (m, 8H, $(-CH_2CH{=}CH-)_4$), 1.96 (s, 3H, $-COCH_3$), 3.91 (t, 2H, $-CH_2OCOCH_3$), and 5.33 (m, 4H, $(-CH{=}CH-)_2$).

The above product gave a single peak in GLC (3% OV-17, 160°, 15 lb/in.^{2}-N_2, R_t = *ca* 8 min). However, an epoxidised sample (obtained by treatment with excess *m*–CPBA) separated into two distinct peaks (R_t = *ca* 19 and 21 min, respectively) with an area-ratio of *ca* 55:45 which obviously corresponded to the two pheromone-components **1b** and **1a**, respectively.

Cleavage of aleuritic acid (**10**). To a stirred suspension of **10** (30 g, 0.1 M) in water (50 ml), a 1 M soln (60 ml) of Na_2CO_3 was added. The mixture was stirred vigorously till the evolution of CO_2 ceased, and then filtered. The filtrate

was treated dropwise with 10% H_3PO_4 till a faint turbidity appeared (pH *ca* 7). $CHCl_3$ (200 ml) was then added, the mixture was warmed to 30° while a soln of $NaIO_4$ (22 g, 0.1 M) in water (200 ml) was added over a period of 30 min. A mildly exothermic reaction ensued which raised the temp of the mixture to 40°. After stirring for 15 min, the mixture was cooled (5–10°) rapidly, acidified to pH 3 with 20% H_3PO_4, and filtered. The organic layer was separated, and extracted thoroughly with sat $NaHCO_3$aq (2 × 50 ml) followed by 5% Na_2CO_3aq (1 × 50 ml). It was then washed with water, brine, and dried over Na_2SO_4.

The combined aqueous portion was acidified, and extracted with $CHCl_3$. Usual work-up provided **11** (17 g crude, almost quantitative).

7-(2'-Tetrahydropyranyloxy)heptan-1-al (**13**). The $CHCl_3$ extract (containing crude **12**) from the above described experiment, was filtered through a short pad of silica gel. The filtrate was cooled (0–5°), and treated with dihydropyran (11 ml, *ca* 0.12 M) followed by PPTS (1 g). The mixture was stirred at 0–5° for 1 hr, and then at the ambient temp for 3 hr. Thereafter, it was washed with a 5% Na_2CO_3aq follwoed by brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by "flash chromatography" to acquire **13** (17 g, 81% from **10**). An analytical sample was prepared by short-path distillation; b.p. 100–105°/0.1 torr (lit.[17] 78–106°/0.1 torr), IR: 2965, 2740, 1740, 1450, 1360, 1145, 1125, 1080, 1035, 910, 870 and 815; PMR: 1.3–1.8 (m, 14H, $(-CH_2-)_7$), 2.1–2.4 (m, 2H, $-CH_2CHO$), 3.2–3.9 (m, 4H, $(-CH_2O-)_2$), 4.52 (br. s, 1H, $-O\dot{C}HO-$), and 9.83 (t, J = 1Hz, 1H, –CHO).

4-Nonyn-1-ol (**14**). Preparation of this compound involved treatment of **3** (25.2 g, 0.3 M) with $LiNH_2$ (0.6 M, from 4.2 g Li) in liquid NH_3 (600 ml), and then an alkylation of the resulting dianion with n-butyl bramide. The experimental procedure was the same as described earlier (for the preparation of **6**). The only difference in this case was that no co-solvent (e.g. THF) was employed, and the reaction was terminated 4 hr after the addition of the bromide. The product was carefully fractionated to afford pure **14** (34 g, 81%); b.p. 107–110°/10 torr (lit.[15] 102–105°/9 torr); IR: 3350, 2985, 1450, 1065 and 930; PMR($CDCl_3$): 0.93 (t, 3H, $-CH_3$), 2.0–2.4 (m, 4H, $-CH_2CH{=}CHCH_2-$), 3.33 (s, D_2O-exchangeable, OH), and 3.72 (t, 2H, $-CH_2OH$).

4-Nonen-1-ols (**15** and **16**). Following essentially the procedures reported by Ohloff *et al.*,[15] the alkenols (**15** and **16**) were prepared by the partial reduction of **14**. The semihydrogenation, however, was carried out using P-2 Ni, rather than Pd as the catalyst.

Compound **15**: b.p. 107–109°/10 torr (lit.[15] 95–97°/10 torr); IR: 3340, 2980, 1460 and 1055; PMR ($CDCl_3$): 0.93 (t, J = 6 Hz, 3H, $-CH_3$), 1.2–1.9 (m, 6H, $(-CH_2-)_3$), 1.9–2.4 (m, 4H, $-CH_2CH{=}CHCH_2-$), 3.57 (t, J = 7 Hz, 2H, $-CH_2OH$), 3.60 (s, D_2O-exchangeable, –OH), and 5.37 ("t", J = 4 Hz, 2H, –CH=CH–).

Compound **16**: b.p. 106–108°/10 torr (lit.[15] 94–95°/10 torr); IR: 3335, 2970, 1465, 1070, and 965; PMR ($CDCl_3$): 0.91 (t, J = 6 Hz, 3H, $-CH_3$), 1.2–1.8 (m, 6H, $(-CH_2-)_3$), 1.9–2.4 (m, 4H, $-CH_2CH{=}CHCH_2-$), 2.70 (s, D_2O-exchangeable, –OH), 3.67 (t, 2H, $-CH_2OH$), and 5.45 (m, 2H, –CH=CH–).

1-Bromo-4-nonenes (**17** and **18**). A stirred and cooled (0–5°) soln of triphenylphosphine (18.3 g, 70 mM) in anhyd CH_2Cl_2 (120 ml), was treated dropwise with Br_2 (12 ml of 5.5 M in CCl_4, 66 mM). To the resulting thick white suspension, a soln of **15** (8.6 g, 60 mM) and anhyd pyridine (5.6 ml, 70 mM) in CH_2Cl_2 (10 ml) was added over a period of 15–20 min. The mixture was then stirred at the ambient temp for 2 hr. Thereafter, it was carefully concentrated under reduced pressure, and the residue was thoroughly extracted with ether-pentane (1 : 1). The extract was filtered through a short pad of neutral alumina (act. I), concentrated, and the residue distilled under reduced pressure to obtain **17** (11.2 g, 78%); b.p. 102–105°/10 torr (lit.[15] 91–94°/10 torr); IR: 2970, 1460, 1435, and 1260. The product exhibited a single peak on GLC.

Similarly, bromination of the (*E*)-alkenol provided **18** (11.6 g, 81%); b.p. 101–104°/10 torr, IR: 2980, 1465, 1430, 1250 and 970; PMR: 0.87 (t, 3H, $-CH_3$), 1.2–1.8 (m, 6H, $(-CH_2-)_3$), 1.9–2.5 (m, 4H, $-CH_2CH{=}CHCH_2-$), 3.40 (t, 2H, $-CH_2Br$), and 5.36 ("t", 2H, –CH=CH–).

(4-Nonenyl)triphenylphosphonium bromides (**19** and **20**). A soln of the (*Z*)- **17** (10.3 g, 50 mM) and triphenylphosphine (14.4 g, 55 mM) in freshly distilled acetonitrile (50 ml), was refluxed for 24 hr. The solvent was then removed using a rotary evaporator, the residue was dissolved in CH_2Cl_2 (30 ml) and precipitated out by adding ether (150 ml). The solvent layer was decanted off from the semisolid residue of **19** (23.4 g, quantitative). Since attempts to solidify or crystallise the salt failed, it was dried thoroughly (5–10 mm, 100–110°) and dissolved in a known volume (100 ml) of anhydrous THF for subsequent use.

The above procedure was repeated for the preparation of **20** from the (*E*)- **18**.

(7Z, 11Z) and (7Z,11E)-1-(2'-Tetrahydropyranyloxy) hexadeca-7,11-dienes (**21** and **22**).

A suspension of NaH (3 g of 80% dispersion, 0.1 M) in anhyd DMSO (50 ml), was stirred at 65–70°, till the evolution of H_2 ceased (*ca* 1 hr). This resulted in the formation of a (light grey coloured) 2 M "dimsyl" soln.

In another flask, a soln of **19** (40 ml of 0.5 M in THF, 20 mM) was placed, cooled by immersing in an ice-bath, and treated dropwise with the above "dimsyl" soln (10 ml, 20 mM). After the addition, the cooling bath was removed, and the mixture was stirred at the ambient temp for 30 min. The resulting red coloured ylide soln was cooled to −30°, and treated with **13** (4.3 g, 20 mM) dissolved in DMSO (10 ml). The mixture was then slowly warmed (over a period of 1 hr) to room temp, and continued to stir for further 3 hr. Thereafter, it was diluted with water, and extracted thoroughly with petroleum ether. The product obtained following the usual work up, was absorbed on celite (20 g), and loaded over a column of neutral alumina (200 g, act. II). Elution with 0–20% (gradient) ether in petroleum ether, provided **21** (4.1 g, 64%); TLC: silica gel, 20% ether in hexane, $R_f = 0.43$. An analytical sample was obtained by a "short path" distillation (b.p. 150–153°/0.02 torr). IR: 2995, 1455, 1190, 1080, 1035, 975, 910, 875, 815 and 720; PMR: 0.91 (dist. t, 3H, $-CH_3$), 1.2–1.9 (m, 18H, $(-CH_2-)_9$), 1.9–2.4 (m, 8H, $(-CH_2CH{=}CH-)_4$), 3.2–3.9 (m, 4H, $(-CH_2O-)_2$), 4.51 (br. s, 1H, $-O\dot{C}HO-$), and 5.40 (m, 2H, –CH=CH–); MS: *m/e* = 322 (M^+), 238, 221, 124 and 86; (Found: C, 78.01; H, 12.09; Calc. for $C_{21}H_{38}O_2$: C, 78.20; H, 11.88).

Likewise, a Wittig reaction between **20** and **13**, yielded the corresponding (7*Z*, 11*E*)-isomer **22**; IR: 2290, 1450, 1190, 1130, 1075, 980, 965, 910, 880 and 810; PMR: 0.93 (dist. t, 3H, $-CH_3$), 1.2–1.9 (m, 18H, $(-CH_2-)_9$), 1.9–2.4 (m, 8H, $(-CH_2CH{=}CH-)_4$), 3.2–3.9 (m, 4H, $(-CH_2O-)_2$), 4.54 (br. s, 1H, $-O\dot{C}HO-$), and 5.38 (m, 4H, $(-CH{=}CH-)_2$).

(7Z, 11Z) and (7Z, 11E)-7, 11-Hexadecadienyl acetates (**1a** and **1b**). The OTHP-dienes (**21** and **22**) were converted to **1a** and **1b** respectively by acetolysis which was carried out as described in the earlier experiment. The resulting products were purified by column chromatography (silica gel, 20% ether in hexane) followed by a "short-path" distillation.

Compound **1a**: b.p. 125–127°/0.1 torr (lit.[19] 86–89°/0.05 torr), n_D^{25} 1.4588 (lit.[19] n_D^{20} 1.4577).

Compound **1b**: b.p. 124–126°/0.1 torr (lit.[19] 92–94°/0.8 torr), n_D^{25} 1.4585 (lit.[19] n_D^{25} 1.4591).

Baring a slight difference in the multiplicity of olefinic proton signals, the PMR spectra of the two pheromone-components were almost identical with that of the mixture (gossyplure). The IR spectrum of 1b however, was characterised by the presence of a strong absorption band at 965 cm^{-1}.

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