confidently established the hydroxyl group on the *cis* side of the olefin at C1. Under these conditions, and as expected, enhancement of the olefin methyl (C13) was not observed.

The discovery of bisabolene derivatives in *Pseudopterogorgia* species is precedented by our earlier report of curcumene derivatives from the related Caribbean gorgonian *P. rigida*[13]. Hydrocarbons possessing this common ring system have also been reported from gorgonians of the genera *Plexaurella* and *Muricea*[14-16]. Despite the widespread occurrence of numerous common carbon skeletons, our observations suggest that specific chemical components characterize discrete species of gorgonian octocorals. The potential use of secondary metabolites in gorgonian taxonomy has recently been reviewed[17], and while more data must be accumulated, this approach to complex problems in taxonomy appears promising.

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[6] Other physical and spectral features for alcohol **2** include: oil, UV λ_{max} (MeOH) = 250 nm (ε = 4900), IR ($CHCl_3$): 3350–3450, 2960, 2930, 1715, 1670, 1450, 1380 cm^{-1}, HRMS: M^+ m/z obsd. 219.1746 (M^+-H, 25.5), $C_{15}H_{23}O$ requires 219.1749, 201.1633 M^+-H_3O, $C_{15}H_{21}O$, 13).

[7] Compound **3** exhibited the following spectral characteristics: (IR ($CHCl_3$): 2940, 1720, 1670, 1510, 1420, 1380, 1210 cm^{-1}, LRMS: M^+, m/z 262 for $C_{17}H_{26}O_2$; ^1H NMR (360 MHz, CCl_4): δ 5.50 (1 H, bs), 5.37 (1 H, bs), 4.44 (2 H, bs), 2.72 (2 H, bs), 2.30 (2 H, bt), 2.08 (3 H, s), 2.11 (4 H, bs), 2.08 (3 H, s), 1.98 (2 H, bt), 1.67 (9 H, s).

[8] Compound **4** exhibited the following spectral characteristics: UV: λ_{max} (MeOH) = 247 nm (ε = 2200), IR ($CHCl_3$): 2960, 1720, 1450, 1360 cm^{-1}, LRMS: M^+, m/z (relative intensity) 260 (0.3) for $C_{17}H_{24}O_2$, 200 (M^+-HOAc, 5), 158 (6), 145 (11), 143 (22), 132 (37), ^1H NMR (360 MHz, $CDCl_3$): δ 7.11 (4 H, m), 5.42 (1 H, bt), 4.43 (2 H, bs), 2.67 (1 H, m), 2.32 (3 H, s), 2.09 (3 H, s), 1.59 (3 H, s), 1.22 (3 H, d, J = 6.9 Hz).

[9] Epoxide **5** exhibited the following spectral characteristics: IR ($CHCl_3$): 3410, 2980, 2950, 2920, 1430, 1370 cm^{-1}, LRMS: M^+, m/z 236 for $C_{20}H_{24}O_2$, 218 (M^+-H_2O); ^1H NMR (360 MHz, $CDCl_3$): δ 5.42 (1 H, bt), 5.36 (1 H, bs), 4.00 (2 H, bs), 2.38 (1 H, bs), 2.33 (1 H, bs), 2.16 (2 H, m), 2.04 (2 H, m), 1.76 (2 H, m), 1.70 (3 H, s), 1.68 (3 H, s), 1.62 (2 H, m), 1.33 (3 H, s).

[10] Compound **6** exhibited the following spectral characteristics: IR ($CHCl_3$): 3300 (brd), 2920, 1715, 1350 cm^{-1}, LRMS: M^+, m/z 124 for $C_8H_{12}O$ (M^+-H_2O); ^1H NMR (360 MHz, $CDCl_3$): δ 5.37 (1 H, bt), 4.00 (2 H, bs), 2.51 (2 H, t), 2.32 (2 H, t), 2.15 (3 H, s), 1.68 (3 H, s).

[11] The reported values for C7, C11 and C14 for *E*-γ-bisabolene are 29.7, 27.4 and 18.4 ppm. The *Z* isomer shows resonances at 26.8, 29.4 and 17.8 ppm[12]. Since **2** shows bands at 29.9, 27.2 and 18.4 ppm it is assumed to be the *E* isomer.

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Fluorinated analogs of insect sex pheromones[1]

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Summary. The syntheses of fluorinated mimics of pheromones of *Spodoptera littoralis, Diparopsis castanea, Laspeyresia pomonella, Bombyx mori* and *Thaumetopoea pityocampa* are described. These analogs showed biological activities similar to those of the natural pheromones in laboratory assays (EAG).

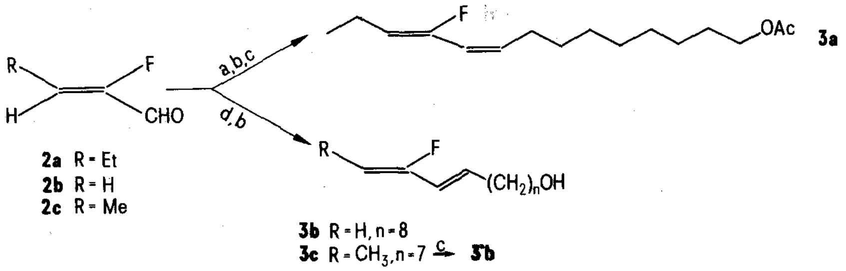
Key words. Pheromones, insect sex; *Spodoptera littoralis; Diparopsis castanea; Laspeyresia pomponella; Bombyx mori; Thaumetopoea pityocampa;* pheromone analogs, fluorinated.

In connection with our ongoing interest on the study of bioactive fluorinated compounds in insect biochemistry[3,4], we describe in the present communication the previously unreported synthesis of fluorinated analogs of several insect sex pheromones, along with their biological activity on EAG.

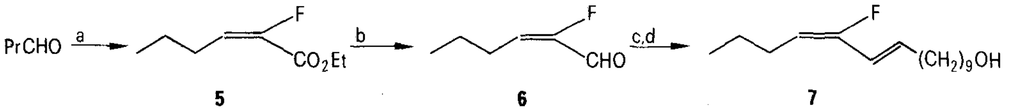
Replacement of hydrogen atoms by fluorine at definite sites of a given pheromone molecule could eventually disrupt the mating communication system by irreversible binding of these fluorinated analogs with specific pheromone receptors. Furthermore, an enhancement of the chemical stability of the pheromone molecule, which might be essential under experimental field conditions, could also be expected.

As shown in scheme 1, synthesis of (Z)-9,(Z)-11,11-fluorotetradecadien-1-yl acetate **3a**, a fluorinated mimic of the sex pheromone of the Egyptian cotton leafworm *Spodoptera littoralis* (Boisd.)[5] was accomplished by Wittig reaction of the tetrahydropyranyl derivative of 9-hydroxy *n*-nonyltriphenylphosphonium ylide **1** with fluoroaldehyde **2a**[6]. The stereochemistry of **3a** was Z/E 92/8 according to GC analysis (glass capillary column OV-1 20 m, 0.30 mm i.d., 0.15 µl).

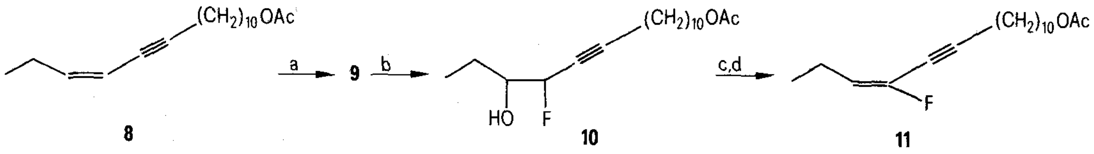
Analogously, aldehydes **2b**[6] and **2c**[6] were allowed to react with the required Wittig ylides under Schlosser procedure[7] (addition of 1 equivalent of *n*-BuLi. LiBr to the initially formed betaine), to yield the expected dienic alcohols, **3b** and **3c**, with predominantly the desired E stereochemistry of the newly formed double bond (Z/E 4/96 by GC analysis). Alcohol **3c** is a fluorinated mimic of the sex pheromone of the codling moth *Laspeyresia pomonella* L.[8] (Lepidoptera, Tortricidae). Acetylation of **3b** under standard conditions afforded (E)-9,11-fluorododecadien-1-yl acetate, **3'b**, a fluorinated analog of the sex pheromone of the red bollworm moth *Diparopsis castanea* Hampson[5] (Lepidoptera, Noctuidae).



Scheme 1. Synthesis of the fluorinated mimics of the sex pheromones of the Egyptian cotton leafworm, **3a**; red bollworm moth, **3b**; and codling moth, **3c**.
a, $Ph_3P^+(CH_2)_9$ OTHP Br^-, *n*-BuLi/−78°C; b, camphosulfonic acid/MeOH, 64% overall; c, Ac_2O/Py, 80%; d, 1) $Ph_3P^+(CH_2)_n$-OTHP Br^-, *n*-BuLi.LiBr/−78°C, 2) *n*-BuLi, 3) *t*-BuOH, 58% for **3a**, 56% for **3b**.



Scheme 2. Synthesis of 12-fluorobombykol, a fluorinated analog of the sex pheromone of the silkworm moth *Bombyx mori*.
a, $(EtO)_2P(O)CHFCO_2Et$ **4**, LDA, 50%; b, DIBAH/−78°C, 62%; c, 1) PH_3P^+ $(CH_2)_{10}OTHP$ Br^-, *n*-BuLi. LiBr/−78°C, 2) *n*-BuLi, 3) *t*-BuOH; d, camphosulfonic acid, 60% overall.



Scheme 3. Synthesis of the fluorinated mimic of the sex pheromone of the processionary moth, **11**.
a, *m*-CPBA, 60%; b, $C_5H_5NH^+F(HF)_n^-$, 16%; c, TsCl/Py, 83%; d, *t*-BuOK/DMSO, 89%.

A new approach was undertaken to prepare (E)-10,(E)-12,12-fluorohexadecadien-1-ol **7**, a fluorinated analog of bombykol, sex pheromone of the silkworm moth *Bombyx mori*[9]. Wittig-Horner reaction of lithium triethylphosphonofluoroacetate[10] **4** with butyraldehyde afforded ester **5** in a Z/E 9/91 isomer ratio. The E isomer was purified by column chromatography and reduced to the corresponding fluoroaldehyde **6** (DIBAH/hexane, −78°C). New Wittig reaction of **6** with the tetrahydropyranyl derivative of 10-hydroxy *n*-decyl-triphenylphosphonium bromide, under the Schlosser modification, yielded 12-fluorobombykol **7** (E, E/Z, E 94/6) (scheme 2).

The fluorinated mimic of (Z)-13-hexadecen-11-yn-1-yl acetate **8**, sex pheromone of the processionary moth *Thaumetopoea pityocampa* (Denis and Schiff)[11] (Lepidoptera, Notodontidae), has also been prepared by ring opening reaction of the corresponding epoxide **9** with pyridinium poly(hydrogen fluoride)[12] to furnish the mixture of *erythro* and *threo* fluorohydrins **10**. Separation of the diastereoisomers on silica gel chromatography followed by dehydration yielded the expected (E)-13,13-fluorohexadecen-11-yn-1-yl acetate **11** (scheme 3).

The fluorinated pheromone mimics **3a** and **11** showed EAG (electroantennogram) activities similar to those of the corresponding natural pheromones. Thus, whereas 1 µg of (Z)-9,(E)-11-tetradecadien-1-yl acetate, the major component of the sex pheromone of the Egyptian cotton leafworm *Spodoptera littoralis*[5] elicited 0.9 mV response and 1 µg of the (Z)-9,(E)-12 isomer, the minor component of the pheromonal secretion[13], deflects a 0.80 mV amplitude as average, the fluorinated mimic **3a** induced a 0.85 mV response on the male's antenna. Different blends of the 3 compounds gave rise to slightly higher EAG deflection amplitudes.

On the other hand, compound **11**, fluorinated pheromone mimic of the processionary moth *Thaumetopoea pityocampa*, elicited a 0.9 mV response compared with 0.8 mV of the natural pheromone **8**. Blends of **8** and **11** induced higher depolarizations, ranging from 1.0 to 1.5 mV according to the **8**/**11** ratio.

The above results suggest that a variety of studies, using flight tunnel behavioral assays as well as studies at single cell receptor level should be carried out to assess the correct nature of the activity exhibited by the fluorinated analogs of the insect sex pheromones.

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