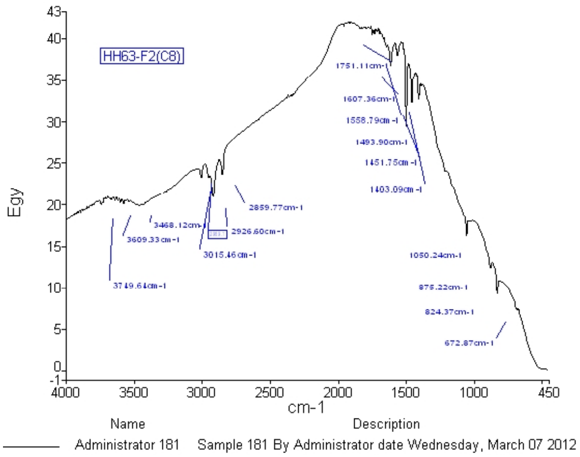
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40
35
30
25
20
15
10
5
0
-1
4000
3500
3000
2500
2000
1500
1000
450
cm-1
1751.11cm-1
1607.36cm-1
1558.79cm-1
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1451.75cm-1
1403.09cm-1
2859.77cm-1
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2926.60cm-1
3609.33cm-1
3015.46cm-1
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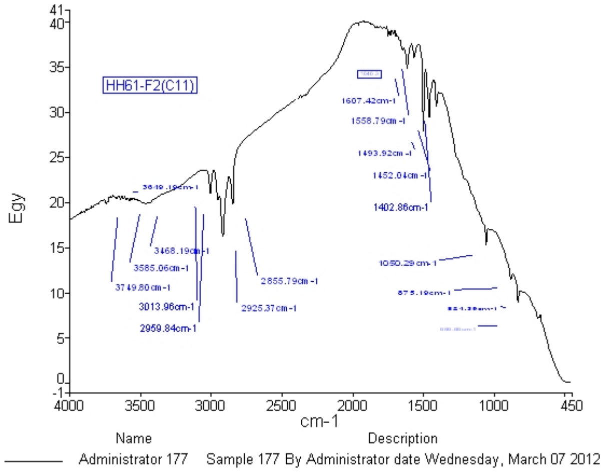
Name
Description
Administrator 181
Sample 181 By Administrator date Wednesday, March 07 2012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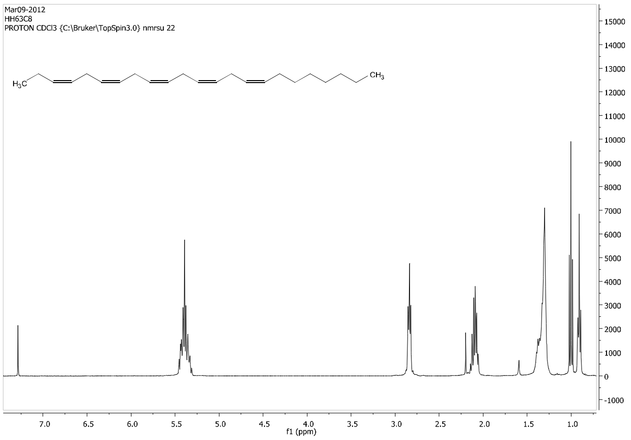
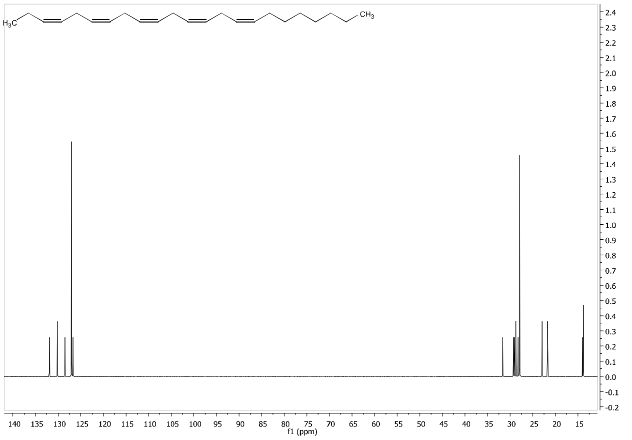
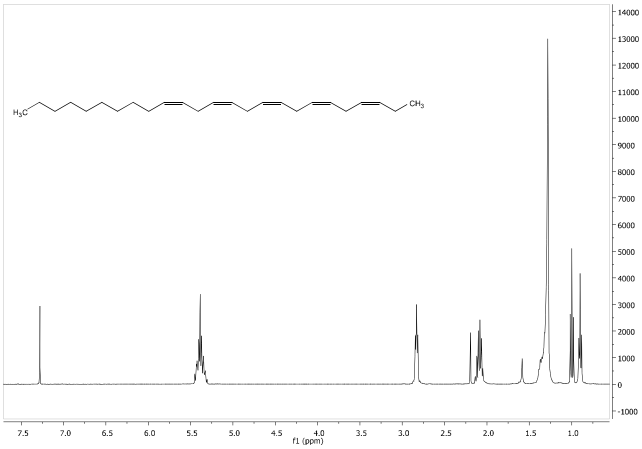
Sample 177 By Administrator date Wednesday, March 07 2012





IR spectrums for (3Z,6Z,9Z,12Z,15Z)-tricosa-3,6,9,12,15-pentaene and (3Z,6Z,9Z,12Z,15Z)-pentacosa-3,6,9,12,15-pentaene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CH3
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12000
11000
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4000
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7.5
7.0
6.5
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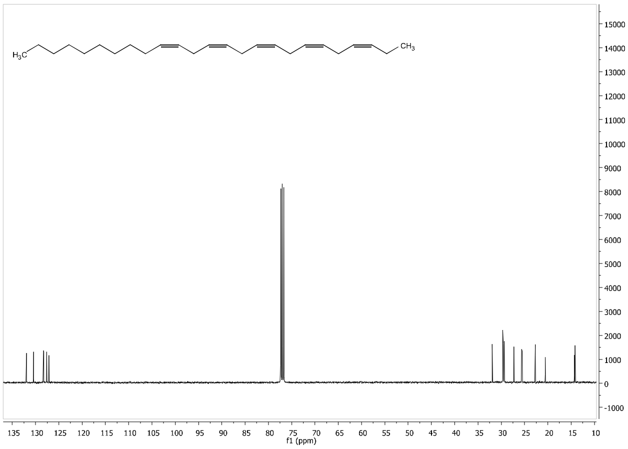
1.0
f1 (ppm)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135
130
125
120
115
110
105
100
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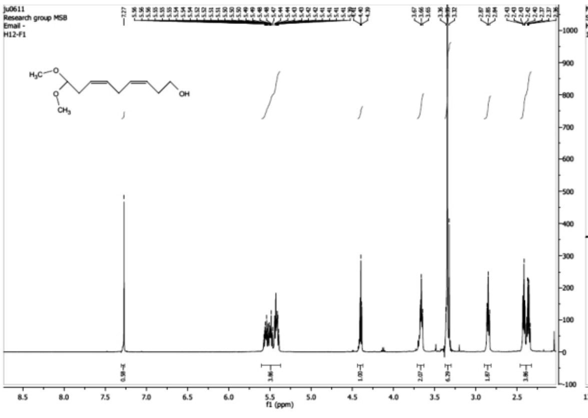
f1 (ppm)


ju0611
Research group MSB
Email -
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H3C
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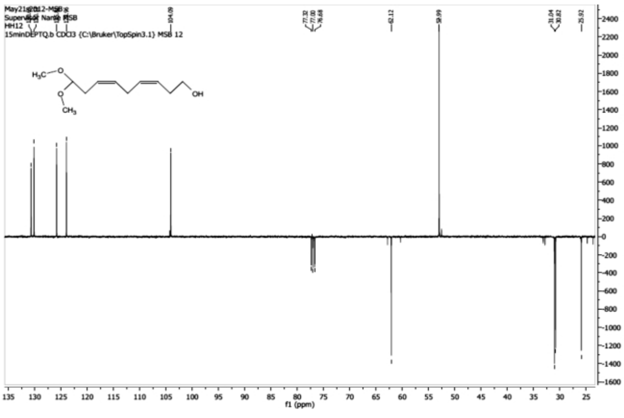
O
CH3
OH
f1 (ppm)


May21-2012-MSB
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52.99
31.04
30.82
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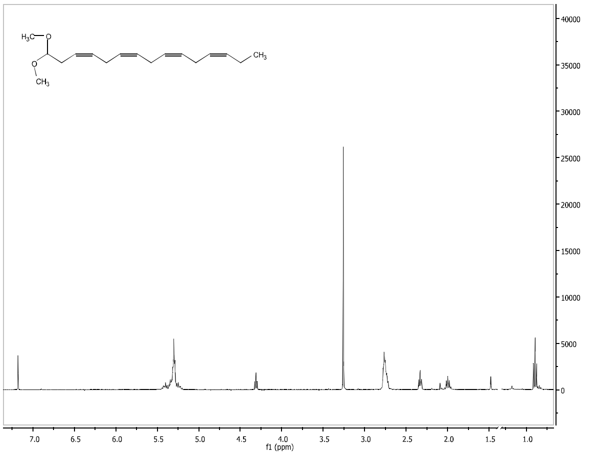
H3C
O
O
CH3
OH
f1 (ppm)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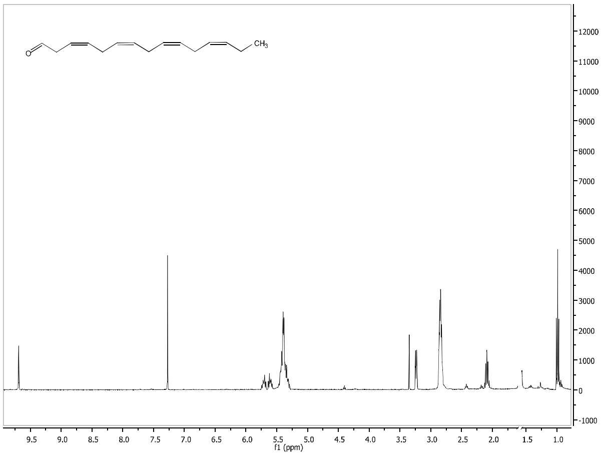
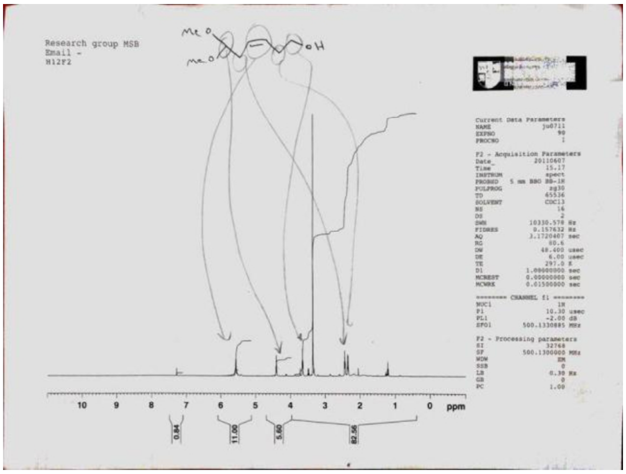
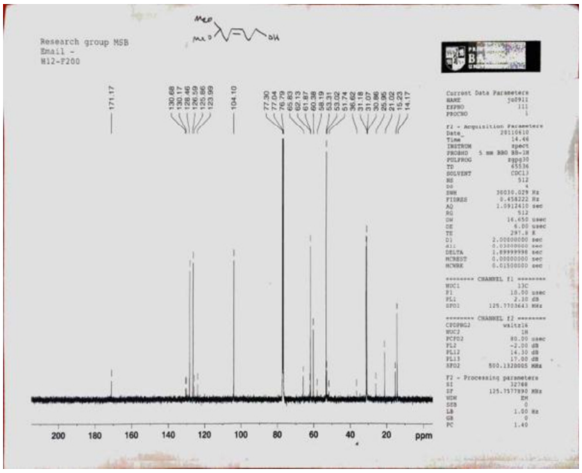
CH3
f1 (ppm)


O
CH3
f1 (ppm)

Supplementary Information Section

Proton and Carbon NMR of Preparing Compounds





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Starting materials	Weight / g or ml	Price (EUR)
Linolenic acid	5 g	667
3-butyn-1-ol	5 g	42
1,5-Cyclooctadiene	250 Ml	26

Acknowledgements

Hussein H. Mustafa wishes to thank Supervisor Professor Mark S. Baird and I wish to thank the Bangor University for providing accurate NMR, IR and mass measurements.

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1. Shani, A., "Integrated pest management using pheromones," **1998**, Chemtech 28 (3), 30-35.
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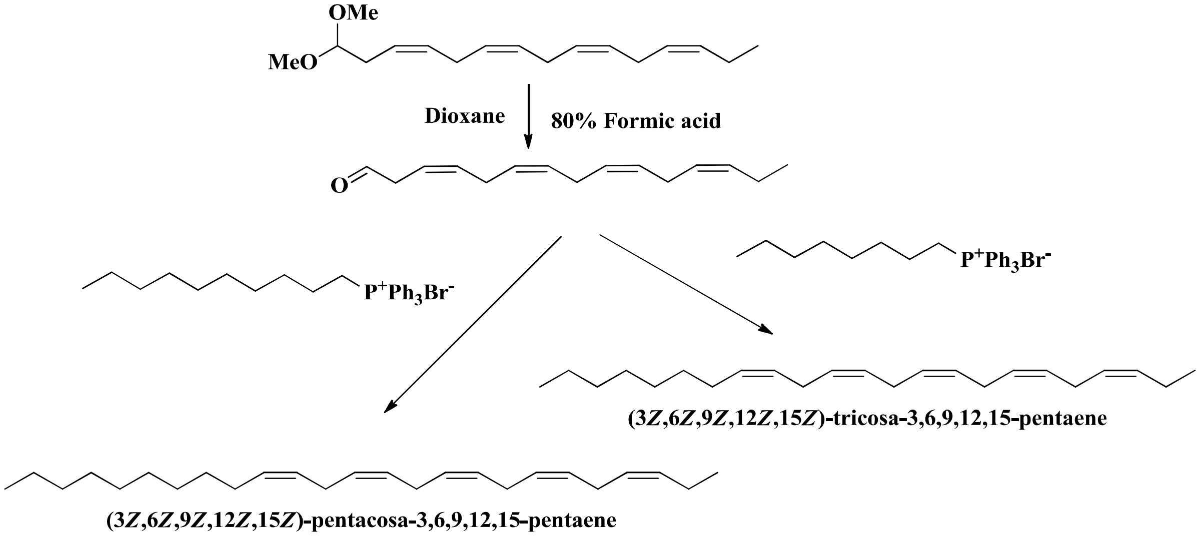
3,6,9,12,15-pentaene. These are the required pheromones in our aim of this work.

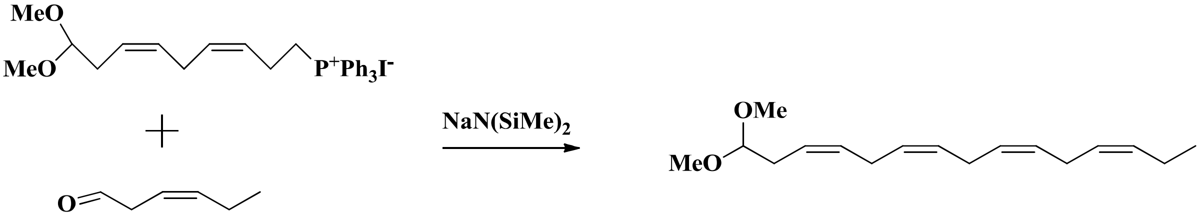


These pheromones had been prepared before in different routes, and usually, all the method were depended on using 3-butyn-1-ol, or using linolenic acid,(4,19) or prepared from acetylene which has a disadvantages relate to the high cost of starting material, use of acetylene couplings and the difficulty of controlling the hydrogenation.[20]

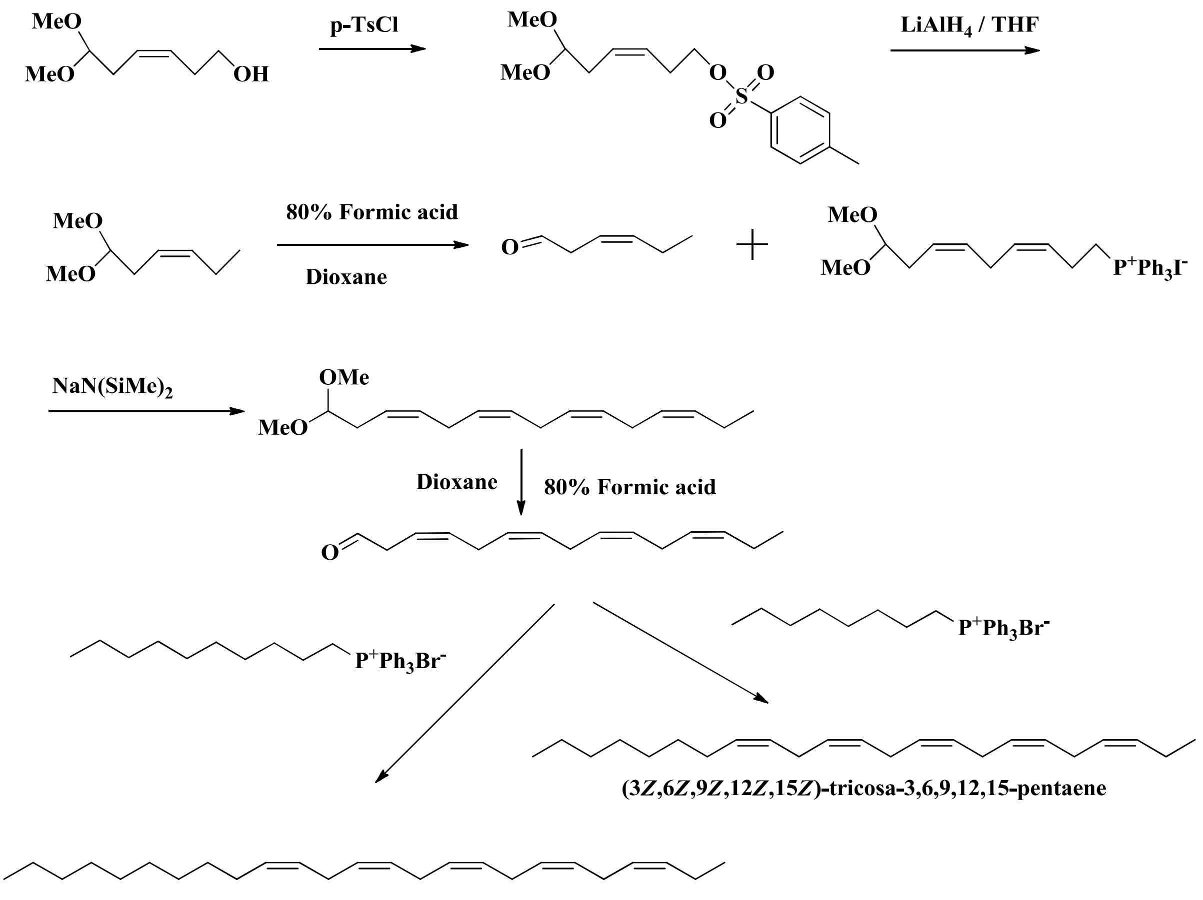
Feasibility:

Economic feasibility shows the importance of the method used in this research through the economic cost of manufacturing, there was a difference in the prices of raw materials used previously for manufacturing, and the price of raw material used in our way.(21) The price of the used starting material 1,5-Cyclooctadiene was 26 EUR which is much lower than other raw materials these had been used previously.

aluminium hydride was used as reduction agent, followed by the deprotection step for the two methoxy groups of the acetal by the using formic acid 80 %,(17) to provides the (Z)-hex-3-enal.(6,7) The phosphonium salt ((3Z,6Z)-9,9- dimethoxy-nona-3,6-dien-1-yl)-triphenyl-phosphonium iodide that had been synthesised before could be applied to synthesis a number of important molecules which characterized by containing four skip conjugated Z- double bonds.(8,18) Here, and by the coupling of this mention phosphonium salt with the aldehyde ((Z)-hex-3-enal) in present of sodium bis-(trimethyl-silyl)-amide as a strong base, tetraene acetal (3Z,6Z,9Z,12Z)-1,1-dimethoxypentadeca-3,6,9,12-tetraene had been prepared.



The tetraene acetal was underwent to a commercial reaction to deprotected the dimetoxy groups by the using of a formic acid to obtain a pentaenal (3Z,6Z,9Z,12Z)-pentadeca-3,6, 9,12-tetraenal. In the final and to extension the chain, two types of phosphonium salt decyltriphenylphosphonium bromide times and octyltriphenylphosphonium bromide in other times were cou-pled to the preparing aldehyde using sodium bis-(trimethyl-silyl) amide to obtain, respectively, (3Z,6Z,9Z,12Z,15Z)-pentacosa-3,6,9,12,15-pentaene and give (3Z,6Z,9Z,12Z,15Z)-tricosa-



(3*Z*,6*Z*,9*Z*,12*Z*,15*Z*)-tricosa-3,6,9,12,15-pentaene

(3*Z*,6*Z*,9*Z*,12*Z*,15*Z*)-pentacosa-3,6,9,12,15-pentaene

The reaction include, first using a large amount of ozono which pass through around flask contain a 1,4,7-cyclononatriene which dissolved in the methanol. In the second step and without separating, the reaction mixter was treated with p-toluene sulfonic acid. The resulting product was undergo to the reduction reaction by using sodium boro-hydride to get an acetal ((Z)-6,6-dimethoxyhex-3-en-1-ol) which has one double bond more than the second product of (3Z,6ZZ)-9,9-Dimethoxynona-3,6-dien-1-ol).

The acetal ((Z)-6,6- dimethoxy-3-hexen-1-ol under went to the tosylate reaction. After that, lithium

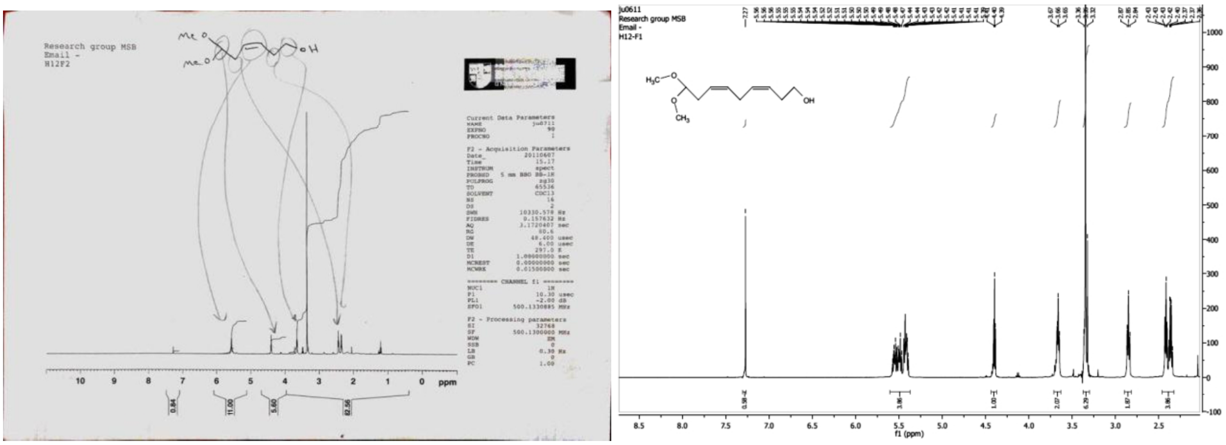


Fig.1: ^{1}HNMR spectrums of (z)-6,6–dimethoxy-3-hexen-1-ol & (3z,6z)- 9,9-dimethoxy-nona-3,6-dien-1-ol

1,4,7-cyclononatriene had been prepared from 1,5-cyclooctadiene through a few steps,(8) this product was subjected to ozonolysis reaction. Controlling the amount of ozone could be lead to formation of two types of acetal with an exclusively Z-olefin, one with one double bond and the second with two double bonds. The second compound has been successfully used in the synthesis of several pheromones compounds which contain Z-alkenes,(15,16) while the aim of the current work was to apply the same ozonolysis reaction on the same 1,4,7-cyclononatriene compound but to get another goal that was increase the yield of the (Z)-6,6-dimethoxy-3-hexen-1-ol product, and make it as a basic intermediate in our other reaction, then coupled with different compounds using Wittig reaction as a main coupling reaction in this strategy to synthesis of pheromones.

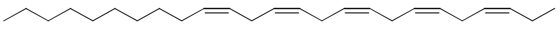
Results and discussion:

There are many pheromones containing double bonds which known as a skip conjugated double bonds systems. because the (3Z,6Z,9Z,12Z,15Z)-pentacosapentaene and (3Z,6Z,9Z,12Z,15Z)-tricosapentaene considered as a crucial components of the pheromone mixture of the fir coneworm, and more important pheromone-based monitoring lures for detecting and monitoring navel Orangeworm in pistachios, almonds and walnuts. Therefore; we focused on its preparation economically. These pheromones works on adult male monitor and identify the population gathered, and the occurrence of disorder in mating in the crop. Several factors affect to these types of reactions - amount of ozone, temperature and the time, but Ozone amount is the main factor that determine the cleavage's numbers of the double bonds in the cyclonona-1,4,7-triene compound (which readily could be obtained from cyclo-octa-1,5-diene).(14) As shown below, the NMR spectrum showed that, when we used (4 Liter / minute O2 while ozone is used 6.36 mmols / minute) it lead to cleavage one double bond and give (3Z,6Z)- 9,9- dimethoxy-nona-3,6-dien-1-ol in high yield, it can be noticed increasing the amount of ozone gas, which pass through the reaction to (4 Liter / minute O2 and 7 mmols / minute O3) leads to cleavage two double bonds of cyclonona-1,4,7-triene to produce another compound which known a (Z)-6,6–dimethoxy-3-hexen-1-ol.

The chemical structures of the obtained products were confirmed by NMR and IR as shown in Supplementary Information Section.

(3Z,6Z,9Z,12Z,15Z)-tricosa-penta-3,6,9,12,15-ene (0.23 g, 82 %), The product showed the same NMR spectrum to the one reported in the literature. δ_H (400 MHz): 5.44 - 5.30 (10H, m), 2.82 (8H, t, J 6.08 Hz), 2.10 (4 H, m), 1.30 (10 H, m), 0.99 (3 H, t, *J* 7.56Hz), 0.89 (3 H, t, *J* 6.64 Hz). δc (126 M Hz): 131.9, 130.5 , 128.6, 128.4, 128.2, 128.16, 127.8, 127.7, 127.6, 127.1, 31.8, 31.7, 29.7, 29.3, 29.2, 27.2, 25.6, 25.5, 22.7, 20.6, 14.2, 14.1. ν_{max}/ cm^{-1}: 3015, 2926, 2859, 1751, 1607, 1493, 824, 672.

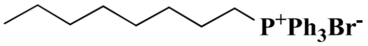
Preparation of (3Z, 6Z, 9Z, 12Z, 15Z)-pentacosa-3, 6, 9, 12, 15-pentaene



(3Z, 6Z, 9Z, 12Z, 15Z)-pentacosa-3, 6, 9, 12, 15-pentaene (0.27 g, 87 %), had been prepared depending to the previous method which reported above from (3Z,6Z,9Z,12Z)-pentadeca -3, 6, 9, 12 -tetraenal (0.2 g, 0.92 mmol), decyltriphenylphosphonium bromide (0.7 g, 1.45 mmol) and a base of sodium bis-(trimethyl-silyl)-amide (2.00 mL, 2.00 mmol) in tetrahydrofuran (20 ml). δ_H (400 MHz): 5.44 (10 H, m), 2.83 (8H, t, J 6.08 Hz), 2.08 (4 H, m), 1.27 (14 H, m), 0.99(3 H, J 7.56 Hz, triplet), 0.89 (3H, J 6.64 Hz, triplet). δc (126 MHz): 131.9, 130.5, 128.6, 128.3, 128.2, 127.8, 127.5, 127.1, 32.0, 29.7, 29.6, 29.5, 29.32, 29.31, 27.2, 25.6, 25.5, 22.7, 20.5, 14.3, 14.1. ν_{max} / cm^{-1}: 3013, 2925, 2855, 1607, 1493, 875, 721. This data had been identical with which reported in behaviours literature which prepared the same product in different method (long and more expensive method).(13)

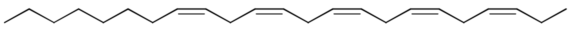
br m), 1.60 (4H, br s), 1.16 (12H, br s), 0.82 (3H, br t, J 6.2 Hz)· δc (126 MHz): 134.9, 134.9, 133.6, 133.5, 130.4, 130.3, 118.6, 117.8, 31.6, 30.4, 30.2, 29.3, 29.1, 29.0, 22.9, 22.5, 22.4, 14.0.

Preparation of octyltriphenylphosphonium bromide



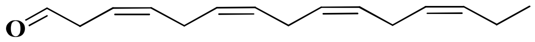
As above, octyltriphenylphosphonium bromide(12) (20 g, 85 %), was prepared by using 1-bromooctane (10 g, 50 mmol), PPh_3 (17.6 g, 67 mmol), toluene (120 ml). δ_H (400 MHz): 7.88-7.78 (9H, br m), 7.73-7.68 (6H, m), 3.84-3.79 (2H, br m),1.63 (4H, br s), 1.34-1.11 (8H, m), 0.88 (3H, br t, J 6.76 Hz). δc (126 MHz): 134.9, 134.9, 133.7, 133.6, 130.5, 130.3, 118.8, 117.9, 31.6, 30.4, 30.2, 29.1, 22.6, 22.5, 22.5, 14.0.

Preparation of (3Z,6 Z,9 Z,12 Z,15 Z)-tricosa-penta-3,6,9,12,15-ene



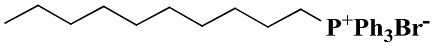
To the mixture of octyltriphenylphosphonium bromide (0.8 g, 1.7 mmol) and 20 mL of dry tetrahydrofuran, Sodium bis-(trimethylsilyl)-amide (2.8 mL, 2.8 mmol) as a base was added slowly at -80 °C. Stirred the reaction mixture for 30 min before cooling down the reaction temperature again to about -80 °C, followed by addition of a mixt of (3Z,6Z,9Z,12Z)-pentadeca-3,6,9,12-tetraenal (0.3 g, 1.35 mmol) with dry tetrahydrofuran (3 ml), and leave it to stirred for one hour. Quenched the reaction by the using of saturated aqueous of NH_4Cl (10 ml), then extracted the product with ethyl acetate, dried, evaporated and finally purified by the using column chromatography to get a

Preparation of (3Z,6Z,9Z,12Z)-pentadeca-3,6,9,12-tetraen-al



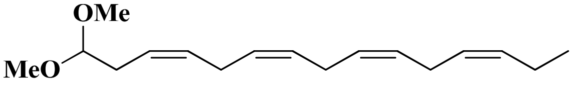
The preparing (3Z,6Z,9Z,12Z)- 1,1-dimethoxypentadeca-3,6,9,12-tetraene (0.2 g, 0.75 mmol) was dissolved in four mL of dioxane, then four mL of solution of formic acid 80 % was added as drops to the reaction mixture. After leaving the mixture to a stir for two hours at room temperature, five mL of water was add to quench the reaction. Extracted the product three times with about 20 mL of CH_2Cl_2, dried, evaporated and purified with column to get the required product of (3Z,6Z,9Z,12Z)-pentadeca-3,6,9,12-tetraenal (0.13 g, 81 %).(9,10) δ_H (400 MHz): 9.69 (1H, t, J 1.72), 5.70 (2H, m), 5.40 (6H, m), 3.20 (2H, br, d, J 7.12, Hz), 2.79 (6H, br pent., J 5.08 Hz), 2.05 (2H, br pent., *J* 7.48 Hz), 1.00 (3H, t, *J* 7.56 Hz). δ_c (126 MHz): 199.2, 132.1, 128.9, 127.8, 127.7, 127.1, 127.06, 126.8, 122.6, 42.0, 27.9, 27.64, 22.5, 21.4, 14.1. $\nu_{max}/\ cm^{-1}$: 2926, 2861, 1731, 1609, 1558, 1494, 1050, 724.

Preparation of decyltriphenylphosphonium bromide



1-Bromodecane (10.0 g, 45 mmol) was added to a stirred solution of triphenylphosphine (15.4 g, 58 mmol) in toluene (120 ml). The mixture was refluxed for 48 hours, then the solvent was evaporated. After that petrol (200 ml) was added and evaporated. The residue was treated with diethylether (100 ml) then stirred for one hour; by this time slurry of crystals had formed. These were filtered, washed with ether and dried to give a white solid of decyltriphenylphosphonium bromide (15.0 g, 71 %).(11) δ_H (400 MHz): 7.84-7.69 (15H, m), 3.71 (2H, 126.4, 126.2, 124.3, 118.3, 117.5, 104.2, 53.4, 31.3, 25.7, 23.5, 23.0, 20.3. ν_{max} / cm^{-1} : 2930, 2863, 1733, 1610, 1485, 1438, 1188, 824, 721.

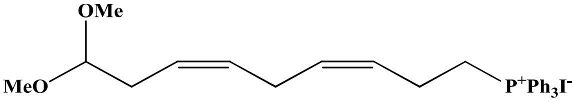
Preparation of (3Z,6Z,9Z,12Z)-1,1-dimethoxypentadeca-3,6,9,12-tetra-ene



To a the stirred slurry of ((3Z, 6Z) - 9,9-dimethoxy-nona-3,6-dien-1-yl)-triphenyl-phosphonium iodide (0.6 g, 0.87 mmol) which dissolved in the drying tetrahydrofuran (15 ml), sodium bis-(tri-methyl-silyl)-amide (2.8 mL, 2.8 mmol) was added as dropwise at -80 °C. The mixture was stirred for 30 mints until the temperature reach to R.T., then leave it to stir for extra 30 min before reducing the temperature again to -80 °C by using liquid nitrogen bath followed by addition of (Z)-hex-3-enal (0.2 g, 2 mmol) which dissolved in (3 ml) of dry tetrahydrofuran. When the reaction temperature reach to the room temperature cooled down again to around 0°C then saturated aqueous of NH_4Cl (10 ml) was add to quenched the reaction. Ethyl acetate was used to extracted the product to the organic layer and dried on the $MgSO_4$ follow by the evaporation and finally purified the resulting product by the column to get a pure compound of (3Z,6Z,9Z,12Z)- 1,1-dimethoxypentadeca-3,6,9,12-tetra-ene (0.45 g, 86 %).(8) δ_H (400 MHz): 5.44 - 5.30 (8H, m), 4.31 (1H, t, *J* 5.4 Hz), 3.26 (6H, s), 2.83 (6H, t, J 6.06 Hz), 2.29 (2H, m), 2.01 (2H, m), 1.03 (3H, t, *J* 6.64 Hz). δc (126 MHz): δ 139.26, 131.92, 127.06, 126.70, 124.57, 106.27, 55.30, 34.38, 27.92, 21.74, 13.84. ν_{max} / cm^{-1} : 3015, 2926, 2859, 1751, 1607, 1493, 824, 721.

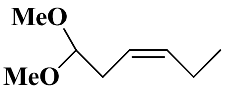
temperature. The reaction mixture was stirred for 1.5 hr, then water (10 ml) was added to quench the reaction, follow by the extraction the product by using dichloromethane (4 x 10 ml). The separated organic layers were washed with $NaHCO_3$ (10 ml), brine (5 ml) then dried with $MgSO_4$ and at the end the solvent was evaporated to obtain (Z)-hex-3-enal (0.17 g, 94 %), %).(6,7) which was used for the next step without purification. δ_H (400 MHz): 9.66 (1H, t, J 1.84), 5.7-5.4 (2H, m), 3.14 (2H, d, J 7.16 Hz), 2.07 (2H, pent, J 7.4 Hz), 0.99 (3H, t, J 7.52 Hz). δc (126 MHz): 199.7, 134.8, 123.9, 42.2, 21.6, 13.9. ν_{max} / cm^{-1} : 2859, 1727, 1646, 1609, 1494, 1452, 1122, 874, 717.

Preparation of ((3Z,6Z)-9,9-dimethoxy-nona-3,6-dien-1-yl)-tri-phenyl-phos-phonium iodide



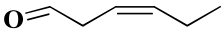
(3Z,6Z)-9-iodo-1,1-dimethoxynona-3,6-diene (0.99 g, 3.20 mmol) was dissolved in the acetonitrile (7 ml), followed by addition of Triphenylphosphine (1.4 g, 5.3 mmol) and calcium carbonate (0.1 g) to the preparing solution then leave the mixture to stir for 72 hours at 50 °C. After that, cooled down the mixture temperature to the room temperature, filtrate, evaporate the organic layers and then purified the residue by the column using a mixt of CH_2Cl_2/MeOH (95:5) as elute to get a pure product of ((3Z,6Z)-9,9-di-methoxynona-3,6-dien-1-yl)tri-phenyl-phosphonium iodide (1.4 g, 71 %).(8) δ_H (400 MHz): 7.80 (15H, br m), 5.65 (1H, br q, J 7.1 Hz), 5.43-5.31 (3H, m), 4.29 (1H, t, J 5.7 Hz), 3.81 (2H, br dt, J 7.8, 12.1 Hz), 3.28 (6H, s), 2.57 (2H, br t, J 5.88 Hz), 2.40 (2H, m), 2.23 (2H, t, J 5.72 Hz). δc (126 MHz): 135.1, 135.1, 133.7, 133.6, 130.6, 130.4, 130.2, 129.3, 127.8, 124.2, 123.4, 104.0, 68.5, , 55.30, 55.30, 34.38, 29.71, 21.13. ν_{max} / cm^{-1} : 2931, 2831, 1598, 1495, 1448, 1361, 1189, 1177, 964, 816.

Preparation of (Z)-1,1-dimethoxyhex -3-ene



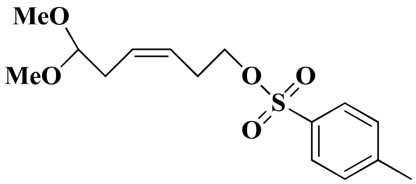
(Z)-6,6-dimethoxyhex-3-en-1-yl 4-methylbenzenesulfonate (0.65 g, 2 mmol) was dissolved in tetrahydrofuran (5 ml) then added as drops to a mixt of a lithium-aluminium hydride (0.5 g, 13.3 mmol) and tetrahydrofuran (15 ml) at -5 °C. This reaction mixture was leaved to stir for 15 hours, after that, and to quench the reaction saturated aqueous of Sodium-sulfate (3 ml) was added to the suspension mixture which diluted with THF (5 ml) between -10 to -5 °C. White precipitate had been formed from the mixture when it stir for about one hour. Tetra hydro furan (5 ml) and $MgSO_4$ were added to the resulting mixture, filtered, evaporated and follow by the purification for the product by the using column technics, and the uses elute was petrol : ethyl acetate in ratio (20:1) to get (Z)-1,1-dimethoxyhex-3-ene (0.25 g, 92 %).(6) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.53-5.44 (2H, m), 4.63 (1H, t, J 5.76 Hz), 3.35 (6H, s), 2.37 (2H, t, J 7.12 Hz), 2.07 (2H, pent, J 7.48 Hz), 0.99 (3H, t, J 7.52 Hz). δc (126 MHz): 139.1, 115.3, 105.0, 55.30, 33.9, 21.5, 14.3. ν_{max} / cm^{-1} : 2961, 2831, 1657, 1462, 1362, 1124, 1061, 756.

Preparation of (Z)-hex-3-enal



To stir mixt of (Z)-1,1-dimethoxyhex-3-ene (0.3 g, 3 mmol) and dioxane (5 ml), 80 % formic acid which was diluted by (6 ml) of water was added carefully as drops at room results were ν_{max} / cm^{-1}: 3410, 2829, 1695, 1365, 1197, 1056.

Preparation of (Z)-6,6-dimethoxyhex-3-en-1-yl 4-methylbenzenesulfonate

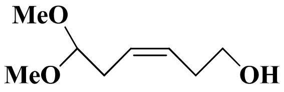


To a stirred solution of (Z)-6,6-dimethoxyhex-3-en-1-ol (0.4 g, 3.12 mmol) which dissolve in pyridine (3 ml), *p*-Toluenesulfonyl chloride (0.7 g, 3.68 mmol) was added at zero degree. The reaction mixture was stirred for 2 hrs at 0 °C. After that the mixture was put it in the fridge for 24 hours, then water (10 ml) was added to the mixture at 0 °C, and pouring in the separating funnel which contained water (20 ml); the resulting product was separated by the extraction with dichloromethane (5 x 20 ml). The collected organic layers were put it in the ice water bath to cooled to -10 °C, then a solution of (2 molare) hydrochloric acid (30 ml) as dropwise was added to make the aqueous layer acidic nature with keeping the temperature around (10 to 0 °C). The reaction mixture was extracted with dichloromethane (25 ml) to separate the organic layer which was dried over magnesium sulphate, filtered and finally evaporated. Purified the crude product by the column chromatography using petroleum ether : ethyl acetate (10:1) as the elute to obtain a pure product of (Z)-6,6-dimethoxyhex-3-en-1-yl 4-methylbenzenesulfonate (0.9 g, 91 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (2H, dd, J 1.95, 8.3 Hz), 7.43 (2H, br d, J 7.9 Hz), 5.45 (2H, m), 4.98 (1H, br ddd, J 1.9, 5.7, 11.45 Hz), 3.61 (2H, ddd, J 1.5, 5.48, 18.96 Hz), 3.34 (6H, s), 2.60 (2H, br t, J 5.4 Hz), 2.35 (2H, br, s), 2.31 (3H, br m). δ_c (126 MHz): 132.4, 129.6, 129.4, relative to chloroform (δ 7.27 ppm), and $CDCl_3$ (δ 77.0 ppm).

Abbreviations and acronyms

b – broad, d – doublet, J - coupling constant, m – meta, q – quartet, s – singlet and t - triplet

Preparation of (Z)-6,6-dimethoxyhex-3-en-1-ol



To a stirred solution contain a mixture of Z,Z,Z-1,4,7-cyclononatriene (2.5 g, 20.8 mmol) and 150 ml of 20 THF : 80 methanol which is collected in a round flask. Ozone was passed through the reaction mixture for 7.5 minutes, with watching the temperature of the flask and keeping it between (-65 to -45) °C using liquid nitrogen. After that, the nitrogen gas was pushed to the mixture for 5 min, followed by addition of p-Toluensulfonic acid monohydrate (0.4 g, 2 mmol) at -35 ─ -20 °C, then stirred vigorously for 3 hrs at room temperature. Sodium borohydride (2.5 g, 66 mmol) was added to the reaction mixture at -10 °C and leave it under stirring for 30 min, at the end the reaction was quenched by using ice water (200 ml) and extracted the resulting product with dichloromethane (3 x 150 ml). The organic layer was dried over anhydrous $MgSO_4$, filtered off then evaporated. The resulting product was Purified by using column chromatography on silica eluting with petrol: ethyl acetate (5:2) to obtain a pure compound.(5) (3.1 g, 93%). The ^{1}H NMR spectrum (500 MHz, $CDCl_3$) showed; δ5.4 (2H, m), 4.29 (1H, t, J 5.15 Hz), 3.64 (2H, t, J 4.71 Hz), 3.33 (6H, s), 2.37 (2H, t, J 6.4 Hz), 2.28 (2H, q, J 6.76 Hz). The ^{13}C NMR spectrum (126 MHz) showed; δ132.4, 124.6, 105.9, 61.6, 53.9, 34.3, 30.8, 25.8. The Infra-red (IR) spectra other moths like the oriental fruit moth and codling moth especially the Cydia pomonella. (2)

In the beginning, it was found that the configuration Ingredients of the navel orangeworm include three main structures, (11Z,13Z)-hexadecadienal, (3Z,6Z,9Z,12Z,15Z)-pentacosapentaene and (3Z,6Z,9Z,12Z,15Z)-tricosapentaene. The first components were described as a weakly attractive, (3) while the other two compounds had been more attractants. (4)

Thus the target of the present study is to develop a cheap and an effective pheromone that could be used in the agriculture to protect crops from insect pests, especially the navel orangeworm (Amyelois transitella) which is considered as a major insect pest that inflicts serious economic damage.

Methodology Section:

All chemicals were purchased from Aldrich Chemical Co. Ltd, Organic solutions were dried over anhydrous magnesium sulfate. All glassware used in anhydrous reactions was dried for not less than 5 h in a 250 °C oven. Column chromatography was conducted under medium pressure using silica gel (BDH, particle size 33–70 mm); TLC was carried out on pre-coated Kieselgel 60 F254 (Art. 5554; Merck) plates. Infra-red spectra were recorded as KBr discs (solids) or thin films on NaCl windows or using a Perkin Elmer 1600 series FT-IR spectrometer. NMR spectra were recorded either on a Bruker AC 250 spectrometer with 5 mm Dual probe or on a Bruker Advance 500 spectrometer with 5 mm BBO probe as solutions in deuterated chloroform ($CDCl_3$) if not differently indicated. Chemical shifts are quoted in δ

Introduction:

Usually, using the classic pesticides result in the development of the resistance in the insect and pests, which lead also to the environmental damages. Therefore, it was necessary to find out and invent a new method to control pests far away from the uses of conventional pesticides, and this has been pheromone which is the best alternatives. (1)

Many chemicals are used by large number of organisms as a communication and understanding means among them with others. Pheromones are one of these chemicals, which secreted by insects as a way to transfer the information among the members of the same type. The pheromones secrete from cells have found in the body wall as a payments invasive. These points are spreading into the air to be received by the receiver on the members of the opposite sex of the same type. There are several types of pheromones, depending on the function; aggregation pheromones, alarm pheromones, trail pheromones and sex pheromones. Sex pheromones are chemicals used for mating in the same species. It is more important and it widely used in the agricultural pest control. One of the hallmarks of pheromones is that they are non-toxic, they tend to be species-specific, that mean they can target a particular species of pest and doesn't affect to other friendly insects. Also, insects tend not to develop resistance to pheromones. This is in contrast to traditional pesticides. Preparing pheromones are effective with the navel orangeworm, which are considered as the principal insect pest and influential in several types of plants like pistachios, almonds and walnuts. The navel orangeworm is more polyphagous comparing to the

Develop new method to preparation of insect pheromones

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Abstract:
New and cheap synthetic method found for the preparation of lepidopteran pheromones which include navel orangeworm pheromones. The structure of these types of pheromones contains pentaene groups which are easier to be prepared through our pathway. These pheromones were synthesized by using directives ozonolysis of cyclonona-1,4,7-triene compounds, which are then converted to a Wittig salt which is using Wittig reaction for coupling with an aldehyde which prepared as a second product from the same ozonolysis step. These synthetic methods involve novel, efficient, and environmentally benign steps.

***Keywords**:* Sex pheromones, (3Z,6Z,9Z,12Z,15Z)-pentacosapentaene, (3Z,6Z,9Z,12Z,15Z)-tricosapentaene, orangeworm and Ozonolysis

تطوير طرق حديثة لتحضير فيرمونات حشرية

م.د. حسين حبيب مصطفى

الخلاصة:

يتضمن البحث ايجاد طريقة جديدة وغير مكلفة اقتصادياً لتحضير فيرمونات حشرية يمكن استخدامها كبديل عن المبيدات الحشرية الكلاسيكية المستخدمة عادةً. تمتاز هذه الفرومونات المحضرة بكونها انتقائية تختص بإبادة الحشرات حرشفيات الأجنحة التي تصيب بساتين ومزارع التين والرمان واللوز والجوز والفستق، وذلك عن طريق إستدراج الحشرات الى مصائد خاصة تعرف بالمصائد الفرمونية تلتصق بها وبعدها يتم طمر أو حرق هذه المصائد والحشرات الملتصقة عليها. تحتوي الصيغة التركيبية لمثل هذه الفرمونات على خمسة اواصر مزدوجة (pentaene groups) وسلسلة طرفية بطول محدد ($(CH_2)_7$ و $(CH_2)_9$). تعتمد طريقة التحضير على عملية تمرير الاوزون على المركب الحلقي ثلاثي الاصرة المزدوجة (cyclonona-1,4,7-triene) وذلك لكسر واحدة من الاواصر المزدوجة مرة، وكسر اصرتين مزدوجتين مرة اخرى اعتماداً على كمية الاوزون الذي يمرر على مزيج التفاعل. تلي هذه الخطوة تحويل احد الناتجين المتكونين الى أملاح فتك والذي يقترن مع المركب الناتج الثاني بعد تحويله الى الالديهايد المقابل باستخدام تفاعل فتك (Wittig reaction). تعتبر هذه الطريقة طريقة حديثة في تحضير هذه الانواع من الفرمونات وتكمن الجدوى الاقتصادية لطريقتنا المستخدمة في الاستغناء عن المواد العالية الكلفة (باهضة الثمن) كالاستلين والمواد الاولية الاخرى التي كانت تستخدم لتحضير هذه الفيرمونات.