

Synthesis of 3Z, 6Z, 9Z-Tricosatriene: A component of the sex pheromone of *Neoleucinodes elegantalis*

Aivlé Cabrera* and Neudo Urdaneta

Departamento de Química, Universidad Simón Bolívar, Apartado 89000
Caracas 1080A, Venezuela

Recibido: 22-09-06 Aceptado: 15-05-07

Abstract

A synthetic route was developed to obtain 3Z,6Z,9Z-tricosatriene from methyl linolenate. 3Z,6Z,9Z-tricosatriene is a sex pheromone component of tomato fruit borer *Neoleucinodes elegantalis*, which exhibits synergistic effect on the attraction of males to the lures, when tested along with the main compound 11E-hexadecen-1-ol. This triunsaturated hydrocarbon belongs to a new family of biologically active compounds recently discovered in Lepidopteran sex pheromones.

Key words: *Neoleucinodes elegantalis*; sex pheromone; 3Z,6Z,9Z-tricosatriene.

Síntesis de 3Z, 6Z, 9Z-Tricosatrieno: Un componente de la feromona sexual de *Neoleucinodes elegantalis*

Resumen

Se desarrolló una ruta de síntesis para la obtención de 3Z,6Z,9Z-tricosatrieno a partir de linolenato de metilo, usando como último paso, una reducción fácil y económica de un mesilato secundario. El 3Z,6Z,9Z-tricosatrieno es un componente clave de la feromona sexual del perforador del fruto del tomate *Neoleucinodes elegantalis*, ya que posee un efecto sinérgico en la atracción de machos hacia trampas que contienen como cebo el componente principal de la feromona, el 11E-hexadecen-1-ol. Este hidrocarburo insaturado es parte de una nueva familia de compuestos biológicamente activos recientemente descubiertos como feromonas sexuales en Lepidoptera.

Palabras clave: Feromona sexual; *Neoleucinodes elegantalis*; 3Z,6Z,9Z-tricosatrieno.

Introduction

Polyunsaturated long chain hydrocarbons have been reported recently as a new important group of components of some Lepidopteran sex pheromones, specifically in the superfamily Pyraloidea. Compounds containing double bonds (up to five) have recently been identified as pheromone components in *Amyelois transitella* (3Z, 6Z, 9Z,12Z,15Z-tricosapentaene and 3Z, 6Z,

9Z,12Z,15Z-pentacosapentaene) and in *Dio-ryctria bietivorella* (3Z, 6Z, 9Z,12Z,15Z-pentacosapentaene) (1,2). An unsaturated hydrocarbon (3Z, 6Z, 9Z-tricosatriene) acting as a synergistic component of a Lepidopteran sex pheromone, was detected for the first time in gland extract of tomato fruit borer *Neoleucinodes elegantalis* females (3). So it is very important to develop new synthetic routes leading to the obtention of this

* Autor para la correspondencia. Fax: +58-212-9063961. E-mail: acabrera@usb.ve

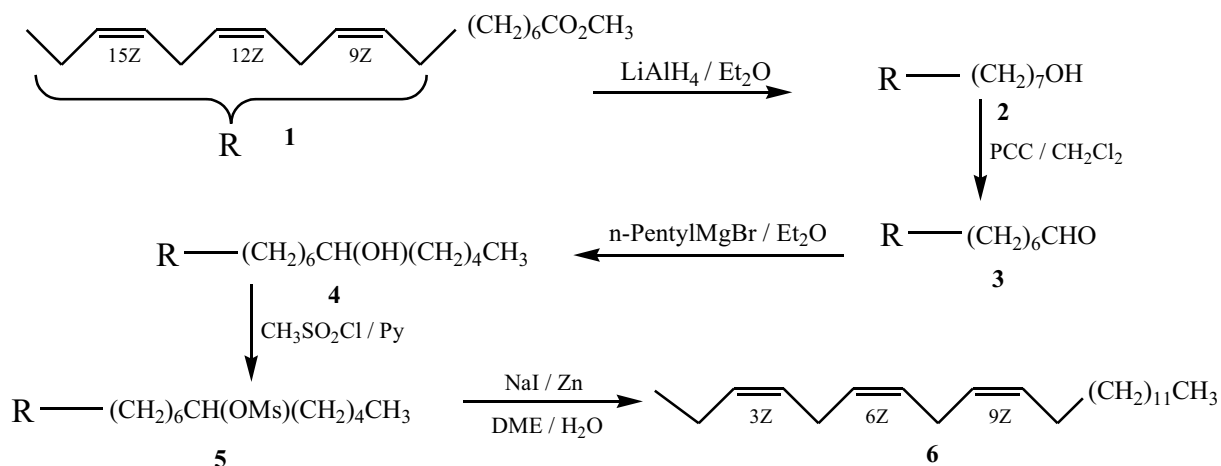


Figure 1. Synthetic scheme of 3Z,6Z,9Z-tricosatriene.

key group of chemicals, in order to evaluate their activity in field experiments.

Materials and Methods

The synthetic scheme (Figure 1) describes the transformation of the commercial linolenic acid methyl ester **1** to 3Z,6Z,9Z-tricosatriene **6**.

The reduction of **1** with LiAlH_4 in dry ether at r.t produced the corresponding linolenol **2** in 92% yield which purity (99%) was corroborated by GC-MS analysis: MS (70 eV): m/z (%) = 264 (2), 121 (10), 108 (26), 79 (100), 67 (82), 55 (78), 41 (79). The resulting linolenol **2** was oxidized with PCC in dry CH_2Cl_2 at r.t to form linolenal **3** in 71% yield (4), MS (70 eV): m/z (%) = 262(2), 121(10), 108(24), 79(100), 67(90), 55(65), 42(96). Pentylmagnesium bromide was added to the obtained aldehyde **3**, to afford alcohol **4** in 65% yield, the purity of this alcohol was determined by GC-MS analysis: MS (70 eV): m/z (%) = 79(100), 55(80), 67(65), 108(63), $317(6) \text{M}^+334(1)$. Treatment of alcohol **4** with methanesulfonyl chloride in dry pyridine produced the mesylate **5** in 84% yield which was characterized by GC-MS analysis: MS (70 eV): m/z (%) = 42(100), 79(95), 55(92),

108(48), 260(4) $\text{M}^+316(3)$. Finally the reduction of mesylate **5** with NaI/Zn dust, in DME in the presence of a little amount of water at refluxing temperature, according the procedure reported in the literature (5), produced 3Z, 6Z, 9Z-tricosatriene **6**, in 74% from mesylate **5**. The final product was fully characterized by ^1H NMR, GC-MS, IR and HRMS. (^1H NMR (CDCl_3 , δ in ppm): δ = 5.35 (m), 2.80 (t), 2.05 (m), 1.25 (m), 0.95 (t) 0.85 (t).- MS (70 eV): m/z (%) = 318 (2), 262 (6), 108 (98), 93 (48), 79 (100), 67 (49). - IR ν = 3000 (=C-H), 2950, 2900, 2850 (C-H), 1650 (C=C), 1450 (C-H). Found by HRMS (m/z) = 318.3270, calculated = 318.3288.

Conclusions

In conclusion the 3Z,6Z,9Z-tricosatriene **6** has been synthesized in 26% overall yield in five steps. The importance of this method is based on its possible use as a generalized and less expensive way to obtain another triunsaturated hydrocarbons with a 3Z,6Z,9Z moiety in their carbon structure.

Acknowledgements

We thank financial support from BID-CONICIT Project QF-36.

References

1. LEAL W.S., PARRA-PEDRAZZOLI A., KAISLING K.E., MORGAN T., ZALOM F., PESAK D.J., DUNDULISE A., BURKS C.S., HIGBEE B.S. **Naturwissenschaften** 92:139-146, 2005.
2. MILLAR J., GRANT G., MCELFRISH S., STRONG W., RUDOLPH C., STEIN J., MOREIRA J. **J Chem Ecol** 31: 1229-1234, 2005.
3. CABRERA A., EIRAS A.E., GRIES G., GRIES R., URDANETA N., MIRÁS B., BADJI C., JAFFE K. **J Chem Ecol** 27:2097-2107, 2001.
4. HENRICK C. **Tetrahedron** 33: 1845-1889, 1977.
5. KOCOVSÝ P., CERNÝ V. **Collect Czechoslov Chem Commun** 44:246-250, 1978.