

Butlerov Communications C Advances in Biochemistry & Technologies ISSN 2074-0948 (print)

2021. Vol.1, No.1, Id.16. Journal Homepage: https://c-journal.butlerov.com/



Full Paper

Thematic section: Preparative Research. *Subsection:* Organic Chemistry.

The Reference Object Identifier – ROI-jbc-C/21-1-1-16 The Digital Object Identifier – DOI: 10.37952/ROI-jbc-C/21-1-1-16 Received 5 February 2021; Accepted 8 February 2021

Methods for the synthesis of the sex pheromone of the pest of grain and grain products – yellow mealworm

Marina P. Yakovleva, Valentina A. Vydrina, Nalia M. Ishmuratova, and Gumer Yu. Ishmuratov

Ufa Institute of Chemistry – Subdivision of the Ufa Federal Research Centre of the Russian Academy of Sciences. Oktyabrya Ave., 71. Ufa, 450054. Republic of Bashkortostan. Russia. Phone: +7 (8347) 235-58-01. E-mail: insect@anrb.ru

*Supervising author; +Corresponding author

Keywords: yellow mealworm *Tenebrio molitor*, sex pheromone, 4*R*-methylnonan-1-ol, synthesis.

Abstract

One of the leading places in the development of fundamentally new plant protection products, characterized by high selectivity of action and safety in relation to the environment, belongs to pheromones – substances formed in the body of insects and affecting the behavior of individuals of the same species. Sex pheromones, which have an impact on the reproduction of the species and thus on its numbers, are most promising in practical terms. The yellow mealworm *Tenebrio molitor* – an insect with complete transformation from the order of *Coleoptera* – is widespread, most often found in bins of flour warehouses, bakeries, and mills. The developing larvae feed on grain, flour, bran, and baked bread. The harm caused by flour beetles is mainly due to the fact that they contaminate the flour with their feces and skins discarded during molting. The sex pheromone of the yellow mealworm *Tenebrio molitor* is 4-methylnonan-1-ol. The review article considers the syntheses of 4R-methylnonan-1-ol with various degrees of optical purity, which is the sex pheromone of the yellow mealworm *Tenebrio molitor*, a malicious pest of grain and grain products. It has been shown that there is considerable interest in the optically active sex pheromone of the yellow mealworm, and the development of effective ways of its synthesis is very urgent. The use of asymmetric synthesis to guide the 4R-center to the target molecule, as well as the use of high-purity optically active substrates, has a number of disadvantages: incomplete stereochemical homogeneity of the products of asymmetric reactions, low availability and high cost of starting compounds and reagents. It has been shown that the most expedient from the point of view of the biological activity/price ratio is the use of (S)-(+)-3,7-dimethyl-1,6octadiene (ee 50%) - the main component of "technical dihydromyrcene", a product of thermolysis cis-(+)-pinan, widely used in the synthesis of aromatic substances in the chemical and perfumery industry.

Copyright © Butlerov Heritage Ltd. & Butlerov Scientific Foundation

For citation: M.P. Yakovleva, V.A. Vydrina, N.M. Ishmuratova, G.Yu. Ishmuratov. Methods for the synthesis of the sex pheromone of the pest of grain and grain products – yellow mealworm. *Butlerov Communications C.* **2021**. Vol.1. No.1. Id.16. DOI: 10.37952/ROI-jbc-C/21-1-16

References

- Y. Tanaka, H. Honda, K. Ohsawa, I. Yamomoto. Absolute configuration of 4-methyl-1nonanol, the sex attractant of the yellow mealmoth, *Tenebrio Molitor. J. Pestic. Chem.* **1989**. Vol.14. No.2. P.197-202.
- [2] A. Baeza, C. Nájera, J.M. Sansano. S_N2'-Alkylation of chiral allylic cyanohydrin *O*-phosphates with organocuprates. *Eur. J. Org. Chem.* **2007**. No.7. P.1101-1112.
- [3] Y. Li, J. Huang, Z. Chen, J. Ren. Synthesis of (R) and (S)-4-methyl-1-nonanol. Journal of North University of China. 2001. Vol.23. No.3. P.247-250.
- [4] Y. Li, J. Huang, Z. Chen, G. Fang. Synthesis of the (*R*)- and (*S*)-sex-attractant of the yellow mealworm from bornanesultam. *Chin. J. Appl. Chem.* 2001. Vol.18. No.10. P.828-830.
- [5] D.T. Genna, C.P. Hencken, M.A. Siegler, G.H. Posner. α-Chloro-β,γ-ethylenic esters: enantiocontrolled synthesis and substitutions. *Org. Lett.* **2010**. Vol.12. No.20. P.4694-4697.
- [6] C. Lu, D. Li, Q. Wang, G. Yang, Z. Chen. Stereoselective synthesis of sex pheromone (*R*)-4methyl-1-nonanol: non-cross-linked polystyrene supported oxazolidinone as a chiral auxiliary. *Eur. J. Org. Chem.* 2009. No.7. P.1078-1081.
- [7] D.L. Li, C.F. Lu, G.C. Yang, Z.X. Chen. Stereoselective synthesis of sex pheromone of the yellow mealworm using (S)-4-benzyloxazolidinone as a chiral auxiliary. *Chem. Nat. Compd.* 2010. Vol.46. No.3. P.440-443.
- [8] I.V. Mineeva. Cyclopropanol methodology in the synthesis of (4*R*)- and (4*S*)-4methyltetrahydro-2*H*-pyran-2-ones. Application in the synthesis of insect pheromones with methyl-branched carbon skeleton. *Russ. J. Org. Chem.* 2015. Vol.51. No.3. P.341-351.
- [9] K. Mori, K. Akasaka. Pheromone synthesis. Part 258. Synthesis of the enantiomers of the beetle pheromones ethyl 4-methylheptanoate, 4-methyloctanoic acid and 4-methyl-1-nonanol, and HPLC analysis of their derivatives to determine their enantiomeric purities. *Tetrahedron: Asymmetry.* 2016. Vol.27. No.4-5. P.182-187.
- [10] A. Carpita, E.De Magistris, R. Rossi. The racemic form and the two enantiomers of 4methyl-1-nonanol, a sex attractant of the yellow mealworm. *Tenebrio molitor* L. *Gazz. Chim. Ital.* **1989**. Vol.119. No.2. P.99-105.
- [11] T. Kitahara, K.S. Hyun, S. Tamogami, R. Kaiser. Synthesis of both enantiomers of methyl 3-methyloctanoate, key component for the scent of african orchids and determination of their absolute configuration. *Nat. Prod. Lett.* **1994**. Vol.5. No.2. P.157-164.
- [12] I.V. Mineeva. Synthesis of the mealworm *Tenebrio molitor* L. pheromone. *Russ. J. Org. Chem.* 2020. Vol.56. No.6. P.994-1000.
- [13] R.L. Safiullin, A.N. Volgarev, G.Yu. Ishmuratov, M.P. Yakovleva, V.N. Odinokov, V.D. Komissarov, G.A. Tolstikov. Decanesulfonic acid as a new oxidant in the Bayer-Villiger reaction. *Reports of the Academy of Sciences*. **1991**. Vol.316. No.3. P.640-642. (Russian)
- [14] V.A. Vydrina, Y.A. Galkina, R.R. Muslukhov, A.A. Kravchenko, G.Yu. Ishmuratov. Oxidation of terpenoids with a cyclohexanone fragment by performic acid. *Chem. Nat. Compd.* 2014. Vol.50. No.4. P.774-775.
- [15] V.N. Odinokov, G.Yu. Ishmuratov, M.P. Yakovleva, R.L. Safiullin, A.N. Volgarev, V.D. Komissarov, R.R. Muslukhov, G.A. Tolstikov. Enantiospecific synthesis of 4*R*methylnonan-1-ol – the sex pheromone of the great flour beetle *Tenebrio molitor* L. *Reports of the Academy of Sciences.* 1992. Vol.326. No.5. P.842-846. (Russian)

- [16] D.V. Banthorpe, D. Whittaker. The preparation and stereochemistry of pinane derivatives. *Chem. Revs.* **1966**. Vol.66. No.4-5. P.643-656.
- [17] L. Lemee, M. Ratier, J.-G. Duboudin, B. Delmond. Flash vacuum thermolysis of terpenic compounds in the pinane series. *Synth. Commun.* **1995**. Vol.25. No.9. P.1313.
- [18] S.S. Poddubnaya, V.G. Cherkaev, S.L. Voitkevich. Synthesis of dihydromyrcene. Wood Chemistry. 1983. No.4. P.93-96. (Russian)
- [19] H. Pines, N.E. Hoffman, V.N. Ipatieff. Studies in the terpene series. XX. The thermal isomerization of pinane at atmospheric pressure. J. Amer. Chem. Soc. 1954. Vol.76. No.17. P.4412-4416.
- [20] R.A. Rienaker. Rhodinal und a-Citronellol aus optisch activen cis-Pinan. *Chimia*. 1973. Vol.27. P.97-99.
- [21] V.N. Odinokov, G.Yu. Ishmuratov, M.P. Yakovleva, O.V. Sokol'skaya, R.Ya. Kharisov. E.P. Serebryakov, G. A. Tolstikov. Insect pheromones and their analogues XLIII. Chiral pheromones from (S)-(+)-3,7-dimethylocta-1,6-diene 3. Synthesis of (4*R*)-4-methylnonan-1-ol sex pheromone of *Tenebrio molitor* and its racemic analogue. *Chem. Nat. Compd.* **1992**. Vol.28. No.6. P.618-621.
- [22] G.Y. Ismuratov, M.P. Yakovleva, A.V. Galyautdinova, G.A. Tolstikov. Synthesis of (4*R*)methylnonan-1-ol and (4*R*, 8*RS*)-dimethyldecanal from (*S*)-(+)-3,7-dimethyl-1,6-octadiene. *Chem. Nat. Compd.* **2003**. Vol.39. No.1. P.31-33.
- [23] Marina P. Yakovleva, Valentina A. Vydrina, Nalia M. Ishmuratova, Gumer Yu. Ishmuratov. Methods for the synthesis of the sex pheromone of the pest of grain and grain products – yellow mealworm. *Butlerov Communications*. 2021. Vol.65. No.2. P.34-42. DOI: 10.37952/ROI-jbc-1/21-65-2-34 (Russian)