Pestycydy/Pesticides, **2010**, 1-4, 33-41.
ISSN 0208-8703

New perspectives to control Colorado potato beetle (*Leptinotarsa decemlineata* Say) – a short review devoted to the recent identification of the aggregation pheromone of Colorado potato beetle

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Abstract: The short review of investigations done in the field of identification, application and synthesis of the aggregation pheromone of Colorado potato beetle, (*S*)-3,7-dimethyl-2-oxooct-6-en-1,3-diol, is presented.

Keywords: Colorado potato beetle (*Leptinotarsa decemlineata*, Say), aggregation pheromone

INTRODUCTION

Colorado potato beetle (*Leptinotarsa decemlineata*, Say) is a difficult to control pest of the potato crops all over the world. Since it has got settled in Poland, what was about 60 years ago, every year the Colorado potato beetle (CPB) abundance exceed the threshold of economical harmfulness and requires the chemical control [1-5]. The threshold of harmfulness in the crop is defined as the presence of 15 larvae on a single plant, 2 beetles on 25 plants or one eggs bed on a single plant [1-2].

The first cases of CPB presence in Europe took place in the last decades of XIX century. Since that time the individual governmental authorities warn against the import of potatoes from the United States. The regular XX century CPB invasion in Europe started after the 1st WW from its emergence in Bordeaux, France, in 1922. Within the next 24 years the beetle migrated and invaded practically all over Europe. In Poland CPB appeared secondarily possibly in 1944, slipping from Germany in the train transports of potatoes designed for German soldiers, that time stationed here as an occupant. At the end of May 1950, a first great invasion of this species took place (about 12000 of individual pockets) and since that date CPB became the most serious pest of potato fields in Poland [6].

A basic method in the integrated programs of CPB control is the use of insecticides, but it must be underlined that a constant treatment of this species by a wide range of agrochemicals caused its persistent genetic changes. This subsequently influences the CPB resistance against different active substances of many chemical groups, as organophosphorus insecticides, carbamates, pyrethroids, derivatives of nereitoxin [7-11].

The efficacy of CPB field control increased due to some relatively new active substances, belonging to the chemical groups of neonicotinoids and phenylpyrazoles, acting as neurotoxin. Between the others, there are acetamiprid, imidachloprid, thiachloprid, thiamethoxam, clothianidin [1-5]. Their mode of action relay on a systemic way of transport inside the plant and on a high toxicity against CPB. The last make possible to apply low doses of active substance on the potato fields. What is also important, there is generated no resistance of CPB to them until now. It must be stated that in the potato crops there are present all the development stages of CPB. Depending on the cultivated potato strain, the weather conditions and the dynamics of the CPB invasion and progress, the effectiveness of the crop protection against this pest may demand from one to three chemical treatments within the season [2].

IDENTIFICATION OF THE AGGREGATION PHEROMONE OF COLORADO POTATO BEETLE

Although the effectiveness of agrochemicals targeted to CPB control is evident – particularly those from the neonicotinoids group, it is still arguable to look for the new solutions to diminish its population. The more so, if they are ecological, assume to use the small quantities of active substance (additionally – not harmful for the environment), and their application does not require the quarantine period. Regarding capability of CPB to generate resistance against many types of insecticides, it seems to be reasonable to make constant efforts within the research of the new possibilities for potato crops protection. The goal of crop protection is not a total eradication of the given pest species, but the limitation of its emergence and minimization damages caused by it [1, 2]. In 2001 J.C. Dickens published the results of his works on the identification of the aggregation pheromone emitted by the males of CPB [12]. The application of traps, containing this pheromone may result in appreciable reduction of the pest number on the potato leaves. In the aspect of looking for the new solutions of crop protection by means the least interfering an environment, possibility to apply pheromone traps to control CPB population is a promising alternative to insecticides. This is of particular interest especially for ecological farms. The traps might also be used complementary to the classical treatment of potato crops.

Considering their high attractiveness, pheromones are applied in small quantities of few micrograms for one trap. There are non toxic – as well for insects as for other animals and humans. Nowadays the pheromones of many insect species are widely used in the pheromone traps to protect woods, orchards, cereals, etc.

The investigations on the identification of CPB attractants have been conducted since seventies of the passed century. In 1974 J.H. Visser [13] described the results of his work on extraction from potato leaves several volatiles revealing the feature of CPB food attractants.

They were identified by GC/MS technique as: (*E*)-2-hexenol,1-hexanol, (*Z*)-3-hexen-1-ol, (*E*)-3-hexen-1-ol and (±)-linalool.

It must be noticed that McIndoo [14] already in 1926 pointed at (±)-linalool and methyl salicylate as for the natural substances attractive for CPB.

J.C. Dickens, who identified (*S*)-3,7-dimethyl-2-oxooct-6-en-1,3-diol as the pheromone of CPB [1], in his earlier works was also concerned with the attractiveness of natural components for CPB [15]. The results he obtained reconfirmed the observations of the mentioned above authors, that some substance – components of a “green leaf” scent play a role of a feed attractants for CPB. Recently also E.M. Hitchner published the results of the examination of *Solanacae* plants (potato, tomato, pepper, eggplant) attractiveness for CPB [16-17].

In 80-ties and 90-ties of 20th century in the Institute of Industrial Organic Chemistry were performed research works within the field of the analytical (GC, GC/MS) and biological (electroantennography) methods oriented on identification the substances extracted from CPB, with the attempt to find a compound exhibiting the properties of pheromone [18]. Many experiments, done in a “head space” technique, was conducted to collect and analyze the volatiles emitted by males, females and mixed populations of CPB. Some experimental works ware carried out to display the leverage of potato leaves flavors with CPB behavior.

In one of performed that time experiments – in the extract from the volatiles emitted by males of CPB and by potato leaves – it was find a substance, not present in the similarly obtained extract from CPB females (GC method).

Unfortunately, in the next repetitions, the obtained result was not confirmed, and finally research project dedicated to the subject of CPB pheromone(s) was abandoned in the Institute.

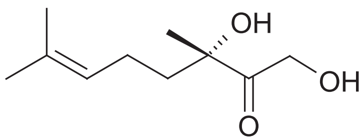
(*S*)-3,7-Dimethyl-2-oxooct-6-en-1,3-diol was identified by J.C. Dickens in 2001 [12] as males produced aggregation pheromone of CPB, with the attractant activity for both genders. It is the first pheromone emitted by males, identified within the species of *Chrysomelidae.* Worth to notice is a fact, that its optical antipode – enantiomer (*R*), was described to be neutral or inhibitive for insects. The pheromone was identified by finding an efficient solution to multiply its production by insects, what was done specifically by connecting two methods – the CPB males population was treated with the juvenile hormone JH III, and then antennoctomy was applied.

Since the publication of this key work, J.C. Dickens and his co workers have published some other articles, regarding the investigations to ascertain the aspects of a new pheromone action; among the others – its effectiveness in a mixture with non pheromonal attractants was studied [16, 19, 20]. In the field tests on the application of CPB pheromone to assemble the adults in the traps was observed the 5-fold higher number of beetles caught in the traps containing a pheromone in proportion to the control traps without pheromone. However it was also stated that pheromone exhibited a highest activity within the first two days. After five days its efficiency decreased and was comparable to results obtained for control [16-17].

Soon the pheromone application was patented, as well "as it is", as in a mixture with (*Z*)-hexenyl acetate, (±)-linalool, methyl salicylate, (*Z*)-3-hexen-1-ol, (*E*)-2-hexen-1-ol [21, 22].

METHODS OF SYNTHESIS

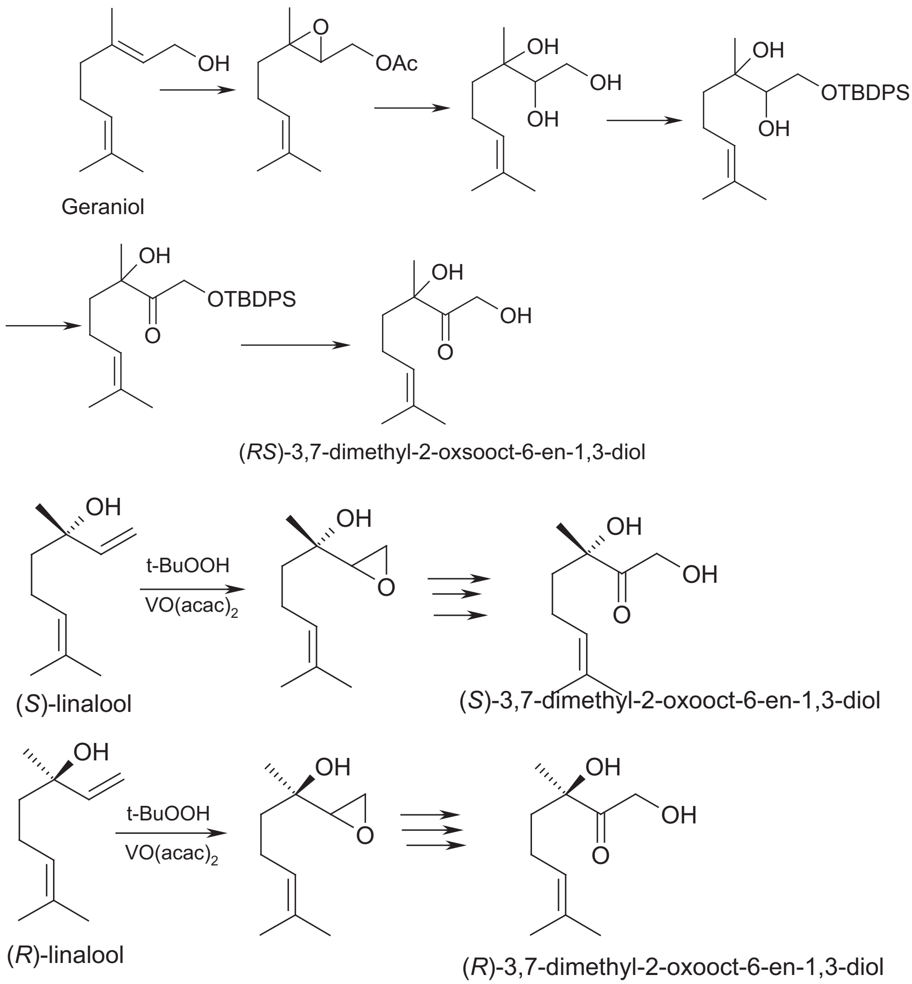
Since the publication of the work about identification of CPB aggregation pheromone in 2002, there were published three articles presented three synthetic pathways to obtain (*S*)-3,7-dimethyl-2-oxooct-6-en-1,3-diol (I) [23-25].



(*S*)-3,7-dimethyl-2-oxooct-6-en-1,3-diol (I)

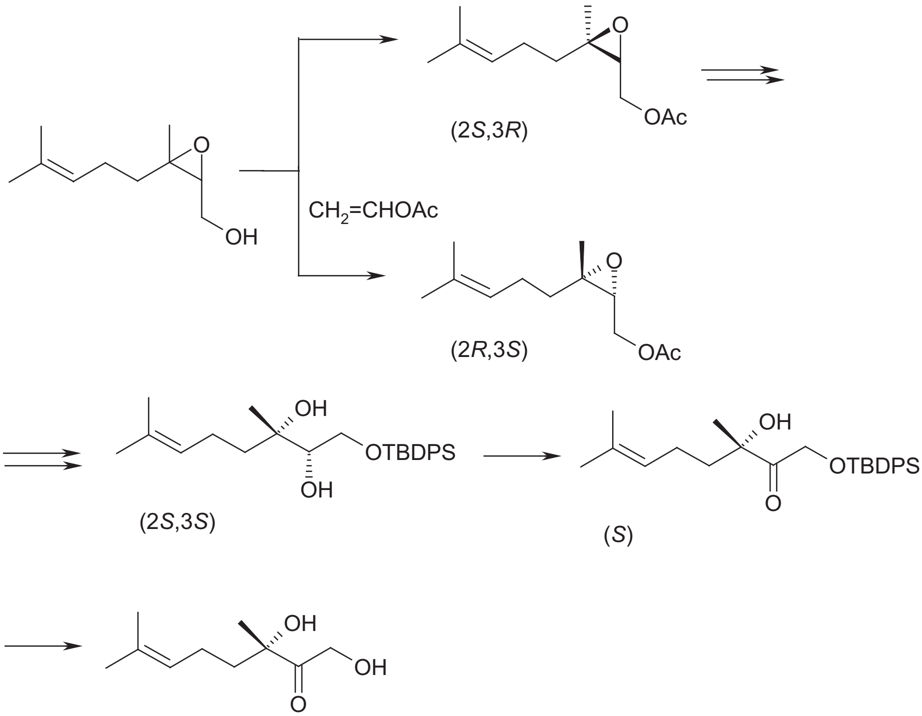
In the first of them, published by J.E. Oliver et al. [23], the racemic

3,7-dimethyl-2-oxooct-6-en-1,3-diol was obtained from geraniol, in reaction sequence as follows: regioselective oxidation of the double bond led to the respective oxirane, next step was the esterification of hydroxyl group with acetic anhydride, then hydrolysis of the resulted epoxy acetate, the protection of a primary hydroxyl group with *t*-(butylchloro)diphenylsilane, selective Swern oxidation and, at the end – a desilylation. The synthetic (*S*) enantiomer, identical to the natural compound, was synthesized by the authors in a repetition of described above way, starting from (*S*)-linalool (Scheme 1).



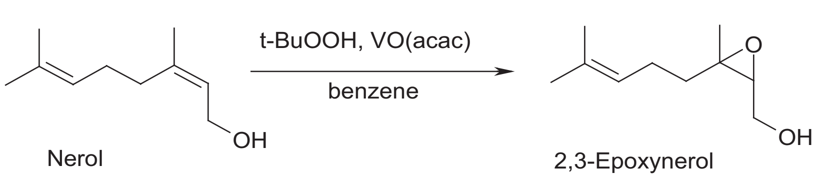
Scheme 1. Synthesis of (*RS*)- (*R*)- and (*S*)-3,7-dimethyl-2-oxooct-6-en-1,3-diol, according to [23].

In 2005 T. Tashiro and K. Mori [24] published the synthesis of both enantiomers of I, from racemic 2,3-epoxynerol and racemic 2,3-epoxygeraniol. In the synthesis was applied the process of asymmetric enzymatic acetalization of racemic epoxides, with the utilization of lipase (Scheme 2).



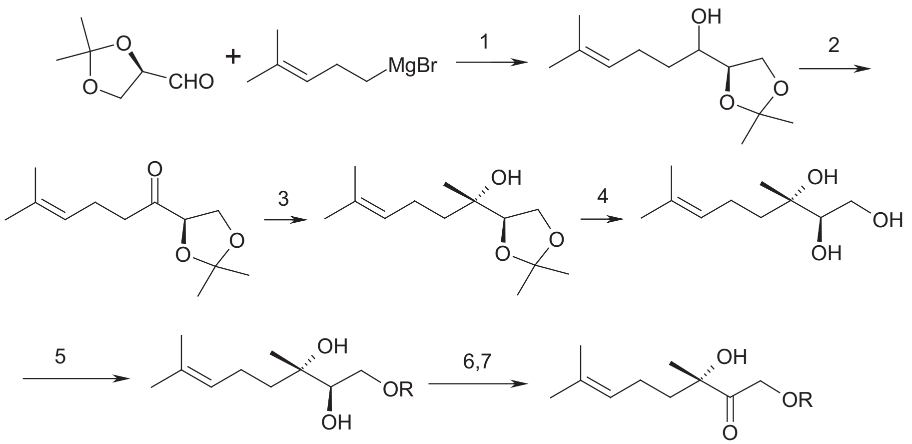
(*S*)-3,7-dimethyl-2-oxooct-6-en-1,3-diol

Scheme 2. Synthesis of (*S*)- 3,7-dimethyl-2-oxooct-6-en-1,3-diol, according to [24].

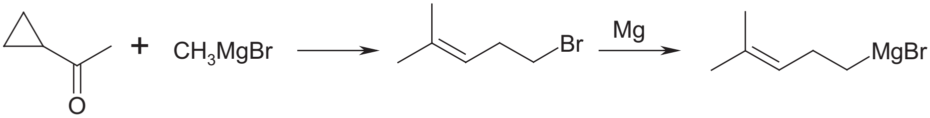


Scheme 3. Preparation of 2,3-epoxynerol [24].

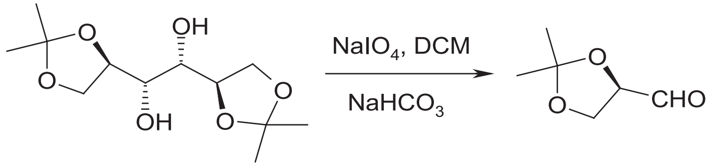
In the third synthetic method to obtain (*S*)-3,7-dimethyl-2-oxooct-6-en-1,3-diol, published in 2009 by B.N. Babu and K.R. Chauhan [25] was used the Grignard reaction of aldehyde (synthesized first from mannitol diacetonide) with (4-methylpent-3-enyl)-magnesium bromide (step 1). The resulted respective secondary alcohol was oxidized with PCC to ketone (step 2). The last was next undertaken the key reaction, crucial for the optical purity of expected product, i. e. a stereoselective catalytic addition of organometallic compound (methyllithium) to the carbon atom of carbonyl group (step 3). At this step catalyst of Lewis acid type was applied, specifically tin tetrachloride. The selectively obtained *anti*-isomer of tertiary alcohol was then transformed into the adequate triol by deprotection of the acetonide group (step 4), followed by silylation of the primary hydroxyl group with *t*-butylchlorodiphenylsilane (step 5), and final selective Swern oxidation of the secondary hydroxyl group (step 6). The desilylation resulted in the expected compound with (*S*) configuration (step 7), (Scheme 5).



Scheme 5. Synthesis of (*S*)-3,7-dimethyl- 2-oxooct-6-en-1,3-diol, according to [25].



Scheme 6. Preparation of 5-bromo-2-methylpent-2-ene [26].



Scheme 7. Preparation of 2,3-*O*-isopropylidene D-glyceraldehyde [27].

CONCLUSIONS

In the paper, some facts concerning the investigations undertaken – over a span of years – by different research groups to identify a pheromone of CPB were reviewed. Identification, in 2001 by J.C. Dickens, of the compound: (*S*)-3,7-dimethyl-2-oxooct-6-en-1,3-diol, as being responsible for the aggregation of these beetles, and thereby defined as an CPB aggregation pheromone, opened the new perspectives to its application in the production of effective and environmentally safe pheromone traps for use in the potato fields. This can be a complementary method to control *Colorado potato* beetle in the fields and help, at least partially, to resolve a problem of an effective fight with this pest.

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