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REVIEWS

Structural Analysis of Sex Pheromones and Attractants in Zygaenidae (Insecta, Lepidoptera): Biochemical and Evolutionary Aspects

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Abstract—The review addresses the data on the chemical composition and structure of all known sex pheromones and attractants in Zygaenidae (Insecta, Lepidoptera). We made an attempt to track possible pathways of the evolution of attractant molecules and to reveal structural features that determine their biological activity. Currently, the structure of sex pheromones and sex attractants is well known for two of the five Zygaenidae subfamilies. Sex attractants of Zygaeninae are esters of acetic acid and fatty alcohols, while in Procridinae they are esters of 2-butanol and higher carboxylic (fatty) acids. Hydrocarbon radicals of fatty alcohols and acids of the known attractant molecules in Zygaenidae contain an even number of carbon atoms (12, 14, 16) and typically one double bond. Species specificity of the chemical signal owes not only the qualitative composition but also the quantitative ratio of components of the pheromone/attractant mixture.

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INTRODUCTION

Although the scientific literature contains extensive factual material on the chemical communication of animals, information about pheromone systems in the vast majority of insect groups is fragmentary and incomplete (http://www.pherobase.com) [1]. A study of the chemical nature of chemical signals has demonstrated that a set of macro- and microcomponents of pheromone compositions is represented by a relatively small number of substances as compared to a huge number of species in this class. Insects are relatively parsimonious in spending energy resources for the biosynthesis of new compounds [2–4]. The application of the probabilistic approach to data processing enabled establishing that the chemical structure of sex pheromones represents a taxonomic character and can be considered in complex with other conventional approaches as an additional marker in solving the issues of phylogeny and biosystematics of some groups of Lepidoptera, specifically Tortricidae and Noctuidae [3, 5]. As a result, the revealed regular patterns of the structure and composition of pheromone components allow not only forecasting the structure of sex attractants and determining the tactics of their field screening but also tracing the evolution of species within a single genus [3, 5].

It is necessary to clearly discriminate between the terms "sex pheromone" and "sex attractant", which are often used in the literature as identical notions. Conventionally, sex pheromones are considered as compounds that are secreted by organisms to the environment, have and excitatory effect on individuals of the opposite sex of the same species, stimulate mating behavior, and influence reproduction [6]. Sex attractants traditionally stand for natural or synthetic substances also attracting and/or exciting individuals of one of the sexes but lacking in pheromone glands of the given species [7]. Thus, sex pheromones of one species may prove to be sex attractants for the other one, although sex attractants cannot be qualified as sex pheromones of the given species until substances with the same structure are detected in the glands of one of the sexes of the given species. In this work, we are holding to this terminology.

As a research object, we chose the family Zygaenidae (Lepidoptera) which, according to the last revision, is divided into five subfamilies: Inouelinae Efetov & Tarmann, 2017; Procridinae Boisduval, 1828; Chalcosiinae Walker, 1865; Callizygaeninae Alberti, 1954; and Zygaeninae Latreille, 1809 [8, 9]. This family, numbering more than 1000 species common to all zoogeographic regions of the world (except the Antarctic) [10–16], is a convenient model group to monitor the state of the environment. Amid Zygaenidae, there are both rare protected species and viticulture and horticulture pests; hence a deeper insight into the mechanisms of chemoattraction is necessary not only for unraveling phylogenetic relationships between taxa within the family but also for developing the measures to defend endangered beneficial species and combat agricultural pests.

This review aimed to analyze the chemical composition and structure of the known sex pheromones and attractants of Zygaenidae, trace the possible evolutionary pathways of attractant molecules, and reveal the structural features that determine their biological activity.

MATERIALS AND METHODS

We used data on the structure and composition of natural sex pheromones and synthetic sex attractants of Zygaenidae borrowed from global database "The Pherobase" (http://www.pherobase.com) [1]. These materials were supplemented with the outcomes of field testing the sex pheromone analogs synthesized in our lab [17–19]. Field testing were carried out in Albania, Greece, Iran, Spain, Laos, Russia, Tajikistan, Thailand, Turkey and Japan in 2013–2018 [20–28].

Chemical names of the attractive compounds were encoded according to the conventional rules:

1. Esters of acetic acid and higher unsaturated alcohols; e.g., (7*Z*)-dodecenyl acetate was encoded as 7*Z*-12:Ac, where 7—the serial number of a carbon atom at a double bond, *Z*—*cis*-isomer of a given substance (or *E* for *trans*-isomer), 12—the number of carbon atoms in an alcoholic radical, Ac—acetate.

2. Esters of 2-butanol and higher unsaturated acids; e.g., (2*R*)-butyl (7*Z*)-tetradecenoate was denoted as 2*R*-7*Z*-14, where 2*R* indicates that the ester is a derivative of the *R*-enantiomer of 2-butanol (or 2*S* for *S*-enantiomer of 2-butanol), 7—the serial number of a carbon atom at a double bond, *Z*—*cis*-isomer of the given substance (or *E* for *trans*-isomer), 14—the number of carbon atoms in an acidic radical.

Full names of the substances were only given on first mentioning.

RESULTS AND DISCUSSION

Component composition and chemical structure of sex pheromones in Zygaenidae

Isolation and identification of sex pheromones of Zygaenidae were preceded by a whole array of studies on various aspects of chemocommunication, namely mating behavior of males and females, electrophysiological responses to odors, effects of the age of individuals and the time of a day on sex pheromone production, mechanisms of chemical signal perception, anatomy and physiology of the secretory glands.

The attraction of Zygaenidae by olfactory signals was first mentioned in the M. Jacobson's extensive review [29] as a fact of the mass flight of *Zygaena* (*Zygaena*) *filipendulae* (Linnaeus, 1758) males (Zygaeninae) to a virgin *Lasiocampa quercus* (Linnaeus, 1758) female (Lasiocampidae). Subsequently, the possibility to attract males of some species of the subfamily Procridinae by sex pheromones of virgin females of another genus or subgenus was confirmed [30]. Absolutely no attractiveness was noted between members of the following genera: *Theresimima* Strand, 1917 and *Adscita* Retzius, 1783; *Theresimima* and *Jordanita* Verity, 1946; *Rhagades* Wallengren, 1863 and *Adscita*; *Rhagades* and *Jordanita*; *Adscita* and *Jordanita*. A negative result was obtained even for individuals of different subgenera of the genus *Jordanita*, namely *Roccia* Alberti, 1954 and *Tremewania* Efetov & Tarmann, 1999. However, a positive response was also observed in a few biotests. For example, *Theresimima ampellophaga* (Bayle-Barelle, 1808) females evoked sexual excitement in *Rhagades* (*Rhagades*) *pruni* ([Denis & Schiffermüller], 1775) males and, vice versa, *Rh.* (*Rh.*) *pruni* females attracted *Th. ampellophaga* males (both species inhabit the Crimea, where they were collected for experiments). The *Jordanita* (*Rjabovia*) *horni* (Alberti, 1937) male (from Armenia) mated the *J.* (*Solaniterna*) *subsolana* (Staudinger, 1862) female (from the Crimea). However, most active sexual behavior was observed between the allopatric species: the *Rh.* (*Wiegelia*) *amasina* (Herrich-Schäffer, 1851) male (from Turkey) got excited in the presence of the *Rh.* (*Rh.*) *pruni* female (from the Crimea). These facts argue in favor of the suggestion that different species may share a similar qualitative composition of sex pheromones, due to which signals of the other species can be misperceived.

The presence in Zygaenidae of intraspecific chemocommunication implemented via volatile sex pheromones was first discovered in a dangerous viticulture pest *Th. ampellophaga*. G.V. Dolidze et al. [31] reported a successful method for male capturing with the use of a sex trap containing virgin females of the given species. Not a single individual of other insect species was finally detected in such a trap, indicative of a high species-specificity of the pheromone signal. The use of pheromones by Zygaenidae females to attract individuals of the opposite sex was experimentally confirmed later on for a whole array of species from the three subfamilies: Procridinae [30, 32], Chalcosiinae [33], and Zygaeninae [34–36].

The chemical structure of the sex pheromone of Zygaenidae was deciphered in a North American viticulture pest *Harrisina metallica* Stretch, 1885 (synonymous to *Harrisina brillians* Barnes & McDunnough, 1910) from the subfamiy Procridinae [37]. From the volatile substances excreted by females of this species, there were indentified 2-butyl decanoate, 2-butyl dodecanoate, isopropyl (7*Z*)-tetradecenoate, and 2-butyl (7*Z*)-tetradecenoate. It was experimentally established that exactly the latter substance is an active component of the sex pheromone in *H. metallica* females. Meanwhile, the absolute configuration of the alcoholic radical in 2-butyl (7*Z*)-tetradecenoate was not determined. Subsequent field testing showed that (2*S*)-butyl (7*Z*)-tetradecenoate (2*S*-7*Z*-14) was most attractive for males, while the presence of the *R*-enantiomer of the given ester decreased the activity of the sex pheromone [38].

Later on, an attempt was made to establish the chemical structure of the pheromone of another species from the subfamily Procridinae, *Illiberis* (*Primilliberis*) *pruni* Dyar, 1905 [39]. The authors managed to detect an unsaturated butyl dodecenoate in female pheromone gland extracts. However, chirality of the alcoholic radical, position and isomerism of the double bond in the fatty-acid hydrocarbon radical remained undetermined.

A complete stereochemical analysis of a sex pheromone was carried out for the viticulture pest *Theresimima ampellophaga* (Procridinae) [40] widespread mainly in the Mediterranean region [30]. The natural pheromone was extracted by hexane from the glands of virgin females raised in laboratory conditions. The authors not only identified the sex pheromone as (2*R*)-butyl (7*Z*)-tetradecenoate (2*R*-7*Z*-14), but also carried out a multi-stage stereoselective synthesis of this ester.

Ten years thereafter, a sex pheromone was isolated and identified in females of the East Asian pest of fruit rosacea *Illiberis* (*Primilliberis*) *rotundata* Jordan, 1907 (Procridinae) [41]. In extracts of the female pheromone glands analyzed by gas chromatography/mass spectrometry, there were detected 2-butyl (7*Z*)-dodecenoate and 2-butyl

(9*Z*)-tetradecenoate. Testing the enantiomers of the esters 2*R*-7*Z*-12 and 2*S*-7*Z*-12, 2*R*-9*Z*-14 and 2*S*-9*Z*-14 both by electroantennography and in natural biotopes (adhesive traps with attractive baits) allowed establishing that the 2*R*-7*Z*-12+2*R*-9*Z*-14 mixtures taken at 30:100 and 50:100 ratios are most attractive for males [41, 42].

Based on the *Jordanita* (*Solaniterna*) *subsolana* biomaterial from the Crimea collected by Prof. K.A. Efetov (Simferopol, Russia) and passed on to Prof. W. Francke (Hambugh, Germany) for examination, the female sex pheromone the given species was found to contain two components: 2-butyl dodecenoate and 2-butyl dodecadienoate (the latter represented a substance with two double bonds discovered in Procridinae for the first time). For some reason, W. Francke did not have his data published but communicated them to Prof. M. Subchev (Sofia, Bulgaria) who included this information to his survey on sex pheromone communication in Zygaenidae [7].

In 2019, a paper by the Chinese research group [43] reported a successful identification of the sex pheromone in females of *Phauda flammans* (Walker, 1854), a species referring to the family Phaudidae [44] and faultily referred by the authors to Zygaenidae [43].

Thus, by now, the structure of sex pheromones has been established in five species of the Zygaenidae subfamily Procridinae: *H. metallica*, *Th. ampellophaga*, *I.* (*P.*) *pruni*, *I.* (*P.*) *rotundata*, and *J.* (*S.*) *subsolana*. In all of them, these are esters of 2-butanol and higher unsaturated carboxylic acids (in *H. metallica*, *Th. ampellophaga* and *I.* (*P.*) *rotundata* found to be *cis*-isomers). The revealed molecular structure of sex pheromones, as well as the topography of the pheromone-secreting glands (in the central region of the female abdomen), appear to be characteristic of the tribe Procridini of the subfamily Procridinae [2, 4, 7]. The chemical composition of natural sex pheromones in representatives of the subfamilies Inouelinae, Chalcosiinae, Callizygaeninae and Zygaeninae is currently unknown.

Alkenyl acetates: synthetic sex attractants of Zygaenidae

Chemical and visual signals provide partner recognition and successful mating in Zygaenidae species [36, 45, 46]. Although most representatives of the subfamily Zygaeninae have a bright, well noticeable, aposematic coloration [47–49], males of this group use exactly olfactory stimuli for long-distance search for individuals of the opposite sex. Sex attractants of Zygaeninae were discovered during field experiments conducted by different research teams with the known sex pheromones of the other lepidopteran families (e.g., Tortricidae, Sesiidae). For example, at the end of the 1970s–beginning of the 1980s the discovery of males of the genus *Zygaena* Fabricius, 1775 (Zygaeninae) in adhesive pheromone traps with unsaturated acetic acid esters [50–52] served as an impetus for a large-scale investigations of chemical communication in members of this genus [53]. For six species of *Zygaena*, there were selected optimal concentrations and compositions of acetic acid esters that attract a maximum number of males to attractive baits in natural biotopes and evoke the same behavioral response in males as in the presence of a “calling” female. In addition, for 12 species of *Zygaena*, one of the genus *Reissita* Tremewan, 1959, and one of the genus *Epizygaenella* Tremewan & Povolny, 1968 (*Reissita* and *Epizygaenella* are phylogenetically close to the genus *Zygaena*), electroantennography revealed a specific sensitivity of receptor cells located in male antennae to esters of acetic acid and seven higher monoenoic alcohols: (5*Z*)-dodecenyl acetate (5*Z*-12:Ac), (7*Z*)-dodecenyl acetate (7*Z*-12:Ac), (9*Z*)-dodecenyl acetate (9*Z*-12:Ac), (7*Z*)-tetradecenyl acetate (7*Z*-14:Ac), (9*Z*)-tetradecenyl acetate (9*Z*-14:Ac), (11*Z*)-tetradecenyl acetate (11*Z*-14:Ac) and (11*Z*)-hexadecenyl acetate (11*Z*-16:Ac).

Subsequently, the attractiveness of *cis*-alkenyl acetates for males of the genus *Zygaena* was repeatedly confirmed in field experiments carried out by different authors [54–56]. Generalized data on sex attractants known from the literature sources for members of the subfamily Zygaeninae are shown in Table 1.

It is well seen that the bulk of the components of synthetic sex attractants of Zygaeninae is represented by esters of acetic acid and unsaturated aliphatic long-chain alcohols with carbon atoms numbering from 12 to 16. An absolute majority of them are *cis*-isomers with the double bond situ-

Table 1. Components and chemical structure of sex attractants that attract males of Zygaeninae (Zygaenidae)*

Species/Subspecies	Sex attractant/attractants	Source
Reissita simonyi (Rebel, 1899)	7*Z*-12:Ac+9*Z*-14:Ac+11*Z*-16:Ac	[53]
Epizygaenella caschmirensis (Kollar, 1844)	9*Z*-14:Ac+11*Z*-14:Ac+11*Z*-16:Ac	[53]
Zygaena (*Mesembrynus*) *tamara* Christoph, 1889	7*Z*-12:Ac+9*Z*-12:Ac+9*Z*-14:Ac+11*Z*-14:Ac	[53]
Zygaena (*Mesembrynus*) *minos* ([Denis & Schiffermüller], 1775)	7*Z*-12:Ac+9*Z*-14:Ac+11*Z*-14:Ac	[53]
Zygaena (*Mesembrynus*) *purpuralis* (Brünnich, 1763)	7*Z*-12:Ac+7*Z*-14:Ac+9*Z*-14:Ac	[53]
	7*Z*-12:Ac+9*Z*-14:Ac	[53]
Zygaena (*Mesembrynus*) *favonia thevestis* Staudinger, 1887	7*Z*-12:Ac+9*Z*-14:Ac+11*Z*-14:Ac	[53]
Zygaena (*Mesembrynus*) *sarpedon* (Hübner, 1790)	7*Z*-12:Ac+9*Z*-12:Ac+9*Z*-14:Ac	[53]
Zygaena (*Agrumenia*) *fausta* (Linnaeus, 1767)	11*Z*-14:Ac	[52]
Zygaena (*Agrumenia*) *hilaris* Ochsenheimer, 1808	11*Z*-14:Ac	[52]
Zygaena (*Agrumenia*) *carniolica* (Scopoli, 1763)	7*Z*-12:Ac+9*Z*-14:Ac+11*Z*-16:Ac	[53]
	7*Z*-12:Ac+9*Z*-12:Ac+9*Z*-14:Ac	[53]
Zygaena (*Agrumenia*) *exulans* (Hohenwarth, 1792)	7*Z*-12:Ac+ 9*Z*-12:Ac+9*Z*-14:Ac	[53]
Zygaena (*Agrumenia*) *viciae* ([Denis & Schiffermüller], 1775)	5*Z*-12:Ac+7*Z*-12:Ac+9*Z*-14:Ac	[53]
Zygaena (*Agrumenia*) *niphona* Butler, 1877	7*Z*-12:Ac+9*Z*-14:Ac	[54]
Zygaena (*Zygaena*) *anthyllidis* Boisduval, 1828	7*Z*-12:Ac+9*Z*-14:Ac	[53]
Zygaena (*Zygaena*) *nevadensis gallica* Oberthür, 1898	11*Z*-14:Ac+11*E*-14:Ac	[52]
Zygaena (*Zygaena*) *osterodensis*** Reiss, 1921	8*Z*-12:Ac+8*E*-12:Ac	[57]
Zygaena (*Zygaena*) *ephialtes* (Linnaeus, 1767)	11*Z*-14:Ac+11*E*-14:Ac+12Ac	[51]
	11*Z*-14:Ac+12Ac	[51]
	11*Z*-14:Ac	[52]
Zygaena (*Zygaena*) *transalpina splugena* Burgeff, 1926	11*Z*-14:Ac+11*Z*-14OH	[50]
Zygaena (*Zygaena*) *transalpina hippocrepidis* (Hübner, 1799)	11*Z*-14:Ac	[52]
Zygaena (*Zygaena*) *angelicae* Ochsenheimer, 1808	11*Z*-14:Ac+12Ac	[51]
Zygaena (*Zygaena*) *filipendulae* (Linnaeus, 1758)	5*Z*-12:Ac+7*Z*-12:Ac+9*Z*-14:Ac	[53]
	5*Z*-12:Ac+7*Z*-12:Ac, 7*Z*-12:Ac+9*Z*-14:Ac	[53]
	11*Z*-14:Ac+11*E*-14:Ac	[58]
Zygaena (*Zygaena*) *lonicerae* (Scheven, 1777)	5*Z*-12:Ac+7*Z*-12:Ac+9*Z*-14:Ac	[53]
Zygaena (*Zygaena*) *trifolii* (Esper, 1783)	5*Z*-12:Ac+7*Z*-12:Ac+9*Z*-14:Ac	[53]

* Systematic position of species and subspecies according to [59].

** Synonim: *Zygaena* (*Zygaena*) *scabiosae* sensu auctorum (nec Scheven, 1777).

ated at an odd position: at the 11th, 9th, 7th, and (less frequently) 5th carbon atoms. The above characters reflect common structural principles of attractant molecules in Lepidoptera [2, 4].

Esters of 2-butanol and higher unsaturated acids: sex attractants of Procridinae

After successful identification of components and molecular structure of sex pheromones in Procridinae, there was carried out a stereoselective synthesis of their structural copies: 2*R*-7-12, 2*S*-7-12, 2*R*-7-14, 2*S*-7-14, 2*R*-9-14, 2*S*-9-14 [40, 41]. All of them are *cis*-isomers. Individually and in various combinations, these esters have begun to be used in ecologo-faunistic studies all over the world, thus leading to a discovery of sex attractants for the whole number of Zygaenidae species from the subfamily Procridinae (Table 2).

Table 2. Components and chemical structure of sex attractants that attract males of Procridinae (Zygaenidae)*

Species/Subspecies	Sex attractant/attractants	Source
Acoloithus falsarius Clemens, 1861	2*R*-7-14, 2*R*-7-14+2*S*-7-14	[60, 61]
Acoloithus novaricus Barnes & McDunnough, 1913	2*S*-7-14, 2*R*-7-14	[61]
Acoloithus rectarius Dyar, 1898	2*R*-9-14	[7]
Neoilliberis fusca (H. Edwards, 1885)	2*R*-9-14	[7]
Neoalbertia constans (H. Edwards, 1881)	2*S*-9-14	[7]
Neoprocris aversa (H. Edwards, 1884)	2*R*-9-14	[7]
Pyromorpha (*Pyromorpha*) *dyari* (Jordan, 1913)	2*S*-7-12	[7]
Triprocris cyanea Barnes & McDunnough, 1910	2*S*-9-14	[7]
Harrisina americana (Guérin-Méneville, 1844)	2*R*-7-14, 2*R*-7-14+2*S*-7-14	[60, 61]
Harrisina coracina (Clemens, 1861)	2*S*-7-14, 2*R*-7-14	[61]
Harrisina guatemalena (Druce, 1884)	2*S*-7-14+2*R*-7-14, 2*S*-7-14, 2*R*-7-14	[61]
Illiberis (*Primilliberis*) *pruni* Dyar, 1905	2*R*-7-12+2*R*-9-14, 2*R*-2-12	[25, 62]
Theresimima ampellophaga (Bayle-Barelle, 1808)	2*R*-2-12+2*S*-2-12, 2*R*-2-12, ClOil 135°**	[18, 19, 23]
Rhagades (*Wiegelia*) *amasina* (Herrich-Schäffer, 1851)	2*S*-2-12, 2*R*-2-12+2*S*-2-12	[26]
Rhagades (*Wiegelia*) *predotae* (Naufock, 1930)	2*S*-2-12	[27]
Rhagades (*Rhagades*) *pruni* ([Denis & Schiffermüller], 1775)	2*R*-7-12, 2*R*-7-12+2*S*-7-12	[63]
	2*S*-2-12, 2*R*-2-12+2*S*-2-12, 2*R*-2-12	[21, 23, 27]
Zygaenoprocris (*Zygaenoprocris*) *chalcochlora* Hampson, 1900	2*R*-7-12, 2*R*-7-12+2*R*-9-14	[7, 64]
Zygaenoprocris (*Zygaenoprocris*) *eberti* (Alberti, 1968)	2*R*-7-12, 2*R*-7-12+2*R*-9-14	[64]
Zygaenoprocris (*Molletia*) *taftana* (Alberti, 1939)	2*R*-7-12	[65]
Adscita (*Procriterna*) *subtristis* (Staudinger, 1887)	2*R*-2-12+2*S*-2-12	[20]
Adscita (*Adscita*) *statices statices* (Linnaeus, 1758)	2*R*-2-12	[22]
Adscita (*Adscita*) *statices drenowskii* (Alberti, 1939)	2*R*-2-12+2*S*-2-12, 2*R*-2-12	[23]
Adscita (*Adscita*) *obscura* (Zeller, 1847)	2*S*-7-12, 2*S*-7-12+2*R*-7-12	[66]
	2*R*-2-12, 2*S*-2-12, 2*R*-2-12+2*S*-2-12	[26]
Adscita (*Adscita*) *geryon* (Hübner, 1813)	2*S*-7-12, 2*R*-7-12+2*S*-7-12	[63, 67]
	2*R*-2-12+2*S*-2-12	[21]
Adscita (*Adscita*) *albanica* (Naufork, 1926)	2*S*-7-12+2*R*-7-12, 2*S*-7-12+2*S*-9-14	[63]
Adscita (*Tarmannita*) *mannii* (Lederer, 1853)	2*S*-7-12, 2*R*-7-12+2*S*-7-12, 2*R*-7-12	[63, 67, 68]
	2*S*-7-12+2*S*-9-14, 2*S*-9-14	[68]
Adscita (*Tarmannita*) *bolivari* (Agenjo, 1937)	2*R*-2-12+2*S*-2-12	[27]
Jordanita (*Tremewania*) *notata* (Zeller, 1847)	2*R*-7-12, 2*R*-7-12+2*S*-7-12	[63, 67, 68]
	2*R*-7-12+2*R*-9-14, 2*R*-7-12+2*S*-9-14	[63, 68]
	2*R*-2-12+2*S*-2-12	[21]
Jordanita (*Tremewania*) *splendens* (Staudinger, 1887)	2*R*-2-12+2*S*-2-12	[20]
Jordanita (*Jordanita*) *graeca* (Jordan, 1907)	2*R*-2-12+2*S*-2-12	[18, 21]
Jordanita (*Jordanita*) *globulariae* (Hübner, 1793)	2*R*-2-12+2*S*-2-12	[18, 21, 23]

Table 2. (Contd.)

Species/Subspecies	Sex attractant/attractants	Source
Jordanita (*Praviela*) *anatolica* (Naufock, 1929)	2*R*-7-12+2*S*-7-12, 2*R*-7-12	[66]
	2*R*-2-12, 2*R*-2-12+2*S*-2-12	[26]
Jordanita (*Praviela*) *rietzschi* Keil, 2016	2*R*-2-12+2*S*-2-12	[69]
Jordanita (*Solaniterna*) *subsolana* (Staudinger, 1862)	2*R*-2-12, 2*R*-2-12+2*S*-2-12	[21, 23, 26]
Jordanita (*Rjabovia*) *horni* (Alberti, 1937)	2*R*-7-12+2*S*-7-12, 2*R*-7-12	[65]
Goazrea lao Mollet, 2016	2*R*-2-12+2*S*-2-12, 2*S*-2-12	[24]

* Systematic position of palearctic species and subspecies according to [70].

** ClOil 135°(cod-liver oil) – esters of 2-butanol and polyunsaturated fatty acids of cod liver oil.

Thus, female sex pheromones of one species can simultaneously serve as sex attractants for males of other species. Keeping in mind the molecular structure of the known sex pheromones and sex attractants of Procridinae (referring to a class of esters formed by 2-butanol and a higher carboxylic acid with the number of carbon atoms varying from 12 or 14), we performed a goal-directed synthesis of the following compounds:

1) ester of 2-butanol and dodecanoic (lauric) acid [71];

2) ester of 2-butanol and dodecenoic acid [17, 18] and its *R*- and *S*-enantiomers;

3) esters of 2-butanol and polyunsaturated fatty acids of cod liver oil (ClOil 135°) [19].

In doing this, we also took into consideration that the known sex pheromones of Procridinae have a double bond in the acidic radical and a chiral center in the alcoholic radical.

Comparative field screening of the resultant compounds in natural biotopes and agrobiocenoses showed that *R*- and *S*-enantiomers of ester of 2-butanol and dodecenoic acid (2*R*-2-12 and 2*S*-2-12, respectively), both individually and/or in a combination (2*R*-2-12+2*S*-2-12), attract males of almost twenty species of Procridinae (Table 2). A high efficiency of these compounds as sex attractants made it possible to detect species with a very low population density. Specifically, there were involved males of *Rhagades* (*Wiegelia*) *predotae* (Naufock, 1930) in Spain [27] and *Rh.* (*Rh.*) *pruni* in Spain and Turkey [23, 27]. Moreover, there were even discovered two new species, *Jordanita* (*Praviela*) *rietzschi* Keil, 2016 [69] and *Goazrea lao* Mollet, 2016 [24], inhabiting Iran, Laos and Thailand. Unfortunately, application of sex attractants that attract males allows detecting individuals of one sex [27, 64, 72].

An analysis of the literature data and results of our experiments demonstrated that the presence of a double bond in the fatty acid radical matters for the perception of a pheromone/attractant molecule by the sensory apparatus of Procridinae males, although the position of this bond can vary. Below are a few examples.

1. 2*R*-2-12 and 2*S*-2-12 represent ester of 2-butanol and a monoenoic fatty acid with twelve carbon atoms and a double bond at the second position. Esters 2*R*-7-12 and 2*S*-7-12, structurally similar but differing by the double bond position at the 7th carbon atom, are also sex attractants for several Procridinae species (Table 2). Specifically, both 2-12 and 7-12 attract males of *Illiberis* (*P.*) *pruni*, *Rhagades* (*Rh.*) *pruni*, *Adscita* (*Adscita*) *geryon* (Hübner, 1813), *Jordanita* (*Tremewania*) *notata* (Zeller, 1847), and *Jordanita* (*Praviela*) *anatolica* (Naufock, 1929). At the same time, testing of biological activity of ester of 2-butanol and lauric (saturated) acid revealed no attractiveness of this compound towards representatives of Procridinae, although it attracted males of the beetle *Tilloidea unifasciata* (Fabricius, 1787) [71].

2. A sex pheromone of *Th. ampellophaga* females is 2*R*-7-14 with minor amounts of 2*S*-7-14 [40]. However, males of this species demonstrate a characteristic sexual behavior and are actively trapped by adhesive traps with the synthetic sex attractants 2*R*-2-12+2*S*-2-12 [18, 28], 2*R*-2-12 [23], ClOil 135° [19]. All esters, as components both of sex pheromones and sex attractants, share identical alcoholic but different acidic radicals. Their structural variations concern the

length of the hydrocarbon acidic radical, as well as the position and the number of double bonds therein. Nevertheless, all the above esters exhibit attractive properties towards *Th. ampellophaga* males, in contrast to 2-butyl dodecanoate.

Importantly, olfactory receptors of Procridinae males demonstrate differential sensitivity to optical isomers of attractant molecules. For example, during simultaneous testing of 2*R*-7-12 and 2*S*-7-12 in a biotope, males of *Adscita* (*Tarmannita*) *mannii* (Lederer, 1853) are mainly attracted to the *S*-enantiomer, while males of *Jordanita* (*Tremewania*) *notata*—to the *R*-enantiomer [67]. Moreover, for males of *J.* (*T.*) *notata*, the presence of 2*S*-7-12 in a racemic mixture 2*R*-7-12+2*S*-7-12, as well as of 2*S*-2-12 in a racemic mixture 2*R*-2-12+2*S*-2-12, does not diminish the attractiveness of the corresponding *R*-enantiomers [21, 67]. An opposite situation is observed in males of *Zygaenoprocris* (*Molletia*) *taftana* (Alberti, 1939): 2*R*-7-12 actively attracts males, while 2*S*-7-12 completely suppresses the attractiveness of 2*R*-7-12 in an equicomponent mixture [65]. Partial inhibition of the sex attractant's action due to the presence of the *S*-enantiomer was demonstrated in *Harrisina americana* (Guérin-Méneville, 1844) and *Acoloithus falsarius* Clemens, 1861, males of which are trapped by traps with 2*R*-7-14 far more efficiently compared to those with 2*R*-7-14+2*S*-7-14 [60]. The species *I.* (*P.*) *pruni* and *J.* (*S.*) *subsolana* are attracted mainly by 2*R*-2-12 [23, 25, 26], while the *Rhagades* species—by 2*S*-2-12 [26, 27].

Thus, structural peculiarities that determine biological activity of the known attractant molecules in Procridinae include the presence of a double bond in the acidic radical and a chiral center in the alcoholic radical of an ester.

Evolutionary aspect of sex pheromones and attractants of Zygaenidae

In the recent years, rapid development of molecular biology enabled detailing the evolutionary relationships in the order Lepidoptera [73], which were formerly analyzed only on the basis of morphology and biology. Studies of numerous nuclear and mitochondrial genes, as well as the RNA structure, allowed reconstructing the phylogeny of Lepidoptera with high reliability, as has been also reflected in taxonomy. We have made an attempt to compare a possible path of sex pheromone evolution in members of the family Zygaenidae and some phylogenetically related groups on the basis of the present-day data on Lepidoptera systematics. As mentioned above, the known sex pheromones and attractants in the family Zygaenidae are represented by two types of compounds: (1) esters of 2-butanol and fatty acids and (2) esters of acetic acid and fatty alcohols. The former are characteristic of the subfamily Procridinae (tribe Procridini), the latter typify the subfamily Zygaeninae (tribe Zygaenini). At the same time, there is a structural similarity in attractant molecules of Zygaenidae and other Lepidoptera. It consists in an analogous structure of long-chain hydrocarbon radicals of esters, with the only exception that in Procridinae it is an acidic radical, while in Zygaeninae (and many Lepidoptera) – an alcoholic one. Some authors explain the chemical/structural uniformity of signaling molecules in Lepidoptera by biosynthetic peculiarities of sex pheromone components and activity of desaturases, which, in turn, reflects genetically determined regularities related to a common phylogenetic descent [3, 74–78]. Specifically, activity of Δ11-desaturase in combination with a cascade of reactions of fatty acid chain shortening by two carbon atoms during β-oxidation allowed the species to produce various unsaturated fatty acids, aldehyde and alcohols from stearic (C_{18}) and palmitic (C_{16}) saturated precursor acids. These acids and alcohols can form esters with 2-butanol and acetic acid, respectively. Thus, nearly all known combinations of sex pheromones and attractants of Zygaenidae can easily be derived from the cascade of the above conversions by restricting the chain shortening stages (Fig. 1).

We analyzed the available data on the structure of sex pheromones and attractants both in Zygaenoidea and systematically related superfamilies Sesioidea and Cossoidea, as well as in the superfamily Tortricoidea taken as a sister group. It turned out that esters of acetic acid and fatty alcohols are sex pheromones and attractants in representatives of the families Sesiidae (Sesioidea) and Cossidae (Cossoidea), as well as in Tortricidae (Tortricoidea) (http://www.pherobase.com) [1].

Therefore, this group of compounds is evolutionarily more ancient than esters of 2-butanol and fatty acids. These data allow speculating with a high degree of probability that the emergence of esters of 2-butanol and fatty acids in the capacity of sex pheromones is an apomorphic character of the tribe Procridini from the subfamily Procridinae (presently, the structure of attractant molecules in Procridinae is known only for the members of this tribe [21, 25, 27, 37, 40, 65, 67]). On the other hand, the presence of esters of acetic acid and fatty alcohols as sex attractants represents a plesiomorphic character which characterizes the subfamily Zygaeninae (Zygaenidae), as well as the families Sesiidae, Cossidae and Tortricidae (Fig. 2).

Within the superfamily Zygaenoidea, sex pheromones and attractants are presently known only for some species of the families Himantopteridae, Phaudidae and Limacodidae. While in Himantopteridae these are esters of acetic acid and fatty alcohols, in Phaudidae and Limacodidae attractant molecules are represented by fatty aldehydes and alcohols (http://www.pherobase.com) [1] which, by their spatial structure, resemble esters of short-chain acids and polyatomic alcohols. Sometimes, the configuration resemblance of the molecules of long-chain aldehyde pheromones with esters of fatty alcohols and, e.g., formic acid can lead to a mistaken binding of the latter to olfactory receptors of males and evoke even a stronger physiological and behavioral response [79]. In some species of the genus *Darna* Walker, 1862 (Limacodidae), the role of sex pheromones is played by esters of methanol, butanol and isobutanol (http://www.pherobase.com) [1], while 2-butanol derivatives are absent.

A statistical analysis of similarities and dissimilarities in the component composition of sex pheromones revealed a taxonomic significance of this character for analyzing phylogenetic relationships within the lepidopteran families [3, 5]. For example, it was shown that evolution of pheromone systems in species of the family Tortricidae proceeded towards (1) an increasing proportion of *trans*-isomers and (2) shortening the carbon chain length from 16 to 12 atoms [5]. In species of the subfamily Zygaeninae (family Zygaenidae), the *trans*-isomers 11*E*-14:Ac or 8*E*-12:Ac (Table 1) emerge as components of sex attractants in species of the younger subgenus *Zygaena* (*Zygaena*) Fabricius, 1775. These species form a cluster that comprises close species of the *nevadensis*-, *transalpina*- and *filipendulae*-groups [59]. At the same time, males of the two species referring to the archaic genera *Reissita* and *Epizygaenella* (Table 1) are sensitive to esters containing a *cis*-isomeristic 16-carbon radical (11*Z*-16:Ac). Although poor knowledge of pheromone/attractant compositions in Zygaenidae complicates the analysis, these facts correlate well with the previously established regularities in the evolution of pheromone systems in other families of Lepidoptera.

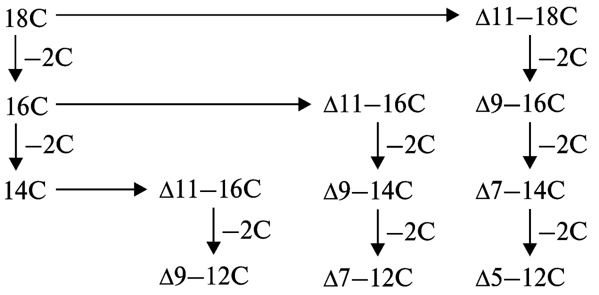

Fig. 1. Possible biosynthetic pathways of monounsaturated sex pheromone components in Lepidoptera. Variants of long-chain hydrocarbon radicals in attractant molecules of Zygaenidae are marked in red.

Many authors tend to believe that chemical cues can play a significant role both in intraspecies pheromone competitiveness and in ensuring reproductive isolation between closely related taxa and hence in speciation [51, 58, 80–84]. The hypothesis that accentuates the importance of pheromone communication in the formation of pre-copulative barriers due to the existence of a species-specific odor finds support also in Zygaenidae. For example, sympatric populations (in Japan, China, Korea) of the two phylogenetically close species of the same genus and subgenus *Illiberis* (*Primilliberis*) *rotundata* and *I.* (*P.*) *pruni* have overlapping flight periods. Peculiarities in the structure of the genitals of these species do not prevent interspecific mating [85]. Moreover, males of both species are attracted by a mixture of the two esters 2*R*-7-12+2*R*-9-14 [42, 62]. However, field testing demonstrated that males of *I.* (*P.*) *rotundata* and *I.* (*P.*) *pruni* respond differ-

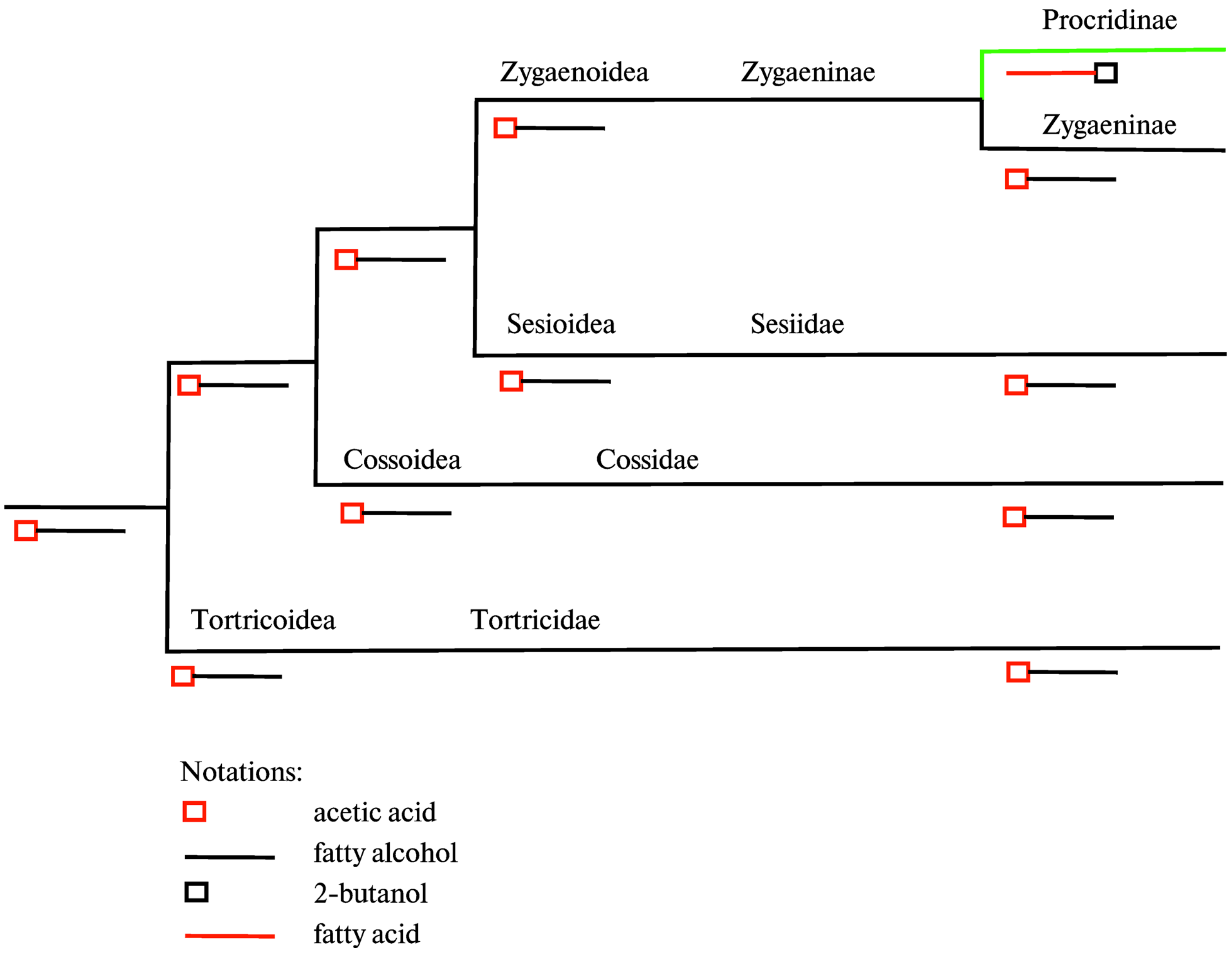

Fig. 2. A scheme showing the evolution of the structure of sex pheromones in Zygaenidae and some other families of Lepidoptera. Acids are marked in red, alcohols—in black; long-chain hydrocarbon radicals are marked by lines, short-chain radicals—by squares. Green branch of the dendrogram shows the subfamily Procridinae in which pheromones represented by 2-butanol and fatty acid esters (but not acetic acid and fatty alcohol esters, as in all the above-mentioned taxa).

entially to different quantitative ratios of these esters in mixtures, and that a percentage of the esters in their compositions is determinative: for *I.* (*P.*) *rotundata* males—30/50:100 while for *I.* (*P.*) *pruni* males—100:10, respectively. By our data, *I.* (*P.*) *pruni* males were attracted by the attractant 2*R*-2-12, whereas *I.* (*P.*) *rotundata* males did not respond to this substance [25]. Thus, the species specificity of a chemical cue is an important isolating mechanism that prevents mating of these two species [86].

Overall, these data indicate that the molecular structure of attractants can serve as an additional character for analyzing relationships between taxa and reconstructing the evolution of Lepidoptera.

CONCLUSION

A survey of the available literature on attractant molecules in Zygaenidae demonstrates that the issues of chemical communication within this family are far from being resolved, and that the structure of sex pheromones and attractants is only elucidated for a small number of species out of the five subfamilies, namely Procridinae and Zygaeninae. While in Zygaeninae the attractive ability characterizes esters of acetic acid and higher unsaturated alcohols, in Procridinae it is inherent to esters of 2-butanol and higher unsaturated carboxylic acids. Long-chain hydrocarbon radicals of the known attractant molecules contain an even number of carbon atoms: 12, 14, 16. At the same time, these radicals are unsaturated in most cases.

Thus, in different subfamilies of Zygaenidae, sex pheromones or attractants are represented by different variants of esters, while within the same subfamily closely related species employ unique combinations of similar components. The species specificity of a chemical cue is determined not only by a qualitative but also quantitative composition of a pheromone/attractant mixture, while the difference between pheromone systems serves as an important isolating mechanism preventing interspecific mating.

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Authors of this study have no conflict of interest. All applicable international, national and institutional principles of handling and using experimental animals for scientific purposes were observed.

REFERENCES

1. El-Sayed, A.M., The Pherobase: database of pheromones and semiochemicals, <http://www.pherobase.com> Accessed 18(10)2019.
2. Ando, T., Inomata, S., and Yamamoto, M., Lepidopteran sex pheromones, *Top. Curr. Chem.*, 2004, vol. 239, pp. 51–96. doi: 10.1007/b95449
3. Grichanov, I. Ya. and Ovsyannikova, E.I., *Feromony dlya fitosanitarnogo monitoring vrednykh cheshuekrylykh* (Pheromones for Phytosanitary Monitoring of Lepidoptera Pests), St. Petersburg: VIZR RAAS, 2005.
4. Francke, W. and Schulz, S., Pheromones of terrestrial invertebrates, *Comprehensive Natural Products II*, Mander, L.N. and Liu, H.-W., Eds., 2010, pp. 153–224. doi: 10.1016/b978-008045382-8.00095-2
5. Safonkin, A.F., Pheromones and phylogenetic relations of leafrollers (Lepidoptera, Tortricidae), *Zool. Zh.*, 2007, vol. 86(12), pp. 1464–1467.
6. Karlson, P. and Lüscher, M., "Pheromones": a new term for a class of biologically active substances, *Nature*, 1959, vol. 183(4653), pp. 55–56. doi: 10.1038/183055a0
7. Subchev, M., Sex pheromone communication in the family Zygaenidae (Insecta: Lepidoptera): a review, *Acta Zool. Bulg.*, 2014, vol. 66(2), pp. 147–157.
8. Efetov, K.A., *Inouela* gen. n. from Japan and Taiwan (Lepidoptera: Zygaenidae, Chalcosiinae), *Entomol. Gaz.*, 1999, vol. 50(2), pp. 91–95.
9. Efetov, K.A. and Tarmann, G.M., The hypothetical ground plan of the Zygaenidae, with a review of the possible autapomorphies of the Procridinae and the description of the Inouelinae subfam. nov., *J. Lep. Soc.*, 2017, vol. 71(1), pp. 20–49. doi: 10.18473/lepi.v71i1.a5
10. Efetov, K.A., The description of the female of *Illiberis (Alterasvenia) yuennanensis* Alberti, 1951 (Lepidoptera: Zygaenidae, Procridinae), *Entomol. Gaz.*, 1996, vol. 47(2), pp. 111–113.
11. Efetov, K.A. and Tarmann, G.M., *Illiberis (Alterasvenia) cernyi* sp. nov. (Lepidoptera: Zygaenidae, Procridinae) from northern Thailand, *Entomol. Gaz.*, 2013, vol. 64(1), pp. 33–39.
12. Efetov, K.A. and Tarmann, G.M., *Chrysartona (Chrystarmanna) mineti* sp. nov. (Lepidoptera: Zygaenidae, Procridinae) from northern Vietnam, *Entomol. Gaz.*, 2013, vol. 64(3), pp. 197–206.
13. Efetov, K.A. and Tarmann, G.M., *Illiberis (Alterasvenia) banmauka* sp. nov. (Lepidoptera: Zygaenidae, Procridinae) from China and Myanmar, *Entomol. Gaz.*, 2014, vol. 65(1), pp. 62–70.
14. Efetov, K.A. and Tarmann, G.M., A new European species, *Adscita dujardini* sp. nov. (Lepidoptera: Zygaenidae, Procridinae) confirmed by DNA analysis, *Entomol. Gaz.*, 2014, vol. 65(3), pp. 179–200.
15. Efetov, K.A. and Tarmann, G.M., *Pseudophacusa multidentata* Efetov & Tarmann, a new genus and species of Procridini from Myanmar, China and Laos (Lepidoptera: Zygaenidae, Procridinae), *SHILAP Revta. Lepid.*, 2016, vol. 44(173), pp. 81–89.
16. Efetov, K.A. and Tarmann, G.M., *Thibetana keili* Efetov & Tarmann, a new species of the genus *Thibetana* Efetov & Tarmann, 1995, from Tibet (Lepidoptera: Zygaenidae, Procridinae, Artonini), *SHILAP Revta. Lepid.*, 2017, vol. 45(180), pp. 581–587.
17. Efetov, K.A., Baevsky, M.Y., Beketov, A.A., Parshkova, E.V., and Poddubov, A.I., Synthesis of 2-butyl 2-dodecenoate, a possible sex attractant for the species of the subfamily Procridinae (Lepidoptera: Zygaenidae), *Tavricheskiy Med.-*

Biol. Vestnik, 2013, vol. 16(4), pp. 53–57.

18. Efetov, K.A., Parshkova, E.V., Baevsky, M.Y., and Poddubov, A.I., *Sec*-butyl ester of dodecenoate: synthesis and attractive properties, *Ukr. Biochim. Zh.*, 2014, vol. 86(6), pp. 175–182. doi: 10.15407/ubj86.06.175
19. Efetov, K.A., Kucherenko, E.E., and Parshkova, E.V., The application of cod-liver oil as a source of polyunsaturated fatty acids for the synthesis of Procridinae sex attractant (Lepidoptera: Zygaenidae), *Tavricheskiy Med.-Biol. Vestnik*, 2016, vol. 19(1), pp. 34–39.
20. Efetov, K.A., Kucherenko, E.E., and Desse, J.-M., Sex attractant for *Adscita (Procriterna) subtristis* and *Jordanita (Tremewania) splendens* (Lepidoptera: Zygaenidae, Procridinae), *Crimean J. Exper. Clin. Med.*, 2016, vol. 6(2), pp. 33–36.
21. Efetov, K.A., Kucherenko, E.E., Parshkova, E.V., and Tarmann, G.M., 2-butyl 2-dodecenoate, a new sex attractant for *Jordanita (Tremewania) notata* (Zeller, 1847) and some other Procridinae species (Lepidoptera: Zygaenidae), *SHILAP Revta. Lepid.*, 2016, vol. 44(175), pp. 519–527.
22. Efetov, K.A. and Gorbunov, O.G., Attraction of the males of *Adscita statices* (Linnaeus, 1758) (Lepidoptera: Zygaenidae, Procridinae) by synthetic sex attractant in Moscow Region, *Tavricheskiy Med.-Biol. Vestnik*, 2016, vol. 19(3), pp. 40–46.
23. Can Cengiz, F., Efetov, K.A., Kaya, K., Kucherenko, E.E., Okyar, Z., and Tarmann, G.M., Zygaenidae (Lepidoptera) of Thrace Region of Turkey, *Nota Lepi.*, 2018, vol. 41(1), pp. 23–36. doi: 10.3897/nl.41.21065
24. Efetov, K.A., Mollet, B., and Kucherenko, E.E., A discovery of the new genus and new species *Goazrea lao* Mollet, 2016 (Zygaenidae, Procridinae) in Laos and Thailand with the help of newly synthesized substances EFETOV-2 and EFETOV-S-S-2, *Abstr. XVI Int. Symp. Zygaenidae* (1–5 May 2018, İzmir, Turkey), İzmir, 2018.
25. Efetov, K.A., Koshio, C., and Kucherenko, E.E., A new synthetic sex attractant for males of *Illiberis (Primilliberis) pruni* Dyar, 1905 (Lepidoptera: Zygaenidae, Procridinae), *SHILAP Revta. Lepid.*, 2018, vol. 46(182), pp. 263–270.
26. Can, F., Efetov, K.A., Burman, J., Kaya, K., Kucherenko, E.E., Ulaşlı, B., and Tarmann, G.M., A study of the Zygaenidae (Lepidoptera) fauna of Central Anatolia, Turkey, *Turk. J. Entomol.*, 2019, vol. 43(2), pp.189–199. doi: 10.16970/entoted.512580
27. Efetov, K.A., Kucherenko, E.E., and Tarmann, G.M., New synthetic sex attractants for the males of two endemic Iberian Procridinae species (Lepidoptera: Zygaenidae), *SHILAP Revta. Lepid.*, 2019, vol. 47(186), pp. 307–315.
28. Vrenozi, B., Toshova, T.B., Efetov, K.A., Kucherenko, E.E., Rredhi, A., and Tarmann, G.M., The first well-documented record of the vine bud moth *Theresimima ampellophaga* (Bayle-Barelle, 1808) in Albania established by field screening of sex pheromone and sex attractant traps (Lepidoptera: Zygaenidae, Procridinae), *SHILAP Revta. Lepid.*, 2019, vol. 47(187), pp. 567–576.
29. Jacobson, M. *Insect Sex Pheromones*, New York and London, Academic Press, 1972.
30. Efetov, K.A., *A Review of the Western Palaearctic Procridinae (Lepidoptera: Zygaenidae)*, Simferopol: CSMU Press, 2001.
31. Dolidze, G.V., Akhaladze, Ts.L., Tatishvili, D., Maruashvili, M.V., and Shalamberidze, N.Sh., Sex-traps as a means of grape and fruit pest control, *Acta et Commentationes Universitatis Tartuensis*, 1980, vol. 545, pp. 88–90.
32. Tanaka, Y. and Koshio, C., Activity pattern and reproductive behavior of the plum moth *Illiberis rotundata* Jordan (Lepidoptera: Zygaenidae: Procridinae), *Jap. J. Entomol. (N. S.)*, 2002, vol. 5, pp. 70–80.
33. Koshio, C. and Hidaka, T., Reproductive behaviour of the white-tailed zygaenid moth, *Elcysma westwoodii* (Lepidoptera, Zygaenidae), I. Mating sequence, *J. Ethol.*, 1995, vol. 13(2), pp. 159–163. doi: 10.1007/BF02350107
34. Zagatti, P. and Renou, M., Les pheromones sexuelles des zygènes. Le comportement de *Zygaena filipendulae* L. (Lepidoptera, Zygaenidae), *Ann. Soc. Entomol. Fr.*, 1984, vol. 20(4), pp. 439–454.
35. Tremewan, W.G., *Ecology, Phenotypes and the Mendelian Genetics of Burnet Moths (Zygaena Fabricius, 1775)*, Wallingford: Gem Publishing Company, 2006.
36. Hofmann, A. and Kia-Hofmann, T., Experiments and observations on pheromone attraction and mating in burnet moths (*Zygaena* Fabricius, 1775) (Lepidoptera: Zygaenidae), *Entomol. Gaz.*, 2010, vol. 61(2), pp. 83–93.
37. Myerson, J., Haddon, W.F., and Soderstrom, E.L., *Sec*-butyl (*Z*)-7-tetradecenoate. A novel sex pheromone component from the western grapeleaf sceletonizer, *Harrisina brillians*, *Tetrahedron Lett.*, 1982, vol. 23(27), pp. 2757–2760.
38. Soderstrom, E.L., Brandl, D.G., Myerson, J., Buttery, R.G., and Mackey, A.E., Sex pheromone for attracting western grapeleaf skeletonizer (Lepidoptera: Zygaenidae), *J. Econ. Entomol.*, 1985,

vol. 78(4), pp. 799–801. doi: 10.1093/jee/78.4.799

39. Li, D., Li, J., and Li, L., Studies on the sex pheromone of the pear leaf borer, *Illiberis pruni* Dyar I – identification of sex pheromone, *J. Shanxi Agr. Sci.*, 1997, vol. 25, pp. 63–66.
40. Subchev, M., Harizanov, A., Francke, W., Franke, S., Plass, E., Reckziegel, A., Schröder, F., Pickett, J.A., Wadhams, L.J., and Woodcock, C.M., Sex pheromone of female vine bud moth, *Theresimima ampellophaga* comprises (2*S*)-butyl (7*Z*)-tetradecenoate, *J. Chem. Ecol.*, 1998, vol. 24(7), pp. 1141–1151; *J. Chem. Ecol.* 1999, vol. 25(5), p. 1203, erratum, i.e. corrected to (2*R*)-butyl (7*Z*)-tetradecenoate. doi: 10.1023/A:1022438717287
41. Subchev, M., Toshova, T., Koshio, C., Franke, S., Tröger, A., Twele, R., Francke, W., Pickett, J.A., Wadhams, L.J., and Woodcock, C.M., Identification and biological activity of sex pheromone components from females of the plum moth *Illiberis rotundata* Jordan (Lepidoptera: Zygaenidae: Procridinae), *Chemoecology*, 2009, vol. 19(1), pp. 47–54. doi: 10.1007/s00049-009-0008-8
42. Subchev, M.A., Koshio, C., Toshova, T.B., and Efetov, K.A., *Illiberis (Primilliberis) rotundata* Jordan (Lepidoptera: Zygaenidae: Procridinae) male sex attractant: optimization and use for seasonal monitoring, *Entomol. Sci.*, 2012, vol. 15, pp. 137–139. doi: 10.1111/j.1479-8298.2011.00485.x
43. Zheng, X.-L., Liu, J.-Y., Zhang, Z.-L., Wang, P., and Lu, W., Diel rhythms of sexual behavior and pheromone responses in *Phauda flammans* Walker (Lepidoptera: Zygaenidae), *Pest Manag. Sci.*, 2019, vol. 75(11), pp. 3070–3075. doi: 10.1002/ps.5423
44. Efetov, K.A., Hofmann, A., Tarmann, G.M., and Tremewan, W.G., Taxonomic comments on the treatment of the Zygaenidae (Lepidoptera) in volume 3 of Moths of Europe, Zygaenids, Pyralids 1 and Brachodids (2012), *Nota Lepi.*, 2014, vol. 37(2), pp. 123–133. doi: 10.3897/nl.37.7871
45. Naumann, C.M., Tarmann, G.M., and Tremewan, W.G., *The Western Palaearctic Zygaenidae (Lepidoptera)*, Stenstrup: Apollo Books, 1999.
46. Toshova, T.B., Subchev, M.A., and Tyth, M., Role of olfactory and visual stimuli in the mating behaviour of male vine bud moths, *Theresimima ampellophaga* (Lepidoptera: Zygaenidae), *Eur. J. Entomol.*, 2007, vol. 104, pp. 57–65. doi: 10.14411/eje.2007.009
47. Efetov, K.A., *Zygaena (Agrumenia) sedi cimmerica* Efetov, a new subspecies from the Crimea (Lepidoptera: Zygaenidae, Zygaeninae), *SHILAP Revta. Lepid.*, 2018, vol. 46(182), pp. 347–351.
48. Knyazev, S.A., Efetov, K.A., and Ponomaryov, K.B., Zygaenidae (Lepidoptera) from Omsk Region, *Zool. Zh.*, 2015, vol. 94(11), pp. 1297–1302.
49. Nazarov, V.V. and Efetov, K.A., On the role of Zygaenidae (Lepidoptera) in pollination of *Anacamptis pyramidalis* (Orchidaceae), *Zool. Zh.*, 1993, vol. 72(10), pp. 54–67.
50. Benz, G. and von Salis, G., Use of synthetic sex attractant of Larch bud moth *Zeiraphera diniana* (Gn.) in monitoring traps under different conditions, and antagonistic action of *cis*-isomer, *Experientia*, 1973, vol. 29(6), 729–730. doi: 10.1007/BF01944802
51. Hrdy, I., Marek, J., and Krampl, F., Sexual pheromone activity of 8-dodecenyl and 11-tetradecenyl acetates for males of several lepidopteran species in field trials, *Acta Entomol. Bohemoslov.*, 1979, vol. 76, pp. 65–84.
52. Decamps, C., du Merle, P., Gourio, C., and Luquet, G., Attraction d'espèces du genre *Zygaena* F. Par des substances pheromonales de tordeuses (Lepidoptera, Zygaenidae et Tortricidae), *Ann. Soc. Entomol. Fr. (N. S.)*, 1981, vol. 17(4), pp. 441–447.
53. Priesner, E., Naumann, C., and Stertenbrink, J., Specificity of synthetic sex-attractants in *Zygaena* moths, *Z. Naturforsch.*, 1984, vol. 39(7–8), pp. 841–844. doi: 10.1515/znc-1984-7-826
54. Toshova, T., Subchev, M., Yano, T., Koshio, C., and Horie, K., Calling behaviour of *Zygaena niphona* Butler, 1887 females and male electroantennographic response to synthetic pheromone compounds, *Abst. XI Int. Symp. Zygaenidae (Lepidoptera) (Sofia, 17–21 September 2008)*, Sofia, 2008.
55. Oleander, A., Thackery, D., and Burman, J., The effect of exposure to synthetic pheromone lures on male *Zygaena filipendulae* mating behaviour: implications for monitoring species of conservation interest, *J. Insect Conserv.*, 2015, vol. 19(3), pp. 539–546. doi: 10.1007/s10841-015-9775-4
56. Thackery, D. and Burman, J., The effect of synthetic pheromone exposure on female oviposition and male longevity in *Zygaena filipendulae* (Linnaeus, 1758) (Lepidoptera: Zygaenidae, Zygaeninae), *Entomol. Gaz.*, 2016, vol. 67(4), pp. 249–256.
57. Hrdý, I., Liška, J., Vrkoč, J., and Hochmut, R., New records on sex attractants for males and faunistic comments on moths (Lepidoptera) from Czechoslovakia, *Acta Entomol. Bohemoslov.*, 1989,

vol. 86(4), pp. 252–268.

58. Grichanov, I.Ya, Bulyginskaya, M.A., Bukzeeva, O.N., Zakonnikova, K.V., and Ovsyannikova, E.I., Ecogeographical variation of species specificity of the artificial sex attractants of Lepidoptera, *Russ. J. Ecol.*, 1995, vol. 26(5), 349–352.
59. Hofmann, A.F. and Tremewan, W.G., *The Natural History of Burnet Moths (Zygaena fabricius, 1775) (Lepidoptera: Zygaenidae), Pt. 1,* Münich: Museum Witt, 2017. doi: 10.3897/alpento.1.22129
60. Landolt, P.J., Heath, R.R., Sonnet, P.E., and Matsumoto, K., Attraction of *Harrisina americana* and *Acoloithus falsarius* males (Lepidoptera: Zygaenidae) to *R*-(–)-2-butyl (*Z*)-tetradecenoate, *Environ. Entomol.*, 1986, vol. 15(4), pp. 959–962. doi: 10.1093/ee/15.4.959
61. Landolt, P.J., Heath, R.R., and Tarmann, G., Zygaenidae trapped with enantiomers of 2-butyl (*Z*)-7-tetradecenoate, *J. Lepid. Soc.*, 1991, vol. 45(1), pp. 63–65.
62. Subchev, M., Toshova, T., Koshio, C., Efetov, K.A., and Francke, W., (2*R*)-butyl (7*Z*)-dodecenoate, a main sex pheromone component of *Illiberis (Primilliberis) pruni* Dyar (Lepidoptera: Zygaenidae: Procridinae)? *Acta Zool. Bulg.*, 2013, vol. 65(3), pp. 391–396.
63. Subchev, M., Efetov, K.A., Toshova, T., Parshkova, E.V., Tyth, M., and Francke, W., New sex attractants for species of the zygaenid subfamily Procridinae (Lepidoptera: Zygaenidae), *Entomol. Gen.*, 2010, vol. 32(4), pp. 243–250.
64. Efetov, K.A., Hofmann, A., and Tarmann, G.M., Application of two molecular approaches (use of sex attractants and DNA barcoding) allowed to rediscover *Zygaenoprocris eberti* (Alberti, 1968) (Lepidoptera, Zygaenidae, Procridinae), hitherto known only from the female holotype, *Nota Lepi.*, 2014, vol. 37(2), pp. 151–160. doi: 10.3897/nl.37.7871
65. Efetov, K.A., Subchev, M.A., Toshova, T.B., and Kiselev, V.M., Attraction of *Zygaenoprocris taftana* (Alberti, 1939) and *Jordanita horni* (Alberti, 1937) (Lepidoptera: Zygaenidae, Procridinae) by synthetic sex pheromones in Armenia, *Entomol. Gaz.*, 2011, vol. 62(2), pp. 113–121.
66. Efetov, K.A., Can, F., Toshova, T.B., and Subchev, M., New sex attractant for *Jordanita anatolica* (Naufock) (Lepidoptera: Zygaenidae: Procridinae), *Acta Zool. Bulg.*, 2010, vol. 62(3), pp. 315–319.
67. Efetov, K.A., Tarmann, G.M., Toshova, T.B., and Subchev, M.A., Enantiomers of 2-butyl 7*Z*-dodecenoate are sex attractants for males of *Adscita mannii* (Lederer, 1853), *A. geryon* (Hübner, 1813), and *Jordanita notata* (Zeller, 1847) (Lepidoptera: Zygaenidae, Procridinae) in Italy, *Nota Lepi.*, 2015, vol. 38(2), pp. 161–169. doi: 10.3897/nl.38.6312
68. Razov, J., Efetov, K.A., Franin, K., Toshova, T.B., and Subchev, M.A., The application of sex pheromone traps for recording the Procridinae fauna (Lepidoptera: Zygaenidae) in Croatia, *Entomol. Gaz.*, 2017, vol. 68(1), pp. 49–53.
69. Keil, T., Eine neue Grünwidderchen-Art aus der iranischen Provinz Kerman (Lepidoptera, Zygaenidae, Procridinae), *Entomol. Nachr. Ber.*, 2016, vol. 60(3/4), pp. 201–203.
70. Efetov, K.A. and Tarmann, G.M., *A Checklist of the Palaearctic Procridinae (Lepidoptera: Zygaenidae)*, Simferopol, Innsbruck: CSMU Press, Nata, 2012.
71. Efetov, K.A., Beketov, A.A., and Parshikov, V.A., Synthesis and biological activity of lauric acid *sec*-butyl ester, *Tavricheskiy Med.-Biol. Vestnik*, 2012, vol. 15(1), pp. 345–347.
72. Gorbunov, O.G. and Efetov, K.A., The clearwing moth genus *Bembecia* Hübner 1819 ["1816"] (Lepidoptera, Sesiidae) in Crimea, with the description of a new species, *Zool. Zh.*, 2018, vol. 97(7), pp. 812–839.
73. Kawahara, A.Y., Plotkin, D., Espeland, M., Meusemann, K., Toussaint, E.F.A., Donath, A., Gimnich, F., Frandsen, P.B., Zwick, A., dos Reis, M., Barber, J.R., Peters, R.S., Liu, S., Zhou, X., Mayer, C., Podsiadlowski, L., Storer, C., Yack, J.E., Misof, B., and Breinholt, J.W., Phylogenomics reveals the evolutionary timing and pattern of butterflies and moths, *PNAS*, 2019, vol. 116(45), pp. 22657–22663. doi: 10.1073/pnas.1907847116
74. Roelofs, W.L., Chemistry of sex attraction, *PNAS*, 1995, vol. 92(1), pp. 44–49. doi: 10.1073/pnas.92.1.44
75. Tillman, J.A., Seybold, S.J., Jurenka, R.A., and Blomquist, G.J., Insect pheromones: an overview of biosynthesis and endocrine regulation, *Insect Biochem. Mol. Biol.*, 1999, vol. 29, pp. 481–514. doi: 10.1016/s0965-1748(99)00016-8
76. Roelofs, W.L. and Rooney, A.P., Molecular genetics and evolution of pheromone biosynthesis in Lepidoptera, *PNAS*, 2003, vol. 100(16), pp. 9179–9184. doi: 10.1073/pnas.1233767100a
77. Blomquist, G.J. and Vogt, R.G., *Insect Pheromone Biochemistry and Molecular Biology: the Biosynthesis and Detection of Pheromones and Plant Volatiles*, London: Elsevier Academic Press, 2003.

78. Byers, J.A., Pheromone component patterns of moth evolution revealed by computer analysis of the *Pherolist*, *J. Anim. Ecol.*, 2006, vol. 75(2), pp. 399–407. doi: 10.1111/j.1365-2656.2006.01060.x
79. Xu, P., Garczynski, S.F., Atungulu, E., Syed, Z., Choo, Y.-M., Vidal, D.M., Zitelli, C.H.L., and Leal, W.S., Moth sex pheromone receptors and deceitful parapheromones, *PLoS ONE*, 2012, vol. 7(7), e41653. doi: 10.1371/journal.pone.0041653
80. Löfstedt, C., Population variation and genetic control of pheromone communication systems in moths, *Entomol. Exp. Appl.*, 1990, vol. 54, pp. 199–218. doi: 10.1111/j.1570-7458.1990.tb01331.x
81. Löfstedt, C., Moth pheromone genetics and evolution, *Phil. Trans. R. Soc. B*, 1993, vol. 340(1292), pp. 167–177.
82. Groot, A.T., Schofl, G., Inglis, O., Donnerhacke, S., Classen, A., Schmalz, A., Santangelo, R.G., Emerson, J., Gould, F., Schal, C., and Heckel, D.G., Within-population variability in a moth sex pheromone blend: genetic basis and behavioural consequences, *Proc. R. Soc. B*, 2014, vol. 281, 20133054. doi: 10.1098/rspb.2013.3054
83. Surov, A.V. and Maltsev, A.N., Analysis of chemical communication in mammals: zoological and ecological aspects, *Zool. Zh.*, 2016, vol. 95(12), pp. 1449–1458.
84. Wyatt, T.D., *Pheromones and Animal Behavior: Chemical Signals and Signatures*, Cambridge: Cambridge University Press, 2014. doi: 10.1017/CBO9781139030748
85. Efetov, K.A., *The Zygaenidae (Lepidoptera) of the Crimea and Other Regions of Eurasia*, Simferopol: CSMU Press, 2005.
86. Subchev, M.A., Efetov, K.A., Toshova, T.B., and Koshio, C., Sex pheromones as isolating mechanisms in two closely related *Illiberis* species – *I. (Primilliberis) rotundata* Jordan, 1907, and *I. (P.) pruni* Dyar, 1905 (Lepidoptera: Zygaenidae, Procridinae), *Entomol. Gaz.*, 2016, vol. 67(1), pp. 51–57.