(Z)-5-Dodecen-1-ol, Another Inhibitor of Pheromonal Attraction in *Coleophora laricella*

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Trap captures of male larch casebearer moths *C. laricella* (Hb.) in response to the primary female pheromone (*Z*)-5-decen-1-ol strongly decreased on addition of either the corresponding acetate analogue (a previously reported inhibitor) or the longer-chain homologue (*Z*)-5-dodecen-1-ol. Various other monoenic acetates or alcohols tested did not affect captures. Comparison with results on other *Coleophora* spp. suggests a role for the two inhibitors in species isolation.

Male larch casebearer moths *Coleophora laricella* (Hb.) (Lepidoptera: Coleophoridae) are strongly attracted to sources of (*Z*)-5-decen-1-ol (*Z*5-10:OH) [1, 2], the identified major component of conspecific female pheromone [3]. We have previously reported [1, 4] on the modification of this response by the corresponding acetate analogue, (*Z*)-5-decenyl acetate (*Z*5-10:Ac). This report describes "inhibitory" effects on male *C. laricella* of the pheromone homologue (*Z*)-5-dodecen-1-ol (*Z*5-12:OH). The results provide the first example, in lepidopterous sex-attractant systems, of a behavioural role of this compound and of an attractant/inhibitor relationship between two (*Z*)-alkenols.

The effects of *Z*5-12:OH on male *C. laricella* became apparent during a comparative study of sexual attractants and their inhibitors in European Coleophoridae. The various sex-attractants and attraction-inhibitors established during this study for some 50 spp. of *Coleophora* [5, 6] included as their essential components the primary alcohols *Z*3-10:OH, *Z*5-10:OH, *Z*7-10:OH, *Z*5-12:OH and *Z*7-12:OH and the acetates *Z*3-10:Ac, *Z*5-10:Ac, *Z*5-12:Ac and *Z*7-12:Ac. These, together with some of their structural analogues, were also tested on *C. laricella* for potential attractive, synergistic or inhibitory properties. The test chemicals, purchased from the Institute for Pesticide Research, Wageningen, The Netherlands, were ≧ 98% pure for geometric or positional isomers. In field tests, rubber cap dispensers (∅ 18 mm; single cap for compound mixtures) suspended in tetratraps [7] or Uni-traps® (Int. Pheromones Ltd., Warrington, UK.) were generally used. Test series consisted of up to 12 formulations, including reference traps baited with different amounts (0.1 to 100 µg) of *Z*5-10:OH, in 4 or 6 concurrent replicates. Placement and inspection of traps and the statistical treatment of trapping data were as in previous *C. laricella* studies [1, 4]. The main test sites were natural stands of *Larix decidua* at Zuoz and Tinizong (Engadin valley in the Swiss Alps) and plantations of *L. decidua* and *L. leptolepis* at Sulzemoos and Hadorf (near Munich, southern Germany) and Lingen (near Münster, northwestern Germany). The tests took place from late May until mid July, in the years 1981 to 1987.

Tests using single compounds revealed low attractive properties for the pheromone stereoisomer *E*5-10:OH and the longer-chain homologue *Z*7-12:OH. For example, at Tinizong in June 1982 traps baited with 100 µg and 1000 µg of these compounds produced *C. laricella* captures corresponding to between 0.1 to 1 µg of *Z*5-10:OH, differing significantly ($P < 0.05$) from control trap captures. In this test, up to 1000 µg of the alcohols *Z*3-10:OH, *Z*7-10:OH or *Z*5-12:OH or some acetate analogues did not produce significant captures [8]. The low attractiveness of the *Z*7-12:OH for male *C. laricella* is illustrated in Table I from another test.

When studying inhibitory effects of *Z*5-10:Ac (acetate analogue of pheromone) on male *C. laricella* at Lingen and Tinizong in 1981/82 [1, 4], some other compounds were included, which were added in varying amounts to the 100 µg *Z*5-10:OH standard. We have already reported the failure of a 10% addition of *Z*7-10:OH or *Z*7-12:OH to modify captures [1]. Similarly, as shown in Table II, a 3% to 100%

Table I. Captures of *C. laricella* males in tetratraps baited with different amounts of *Z*5-10:OH or *Z*7-12:OH. Sulzemoos, June 5 to 15, 1985; four replicates.

Amount [µg/trap] of *Z*5-10:OH	*Z*7-12:OH	$\bar{X}$ males/trap
0.1	0	36.0
1	0	168.0
0	100	99.5
0	1000	308.75
blank		12.25

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Table II. Captures of *C. laricella* males in tetratraps baited with 100 µg of *Z*5-10:OH alone or in combination with varying amounts of the stereoisomer *E*5-10:OH, in two test series: A, Lingen, May 31 to June 3, 1982; B, Tinizong, June 18 to 22, 1982; six replicates per series [8].

Amount [µg/trap] of *Z*5-10:OH	*E*5-10:OH	$\bar{X}$ males/trap in series A	B
100	0	268.8	270.3
100	3	371.7	332.8
100	10	293.5	321.3
100	30	344.2	212.8
100	100	407.5	308.7
blank		0	3.5

addition of the pheromone stereoisomer *E*5-10:OH had no modifying effect. Tests were continued in 1985 after *Z*3-10:OH and *Z*5-12:OH had been found to be strong pheromonal inhibitors in some other *Coleophora* spp. attracted by *Z*5-10:OH [5, 6]. Results presented in Table III show that a 100% addition of *Z*3-10:OH or *Z*7-12:OH had no effect on *C. laricella* captures, whereas the same amount of *Z*5-12:OH reduced captures to 2% of those obtained with 100 µg *Z*5-10:OH alone. Effects of this inhibitor were further studied, in a subsequent series, by comparison with the previously established inhibitor *Z*5-10:Ac. The three formulations containing 0.3, 1 and 3% of the acetate produced captures corresponding to approx. 11, 2 and 1%, respectively, of those obtained with the 100 µg *Z*5-10:OH standard (Table IV). These figures compare well with trapping data with the same compound combinations at two test localities in 1981 [1]. The *Z*5-12:OH revealed comparable reduction effects at a 10–30-fold higher amount (Table IV). The inhibitory threshold of this compound (causing significant reduction of catches in comparison to pure *Z*5-10:OH alone), not apparent from this test, was determined in a subsequent series (Table V) as about a 1% addition.

Table III. Effect of four additives on captures of *C. laricella* males with 100 µg *Z*5-10:OH. Sulzemoos, June 6 to 15, 1985; tetratraps, four replicates.

Additive [100 µg]	$\bar{X}$ males/trap
none	547.0
*Z*3-10:OH	442.5
*Z*5-12:OH	11.0
*Z*7-12:OH	587.3
*Z*3-10:Ac	505.3

Table IV. Effect of varying amounts of *Z*5-12:OH or *Z*5-10:Ac on captures of *C. laricella* males with 100 µg *Z*5-10:OH. Lingen, May 27 to June 25, 1985; unitraps, three replicates.

Additive [µg]		$\bar{X}$ males/trap	%
none		2341.7	100
*Z*5-12:OH,	0.3	1247.3	53.3
	1	1074.7	45.9
	3	527.0	22.5
	10	131.3	5.6
	30	39.7	1.7
*Z*5-10:Ac,	0.3	260.7	11.3
	1	51.3	2.2
	3	22.7	1.0

Table V. Effect of varying amounts of *Z*5-12:OH on captures of *C. laricella* males with 100 µg *Z*5-10:OH. Hadorf, June 12 to 25, 1987; tetratraps, six replicates.

Amount [µg] of added *Z*5-12:OH	$\bar{X}$ males/trap[a]
0	480.3 ab
0.03	505.0 a
0.1	458.5 ab
0.3	433.0 b
1	209.3 c
3	51.0 d

[a] Capture means followed by common letters are not significantly different (P = 0.05, Duncan's multiple range test).

This again differs by one order of magnitude from the threshold value of 0.1% previously determined for the *Z*5-10:Ac [1, 4].

The lower inhibitory threshold of *Z*5-10:Ac than of *Z*5-12:OH seems reasonable given the mode of sensory perception of these compounds. The respective single cell recordings have not yet been made in *C. laricella* but studies in other Lepidoptera have shown that pheromone inhibitors are generally perceived *via* specialized types of "inhibitory cells", located with the pheromone receptor cells within the same male antennal hair sensilla [9–14]. Different types of receptor cells specialized for *Z*5-10:OH, *Z*5-10:Ac and *Z*5-12:OH respectively are thus likely to occur in the antennal receptor system of male *C. laricella*. Furthermore, as shown by studies in other Lepidoptera [9–11, 15], cells specialized for a particular (*Z*)-alken-1-ol are approx. 100 times less sensitive (from equipotent stimulus amounts) to an isomer or homologue differing from the "key" com-

pound by 2 carbon units in chain length and/or double bond position, whereas (*Z*)-alkenyl acetate receptors are approx. 1,000-fold less sensitive to the corresponding alcohol analogue. If these statements also hold for *C. laricella*, cross-activation by *Z*5-10:OH (the primary pheromone) would require an approx. 100-fold increase in stimulus amount for the postulated *Z*5-12:OH receptor and one of 1,000-fold for the *Z*5-10:Ac receptor, thus limiting the lower perception of these compounds in a pheromone/inhibitor blend to approx. 1% and 0.1%, respectively. This would correspond well with the threshold values determined for the two inhibitors in the present field study.

Further tests (data not given) showed that 100% additions of the acetates *Z*3-10:Ac, *Z*7-10:Ac, *Z*5-12:Ac or *Z*7-12:Ac had virtually no effect on *C. laricella* trap captures by *Z*5-10:OH. This pattern also holds for other *Coleophora* spp. attracted by *Z*5-10:OH, such as *C. alticolella* Zell., *flavipennella* (Dup.), *glitzella* Hofm., *serratella* (L.) (= *fuscedinella* Zell.) and *trigeminella* Fuchs [5, 6]. These four acetates are, however, strong behavioural inhibitors in some other *Coleophora* spp. attracted either by *Z*5-10:OH / *Z*5-10:Ac blends, such as *C. amellivora* Bald., *coracipennella* (Hb.), *juncicolella* Staint., *lineolea* (Haw.), *lithargyrinella* Zell., *ochripennella* Zell. and *prunifoliae* Doets, or by *Z*5-10:Ac alone, such as *C. binderella* (Koll.), *clypeiferrella* Hofm., *glaucicolella* Wood, *gryphipennella* (Hb.), *mayrella* (Hb.), *orbitella* Zell., *ornatipennella* (Hb.), *vacciniella* H. Sch. and *virgaureae* Staint. [5, 6].

A pheromone/inhibitor relationship between homologous (*Z*)-alkenols, reported here for *C. laricella*, is a novel pattern for insect pheromone systems. As with *Z*5-10:Ac [4], the biological significance of the inhibition by *Z*5-12:OH of pheromonal responses in *C. laricella* remains unknown. A role in species isolation does not seem unlikely considering that certain other *Coleophora* spp. respond to particular OH/Ac or OH/OH blends ([5, 6]; see also above). The two inhibitors established for the sex-attractant system of *C. laricella* should provide effective reproductive isolation from other spp. of the genus using either a *Z*5-10:OH / *Z*5-10:Ac or a *Z*5-10:OH / *Z*5-12:OH blend as their sexual pheromones.

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