The reaction starts from a RO· radical which exhibits 2 other resonance hybride Rβ· and R5· radicals (see scheme). Coupling between Rβ· radical and R5· radical generates **2**[7d] and the combination of 2 Rβ· radicals yields **3**. **3** is oxidized with oxygen and $FeCl_3$ as catalyst[11] to the endoperoxide **9** which is reduced by Fe^{2+} ion and finally rearranged by $FeCl_3$ to give **5** and **6a**. **4a** is formed by dehyration of **5** and **6a** during the separation.

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Ortho-aminoacetophenone: A component of the sex pheromone system of the web-spinning larch sawfly, *Cephalcia lariciphila* wachtl

R. Baker, C. Longhurst[1], D. Selwood and D. Billany

Chemical Entomology Unit, Departments of Biology and Chemistry, The University of Southampton, Southampton SO9 5NH (England), and Forestry Commission, Alice Holt Lodge, Wrecclesham, Farnham, Surrey GU10 4LH (England), January 5, 1983

Summary. The ortho-isomer of aminoacetophenone was found in females of *Cephalcia lariciphila*. The pheromone released antennal movement, abdominal flexing and short flights in males, but did not release orientated upwind flight in these activated males.

Males of *Cephalcia lariciphila* have been shown to respond to a sex pheromone produced by the female[2]. In an attempt to identify the pheromonal components of female *C. lariciphila* large scale collections of prepupae were made from the Forest of Dean (SO 650160) and Mortimer Forest (SO 625350) in February and March of 1979–1981.

Females were extracted into pentane using a procedure similar to that developed for *Diprion* spp.[3]. The insects were macerated in methanol and ultrasonicated. The mixture was then refluxed for 24 h; after centrifugation the supernatant methanol was refluxed with KOH. The methanol was then evaporated and following addition of water the residue was extracted with pentane. Volatile compounds in the pentane extract were resolved on a SCOT capillary GLC column (5% carbowax 20 M, 0.2 mm × 50 m; 130–200 °C at 4 °C/min) or a 2% OV17 on diatomite CLQ column (100–200 mesh, 3 mm × 3 m; 130–315 °C at 6 °C/min). Mass-spectra of the eluting compounds were recorded at 70 eV on an A.E.I. MS30 spectrometer with a Kratos DS55 data system. One of the major non-hydrocarbon peaks (< 0.5 µg/female) was identified as an isomer of aminoacetophenone, m/e (%), 136 (8), 135 (81), 121 (10), 120 (100), 93 (5), 92 (46), 65 (22), 39 (7). Comparison with authentic samples of *o*-, *p*- and *m*-aminoacetophenone (aap) confirmed the natural product to be the *ortho*-isomer. This compound has previously only been reported in the

Table 1. Responses of male *Cephalcia lariciphila* to virgin females, female extract and *o*-aminoacetophenone*

Behavioral response	Number of males giving the behavioral response (number tested)				
	Virgin female (10)	Female extract (12)	*o*-Amino aceto-phenone (15)	Solvent control (10)	Virgin male (10)
1. Antennal movement	10	12	15	0	4
2. Abdomenal flexing	10	12	15	0	1
3. Short flights (100 mm)	9	7	12	0	1
4. Upwind flight	6	4	0	0	0
5. Courtship	3	0	0	0	0

* Assay chamber of same basic design as Jones et al.[6] but with a 1.1 m diameter × 2 m chamber and without hexagonal interface to give a laminar airflow. Males released from 200 × 200 mm platform 0.5 m above the chamber floor and upwind of the female. Females and test substances were placed on a 100 × 100 mm platform at the other end of the chamber. Females were placed in 40 × 35 mm high perforated plastic chambers.

Table 2. Response of male *C. lariciphila* to delta and horizontal board traps baited with isomers of aminoacetophenone, female extracts or virgin females

	Trap type	Mean number of males/trap		
		Experiment 1	Experiment 2	Experiment 3
o-Aminoacetophenone	Delta		3.2b	4.4c
	Board	36.0b		29.6b
m-Aminoacetophenone	Delta		0.8b	
	Board	5.6c		
p-Aminoacetophenone	Delta		2.4b	
	Board	10.2c		
Female extract (0.5 equivalent)	Delta		27.8a	
	Board	42.4b		
Virgin female	Delta			96.6a
	Board	94.2a		
Control	Delta		1.4b	3.4c
	Board			10.2c

Mean trap catches followed by the same letter in any experiment are not significantly different at $p > 0.05$; ANOVA followed by Newman Keul's test. Experiment 1 performed in 1980, experiment 2 in the period 7.–12.5.81 and experiment 3 in the period 12.–19.5.81.

Hymenoptera from the primitive-growing ants, *Mycocepurus goeldii*[4].

Electroantennograph (EAG) measurements on the 3 isomers were obtained using whole insect preparations. The body of the insect was immobilized on a block of plasticine and the antennae secured with microstaples. Glass electrodes drawn out of capillary tubing (Medde GC-100 F-4) were filled with insect ringer solution and connected to a high impedance (10^{12} Ω) differential amplifier via chloridized silver wires inserted down the center of each electrode. The EAG response was recorded on a digital transient recorder (DTR Type DL901). A test substance in solution was applied to the inside of a pasteur pipette and any solvent allowed to evaporate; the substance was then puffed over the antennae by hand. The pipette tip was 10–20 mm from the insect antenna. The mean response of the male antennae to 1 µg of o-aap was 2.4 mV, to m-aap 0.63 mV and *p*-aap 0.30 mV. Live females elicited a 1.8 mV response, while female extracts a 0.8 mV response compared to 0.25 mV for the solvent control. The EAG responses to *o*-aap, as well as those of live females and female extracts, had a sharp leading edge characteristic of genuine pheromone responses[5]. This sharp edge was lacking in the responses from other isomers.

Laboratory observations of the behavioral responses of male *C. lariciphila* to females and experimental compounds were carried out in a plastic wind tunnel[6] of 1.1 m diameter. The behavioral responses leading to close range courtship and mating can be classified into the following sequence[7]: 1. Movement of the antennae (including searching of the substrate), accompanied by extrusion of the genitalia and opening of the mandibles. 2. Vertical flexing of the abdomen from the horizontal and 'flitting of the wings'. 3. Short flights (< 100 mm). 4. Upwind flight. 5. Close range courtship and mating.

Only calling virgin females elicited this full behavioral sequence (table 1); extracts of females on rubber sleeve stoppers did elicit upwind flight. but males did not attempt to perform close range courtship displays or mate with the pheromone source. The *ortho*-aminoacetophenone released the first 3 sequences of the behavioral repertoire, but did not elicit upwind flight.

Field testing was carried out in larch plantations at Wopley Hill (Mortimer Forest) in 1980 and 1981. Horizontal plywood traps (200×200 mm), with removable sticky surfaces (190×210 mm), were mounted on stakes 1 m above the ground. A 5×5 latin square experimental design was utilized to compare the responses of males to virgin female *C. lariciphila* (in plastic chambers[2]), female extracts (0.5 female equivalents/trap) and the 3 isomers of aap at 1 µl/trap. The aminoacetophenones were dissolved in dichloromethane and applied to 7×20 mm rubber sleeve stoppers (West Pharma Rubber).

When deployed on open horizontal board traps the *ortho*-isomer caught significantly more males of *C. lariciphila* than the other isomers (table 2, experiment 1) and as many as the female extract. In 1981 an attempt was made to repeat this experiment using plastic delta traps (Wolfson Unit, Southampton University; 190×210×120 mm high). In this experiment (table 2, experiment 2) no significant differences could be seen between the different isomers of aap and control traps. Previous experiments[7] had demonstrated that delta traps baited with live females perform as well as horizontal board traps; it was, therefore, concluded that the differences between experiments 1 and 2 were due to trap design interacting with the pheromone. A comparison was made between delta traps and board traps (table 2, experiment 3) which showed that board traps baited with *o*-aap caught significantly more males than enclosed delta traps baited with the same compound.

These data, from laboratory and field studies, are interpreted as indicating a role for *o*-aap in a multicomponent sex pheromone. It is apparent that the aap does not release attraction of males to the pheromone source but only activates the early stages of the courtship sequence. The behavior released by the *o*-aap leads to an increased activity in the vicinity of the trap in the form of non-orientated random flights. This leads to an increased catch of male sawflies on the exposed sticky surface near the source of the activation stimulus. In contrast, to be captured in a delta trap, a male sawfly must make an orientated flight through the trap entrance. Laboratory studies (table 1) also indicate the role of *o*-aap in increasing flight activity. The significantly larger numbers of males found in delta traps baited with females (table 2, experiment 3) or female extracts (table 2, experiment 2), together with laboratory data from females and their extracts, indicate that other behavioral releasing chemicals, such as an orientation stimulant, are present in the complete pheromone system.

Our results also indicate the unsuitability of unenclosed traps for pheromone research as they do not distinguish orientated responses from unorientated action responses when the density of flying insects is high, as in this sawfly infestation[2].

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Condensation of an alkyl chain on 1,7,7-trimethylbicycloheptane: A model for the effect of camphor on lipid membranes

G.J. Smith[1]

Physics and Engineering Laboratory, DSIR, Private Bag, Lower Hutt (New Zealand), January 18, 1983

Summary. Enthalpies of mixing of the hydrocarbon portion of camphor with n-octane show that it exerts a condensation interaction on adjacent alkyl chains. This is a similar interaction to that displayed by cholesterol in cell membranes which results in an alteration of the membrane fluidity.