Table 1. Spectral data of derivatives of 7-oxy-coumarin (umbelliferon, UBF) in water (ionic strenght between 0.0 and 0.1 *M*), ethanol and vesicle suspensions (ionic strength 0.1 *M*)

Probe	Water		Ethanol 95%		Egg-PC vesicles	
	λ_{max} [nm] (±2 nm)	ε [$10^4 M^{-1}$ cm^{-1}] (±5%)	λ_{max} [nm] (±2 nm)	ε [$10^4 M^{-1}$ cm^{-1}] (±5%)	λ_{max} [nm] (±2 nm)	ε [$10^4 M^{-1}$ cm^{-1}] (±10%)
I. 3A-UBF	361	2.3	364	2.4	360	
3A-UBF$^-$	414	4.4	431	4.6	416	
II. 3P-UBF	insoluble		365	2.2	368	2.0
3P-UBF$^-$			430	4.5	424	3.3
III. UBF	325	1.5	326	1.5	(325)	
UBF$^-$	369	1.9	3.77	2.1	(369)	
IV. C_{15}-UBF	insoluble		326	1.5	327	1.5
C_{15}-UBF$^-$			376	2.1	380	1.7

density and the chemical structure of the polar region in a manner similar to IV [5, 6]. Then we may try to incorporate it into biological membranes to probe structure and structural changes there.

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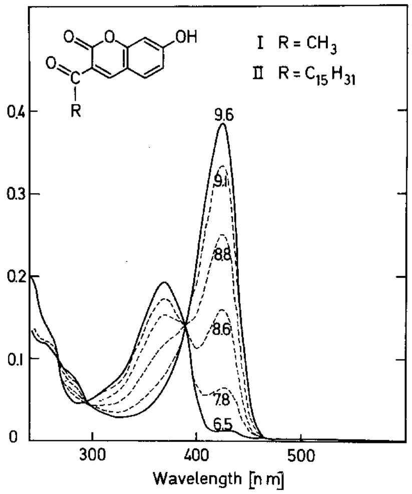

Fig. 1. Absorption spectra of 3-palmitoyl-7-oxy-coumarin (II) in egg-phosphatidylcholine(PC) microvesicles. Molar ratio (egg-PC:II) about (200:1). Aqueous phase 0.1 *M* NaCl of the indicated pH. Reference was an identical microvesicle preparation without II

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(−)-Grandisol, the Antipode of the Boll Weevil Pheromone, is Biologically Active

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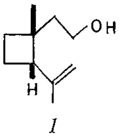
(1R,2S)-(+)-Grandisol (*1*) is one of the four pheromone components isolated from male boll weevils, *Anthonomus grandis* Boheman [1, 2]. We synthesized its antipode and found it to be as biologically active as an isolated pheromone component. Antipodes of bioactive chiral molecules were generally believed to be devoid of biological activity. This dogma was proved to be untrue in the present case. Many syntheses of (±)-grandisol were reported [3], but only two reports were concerned with the synthesis of optically active grandisol. Hobbs and Magnus described the synthesis of natural (+)-grandisol of 90% optical purity ($[\alpha]_D^{21.5}+16.6°$; $c=1$, n-hexane) [4], while Mori published a synthesis of both (+)- ($[\alpha]_D^{20}+15.7°$; n-hexane) and (−)-grandisol ($[\alpha]_D^{20}-16°$; n-hexane) of about 80% optical purity [5]. The synthesis of highly optically pure (−)-grandisol (*1′*) was essential in clarifying the chirality-boll weevil pheromone activity relationship.



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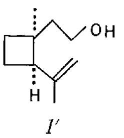
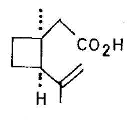
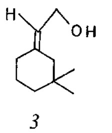


1′



(1S, 2R)-*2*



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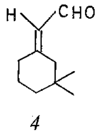

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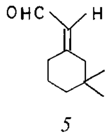

5

Our synthesis was accomplished as follows. We prepared 2.7 g of (±)-*2*, m.p. 39.0~40.0 °C, by oxidizing (±)-grandisol with CrO_3-C_5H_5N-HCl in CH_2Cl_2 and Ag_2O-NaOH in 50% EtOH. The optical resolution of (±)-*2* (2.7 g) with quinine (5.2 g) in 99% EtOH yielded, after ten recrystallizations, 0.75 g of the quinine salt, m.p. 137.0~138.5 °C, $[\alpha]_D^{21}-140.1°$ ($c=$ 0.352, MeOH); found: C 70.90; H 8.24; N 5.54. $C_{30}H_{40}O_4N_2 \cdot H_2O$ requires: C 70.56; H 8.28; N 5.48%. This, upon acidification (dil. HCl), afforded the (−)-acid *2* (0.27 g, 20%), m.p. 39.5~40.0 °C; $[\alpha]_D^{23}-49.3°$ ($c=0.74$, n-hexane); found: C 71.64; H 9.59. $C_{10}H_{16}O_2$ requires: C 71.39; H 9.58%. This acid *2* was reduced with $LiAlH_4$ (130 mg) in dry ether (10 ml) to give 0.2 g (87%) of (−)-grandisol (*1′*), b.p. (bath temp.) 110~113 °C/13 mmHg; n_D^{22} 1.4731; m/e 154 (M^+); GLC (3% SE-30 1.5 m × 2 mm at 80 °C; Carrier gas N_2, 1 kg/cm^2): R_t 7.0 min (single peak); $[\alpha]_D^{22}-18.2°$ (±0.2°) ($c=1.3$, n-hexane). From this $[\alpha]_D$ value, the optical purity of our (−)-grandisol was thought to be 91% (based on Mori's data [5]) or 98% (based on Magnus' data [4]). This (−)-grandisol

Table 1. Laboratory response of female *Anthonomus grandis* to a pheromone mixture containing (+)-grandisol (*1*) or (−)-grandisol (*1'*)

	Responding to test	Responding to check	Not responding
(+)-Grandisol[a]	11	0	9
	13	0	7
	8	0	12
	6	0	14
mean	9.5	0	10.5
(−)-Grandisol	12	0	8
	7	2	11
	10	1	9
	12	2	6
mean	10.3	1.3	8.5

[a] 8 µg of a mixture of *1* or *1'*:*3*:*4*:*5*=30:40:15:15 in 0.1 ml of heptane applied to 60/80 Chromosorb W: insects were counted after 1 h

(*1'*) and the previously synthesized (+)-isomer *1* of about 80% optical purity [5] were bioassayed in the USA. The grandisol isomers were formulated with the other pheromone components *3*, *4* and *5* in a ratio of *1* or *1'*:*3*:*4*:*5*=30:40:15:15. After formulation, the ratios were verified by GLC. The results of four replicated bioassays are shown in Table 1. As can be seen, the calculated net % response was 47.5 to (+)-grandisol and 45.0 to (−)-grandisol. The responses were very good for this bioassay. The average net response is typically about 40. Because the ratio of the four components is important for activity, it does not seem possible that the small amount of (+)-isomer in our (−)-grandisol would support full activity. From this bioassay, it is deduced that both of the grandisol isomers are fully active, although there might be a slight preference for the (+)-isomer.

This lack of chiral specificity in the pheromone receptor of boll weevil is in sharp contrast with the strong specificity among other insects, *Dendroctonus brevicomis* [6], *Ips grandicollis* [7], *Ips calligraphus* [8] and *Porthetria dispar* [8, 9], etc. Synthesis of other chiral pheromones will be further pursued to increase our knowledge of the chirality-pheromone activity relationship.

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Observations of an Aphid Infestation on Hawthorn in the Vicinity of a Motorway

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In previous reports we have shown that the microclimate and the vegetation near a motorway with a frequency of 30000 vehicles per day are drastically affected. Measurements of the soil and air temperature in the dividing strip during hot summer days showed that a motorway may function as a heat accumulator [1]. Trees and shrubs, growing along the motorway and covered by road dust, showed, during warm and sunny days, significantly lower stomatal diffusive resistances and an increased leaf temperature [1, 2].

Young birch trees showed marked biochemical responses, similar to these biophysical changes, relative to their distance from the motorway [3]. Corresponding findings have now been observed with the hawthorn (*Crataegus monogyna*) (Fig. 1). In July, the quantity of reducing sugars was 25% higher, while the quantity of ascorbic acid was 30% lower in plants growing in the dividing strip, as compared with the quantities in plants growing at a distance of 50 m. The quantity of free amino acids increased slightly as the distance to the motorway became shorter.

During the past three years, we have observed on these *Crataegus* plants a conspicuous infestation by *Aphis pomi*, which decreased with the distance from the dividing strip (Fig. 2). Investigations during the generally cool season of April revealed that hawthorn plants growing in the dividing strip suffered from heavy attacks, even in the very early stages of leaf development, whereas shrubs at a distance of 10 m from the motorway showed evidence of only a few, and at a distance of 50 m, no *Aphis pomi*. This suggests that changed microclimate conditions along the motorway might favor aphid development, especially during cool seasons. On the other hand, it cannot be discounted that the air pollution along the motorway may also influence the host plant–parasite relationship, e.g., as a result of changes in the plant biochemistry as mentioned above which may alter the food quality for parasites. Results of various investigators demonstrate that, in particular, the pattern of amino acids is changed and the quantity of free amino acids is increased when the plants are exposed to air pollution [4]. An increased formation of soluble nitrogen favors the mass propagation of aphids [5]. However, hawthorn leaves, growing in the dividing strip, showed, in contrast to previous findings in birch trees, only significantly more free amino acids, when they were infested by aphids (Fig. 1).

Observations by various authors have revealed that a great number of plant parasites can appear as a result of emissions. Pines showed an increase in parasite population, possibly as a result of changed water relations, after exposure to SO_2 [6]. In the vicinity of a wood-carbonization plant, which emitted various gases, an unusual mass propagation of the spruce sawfly (*Pristiphora abietina*) was evidenced [7]. Spruce, damaged by fluoride, suffered an exceedingly high rate of infestation by the spruce gall aphid [8].

On the basis of existing literature and of our findings, it is therefore suggested that the motorway has a stimulatory effect on the aphid infestation of the hawthorn. It is to be hoped that further investigations of the system of aphids and host plant, as well as the development of enemies of the aphids in the proximity of the mo-