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Chemical Basis for the Relationship between *Ophrys* Orchids and Their Pollinators

I. Volatile compounds of *Ophrys lutea* and *O. fusca* as insect mimetic attractants/excitants

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Abstract

The composition of volatiles from the form complexes of *Ophrys lutea* and *Ophrys fusca* orchids were analysed chemically and compared with each other as well as the volatile compounds from 15 potential or established pollinator species among the solitary bee genus *Andrena*. The volatile compounds were isolated by solvent extraction or adsorption and analysed by gas chromatography and mass spectrometry. Of particular interest as possible pollinator excitants/attractants were the series of aliphatic 1- and 2-alcohols, the terpenes geraniol, nerol, geranial, neral and E,E-farnesol, since they were found in the secretions of the mandibular or Dufour glands of many species of *Andrena*. Chemical similarities between orchids and their pollinators are discussed in terms of chemical mimesis.

Introduction

The nectarless orchids of the genus *Ophrys* L. are pollinated by sexually stimulated hymenopteran males (Apoidea, Scoliidae and Sphecidae). The attraction of the males to and their behavioural excitation on the flowers is based on chemical, visual and tactile stimuli [1].

Males of several species of *Andrena* F. bees have been reported to be frequent pollinators of the various forms of *O. lutea* Cav. and *O. fusca* Link [2]. For example, males of *A. flavipes* Pz. have been observed to pollinate *O. fusca* in Alger [3, 4], and on Cyprus [5, 6]. *A. flavipes* ssp. *puber* was observed to pollinate *O. fusca* in Morocco and Majorca [1, 6] and a form labelled as *O. fusca fusca* in Spain [7, 8]. Other *Andrena* species known to pollinate *O. fusca* are *A. nigroaenea* (K.) in Southern France [4, 9, 10–12], *A. ovatula* (K.) in Spain [7, 8] and *A. panurgimorpha* Mavr. in Southern Greece [2]. In a field experiment performed in Sweden [1, 2] *A. ovatula* (Fig. 13), *A. bicolor* Fabr. and *A. nigroaenea* males were shown to be effective pollinators of *O. lutea* plants collected in Southern France. In Herault (France) *A. cinerea* Brullé were shown to be an effective pollinator of *O. lutea lutea* (38).

Earlier results from field studies of the pollination of the pollination relationship [6, 13, 14]. Both male and female cephalic secretion as well as various extracts of *Ophrys* flowers were found to be highly attractive to male *Andrena* bees [14, 15]. It has been hypothesized [1] that *Ophrys* species and forms in the section *Fusci–Luteae* produce a set of substances that mimic the odour of *Andrena* females. Preliminary isolations and identifications of volatile compounds from orchid flowers have been reported in references [16–19]. The volatiles from all *Andrena* bee species except for *A. panurgimorpha* and the *Colletes* bee are compiled from references [14, 20–24].

We now report our results of the chemical analysis of the volatile material from two forms of *O. lutea* and six forms of *O. fusca*. After a comparison between the volatile compounds from these *Ophrys* species/forms, the flower volatiles are compared to volatiles in the cephalic secretions of 15 species of *Andrena* and 1 species of *Colletes* all of which can be regarded as potential pollinators (see Table II). Chemical identities and resemblances between the orchids and their pollinators are discussed in terms of chemical mimesis.

Materials and methods

Solvent extracts

Ophrys labella (species and forms described later in the text) were extracted in methanol (M) (pa Merck), redistilled pentane (P) or hexane (H) (pa Merck) at 20 °C for 3 days. The labella were then removed and the organic solvent phase was used for GC–MS analysis. Before chemical analysis of the methanol extracts the compounds soluble in non-polar solvents were transferred to pentane by a (1:5:1) methanol/water/pentane (MWP) distribution [14]. Sodium chloride was added to the methanol–water mixture until saturation.

One *Andrena panurgimorpha* male head with the mandibles detached was extracted in 2 ml hexane at 20 °C for 3 days.