Species and Sex Specificity in the Odour Composition of Two Panurgine Bees (Hymenoptera, Andrenidae)

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From the volatile constituents of the solitary bee species *Panurgus banksianus* Kirby and *P. calcaratus* Scopuli 31 compounds could be identified. The cephalic secretion of *P. banksianus* is a sex specific multicomponent mixture of terpenes and aliphatic carboxylic acid esters while *P. calcaratus* contains monoterpenes only. The major component in the Dufour's gland secretion of *P. banksianus* is a macrocyclic lactone, eicosanolide, which is absent in *P. calcaratus*. In contrast, the new terpenoid ester, geranyl citronellate, is present in large amounts in the Dufour's gland secretion of *P. calcaratus*.

Introduction

In continuation of our investigations on the communication systems of solitary bees [1] we studied the volatile secretions of both sexes of *Panurgus banksianus* (Kirby) and *P. calcaratus* (Scopuli). Our results show that the odour bouquets of *P. banksianus* and *P. calcaratus* are made up by blends of terpenoids and aliphatic compounds. Though some of the identified compounds are found in both species, the chemical compositions of the cephalic secretions as well as the Dufour's gland secretions of the two species are distinctly different. While acetogenines are prevailing in the *P. banksianus* secretions, *P. calcaratus* produces predominantly terpenes.

P. banksianus and *P. calcaratus* are two palaearctic panurgine species occurring in sandy areas. They are often found at the same localities, but their flight periods are separated or only slightly overlapping. They are morphologically and taxonomically close and share several basic characteristics. All populations studied by us are pollen oligolectic on *Hypochoeris radicata* L. (Asteraceae). The bright yellow flowers of these plants are furthermore the rendezvous places of the two species, intensely patrolled by the mate-searching males.

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Materials and Methods

Insects, caught in the field, were kept alive over night at 5–8 °C. The following morning they were killed by deep freezing and subsequently dissected. For the analyses of cephalic secretions the heads were cut off and, after loosening of the mandibles, extracted with pentane. Analyses of Dufour's glands were carried out using pentane extracts of freshly dissected glands.

Gaschromatographic separations were performed on 50 m glass capillary columns with WG 11 as a stationary phase. The identification of components was carried out on GC/MS-coupling systems, LKB 2091 or Varian MAT 311 A; synthetic samples were used as reference compounds.

Results and Discussion

The cephalic secretion of *P. banksianus* is much more complex than that of *P. calcaratus* and shows considerable qualitative and quantitative individual variation. Geranyl hexanoate, also known from other bee species [2, 3], was specifically found in the females of *P. banksianus*. In addition to terpenes, *P. banksianus* contains non-terpenoid ketones, alcohols, and relatively low boiling esters. Esters are particularly widespread among bees [2] and most of them are even numbered both at the alcohol side and at the acid side. Besides heptanol which may reach considerable amounts in both sexes, *P. banksianus* produces an interesting series of heptyl esters. Because of its unusual structure, the male specific heptyl heptanoate should give a particularly characteristic information in chemical communication. Heptyl hexanoate occurs almost specifically in the males, while heptyl octanoate is a typical component of females; these compounds were identified only once in the samples of the opposite sex. The cephalic secretions of both sexes of *P. calcaratus* are consistently dominated by large amounts of the widespread terpene aldehydes, geranial and neral, and by the respective acids.

Striking species specific differences are found in the Dufour's gland secretions. While *P. calcaratus* contains geranyl citronellate in high concentrations

Table I. Volatile constituents in the cephalic and Dufour's gland secretions of both sexes of *Panurgus banksianus* and *P. calcaratus*.

Compound	*P. banksianus* Cephalic ♂	*P. banksianus* Cephalic ♀	*P. banksianus* Dufour ♂	*P. calcaratus* Cephalic ♀	*P. calcaratus* Cephalic	*P. calcaratus* Dufour
Number of samples analysed 1978–84	8	5	10	2	5	5
A. Terpenes and terpenoids						
Geranolic acid		x		M	M	
Nerolic acid		x		M	M	
Citronellal					x	
Geranial		x	p	M	M	x
Neral		x		M	M	
6-Methyl-5-hepten-2-one		x		x	x	
Geraniol	p	p	p			p
Nerol		p				
2,6-Dimethyl-5-hepten-1-ol	x	x				
Geranyl citronellate			x			M
Neryl citronellate						p
Geranyl hexanoate		p				
Geranyl octanoate		x				
B. Aliphatic compounds						
2-Heptanone	x					
2-Nonanone	x					
Heptanol	p	p				
Octanol	x					
Nonanol	x					
iso-Pentyl hexanoate	x	x				
iso-Pentyl heptanoate	x	x				
iso-Pentyl octanoate		x				
Heptyl acetate	x					
Heptyl *iso*-pentanoate	x					
Heptyl pentanoate	x					
Heptyl hexanoate	p	x				
Heptyl heptanoate	p					
Heptyl octanoate	x	p				
Ethyl hexadecanoate	x					
Octadecanolide			m			
Eicosanolide			M			
C. Other compounds						
β-Phenylethanol	p	p				
Unknown, M = 296			m			m
Unknown, M = 332						m

M = main component; m = minor component; p = present, varying from traces to minor components in different runs; x = not consistently present.

and traces of its isomer, neryl citronellate, *P. banksianus* shows large amounts of the macrocyclic lactone, eicosanolide, and traces of octadecanolide. These latter compounds could not, so far, be detected in *P. calcaratus,* while the *P. banksianus* secretion, if ever, shows only traces of geranyl citronellate. The mass spectrum of this new natural product is shown below. While macrocycles and esters formed from terpene alcohols and straight chain even numbered carbocyclic acids are well known as volatile constituents of bee secretions [2], esters formed from two terpenes are seldomly found. Citronellyl citronellate and citronellyl geranoate have been identified from workers of the European hornet, *Vespa crabro* [4], and from *Panurginus* bees [5]. Geranyl geranoate was found in *Protandrena* which

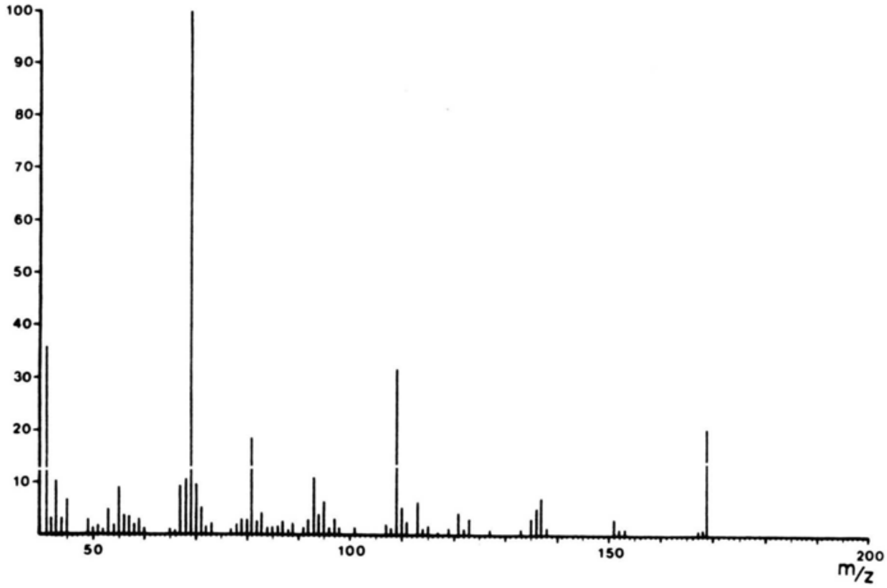

Fig. 1. 70 eV mass spectrum of geranyl citronellate; Finnigan MAT 311 A.

also contains farnesyl geranoate, while *Pseudopanurgus aethiops* contains farnesyl farnesoate [3]. Our results are particularly relevant in the view of taxonomic and evolutionary aspects on the genus *Panurgus* which will be discussed in detail in a separate publication. Behavioral experiments using synthetic mixtures of the identified compounds are presently under investigation.

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