The Odor-Bouquet of *Ips schmutzenhoferi* Holzschuh (Col.: Scol.)

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Dedicated to Professor Kurt Heyns on the occasion of his 80th birthday

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Ipsenol, Ipsdienol, and *E*-myrcenol are male specific compounds of *Ips schmutzenhoferi*. Overall 46 compounds could be identified from males and females. The diversity of oxygenated terpenes is particularly high in males.

Preliminary studies on the pheromone system of *Ips schmutzenhoferi*, a new species of the Southeastern Himalaya region of Bhutan, showed high attractivity of mixtures of racemic ipsenol and (S)-*cis*-verbenol [1]. As a result of further investigations, we now wish to present a detailed list of compounds identified from males and females.

Using a closed loop stripping system [2], volatile compounds emanating from the system, *Pinus sylvestris*/feeding beetles, were trapped on charcoal. Odor patterns from uninfested billets and from those containing males or females were compared. In addition, the contents of the hindguts of dissected males and females [1] were analysed. Conditions for gas chromatographic separation of terpenes and gc/ms-analyses have been previously described [3]. Identifications of natural products were based on comparison of gc-retention times and mass spectra with respective data of authentic samples. Results are compiled in Table I; typical gas chromatograms of pentane extracts of hindguts of both sexes ore shown in Fig. 1.

Similar to many other bark beetle species, the odor bouquets of males and females of *I. schmutzenhoferi* are complex mixtures of mostly monoterpen hydrocarbons and oxygenated monoterpenes. While the former are typical host constituents, the latter represent products of secondary reactions: En-

Table I. Volatile compounds identified from males and females of *Ips schmutzenhoferi*. + = present, * = not consistently.

No.	Compound	♂	♀	No.	Compound	♂	♀
1)	α-Pinene	+	+	24)	Pinocarvone*	+	
2)	β-Pinene	+	+	25)	Isophorone*	+	+
3)	Verbenene	+		26)	Terpinen-4-ol*	+	+
4)	3-Carene	+	+	27)	Myrtenal*	+	+
5)	Myrcene	+	+	28)	*trans*-Pinocarveol*	+	
6)	M = 134	+	+	29)	*cis*-Verbenol	+	+
7)	Limonene	+	+	30)	*trans*-Verbenol	+	+
8)	β-Phellandrene	+	+	31)	Ipsdienol	+	
9)	γ-Terpinene*	+		32)	Limonen-4-ol*	+	
10)	p-Cymene*	+		33)	α-Terpinylacetate*	+	
11)	Acetoin*	+	+	34)	*E*-Myrcenal*	+	
12)	Terpinolene	+	+	35)	Borneol*	+	+
13)	Pinol*	+		36)	α-Terpineol*	+	+
14)	Nonanal*	+		37)	Verbenone	+	+
15)	Fenchone*	+		38)	α-Phellandren-8-ol*	+	+
16)	Ipsenone	+		39)	Perillaaldehyde*	+	
17)	Chrysanthenone*	+		40)	Myrtenol	+	+
18)	Camphor*	+		41)	*p*-Cymol-8-ol*	+	+
19)	Benzaldehyde*	+	+	42)	Carvacrol*	+	+
20)	Pinocamphone*	+		43)	Geraniol*	+	
21)	Ipsenol	+		44)	β-Phenylethanol*	+	+
22)	Isopinocamphone*	+		45)	*E*-Myrcenol	+	
23)	Bornylacetate*	+		46)	Perillaalcohol*	+	

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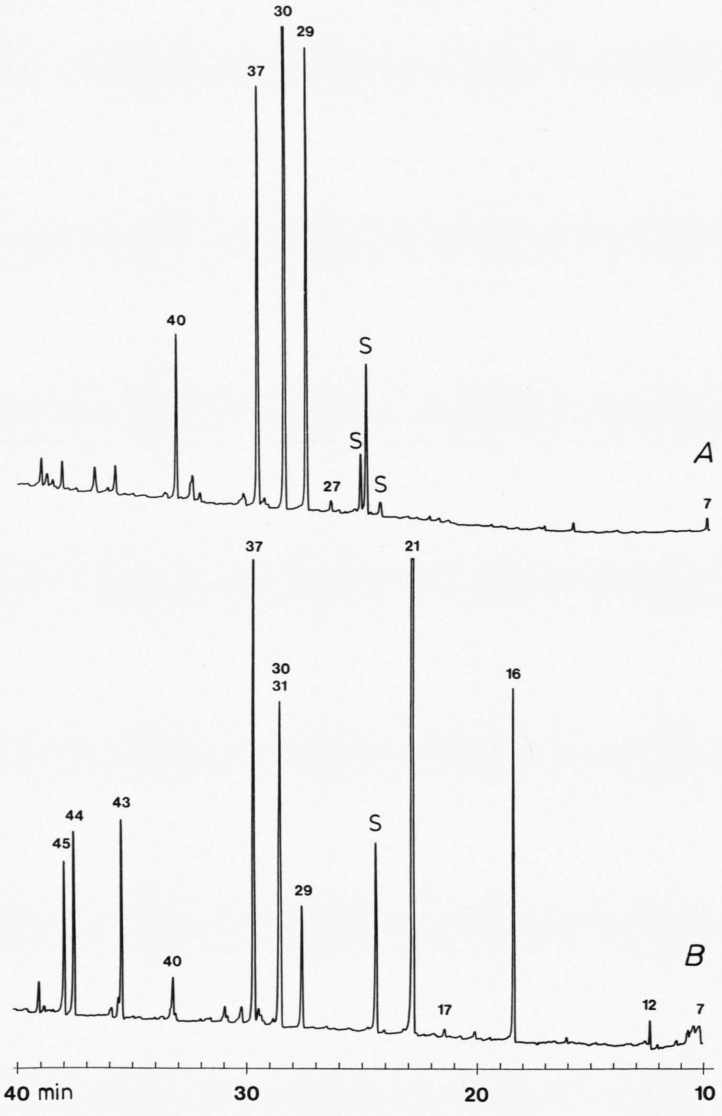

Fig. 1. Gas chromatograms of pentane extracts of hindguts of females (A) and males (B) of *Ips schmutzenhoferi*; WG-11 Q (50 m/0,25 mm), 60–230 °C; 3 °C/min; peak numbers follow Table I, S = Sesquiterpen hydrocarbons.

zymatic oxidation or hydration of the hydrocarbons by either the beetles [4, 5] or their associated microorganisms [6, 7] as well as simple autoxidation processes (sometimes followed by rearrangements) lead to the formation of a variety of terpene alcohols and respective carbonyl compounds. As in other *Ips* species, males of *Ips schmutzenhoferi* are particularly productive in the formation of oxygenated monoterpenes, however, with the exception of 8 compounds (the α-pinene derivatives, *cis*-/*trans*-verbenol, verbenone and myrtenol, and the mycrene derivatives, ipsdienol, ipsenol, ipsenone and E-myrcenol) none of them proved to be consistently present in all samples. This may be due to seasonal variation in the activity of the beetles and the host respectively as well as to the method of sample collection and analytical work up.

Allylic oxidation of α-pinene and myrcene yields particularly important behavior mediating compounds both in *Dendroctonus* and *Ips* species [8]. While oxygenation of α-pinene is neither genus- nor sex-specific, the ability to transform myrcene to 2-methyl-6-methylene-2,7-octadien-4-ol, ipsdienol [9], is restricted to males only. Though a typical aggrega-

tion pheromone of many *Ips* species, ipsdienol could also be identified in males of *Dendroctonus* species after exposure to myrcene [10–13]. In contrast, both sexes of *D. brevicomis* and *D. ponderosae* proved to convert myrcene vapors to 2-methyl-6-methylene-2,7-octadien-1-ol, myrcenol, the other possible product of an allylic oxidation [11, 13]. Interestingly, females of the bollweevil, *Anthonomus grandis* [14], as well as several *Pseudomonas* species (W. Francke, unpublished data) produce myrcenol from myrcene.

In a particularly careful analysis of the abdominal volatiles from *D. ponderosae* fed in ponderosa pine, *E*-myrcenol was found to be produced by these bark beetles also under natural conditions [5]. The compound, first identified as a constituent of thyme [15], represents a new male specific component among the volatiles of *Ips* species. Since we found *E*-myrcenol also in the European *I. sexdentatus*, this alcohol or its corresponding aldehyde may be particularly widespread among *Ips* species. Their biological significance as chemical messengers in bark beetle communication is presently under investigations.

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