Cephalic Volatiles Identified in Workers of *Mourella caerulea*, a Rare Stingless Bee Recently Rediscovered in Southern Brazil

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From workers of *Mourella caerulea*, an extremely rare and primitive species of neotropical stingless bees, 101 cephalic volatiles were identified by GC/MS analyses.

The stingless bee species *Mourella caerulea* was first described in 1900 by Friese [1]. Since then only a few worker specimens were recorded in subtropical Brazil. The nest architecture, males and the queen were unknown until several of the subterraneous nests were recently discovered during a four years survey of the bees of Rio Grande do Sul, the southernmost State of Brazil [2]. Apart from our interest in chemical communication in stingless bees [3–8], we are aware of the potential information which an analysis of cephalic volatiles, together with comparative studies on morphology and nest architecture [9] as well as on intranidal behavior [10] will contribute to a proper taxonomic collocation of *M. caerulea*, a species which has often been considered one of the most primitive living stingless bees of the neotropics.

A nest collected at Canguçu, Rio Grande do Sul, Brazil, was transferred to the laboratory. Heads of adult worker bees of different age, mostly field bees, were cut off and extracted in pentane. Extracts were analyzed using the coupled gas chromatographic/mass spectroscopic system Varian MAT 311 A [3]. The relative proportions of the identified volatile components were determined and classified as: + = < 0.05%, ++ = 0.05–0.5%, +++ = 0.5–20%, ++++ = > 20%. The following compounds were found:

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Hydrocarbons	
Pentadecane	+
Heptadecane	+
7-Heptadecene	+
9-Heptadecene	+
Heptadecadiene	+
Octadecane	+
Nonadecane	+
7-Nonadecene	+
9-Nonadecene	+
Eicosane	+
Heneicosane	++
7-Heneicosene	+
9-Heneicosene	+
Docosane	+
Tricosane	+++
7-Tricosene	+
9-Tricosene	+
2-Methyltricosane	++
Pentacosane	+++
7-Pentacosene	+
9-Pentacosene	+
Heptacosane	+++
Heptacosene*	+++
Nonacosane	+++
Nonacosene**	+++
Hentriacontane	+++
Hentriacontene***	+++
Alcohols	
2-Pentanol	+
2-Hexanol	+
2-Heptanol	++
2-Octanol	+
2-Nonanol	+
2-Pentadecanol	+
Ketones	
2-Hexanone	+
2-Heptanone	+++
2-Octanone	++
2-Nonanone	+
2-Decanone	+
2-Undecanone	+
2-Tridecanone	++
2-Pentadecanone	+
2-Heptadecanone	+
6-Methylhept-5-en-2-one	+
Aldehydes	
Hexadecanal	+
Octadecanal	++
Carboxylic acids	
Acetic acid	+
2-Methylpropionic acid	+
Butanoic acid	+
3-Methylbutanoic acid	++
Pentanoic acid	+
Hexanoic acid	+
Heptanoic acid	+
Octanoic acid	+
Nonanoic acid	+
Decanoic acid	++

Dodecanoic acid	+++
Tetradecanoic acid	+++
Hexadecanoic acid	+++
Octadecanoic acid	+++
9-Octadecenoic acid	++++
Octadecadienoic acid	++++
Octadecatrienoic acid	++++
Benzoic acid	+
Phenylacetic acid	+
Esters	
Ethyl octanoate	+
Ethyl nonanoate	+
Ethyl decanoate	+
Ethyl dodecanoate	+
Methyl tetradecanoate	+
Ethyl tetradecanoate	+
Methyl hexadecanoate	+
Ethyl hexadecanoate	++
Ethyl 7(?)-hexadecenoate	+
Methyl heptadecanoate	+
Methyl octadecanoate	+
Ethyl octadecanoate	++
Methyl 9-octadecenoate	++
Ethyl 9-octadecenoate	+++
Methyl octadecadienoate	++
Ethyl octadecadienoate	+++
Methyl octadecatrienoate	+
Ethyl octadecatrienoate	+++
2-Heptyl acetate	+
2-Heptyl octanoate	+
2-Heptyl nonanoate	+

Mixtures of positional isomers: * = 7, 9, 10, 13; ** = 7, 9–14; *** = 7, 9–15.

Up to now pheromonal bouquets of only a few species of stingless bees have been studied [11]. Recently we described the occurrence of 70 volatile compounds in cephalic secretions of *Scaptotrigona postica* workers [7]. The analyzed head extracts contain secretions of the mandibular glands, however, we cannot exclude that some of the compounds are extracted from the hypopharyngal and labial glands and/or the cuticula. The list of cephalic volatiles presented here shows that *Mourella caerulea* has a complex bouquet comparable to other stingless bee species: It is made up by uneven numbered, saturated and unsaturated hydrocarbons, methylcarbinols, respective methylketones, carboxylic acids and esters. Only very few compounds show a branched carbon skeleton. The ester fraction is particularly interesting, since it contains, with three exceptions, only methyl and ethyl esters which are known as typical volatile compounds of blossoms. Only three esters of 2-heptanol were recorded. The wax ester type, represented by compounds formed from alcohols and carboxylic acids of comparable chain length, is entirely absent. Esters of this type were repeatedly recorded in many bee species and represent characteristic constituents of their cephalic secretions [12, 13].

The monospecific genus *Mourella* is probably related to *Plebeia* [14]. A comparative study of cephalic secretions in *Plebeia* species seems desirable before any chemotaxanomic conclusions can be drawn. The list of identified *Mourella* volatiles, on the other hand, can be used for bioassays in order to decode the significance of pheromonal signals in the social behavior of these bees.

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[1] H. Friese, Jur. Természetrajzi Füzetek **23,** 381 (1900).
[2] D. Wittmann and M. Hoffmann, Iheringia (1989), in press.
[3] W. Francke, W. Schröder, E. Engels, and W. Engels, Z. Naturforsch. **38c,** 1066 (1983).
[4] W. Engels, Adv. Invertebr. Reprod. **4,** 285 (1986).
[5] W. Engels, Mem. Inst. Oswaldo Cruz **82,** III, 35 (1987).
[6] E. Engels, W. Engels, W. Schröder, and W. Francke, J. Chem. Ecol. **13,** 371 (1987).
[7] D. Wittmann, R. Radtke, W. Francke, and W. Schröder, Abstr. IUSSI Bayreuth, 26 (1987).
[8] R. Radtke, D. Wittmann, W. Francke, and W. Schröder, Abstr. IUSSI Bayreuth, 27 (1987).
[9] J. M. F. Camargo and D. Wittmann, Stud. neotrop. Fauna and Environm., in preparation.
[10] D. Wittmann, L. Bego, and R. Zucchi, in preparation.
[11] M. Blum, Academic Press, N.Y. 1981.
[12] W. Francke, W. Schröder, G. Bergström, and J. Tengö, Nova Acta Regea Societates Scientiarium Upsaliensis, Ser. V: C, III, 127–136 (1984).
[13] W. Francke, Adv. Invertebr. Reprod. **4,** 327 (1986).
[14] H. F. Schwarz, Bull. Am. Mus. Nat. Hist. **90,** 500 (1948).