

## Summary

This thesis deals with structure elucidation and synthesis of possible semiochemicals that various vertebrate species may use for intra- and interspecific communication. The study is structured into four parts. The first part covers analytical investigations on volatile substances in the urine of female Asian elephants (*Elephas maximus*), which may signalize the state of the oestrous cycle and play a role in mate choice. Subject of the second part is the analysis of the interdigital secretion of the bontebok (*Damaliscus pygargus pygargus*) and the stereoselective synthesis of an unsaturated lactone as a main component of the secretion. Content of the third part is the identification of volatiles released by freshwater fish and the stereoselective synthesis of  $\alpha$ -Hydroxyalkyllactones, with a potential kairomonal function in the predator-prey relationship between planktivorous fish and zooplankton (*Daphnia*). Finally, the thesis describes the identification of volatile compounds in human colostrum and in secretions of *areola* glands that have a possible biological activity in human mother-offspring interactions.

In the first part of the present investigations a method for the enrichment and isolation of an unknown substance cluster in the urine of female Asian Elephants was developed. The occurrence of this substance cluster is linked to the oestrous cycle, and the structure elucidation could be helpful to understand the mate choice in Asian elephants and to detect the time of ovulation for captive breeding activities. The investigation of the compounds in urine was carried out using HS-SPME for sample preparation followed by coupled gas chromatography-mass spectrometry (GC/MS). A total number of more than 180 compounds have been identified in this complex mixture, mostly terpenes and terpenoids. The unknown substance cluster eluted at retention times between the steroids  $5\alpha$ -androst-2-en-17-one (**38**),  $5\alpha$ -androst-3-en-17-one (**E159**),  $5\alpha$ -androst-2-en-17 $\beta$ -ol (**39**),  $5\alpha$ -androst-3-en-17 $\beta$ -ol (**E161**),  $5\alpha$ -pregn-2-en-20-one (**E173**) and  $5\alpha$ -pregn-3-en-20-one (**E174**) which initially led to the hypothesis that the unknowns were steroids. Approximately less than 1 mg of the main components of the substance cluster were isolated by preparative gas chromatography and HPLC and proved to be oxygenated diterpenes. 2-hydroxyisopimaric acid lactone (**E176**), 2-hydroxy-7,8-dihydroabietic acid lactone (**E177**), 2-hydroxydehydroabietic acid lactone (**E181**) and 2-hydroxyabietic acid lactone (**E182**) were verified by NMR spectroscopy. In addition, 2-hydroxypimaric acid lactone (**E175**) was proposed on the basis of partial NMR data and mass spectral data.

The structures of 2-hydroxyneoabietic acid lactone (**E184**), 2-hydroxypalustric acid lactone (**E178**) and 2-hydroxylevopimaric acid lactone (**E179**) were deduced from mass spectral data. It is the first time that these structures are reported in the urine of Asian elephants, and they represent new natural products.

The second part of this thesis deals with the stereoselective synthesis of the lactone (6*Z*)-dodec-6-en-4-olide (**18**), which is a major constituent among the approximately 100 identified volatiles of the Bontebok's interdigital secretion. The stereoselective synthesis was optimized to not only obtain reference material for the determination of the absolute configuration but also to gain enough material for field testings in the semi-deserts of South Africa. The natural product was shown to exclusively keep (*S*)-configuration.

The third chapter describes the identification of volatiles released by planktivorous fish. Unknown chemical cues called "Fischfaktor" induce a diel vertical migration (DVM) on *Daphnia* populations in freshwater. The investigation of possible kairomones was carried out by GC/MS after sample preparation with solid phase extraction (SPE) of water from perch cultivations. The extract consists mainly of diketopiperazines and the new  $\alpha$ -hydroxy-alkyllactones 5-hydroxy-4-decanolide (**B88**), 6-hydroxytetradecan-5-olide (**F59**) and 6-hydroxytetradec-2-en-5-olide (**F56**). **F56** was synthesized enantioselectively by Sharpless asymmetric dihydroxylation (AD). **B88** and **F59** were already synthesized enantioselectively in an earlier study. The absolute configuration of the natural compounds **F56**, **B88** and **F59** were elucidated using enantioselective gas chromatography coupled with high-resolution mass spectrometry and the synthetic reference material. The natural products were found to consist of the following enantiomeric ratios: 68 % (*S,S*) / 32 % (*R,R*)- **B88**, 88 % (*S,S*) / 12 % (*R,R*)- **F59** and 90 % (*S,S*) / 10 % (*R,R*)- **F56**. **F56** is a new natural product.

Finally, volatiles of human colostrum and the secretions of *areola* glands (SAG) were compared upon analysis by GC/MS on different stationary phases. Both secretions contained a complex mixture of more than 100 compounds with no obvious qualitative differences. Results from earlier studies of human colostrum could be confirmed and more than 70 additional volatiles were identified by comparison of mass spectral data and retention indices. This data set serve as a base for further investigations of biologically active compounds in this secretions and biological tests with neonates.