# 2. Summary

Fungi of the genus *Hygrophorus* are obligate symbionts (as mycorrhiza) with deciduous or coniferous trees. Most of the species in this genus are edible. Contrary to fruit bodies of most other basidiomycetes they are hardly ever attacked by parasitic fungi. The ecological defence observations prompted us to look for the underlying chemical principles.

Twenty new cyclopentenone derivatives (hygrophorones) were isolated from fruitbodies of *Hygrophorus latitabundus*, *H. olivaceoalbus*, *H. persoonii*, and *H. pustulatus*. Their structure was elucidated by NMR and MS. The hygrophorones are 2-cyclopentenones with hydroxy or acetoxy substituents at C-4 and C-5. Furthermore, there is an odd numbered alkyl chain ($C_{11}$, $C_{13}$, $C_{15}$ or $C_{17}$) at C-5 which is additionally hydroxylated, acetoxylated, or oxidized at C-6 (see figure 1.1). Additionally, two new $\gamma$-butyrolactone derivatives 5-(*E*)-2-hydroxytetradecylidene-5*H*-furan-2-one and 5-(*Z*)-2-hydroxytetradecylidene-5*H*-furan-2-one were isolated.

The relative configuration of the substituents of the cyclopentenone ring was assigned based on nuclear overhauser effects (NOE), comparison of coupling constants, and formation of cyclic methylboronates. Hygrophorones A (from *H. persoonii*) and hygrophorones D (from *H. latitabundus*) are *trans* configured, hygrophorones B (from *H. olivaceoalbus*) and hygrophorones C (from *H. pustulatus*) are *cis* configured.

First activity studies showed that hygrophorones have significant antibacterial and antifungal potential. The antibacterial effect against Gram positive bacteria is stronger than against Gram negative bacteria. The hygrophorones are even active against vancomycin, methicillin and ciprofloxacin resistant bacteria. Polar compounds are more active than nonpolar.

Mass spectral studies of cyclopentenone derivative are rarly described in literature. Therefore the mass spectral behaviour of hygrophorones after electrospray ionisation was investigated. Although the substituent fragmentations (loss of water, ketene, acetic acid) are the most dominating processes, there are some key ions allowing an assignment into two types: type I hygrophorones have a hydroxy- or an acetoxygroup at C-6, while type II hygrophorones are oxidized at C-6 to a ketone. An interesting and unusual fragmentation is the loss of $CO_2$ from the $[M-H]^-$ ion which is only possible by a rearrangement including an oxygen of a hydroxyl function.

Knowledge of the MS-fragmentation behaviour of hygrophorones allowed to detect hygrophorones also in *H. agathosmus*, *H. nemoreus*, and *H. poetarum* by selected reaction monitoring (SRM).

The biosynthesis of the hygrophorones was investigated by inoculation of $^{13}C$ marked acetate and $^{13}C$ marked glucose. An incorporation was not observed. In parallel, the biosynthesis of similar compounds from *Rigidoporus lineatus* was investigated. A statistic incorporation of $^{13}C$ marked acetate was observed here.