Beer flavour is known to deteriorate through ageing due to the release of compounds like trans-2-nonenal (1), dimethyltrisulfide (2), 4-vinylsyringol (3), … Polyfunctional thiols have been recently identified as key-flavours of a fresh beer (4). Their evolution through ageing is therefore prime of concern for the brewers. Different kinds of lager (L1, L2, L3, L4), wheat (W) and top-fermented (T) beers have been studied for five months at 20°C. The polyfunctional thiols have been trapped by a specific extraction with pHMB (p-HydroxyMercuriBenzoic acid) (5). The extracts have been then analysed by GC-MS, GC-O and GC-PFPD.

### INTRODUCTION

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#### Roasted/burned flavours brought by mercaptoacetates

2-Mercaptoethyl acetate and 3-mercaptopropyl acetate are known as responsible of a roasted/burned flavour in wines (6). Vermeulen et al. (4) identified them in lager beers. Six commercial beers have been here analysed through a five-months storage at 20°C. The GC-O analyses revealed that 2-mercaptoethyl acetate and 3-mercaptopropyl acetate are already present in the six fresh beers. However, their detection and quantification were possible by GC-PFPD only after ageing (Figure 1).

![Figure 1: Evolution of (a) 2-mercaptoethyl acetate and (b) 3-mercaptopropyl acetate in six commercial beers during ageing at 20°C. L1, L2, L3 and L4 = lager beers, W = wheat beer, T = top-fermented beer.](image)

In most beers, the concentration of 2-mercaptoethyl acetate revealed maximum after three months (up to 6.4 ppb IST equivalents) in L2. The concentration of 3-mercaptopropyl acetate was in all cases much lower (up to 313 ppb IST equivalents). Its concentration also increased during ageing except in the wheat beer. Given their threshold value (close to 40 ppb (6)) and probable synergy, they could impart strong defects in some aged beers.

![Figure 2: Hypothetical pathway of 2-mercaptoethyl acetate and their corresponding acetates.](image)

As shown in Figure 2, mercaptoacetates are most probably synthesized from their corresponding mercaptoalcohols. However, neither 2-mercaptoethanol nor 3-mercaptopropionaldehyde have been detected by GC-olfactometry or GC-PFPD in fresh samples. Only two 5 months aged beers allowed us to detect them at the sniffing port (L3 and L4).

#### Onion-like flavour brought by mercaptoalcohols

2-Mercapto-3-methyl butanol has been detected by GC-O in all our fresh and aged extracts, except for the wheat beer. 3-Methyl-2-buten-1-thiol (MBT), responsible of hop flavour at low concentration, and the light-struck off-flavour at higher level, was also perceived by GC-O in all our extracts (beer stored without light).

![Figure 3: Evolution of the concentration of 2-mercapto-3-methyl butanol in three lager beers (L2, L3, L4) stored at 20°C.](image)

Figure 3. Evolution of the concentration of 2-mercapto-3-methyl butanol in three lager beers (L2, L3, L4) stored at 20°C.

Vermeulen et al. (4) proposed a hop constituent, 3-methyl-2-buten-1-ol, as the common precursor of 2-mercapto-3-methylbutanol, 3-mercaptopropyl butanol and 3-methyl-2-buten-1-thiol (MBT) (Figure 4). The two latter were detected by Vermeulen et al. in four different lager beers (4). 3-Mercapto-3-methyl butanol has been detected by GC-O in all our fresh and aged extracts except for the wheat beer. 3-Methyl-2-buten-1-thiol (MBT), responsible of hop flavour at low concentration and the light-struck off-flavour at higher level, was also perceived by GC-O in all our extracts (beer stored without light).

![Figure 4: Hypothetical formation pathway of 3-mercapto-3-methylbutanol, 3-mercaptopropyl butanol and MBT in beer (4).](image)

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#### CONCLUSIONS

Polyfunctional thiols are compounds which confer to beer its typical aroma. 4-Mercapto-4-mercapto-2-pentanone, 3-mercaptopentanole and traces of MBT most probably participate to the fresh hoppy flavour required in a lager. The present study shows that some thiols are generated through ageing. They could induce some roasted/burned (2-mercaptoethyl acetate and 3-mercaptopropyl acetate) and onion-like (U2 and U3) off-flavours after a few months of ageing.

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