91

Polyfonctional thiols and drinkability of beer

Catherine Vermeulen, Sara Lecocq & Sonia Collin

Université catholique de Louvain, Laboratoire de brasserie et des industries alimentaires, Croix du sud 2 bte 7, B-1348 Louvain-la-Neuve, Belgium (e-mail: vermeulen@inbr.ucl.ac.be)

Descriptors:
Beer aroma, drinkability, gas chromatography, sensory analysis, thiol

SUMMARY
In the last decade, the organoleptic role played by polyfunctional thiols has been well documented for many foods and beverages. Nevertheless, our knowledge on this kind of sulfur compounds beer occurrence is currently deficient. Recently, combinatorial chemistry coupled with gas chromatography was used in our laboratory to create a database where more than sixty polyfunctional thiols mass spectra and sensorial properties were reported. On those bases, GC-Olfactometry analyses were performed on beer extracts. They revealed 4-mercapto-4-methyl-pentan-2-one and 3-mercapto-hexan-1-ol as natural components in fresh lager beers. Sensorial analyses finally proved that thiols can oddly influence beer aroma.

Polyfunktionale Thiole und die Trinkbarkeit von Bier

Deskriptoren:
Bieraroma, Durchtrinkbarkeit, Gaschromatographie, sensorische Analyse, Thiol

ZUSAMMENFASSUNG
Im letzten Jahrzehnt wurde die organoleptische Rolle, die polyfunktionale Thiole gespielt haben, für viele Lebensmittel und Getränke gut dokumentiert. Trotzdem ist unser Wissen über diese in Bier vorkommende Art der Schwefelverbindungen derzeit unzulänglich. Kürzlich wurde in unserem Labor die kombinatorische Chemie mit der Gaschromatographie gekoppelt, um eine Datenbank aufzubauen, die das Massenspektrum und die sensorischen Eigenschaften von mehr als 60 polyfunktionalen Thiolen speichert. Auf dieser Grundlage wurden GC-olfaktorische Analysen von Bierextrakten durchgeführt. Sie erkannten 4-Mercapto-4-methylpentan-2-on und 3-Mercaptohexan-1-ol als natürliche Verbindungen in frischen, untergärigen Bieren. Sensorische Analysen haben endlich bewiesen, dass Thiole das Bieraroma eigenartig beeinflussen können.

Thiol poly-fonctionnels et l'appréciation de la bière

Descripteurs:
Analyse sensorielle, arôme de la bière, buvabilité, chromatographie en phase gazeuse, thiol

RESUME
Depuis peu, le rôle organoleptique joué par les thiols polyfonctionnels dans certaines denrées fait l'objet de nombreuses publications. Néanmoins, nos connaissances concernant l'occurrence de ces composés dans la bière souffrent d'énormes lacunes. Récemment, une banque de données décrivant les spectres MS et propriétés sensorielles de plus de soixante thiols polyfonctionnels fut créée grâce à la chimie combinatoire. Forts de ces données, des extraits de bière furent analysés par GC-Olfactométrie. Ils révélèrent la présence naturelle de 4-mercapto-4-méthyl-pentan-2-one et 3-mercaptohexan-1-ol dans la bière fraîche. Enfin, des analyses sensorielles démontrèrent combien les thiols influencent curieusement l'arôme de cette boisson.

Tioles polifuncionales y "drinkability" de la cerveza

Palabras claves:
Análisis sensorial, aroma de cerveza, cromatografía de gases, 'drinkability', tiol

RESUMEN
En la década pasada, el papel organoléptico desempeñado por los tioles polifuncionales ha sido bien documentado para muchos alimentos y bebidas. Sin embargo, nuestro conocimiento acerca de la ocurrencia de este tipo de compuestos azufrados en la cerveza es actualmente deficiente. Recientemente se han utilizado la química combinatoria junto con la cromatografía de gases en nuestro laboratorio para crear una base de datos con más de sesenta espectros de masas de tioles polifuncionales y se describieron las características sensoriales. En esas bases, fueron realizados los análisis por CG-Olfatometría en extractos de cerveza. Revelaron al 4-mercapto-4-metil-pentano-2-ona y al 3-mercapto-hexan-1-ol como componentes naturales en cervezas lager frescas. Los análisis sensoriales finalmente probaron que los tioles pueden influir singularmente en el aroma de la cerveza.

INTRODUCTION

In the last decade, the organoleptic role played by polyfunctional thiols has been well documented for many foods (cooked meat, *Allium* vegetables, grapefruit, passion fruit,...) and beverages (wine, tea, coffee,...). Even if they often occur as traces, their extremely low odor threshold – sometimes below the ppt level – render them able to alter the whole flavor of a matrix. Recently and against all expectations, it has also been proved that those sulfur compounds, sometimes characterized by very pleasant and fruity notes, are highly desired by the consumers. Nevertheless, due to their high reactivity, their commercial unavailability and their minute concentrations in foods, our thiol knowledge is currently deficient (*1*).

In a first time, we decided to create a database where the mass spectra and the sensorial properties of more than fifty unknown polyfunctional thiols would be reported. To achieve this, combinatorial chemistry was used. This is a very rapid and useful method, which in a way consists in performing "one-pot syntheses". So, similarly reactive compounds are put together with another chemical to obtain after reaction, a mixture of analogs. The later are then separately analyzed by gas chromatography (*2-5*). In a second time, we applied an XAD extraction procedure on fresh lager beer to obtain an extract with a representative odor of the original product (*6*). Thanks to GC-Olfactometry and sensorial analyses, we were finally able to prove that polyfunctional thiols occur naturally in beer and have a relevant odor impact on this beverage.

EXPERIMENTAL AND ANALYTICAL METHODS

Combinatorial chemistry

The synthetic pathways used to obtain mercapto-ketones, mercapto-aldehydes, mercapto-alcohols et mercapto-esters are summarized in figure 1. The 3-methyl-2-buten-1-thiol was individually synthesized from its unsaturated bromo analog and thiourea.

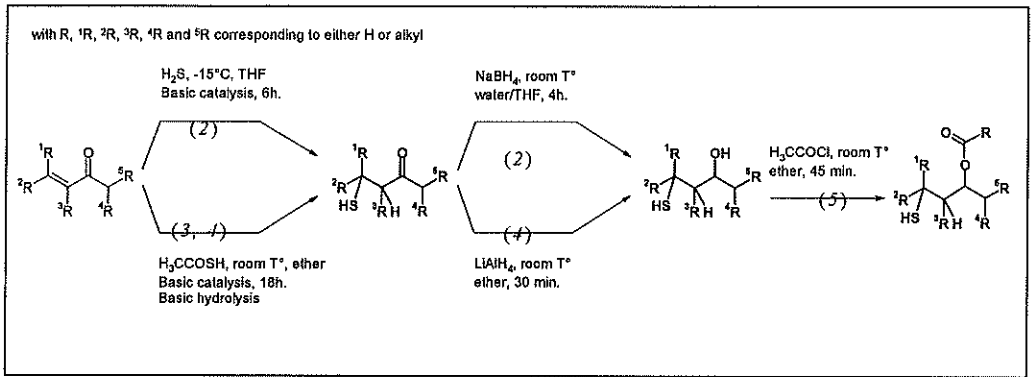

Figure 1: The polyfunctional thiols synthetic pathways used for combinatorial chemistry. For more details, read references (*2-5*).

Beer extraction procedure

The XAD amberlite resin extraction procedure has been previously published by Lermusieau *et al.* (*6*).

Solid phase microextraction (SPME) of a model solution

A stableflex Carb/PDMS fiber (Supelco, Belgium) was used to extract thiols from the headspace of an aqueous model solution containing about 250 ppb of 4-mercapto-4-methyl-2-pentanone and the same amount of 3-mercapto-1-hexanol. The sample (18 ml) placed in a 20 ml vial was submitted to the extraction for 30 minutes at 30 °C. The thiols were thermally desorbed from the fiber in a split/splitless injector and then analyzed by GC-MS. The same procedure was applied on the same sample spiked with 1 ppm of Cu^{++} ions. This was realized in triplicate.

Gas chromatography analyses

Gas Chromatography coupled with Sulfur Chemiluminescence Detection (GC-SCD): GC was performed using a Chrompack CP9001 chromatograph equipped with a splitless injector maintained at 250 °C and opened after 0.5 min. Analysis of sulfur compounds was performed using a 50 m × 0.32 mm i.d., wall-coated 1.2 µm film thickness open tubular (WCOT fused silica) apolar CP-Sil 5 CB capillary column (Middelburg, The Netherlands) connected to a sulfur chemiluminescence detector (Sievers, Model 355 SCD) and Shimadzu CR3A integrator. An initial oven temperature of 40 °C was maintained for 4 min and then programmed to rise from 40 – 132 °C at 2 °C/min followed by 132-250 °C at 10 °C/min. The final temperature was then held for 45 min. Helium carrier gas was used at a flow of 32.0 cm/s (flow rate = 1.0 ml/min). Air and hydrogen flows were maintained at 40 and 100 ml/min, respectively in the 800 °C combustion chamber. The airflow rate in the ozone generator was 6 psi and a vacuum of 150-275 Torr was applied to the entire system.

Gas Chromatography coupled with Electronic Impact Mass Spectrometry (GC-MS):

Mass spectra (*m/z* 40 to 380) were recorded at 70 eV on a ThermoFinnigan Trace MS mass spectrometer connected to a ThermoFinnigan Trace GC 2000 gas chromatograph equipped with a splitless injector and either the previously described column or a 25 m × 0.32 mm i.d., wall-coated 0.3 µm film thickness open tubular fused silica (WCOT fused silica) polar FFAP CB capillary column (Middelburg, The Netherlands). Oven temperature, initially kept at 40 °C for 4 minutes, was programmed to rise from 40 to 132 °C at 2 °C/min and thereafter, from 132 to 250 °C at 10 °C/min, remaining at the maximum temperature for 15 minutes. Spectrometric recording was automatic throughout elution using the Xcalibur software. The compounds were identified on the basis of their fragmentation patterns and library matching of spectra.

Gas Chromatography coupled with dual Flame Ionization and Olfactometric Detection (GC-FID-O):

This was performed using a Chrompack CP9001 gas chromatograph which was equipped with a splitless injector maintained at 250 °C and opened after 0.5 min. Sulfur compounds were analyzed using a 50 m × 0.32 mm i.d., wall-coated 1.2 µm film thickness open tubular (WCOT fused silica) apolar CP-Sil 5 CB capillary column (Middelburg, The Netherlands). An initial oven temperature of 40 °C was maintained for 4 min and then programmed to rise from 40 to 132 °C at 2 °C/min followed by 132 to 250 °C at 10 °C/min. The final temperature was held for 15 min. A fused silica T-junction was used at the end of the capillary column. Fifty percent of the eluent was sent to a FID maintained at 250 °C and connected to a Shimidazu C-R3A integrator, while the other part was directed to a GC-odor port at 250 °C. In the latter case, the eluent was diluted with a large volume of air (20 ml/min) previously humidified in an aqueous copper (II) sulfate solution to improve the transport of the effluent out of the funnel. The volume brought by the GC is too low to really prevent odor assessors' mucuous membranes from drying. In order to be sure that no oxidation occurred in the sniffing port, all compounds were also smelled one time without air. The Best Estimated GC-Lower Amount Detected by Sniffing (BE-GC-LoADS) is defined as the geometric mean between the lowest mass of compound perceived at the outlet of the GC-odor port and the highest undetected amount injected onto the column (*7*). Experiments were performed by injecting 2 µl of each solution at the following dilutions: 1/50, 1/100, 1/200, 1/500, 1/1000, 1/2000, 1/5000 and so on up to the 1/50000 dilution. Two judges working completely independently of each other performed sensory analyses. During the course of all sensory analyses the verbal odor descriptions of the judges were recorded.

Sensorial analyses

Five coded beer samples among which two contained 50 ppm of Cu^{++} ions were presented to 10 assessors. Assessors were asked to smell each sample under green

light and select the two samples that were different from the other three. Note that the copper was added just before the test in order to avoid thiol oxidation.
It was also asked to few panelists to compare a fresh beer to the same one spiked with 10 ppt of 4-mercapto-4-methyl-2-pentanone.

RESULTS

Polyfunctional thiol sensorial characterization after synthesis by combinatorial chemistry

Tables 1 to 5 compile the physico-chemical and sensorial properties of more than sixty polyfunctional thiols: 8 mercapto-ketones, 13 mercapto-aldehydes, 21 mercapto-alcohols (8 primary and 13 secondary alcohols) and 21 mercapto-esters. They were all synthesized by combinatorial chemistry. Note that the different protocols mentioned in figure 1 lead to various reaction yields. In general, those involving H_2S or $NaBH_4$ give more by-products.

Table 1: Physico-chemical and sensorial properties of mercaptoketones.

Name	Kovats index (CP Sil5 CB)	Kovats index (FFAP)	5 Major MS fragments, *m/z*	BE-GC-LoADS [ng]	Odor at the sniffing port
1-Mercaptobutan-3-one	844	1445	43, 71, 61, 55, 104	0.01	Potato
4-Mercaptopentan-2-one	884	1422	43, 85, 41, 118, 61	0.03	Greenery, potato, blackcurrant
4-Mercapto-4-methylpentan-2-one	915	1382	43, 132, 75, 55, 99	0.004	Blackcurrant, catty, broom
1-Mercaptopentan-3-one	947	1517	57, 61, 85, 118, 47	0.009	Cheese, solvent, skunky, pungent
4-Mercapto-3-methylpentan-2-one	959[a] 967[a]	1469[a] 1477[a]	43, 99, 55, 61, 132	0.02[a] 0.4[a]	Sweat[a] Cooked milk[a]
5-Mercaptohexan-3-one	984	1487	57, 61, 75, 132, 99	0.02	Box tree, fresh, empyreumatic
5-Methyl-4-mercaptohexan-2-one	1069	1585	43, 112, 113, 55, 146	0.03	Exotic fruit, sweet
4-Mercaptononan-2-one	1292	1802	43, 55, 41, 141, 71	0.02	Rhubarb, lemon, cannabis, spicy

[a] the data correspond to diastereoisomers

Table 2: Physico-chemical and sensorial properties of mercapto-aldehydes.

Name	Kovats index (CP-Sil 5 CB)	Kovats index (FFAP)	5 Major MS fragments, *m/z*	BE-GC-LoADS [ng]	Odor at the sniffing port
3-Mercaptopropanal	756	1382	72, 90, 62, 57, 61	0.06	Rotten potatoes, broth
3-Mercaptobutanal	803	1372	41, 42, 86, 71, 61	4	Broth, cheese, pungent
3-Mercapto-3-methylbutanal	842	1353	41, 56, 57, 55, 59	0.06	Broth, cheese, pungent
3-Mercapto-2-methylpropanal	826	1400	41, 71, 42, 47, 76	3	Meat, broth, raw bread paste
3-Mercapto-2-methylbutanal	892	1424[a] 1429[a]	56, 61, 85, 55, 41	0.002	Broth, onion, meat, cheese [a] Broth, onion, meat, cheese [a]
3-Mercaptopentanal	910	1476	41, 56, 100, 55, 45	1	Broth, raw onion, flowery
3-Mercapto-2-ethylpropanal	926	1481	85, 56, 55, 41, 47	13	Broth, rotten potatoes, plastic, groundnut
3-Mercapto-2-methylpentanal	991[a] 995[a]	1508[a] 1524[a]	70, 41, 55, 75, 43	0.003[a] 0.1[a]	Broth, meat, onion [a] Broth, pepper [a]
3-Mercaptohexanal	1004	1560	55, 41, 70, 42, 61	0.003	Citrus fruit peel, fresh
3-Mercaptoheptanal	1108	1659	41, 69, 56, 55, 43	0.03	Flowery, citrus fruit peel
3-Mercapto-2-butylpropanal	1133	1667	55, 57, 56, 41, 43	0.4	Plastic, rhubarb, pungent
3-Mercaptooctanal	1214	1764	55, 41, 70, 56, 69	0.001	Citrus fruit peel, grapefruit, greenery, fresh
3-Mercaptononanal	1320	1873	55, 41, 70, 43, 69	-	Stale odor, greenery

[a] the data correspond to diastereoisomers

Table 3: Physico-chemical and sensorial properties of mercapto secondary-alcohols.

Name	Kovats index (CP-Sil 5 CB)	Kovats index (FFAP)	5 Major MS fragments, *m/z*	BE-GC-LoADS [ng]	Odor at the sniffing port
1-Mercaptobutan-3-ol	881	1622	45, 43, 47, 55, 72	0.005	Caramel, solvent, lemon, fresh
4-Mercaptopentan-2-ol	914[a] 926[a]	1587[a] 1614[a]	45, 86, 71, 61, 69	0.002[a] 0.02[a]	Broom, blackcurrant, catty[a] Raw onion[a]
4-Mercapto-4-methylpentan-2-ol	952	1547	57, 85, 45, 100, 41	0.009	Broom, blackcurrant, solvent,...
1-Mercaptopentan-3-ol	981	1698	47, 57, 59, 45, 41	0.05	Stinging nettle
5-Mercaptohexan-3-ol	1012[a] 1023[a]	1658[a] 1682[a]	61, 59, 71, 100, 116	0.02[a] 0.06[a]	Sweat, meat broth, citrus fruit[a] Sweat, cooked milk[a]
4-Mercapto-3-methylpentan-2-ol	1022[a] 1037[a]	1671[a] 1677[a] 1687[a] 1739[a]	56, 45, 55, 61, 100	0.06[a] 0.0001[a]	Sweat, cooked milk[a] Onion, leek, sweat, soup[a]
5-Methyl-4-mercaptohexan-2-ol	1097[a] 1107[a]	1747[a] 1762[a]	71, 45, 55, 61, 114	0.002[a] 0.002[a]	Rhubarb, lemon[a] Spicy, peppery, meaty[a]
4-Mercaptononan-2-ol	1315[a] 1323[a]	1971[a] 1985[a]	45, 71, 41, 43, 55	0.002[a] 0.008[a]	Rhubarb, sweat[a] Rhubarb, mushroom[a]

[a] the data correspond to diastereoisomers

Table 4: Physico-chemical and sensorial properties of mercapto primary-alcohols.

Name	Kovats index (CP-Sil 5 CB)	Kovats index (FFAP)	5 MajorMS fragments, *m/z*	BE-GC-LoADS [ng]	Odor at the sniffing port
3-Mercaptopropanol	852	1665	57, 41, 58, 45, 47	0.2	Potato, broth
3-Mercaptobutanol	898	1665	57, 55, 41, 72, 43	0.1	Cheese, onion, cabbage, pungent
3-Mercapto-2-methylpropanol	920	1698	41, 47, 57, 55, 72	0.07	Leek, onion
3-Mercapto-3-methylbutanol	944	1671	41, 69, 71, 86, 43	0.2	Cooked onion, tartare, chervil
3-Mercapto-2-methylbutanol	987	1738	41, 60, 45, 61, 71	0.01	Leek, broth, pepper
3-Mercaptopentanol	1002	1765	41, 57, 55, 61, 69	0.001	Broth, greenery, stinging nettle
3-Mercapto-2-ethylpropanol	1020	1790	57, 41, 47, 55, 45	0.01	Onion
3-Mercapto-2-methylpentanol	1082[a] 1084[a]	1822[a] 1828[a]	41, 74, 55, 71, 45	0.007[a] 0.004[a]	Burned plastic, gas, citrus fruit[a] Greenery, vinaigrette[a]
3-Mercaptohexanol	1095	1853	55, 41, 57, 61, 67	0.004	Rhubarb, lime
3-Mercaptoheptanol	1198	1962	55, 41, 57, 61, 81	0.006	Citrus fruit, vinaigrette, carrot
3-Mercapto-2-butylpropanol	1218	1985	43, 74, 45, 47, 57	0.005	Plastic, pungent
3-Mercaptooctanol	1302	> 2000	41, 55, 57, 69, 43	0.004	Rhubarb, carrot greenery
3-Mercaptononanol	1424	> 2000	41, 55, 57, 43, 69	0.08	Carrot greenery

[a] the data correspond to diastereoisomers

Table 5: Physico-chemical and sensorial properties of mercapto-esters.

Name	Kovats index (CP-Sil 5 CB)	Kovats index (FFAP)	5 Major MS fragments, *m/z*	BE-GC-LoADS [ng]	Odor at the sniffing port
1-Mercaptobutyl-3-acetate	1025	1539	43, 88, 55, 60, 47	3	Onion, plastic, pungent
4-Mercaptopentyl-2-acetate	1053[a] 1063[a]	1509[a] 1531[a]	43, 69, 60, 102, 61	2[a] 0.8[a]	Plastic, burned[a] Mold, pungent[a]
4-Mercapto-4-methylpentyl-2-acetate	1096	1518	43, 83, 55, 41, 118	8	Coffee, mocha, burned, vinegar
1-Mercaptopentyl-3-acetate	1118	1611	43, 102, 87, 55, 60	4	Potato, raw carrot, celery
2-Mercaptohexyl-4-acetate	1149[a] 1157[a]	1578[a] 1596[a]	43, 61, 74, 116, 87	3[a] 0.4[a]	Greenery, plastic[a] Carrot greenery[a]
4-Mercapto-3-methylpentyl-2-acetate	1166[a] 1170[a]	1613[a] 1623[a]	43, 61, 83, 118, 55	2[a] 0.1[a]	Broom, catty, blackcurrant[a] Groundnut, broth[a]
5-Methyl-4-mercaptohexyl-2-acetate	1224[a] 1238[a]	1650[a] 1675[a]	43, 87, 55, 130, 97	8[a] 5[a]	Rhubarb, lemon, fresh[a] Pepper[a]
4-Mercaptononyl-2-acetate	1430[a] 1438[a]	1857[a] 1871[a]	43, 55, 69, 87, 102	44[a] 115[a]	Garlic, sweet[a] Garlic, sweet, greenery[a]
3-Mercaptopropyl-acetate	992	1565	43, 74, 41, 47, 61	0.9	Grilled, roasted meat
3-Mercaptobutyl-acetate	1035	1559	43, 88, 55, 59, 61	0.9	Pungent, stinging nettle, hazelnut
3-Mercapto-2-methylpropyl-acetate	1051	1583	43, 88, 55, 47, 41	11	Plastic, roasted hazelnut
3-Mercapto-3-methylbutyl-acetate	1082	1568	69, 43, 41, 102, 75	0.3	Green pepper, vinegar, plastic
3-Mercapto-2-methylbutyl-acetate	1119[a] 1122[a]	1612[a] 1619[a]	43, 61, 69, 60, 102	2[a] 2[a]	Roasted meat[a] Onion, vinegar, fruity[a]
3-Mercaptopentyl-acetate	1144	1649	43, 73, 102, 69, 41	1	Exotic fruit, candy
3-Mercapto-2-ethylpropyl-acetate	1154	1665	43, 102, 60, 69, 87	11	Vinaigrette
3-Mercapto-2-methylpentyl-acetate	1207	1687[a] 1692[a]	43, 74, 41, 116, 83	0.07	Rhubarb, exotic fruit, candy
3-Mercaptohexyl-acetate	1227	1727	43, 55, 88, 116, 63	0.02	Candy, blackcurrant, passion fruit
3-Mercaptoheptyl-acetate	1324	1823	43, 69, 88, 55, 41	0.06	Onion, exotic fruit, candy
3-Mercapto-2-butylpropyl-acetate	1331	1835	43, 55, 41, 60, 130	1	Greenery
3-Mercaptooctyl-acetate	1425	1930	43, 88, 55, 41, 69	0.9	Citrus fruit peel, rhubarb, carrot
3-Mercaptononyl-acetate	1526	> 2000	43, 88, 55, 41, 69	15	Carrot, sweet

[a] the data correspond to diastereoisomers

Polyfunctional thiol occurrence in a fresh beer

GC-O of fresh beer extracts (XAD extraction procedure) revealed the presence of 4-mercapto-4-methyl-pentan-2-one (4MMP) and 3-mercaptohexan-1-ol (3MH). Those results have been confirmed on two different capillary columns. On the other hand, usual techniques like GC-MS or GC-SCD revealed to be inappropriate for the detection of such traces. Noteworthy is the occurrence of 4MMP and 3MH in wine, another yeast fermented beverage (*8-11*). Surprisingly, 3-methyl-2-buten-1-thiol (MBT) was also found as a very strong odor of the fresh beer extract (beer although protected from light). Here, the GC-MS used in SIM mode allowed to confirm the structure.

Polyfunctional thiol impact on the global aroma of a Pils beer

The impact of thiols on the overall flavor of a lager beer was assessed by sensory analyses of fresh samples spiked or not with copper (Cu^{++}). As depicted in figure 2 (SPME data), copper is very efficient to decrease thiol volatility. Eight panelists out of 10 managed to perceive a difference when beer thiols were trapped ($p < 0.1$ %) but they had trouble to describe it clearly and unanimously (rather unpleasant). In a second experience, the 10 ppt spiking of 4MMP in fresh beer was described by the panelists as fresh and fruity.

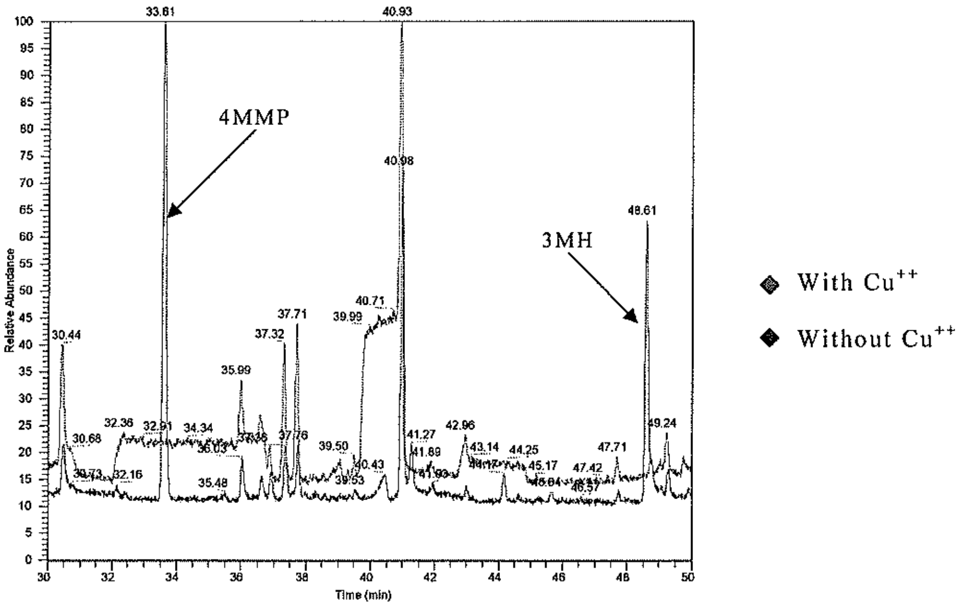

Figure 2: Thiol trapping by copper ions confirmed by GC-SPME.

CONCLUSIONS

Thanks to combinatorial chemistry and GC-Olfactometry, 4-mercapto-4-methyl-2-pentanone (4MMP), 3-mercaptohexanol (3MH) and 3-methyl-2-buten-1-thiol (MBT) were detected in fresh lager beer. Sensorial analyses emphasized the relevance of those thiols in beer flavor.

REFERENCES

1. Vermeulen, C. & Collin, S., Sensorial contribution and formation pathways of thiols in foods: a review, J. Agric. Food Chem., 2003, submitted.
2. Vermeulen, C., Pellaud, J., Gijs, L. & Collin, S., Combinatorial synthesis and sensorial properties of polyfunctional thiols, J. Agric. Food Chem., 2001, 49, 5445-5449.
3. Vermeulen, C. & Collin, S., Synthesis and sensorial properties of mercaptoaldehydes, J. Agric. Food Chem., 2002, 50, 5654-5659.
4. Vermeulen, C., Guyot-Declerck, C. & Collin, S., Combinatorial synthesis and sensorial properties of mercapto primary-alcohols and analogs, J. Agric. Food Chem., 2003, in press.
5. Vermeulen, C. & Collin, S., Combinatorial synthesis and sensorial properties of mercaptoesters, J. Agric. Food Chem., 2003, in press.
6. Lermusieau, G., Bulens, M. & Collin, S., Use of GC-Olfactometry to identify the hop aromatic compounds in beer, J. Agric. Food Chem., 2001, 49, 3867-3874.
7. Berger, C., Martin, N., Collin, S., Gijs, L., Khan, J.A., Piraprez, G., Spinnler, H.E. & Vulfson, E.N., Combinatorial approach to flavor analysis 2. Olfactory investigation of a library of S-methyl-thioesters and sensory evaluation of selected components, J. Agric. Food Chem., 1999, 47, 3274-3279.
8. Tominaga, T., Furrer, A., Henry, R. & Dubourdieu, D., Identification of new volatile thiols in the aroma of Vitis vinifera L. var. Sauvignon blanc wines, Flavour Fragr. J., 1998, 13, 159-162.
9. Tominaga, T., Murat, M.-L. & Dubourdieu, D., Development of a method for analysing the volatile thiols involved in the characteristic aroma of wines made from Vitis vinifera L. cv. Sauvignon blanc, J. Agric. Food Chem., 1998, 46, 1044-1048.
10. Tominaga, T., Peyrot des Gachons, C. & Dubourdieu, D., A new type of flavor precursors in Vitis vinifera L. cv. Sauvignon blanc: S-cysteine conjugates, J. Agric. Food Chem., 1998, 46, 5215-5219.
11. Tominaga, T., Baltenweck-Guyot, R., Peyrot des Gachons, C. & Dubourdieu, D., Contribution of volatile thiols to the aromas of white wines made from several Vitis vinifera grape varieties, Am. J. Enol. Viticult., 2000, 51, 178-181.