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Identification of Volatiles Emitted during the Blanching Process of Brussels Sprouts and Cauliflower

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Volatiles produced during the blanching process of Brussels sprouts (Brassica oleracea *L var* gemmifera *DC) and cauliflower* (Brassica oleracea *L var* botrytis *subvar* cauliflora *DC) in laboratory and industrial conditions were identified. Thiols, sulphides, polysulphides, isothiocyanates, nitriles, carbonyl compounds, furans, esters and terpenes were identified in the head space of both vegetables. Isothiocyanates and nitriles were predominant in Brussels sprouts whereas aldehydes were the most abundant cauliflower volatiles. Several volatiles were identified for the first time. 2-Methylbutyl isothiocyanate and 3-methylpentanenitrile, breakdown products of 2-methylbutylglucosinolate, were identified in the head space of Brussels sprouts. The presence of this glucosinolate in Brussels sprouts has not previously been reported.*

Samples were taken in laboratory conditions and in an industrial blanching installation. For laboratory-scale experiments a three-necked glass flask (2 litres) was provided with a glass tube allowing supply of helium gas, a thermometer and a small water condenser. Tenax tubes (0·75 g per tube) were mounted on top of the condenser. The adsorption tube outlet was connected with a wet volume meter. One litre of distilled water was placed in the flask and heated to 90°C. Raw vegetables were added, the system was closed and helium gas (0·5 litre min^{-1}) was bubbled through the flask to transfer volatiles to the adsorption tube. In the industrial process, fume hoods are constructed above the inlet and outlet of the rotary drum. Blanching vapours are evacuated via these fume hoods. A Teflon tube was put in the waste gas duct and connected with a Tenax GC tube to take waste gas samples.

Interpretation of mass spectra was based on literature data and analyses of reference compounds, which were normally bought from local suppliers. Propyl, 2-methylpropyl, 1-methylpropyl, 1-methylbutyl and 2-methylbutyl isothiocyanates, 2-methyl and 3-methylpentanenitrile were prepared according to methods described by Furniss *et al* (1989).

Although there is a great similarity in the chemical nature of volatiles in both vegetables, differences in relative composition are obvious. In Brussels sprouts, breakdown products from glucosinolates (isothiocyanates and nitriles) are predominant. These groups represent 82·6% of volatiles in the laboratory experiments and 91·8% of volatiles in industrial samples. In cauliflower, aldehydes are 70·8% of head space volatiles in laboratory experiments and 75·1% of volatiles in industrial samples. Glucosinolate breakdown products and organic sulphur compounds represent 15% of cauliflower volatiles.

Dimethyl disulphide is the most abundant sulphur compound in both Brussels sprouts and cauliflower. This compound contributes about 10% to the head space composition of cauliflower and 2·8% only in Brussels sprouts. Of all sulphur compounds detected, carbon disulphide was identified for the first time in both vegetables, and dimethyl tetrasulphide was identified for the first time in Brussels sprouts.

Isothiocyanates and nitriles originate from glucosinolates. In the presence of myrosinase, glucosinolates are hydrolysed to β-D-glucose, sulphate, sulphur and organic compounds. In neutral pH conditions formation of isothiocyanates is favoured. In acid conditions and in the presence of ferrous ions, nitriles are predominant. Prop-2-enyl isothiocyanate, but-3-enyl isothiocyanate and the corresponding but-3-enenitrile and pent-4-enenitrile are the most abundant breakdown products of glucosinolates in Brussels sprouts and cauliflower. Other isothiocyanates and nitriles that were identified are only minor compounds.

Methylglucosinolate is characteristic for the Capparaceae. Present results indicate the presence of this glucosinolate in Brussels sprouts and cauliflower.

Propyl isothiocyanate was identified based on the similarity of the spectrum of the compound in the sample and the spectrum of the reference compound. The experimentally determined Kovats retention index of propyl isothiocyanate (869) also agreed with the retention index of the unknown.

Based on the mass spectrum of the reference compounds synthesised, their retention indices (1-methylpropyl isothiocyanate: 900, and 2-methylpropyl isothiocyanate: 932) and the spectra published by Kjaer *et al* (1963), it was concluded that 2-methylpropyl isothiocyanate was present in Brussels sprouts. It was not detected in cauliflower.

2-Methylbutyl isothiocyanate has not been reported as a head space volatile in Brussels sprouts or cauliflower. Identification was based on comparison of the spectra with reference compounds and on Kovats indices (2-methylbutyl isothiocyanate: 1032). Next to the isothiocyanate, the corresponding 3-methylpentanenitrile was identified in Brussels sprouts. (Kovats index for 2-methylpentanenitrile: 792; 3-methylpentanenitrile: 876). Both 2-methylbutyl isothiocyanate and 3-methylpentanenitrile originate from the same precursor, 2-methylbutylglucosinolate.

Aldehydes are predominant in cauliflower. Aldehydes show a very specific pattern, with high relative amounts of octanal and nonanal. Nasirullah *et al* (1984)

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determined fatty acid composition of lipids from edible parts of vegetables. Plant total lipids content was 0·18% for Brussels sprouts and 0·28% for cauliflower. Both vegetables are rich in linolenic acid (58·7% of total fatty acids for Brussels sprouts and 48·9% for cauliflower). Small variations in the fatty acid composition from Brussels sprouts and cauliflower cannot explain the difference in head space volatile composition. Probably aldehydes are produced by lipoxygenase activity. Pentanal, heptanal, non-2-enal, methylbutanone and 3-methylpentan-2-one were not previously identified as cauliflower volatiles. Hexanal, octanal, hex-2-enal, propanone and butanedione have been identified in Brussels sprouts (MacLeod and MacLeod 1970; MacLeod and Pikk 1979). All other carbonyl compounds in Table 1 were identified for the first time as Brussels sprouts volatiles.

TABLE 1

Volatiles identified in Brussels sprouts and cauliflower blanching vapours. Relative composition (%)

Compounds	*Brussels sprouts*		*Cauliflower*	
	Lab	*Ind*	*Lab*	*Ind*
1. Organic sulphur compounds				
Carbon disulphide	+	+	+	+
Methanethiol	+	+	+	+
Propanethiol	–	+	–	–
Dimethyl sulphide	+	+	+	+
Methyl propyl sulphide	+	–	–	–
Dimethyl disulphide	2·8	2·9	13·6	8·8
Dimethyl trisulphide	1·2	1·9	1·9	+
Dimethyl tetrasulphide	0·2	0·6	–	–
2. Isothiocyanates (ITC)				
Methyl ITC	+	+	+	+
Propyl ITC	0·8	–	–	–
2-Methylpropyl ITC	0·1	–	–	–
2-Methylbutyl ITC	0·2	+	+	0·5
Prop-2-enyl ITC	12·8	0·7	2·1	7·8
But-3-enyl ITC	1·7	1·5	–	0·9
3. Nitriles				
Acetonitrile	–	–	+	–
3-Methylbutanenitrile	1·2	–	–	–
2-Methylpentanenitrile	1·7	–	–	–
But-3-enenitrile	51·6	61·1	0·9	6·9
Pent-4-enenitrile	12·5	28·5	–	–
Phenylacetonitrile	+	+	–	–
4. Aldehydes				
Ethanal	+	+	+	+
Propanal	–	+	–	–
Pentanal	+	+	2·1	–
Hexanal	3·6	0·9	4·5	10·7
Heptanal	0·5	0·1	2·6	2·0
Octanal	0·8	0·4	13·6	11·8

TABLE 1—*contd*

Compounds	*Brussels sprouts*		*Cauliflower*	
	Lab	*Ind*	*Lab*	*Ind*
4. Aldehydes *continued*				
Nonanal	1·0	0·3	46·4	50·6
Methylpropanal	+	+	+	+
2-Methylbutanal	+	+	+	−
3-Methylbutanal	+	−	−	+
Propenal	+	+	+	+
Pent-2-enal	−	−	+	−
Hex-2-enal	1·3	−	1·0	+
Non-2-enal	−	−	+	−
Hepta-2,4-dienal	+	−	+	−
Methylpropenal	−	+	−	−
Benzaldehyde	0·5	0·5	0·6	+
5. Ketones				
Propanone	+	+	+	+
Butanone	+	−	+	−
Methylbutanone	−	−	+	−
3-Methylpentan-2-one	−	+	+	+
4-Methylpentan-2-one	+	−	−	−
Heptan-3-one	+	−	−	−
Octan-2-one	+	−	−	−
Octan-3-one	+	−	−	−
Nonan-5-one	+	−	−	−
Butanedione	+	+	−	+
Acetophenone	+	+	−	+
6. Alcohols				
Methanol	+	+	+	+
Ethanol	−	+	+	+
Pentan-1-ol	0·9	−	1·3	−
Heptan-1-ol	−	−	+	−
Octan-1-ol	−	−	8·0	+
Pent-2-en-1-ol	+	−	0·6	−
Hex-3-en-1-ol	+	+	0·7	−
7. Miscellaneous				
2-Methylfuran	+	−	+	−
2-Pentylfuran	+	+	−	+
Hex-3-enyl acetate	3·9	−	−	−
Limonene	+	+	−	+
Terpinolene	+	−	−	+
α-Pinene	−	+	−	−
γ-Terpinene	−	+	−	−

+ Identified but not integrated.
− Not identified.
Lab results from laboratory experiments.
Ind results from industrial sample analyses.
The thermal desorption GC–MS system used was described by Van Langenhove *et al* 1982. Fused silica columns, 30 m in length, 0·52 mm ID coated with RSL-150 and RSL-200 (1·2 μm) were used.

Cauliflower Lab	Ind
46·4	50·6
+	+
+	−
−	+
+	+
+	−
1·0	+
+	−
+	−
−	−
0·6	+
+	+
+	−
+	−
+	+
−	−
−	−
−	−
−	−
−	−
−	+
−	+
+	+
+	+
1·3	−
+	−
8·0	+
0·6	−
0·7	−
+	−
−	+
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−	+
−	+
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−	−

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In conclusion, under blanching conditions alkenyl isothiocyanates and alkenyl nitriles are the most abundant glucosinolate degradation products in Brussels sprouts and cauliflower. Small amounts of alkyl isothiocyanates and alkyl nitriles were also detected. Results indicate the presence of 2-methylbutylglucosinolate, which has not previously been detected in Brussels sprouts. Next to glucosinolate breakdown products aldehydes and organic sulphur compounds are important head space volatiles, especially in cauliflower. Although there are minor differences in composition, there is a good qualitative similarity between the head space volatiles sampled in laboratory conditions and in the industrial blanching process.

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