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Flavour Compounds of a Commercial Concentrated Blackberry Juice

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ABSTRACT

The volatile compounds of a commercial blackberry juice were isolated by a simultaneous distillation–extraction procedure. Seventy compounds were identified by GC–MS (EI and CI mode), GC–IR analysis and comparison of retention indices with those of authentic compounds.

The aroma of this juice is mainly due to the presence of furfural (which represents a third of the total odorous profile), 3-methyl-butanal, 3-methyl-1-butanol, phenylacetaldehyde and trans-*furan linalool oxide.*

INTRODUCTION

A recent study of the flavour-neutral compounds of fresh cultivated blackberries (Evergreen Thornless) led to the identification of 245 volatile compounds (Georgilopoulos & Gallois, 1987*a*). The effect of a heat treatment upon the odorous profile of these berries was then examined (Georgilopoulos & Gallois, 1987*b*).

Although numerous qualitative and quantitative changes occurred, alcohols and aldehydes remained the predominant chemical classes in the laboratory-heated juice which was also characterized by the formation of furanic compounds.

In this work, we studied the flavour compounds of a commercial concentrated blackberry juice (from the same variety Evergreen Thornless) to observe the effects of an industrial heating process on the odorous profile of blackberry juice.

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MATERIALS AND METHODS

Materials

A concentrated pasteurized juice of Thornless Evergreen variety blackberries (*Rubus laciniata* L.) obtained from a commercial juice-concentrating operation was supplied by International Flavors and Fragrances. This juice (66° Brix, pH 3·4) exhibited a rather pleasant and characteristic blackberry aroma. All solvents were purified by distillation.

Extraction procedure

Volatile compounds of 1·5 kg of juice were isolated by a simultaneous distillation/extraction procedure. The extraction was performed for 20 min at atmospheric pressure with 100 ml of dichloromethane as solvent in a modified Likens–Nickerson apparatus (Likens & Nickerson, 1964; Schultz *et al.*, 1977).

The solvent extract was freed from the acidic compounds by washing with a 10% aqueous $NaHCO_3$ solution (w/v) and fractionated as previously described (Georgilopoulos & Gallois, 1987*a*). The three 50 ml fractions obtained by successively eluting the silica gel column with pentane, dichloromethane and diethylether were dried over Na_2SO_4 and carefully concentrated to 100 μl with Dufton-type columns (Loyaux *et al.*, 1981).

Gas chromatography

Chromatographic separations were performed on a Girdel 300 gas chromatograph (Delsi), equipped with a 30 m × 0·32 mm (id) fused silica capillary column DB5 (J & W Scientific Inc.) (film thickness, 1 μm). The hydrogen carrier gas flow rate was 37·5 cm/s. The oven temperature was programmed from 45°C to 220°C at 2°C/min. The injector and flame ionization detector temperatures were 260°C and 270°C, respectively.

Peak areas were recorded with a Minigrator integrator (Spectra Physics). The relative amount of each compound in the dichloromethane fraction was calculated with regard to the total area of the chromatogram, excluding the solvent peak. Retention indices were calculated using these conditions.

Mass spectrometry

Analyses were performed on a Nermag R 10–10 spectrometer coupled with a Girdel 31 gas chromatograph. The GC was equipped with a 60 m × 0·32 mm id fused silica DB5 capillary column directly connected to

the ion source. The operating conditions were the same as described above. Electron impact (EI) mass spectra were taken at 70 eV. Source temperature: 150°C – Interface temperature: 280°C. Scanning rate: 0·8s from 25 to 300 dalton.

Chemical ionization mode (CI) was used to confirm molecular weights with methane as reagent gas. Ionizing energy: 90 eV. Source pressure: 0·3 Torr. Source temperature: 90°C. Repeller tension: 1 V.

Infrared spectrometry

Infrared spectra were recorded with a Bruker IFS 85 coupled with a Carlo–Erba 5160 gas chromatograph, equipped with a 30 m × 0·54 mm id DB5 fused silica capillary column (film thickness, 1·5 μm).

Transfer line temperature: 200°C. Light pipe: 1·5 mm id × 36 cm gold-coated, temperature: 200°C. Detector: M.C.T. large band (4800–600 cm^{-1}).

Sensory evaluation of volatile compounds

Chromatographic effluents were split 1:1 between the FID (of the Girdel 300 chromatograph) and a sniffing port through a microneedle valve (SGE, 1/16 in, OD MNVT).

The odour intensity of each compound was estimated on a three-point scale. Each extract was sniffed twice.

RESULTS AND DISCUSSION

Both diethylether and pentane fractions (which, for the latter, contained only hydrocarbons) did not exhibit any odour of interest and were discarded.

On the other hand, the dichloromethane fraction possessed a very pleasant odour with sweet, caramel-like, warm and old Cognac notes. Fruity and herbaceous notes were also noticed, which were less intense.

Seventy compounds, found in this fraction are listed in Table 1. They represent 82% of the total odorous profile. The remaining unknown compounds were not further studied as they did not possess any perceptible odour.

The odorous profile of concentrated blackberry juice did not contain any impact compound, as already noticed for fresh and heated blackberry juice (Georgilopoulos & Gallois, 1987*a*,*b*).

Furans are the most abundant chemical class, mainly because of furfural which represents a third of the total odorous profile.

TABLE 1
Volatile Compounds Identified in the Blackberry Concentrated Juice

Compounds	%[a] (*OI*)[b]	*RI*
Hydrocarbons		
p-cymene[d]	+ (0)	1 024
limonene[d]	+ (0)	1 044
m-diisopropenyl benzene[e]	+ (0)	
p-diisopropenyl benzene[e]	+ (0)	
Esters		
ethyl acetate[d,f]	1·93 (2)	
ethyl lactate[d,f]	2·17 (1)	836
ethyl levulinate[e]	tr (0)	1 070
trans-2-hexenyl butanoate	tr (0)	1 129
diethyl succinate	0·07 (0)	1 172
methyl salicylate	tr (0)	1 197
ethyl-α-toluate	tr (0)	1 231
Total percentage	4·17	
Aldehydes		
acetaldehyde	+ (1)	
propenal	+ (1)	
3-methyl butanal[d,f]	15·17 (3)	
benzaldehyde[d,f]	0·05 (1)	970
phenylacetaldehyde[d,f]	5·67 (3)	1 068
α-campholenal	0·01 (1)	1 135
safranal	0·05 (1)	1 212
p-9-menthenal[f]	0·05 (0)	1 227
Total percentage	21·00	
Ketones		
2,3-pentanedione	0·26 (1)	
3-hydroxy-2-butanone[d]	0·18 (1)	
5-hexen-2-one	tr (0)	
2-heptanone[d]	0·03 (1)	902
damascenone[d,f]	0·01 (2)	1 385
2,3,6-trimethyl-1-phenyl-buten-3-one-2	0·01 (0)	
p-isopropenyl acetophenone[e]	tr	
Total percentage	0·49	
Acetals		
1,1′-diethoxy ethane[f]	1·38 (1)	
1,1′-diethoxy propane[e,f]	tr (0)	
1,1′-diethoxy butane[f]	0·97 (0)	872
1,1′-diethoxy isopentane[f]	1·59 (0)	
Total percentage	3·94	

TABLE 1—*contd.*

Compounds	%[a] (*OI*)[b]	*RI*
Phenols		
p-cresol[d,e]	tr (0)	1 104
p-vinyl guaiacol[e]	0·01 (3)	1 326
Total percentage	0·01	
Alcohols		
ethanol	+ (0)	
1-propanol[f]	0·44 (0)	
2-methyl-3-buten-2-ol	0·26 (0)	
2-methyl-1-propanol[f]	2·78 (2)	
3-methyl-1-butanol[d,f]	6·26 (2)	
2-heptanol[d,f]	0·19 (1)	919
linalool[d,f]	0·04 (1)	1 114
myrcenol	tr (2)	1 126
phenylethanol[d,f]	tr (0)	1 130
p-cymen-8-ol[f]	0·02 (0)	1 194
α-terpineol[d]	0·19 (0)	1 197
3-phenyl-1-propanol[d]	tr (3)	1 238
Total percentage	10·18	
Lactones		
γ-butyrolactone[d,f]	0·17 (0)	925
Total percentage	0·17	
Furans		
furfural[f]	32·28 (3)	848
furfuryl alcohol[f]	0·09 (0)	874
α-angelica lactone[f]	0·93 (1)	901
2-acetyl furan[f]	0·59 (1)	921
β-angelica lactone	0·03 (2)	946
5-methyl furfural[f]	0·98 (0)	973
4-hydroxy-5-methyl-(4H)dihydro 3-furanone	0·11 (0)	985
isomaltol	0·05 (0)	989
2-furyl-1,2-propanedione	0·04 (0)	1 072
trans-furan linalool oxide[f]	5·09 (3)	1 087
methyl furoate[d,f]	0·93 (3)	1 101
cis-furan linalool oxide[f]	0·27 (2)	1 103
2-methyl benzofuran[e]	tr (0)	
Total percentage	41·67	
Pyrans		
2,6,6-trimethyl-2-vinyl tetra-hydropyran[e]	tr (0)	979
Total percentage	>0·01	

(*continued*)

TABLE 1—*contd.*

Compounds	%[a] (*OI*)[b]	*RI*
Pyrroles		
2-formylpyrrole	0·07 (2)	1 031
2(1H)pyrrolylethanone	0·06 (1)	1 075
Total percentage	0·13	
Imidazoles		
2-(1,1-diethoxy methyl)-imidazole[e]	0·09 (0)	1 091
2-(1,1-diethoxy ethyl)-imidazole	0·02 (3)	1 197
2-(2,2 diethoxy ethyl)-imidazole	0·03 (2)	1 199
2-(3,3-diethoxy propyl)-imidazole	0·04 (1)	1 212
2-(4,4-diethoxy butyl)-imidazole	0·04 (2)	1 309
2-(5,5-diethoxy pentyl)-imidazole	0·02 (3)	
Total percentage	0·24	
Others		
dimethyldisulphide[e]	0·15 (2)	
methional[e]	0·23 (2)	918
vitispirane[f]	0·08 (3)	1 286
Total percentage	0·46	
Identified compounds (% of the total profile)	82·46	

[a] Relative amount in the dichloromethane fraction.
[b] Odour intensity. (0): no odour (1): weak odour (2): medium-intense odour (3): strong odour.
[c] Retention indices determined on DB5 column.
[d] Retention indices identical with those of authentic compounds.
[e] Compounds for which EI mass spectra only have been obtained. For all other compounds, both EI and CI mass spectra were recorded.
[f] Identification positively confirmed by infra-red spectrometry.

The predominance of this class is not surprising as furanic compounds are known to be formed during heating of hydrocarbons (Hodge, 1967).

However, furfural and *trans*-furan linalool oxide are much more abundant than in heated juice obtained on a laboratory scale (Georgilopoulos & Gallois, 1987*b*).

Other compounds, known as Maillard reaction products, have been found here: a pyran, two pyrroles, six imidazoles. These compounds were not produced during the laboratory heating treatment of a blackberry juice (Georgilopoulos & Gallois, 1987*b*) which indicates that the industrial heating process was much more drastic than the laboratory one.

Some of these compounds may also have been produced by Maillard reaction during a long storage period of the concentrated juice.

Despite their very low concentration, both 2-(3,3 diethoxy propyl)-imidazole and 2-(5,5 diethoxypentyl)-imidazole bring very potent fruity notes to the overall aroma.

The occurrence of four acetals should also be noted here. They are much more abundant than in laboratory-heated juice. Except in strawberry oil, where MacFadden *et al.* (1965) identified numerous acetals, these compounds are scarcely reported. They could have been formed during a strong heat treatment. Another hypothesis could be suggested: the level of diethyl acetals is a direct measure of the ethanol content. This ethanol content is dependent on the degree of fermentation of the freshly pressed juice before processing. Thus the abundance of acetals here could suggest that the industrial juice started from more highly fermented blackberry material than the laboratory-made juice.

Aldehydes and alcohols represent, respectively, 21% and 10% of the odorous profile. The quantitative importance of aldehydes is the same as for laboratory-heated juice but the predominant compounds are here 3-methyl-butanal and phenylacetaldehyde instead of nonanal and hexanal.

Among alcohols, a great decrease of 2-heptanol can be noticed (0·19% of the odorous profile instead of 23% for laboratory heated juice) together with an increase of both 2-methyl-1-propanol and 3-methyl-1-butanol concentrations.

Several compounds, present only at trace levels, seem to contribute to the total aroma of the concentrated juice: *p*-vinyl guaiacol (spicy, clove-like note), 3-phenyl-1-propanol (flowery, lilac), vitispirane (flowery), dimethyl-disulfur (onion like). On the other hand, methoxyfuraneol, an important compound of the laboratory-heated juice, was not found here, perhaps because of the strong heating.

CONCLUSION

The modifications which affect the odorous profile of heated blackberry juice are influenced by the kind of treatment used: an industrial rough heat treatment favours the formation of nitrogen- and oxygen-containing heterocyclic compounds, especially furanic derivatives, which contribute to the characteristic flavour of the heated juice.

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REFERENCES

Georgilopoulos, D. N. & Gallois, A. N. (1987*a*). Aroma compounds of fresh blackberries (*Rubus laciniata* L.). *Z. Lebensm. Unters. Forsch.*, **184**, 374–80.

Georgilopoulos, D. N. & Gallois, A. N. (1987*b*). Volatile flavour compounds in heated blackberry juices. *Z. Lebensm. Unters. Forsch.*, **185**, 299–306.

Hodge, J. E. (1967). Non-enzymatic browning reactions. In: *Symposium on foods: The chemistry and physiology of flavors.* (Schultz, H. W., Day, E. A. & Libbey, L. M. (Eds)), The AVI Publishing Co., Westport, 465–91.

Likens, S. T. & Nickerson, G. B. (1964). Detection of certain hop oil constituents in brewing products. *Proc. Amer. Soc. Brew. Chem.*, **22**, 5–13.

Loyaux, D., Roger, S. & Adda, J. (1981). The evolution of Champagne volatiles during ageing. *J. Sci. Food. Agric.*, **32**, 1254–8.

MacFadden, W. H., Teranishi, R., Corse, J., Black, D. R. & Mon, T. R. (1965). Volatiles from strawberries. II. Combined mass spectrometry and gas chromatography on complex mixtures. *J. Chromatog.*, **18**, 10–19.

Schultz, T. H., Flath, R. A., Mon, T. R., Eggling, S. B. & Teranishi, R. (1977). Isolation of volatile components from a model system. *J. Agric. Food. Chem.*, **25**, 446–9.