plantings were roughly parallel.

The private farms from which samples were taken can be segregated into areas. Within an area, the fields which were sampled were no more than 10 miles apart. The centers of the areas, named for the nearest city, were more than 70 miles apart. There were no significant differences in protein content of Centennial due to the area. Jewel roots from the Wake Forest area contained significantly more protein than those from the other two areas. Roots from the Castle Hayne AES contained significantly more protein than those from the Clayton AES and the Dunn area.

We could not explain the cause of these differences. All soils were classed as Norfolk sandy loams, and horticultural practices at the AES farms were essentially the same. The Wake Forest area, with the highest protein roots, was the farthest north. Castle Hayne AES, which had the second highest protein, was the farthest south. Differences of protein content within a cultivar may be a complex function of soil water and soil nitrogen (Constantin et al., 1974; Li, 1976a,b; ARS, 1972), or it may be due to development of different clones within a cultivar.

We have demonstrated the magnitude of variance due to roots, hills, and fields and documented differences due to growing area. These data illustrate difficulties which may arise if nutritional labeling of sweet potatoes were attempted.

Sweet potatoes with 8% protein provide an adequate protein–calorie balance. We have shown that some fields produce roots with protein contents exceeding 8%, although the factors contributing to high protein content are not known. Consistent production of high protein roots could significantly contribute to the world food supply. Hopefully this report will stimulate a search for the factors affecting protein content of sweet potatoes.

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Occurrence of Sesquiterpenes in Mountain Cheese Volatiles

Jean-Pierre Dumont and Jacques Adda*

GC–MS analysis performed on Beaufort cheese volatiles has led to the identification of 140 components including nine sesquiterpenes. Sesquiterpenes were only found in cheeses made from summer milk when cows were grazing on high-altitude pastures. Influence of the traditional ripening process on volatile flavor compounds is also discussed.

Beaufort is a Gruyere type of cheese manufactured on a small scale in a limited area of the French Alps (Davies, 1976). It differs from the Swiss type, the flavor of which is well documented (Langler et al., 1967; Langsrud and Reinbold, 1973), by its smeary coat resulting from repetitive hand rubbings with a brine-soaked-cloth; its maturing temperature is lower (12–14 °C for at least 6 months); and, during summertime, cheeses are made with milk from cows grazing on the upper alpine slopes (1500–2500 m).

The quality of the grass with its specific flora has often been claimed to account for the delicate aroma of mountain cheeses which are highly valued. But, up till now, no definite differences in the flavor composition has ever been put forward. This paper deals with the identification of major neutral flavor compounds both in summer and winter cheeses; the influence of surface bacterial growth has also been considered to explain the formation of some of the volatile components.

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METHODS

Six summer cheeses samples (four 6-months and two 18-months old ones) and three winter cheeses samples (6-months old) were supplied by a cheese cooperative. From each sample, three different parts were studied separately (the rind, a 5-mm thick zone just under the rind, and the core of the cheese). Two samples of smear organisms suspension in brine were also studied. The flavor extracts were obtained as previously described (Dumont et al., 1976; Dumont and Adda, 1972).

Freon 11 extract was fractionated by chromatography on silicic acid (Palmer, 1973). Gas chromatography was carried out on a Giravions Dorand Model 3000 fitted with a metal capillary column, the details of which are described in the caption of Figure 1. The injection port was at 150

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Table I. Cumulative List of Volatile Components Found in Different Samples of Beaufort Cheese

Component	Peak no.	Component	Peak no.
Alcohols		Heptanal	39
Ethanol		Octanal	
1-Propanol		Nonanal	
2-Methyl-1-propanol	8	Benzaldehyde	54
1-Butanol	13	Sulfur compounds	
3-Methyl-1-butanol	21	Hydrogen sulfide	1a
1-Pentanol	27	Methanethiol	2a
1-Hexanol	41	Methyl sulfide	3a
1-Heptanol		Unknown	4a
1-Octanol		Methanethiol acetate	11, 5a
1-Nonanol	84	D.M.D.S.	16, 6a
β-Phenylethanol	80	Methyl trisulfide	50
Benzyl alcohol		2,4-Dithiapentane	37
2-Butanol	4	2,3,5-Trithiahexane	
2-Pentanol	15	Methional	
4-Methyl-2-pentanol[b]	28	3-(Methylthio)propanol	
2-Hexanol	29	Hydrocarbons	
2-Heptanol	42	Octane	25
2-Octanol	75	Methyloctane	33
2-Nonanol	78	3,3-Diethylpentane	35
2-Undecanol	96	Methylethylheptane	45
α-Phenylethanol	88	Dimethyloctane	48
Furfurol		Nonane	
1-Octen-3-ol		Methylnonane	51
Acetoin	20	Decane	58
Esters		Undecane	76
Ethyl acetate	3	Dodecane	
Propyl acetate	13	Tridecane	94
Butyl acetate	27	Pentadecane	109
Isoamyl acetate	27	Hydrocarbon M 128	30
Nonyl acetate	34	Hydrocarbon M 140	46
sec-Butyl acetate	18	Hydrocarbon M 154	62, 63, 64
Ethyl propanoate	12	Hydrocarbon M 156	
Amyl propanoate	60	Benzene	7
Isoamyl propanoate		Toluene	19
Propyl 2-methylpropanoate	38	Ethylbenzene	32
Ethyl butanoate	24	Dimethylbenzene	33, 38
Propyl butanoate		Vinylbenzene	
sec-Butyl butanoate	55	Methylethylbenzene	49
Ethyl 2-methylbutanoate		Isopropylbenzene	47
Methyl 3-methylbutanoate	14	Dimethylethylbenzene	
Ethyl 3-methylbutanoate	31	Naphthalene	86
Ethyl 3-methylvalerate		Methylnaphthalene	95, 99
Ethyl hexanoate	56	Dimethylnaphthalene	
Isoamyl hexanoate	89	1,3-Dimethoxybenzene	44
Ethyl octanoate	83	Limonene	
Methyl decanoate	97	Dihydrovalencene[b]	100
Ethyl decanoate	107	Dihydropinene	
Methyl benzoate	77	α-Copaene[b]	101
β-Phenylethyl acetate		Sesquiterpene	104
Carbonyls		β-Farnesene[b]	105
2-Butanone	2	Caryophyllane[b]	106
2-Pentanone	9	Sesquiterpene	107
3-Methyl-2-pentanone	17	Sesquiterpene	108
2-Hexanone	22	Eremophylane[b]	110
Methyl-2-hexanone[b]		Sesquiterpene	111
2-Heptanone	36	Miscellaneous	
2-Octanone	53	Phenol	87
2-Nonanone	73	Cresol	91
2-Decanone	82	Ethylphenol	
2-Undecanone	93	Pyridine	29
2-Tridecanone	111	Trimethylpyridine	59
3-Octanone	52	Dimethylpyrazine	
2-Nonenone	72	Indole	112
Acetophenone	74	Skatole	
2-Methyl-1-butanal	5	Benzothiazole	90
3-Methyl-1-butanal	6	δ-Decalactone	
Pentanal	10	δ-Dodecalactone	
Hexanal	23	γ-Decalactone	113

[a] Refers to Figure 2. [b] Tentatively identified.

°C and the carrier gas (helium) was at an inlet pressure of 0.5 atm. A split led to the flame ionization detector, the main exit leading to the inlet of an AEI MS 20 organic mass spectrometer via a temperature-programmed membrane separator. Make-up gas was added at the column exit in order to obtain an optimum gas flow through the separator. Ion source temperature was 200 °C, electron current was 50 μA, electron energy was 70 eV, and the accelerating voltage was 2 kV. Scanning range was m/e 25 to 250 in 10 s.

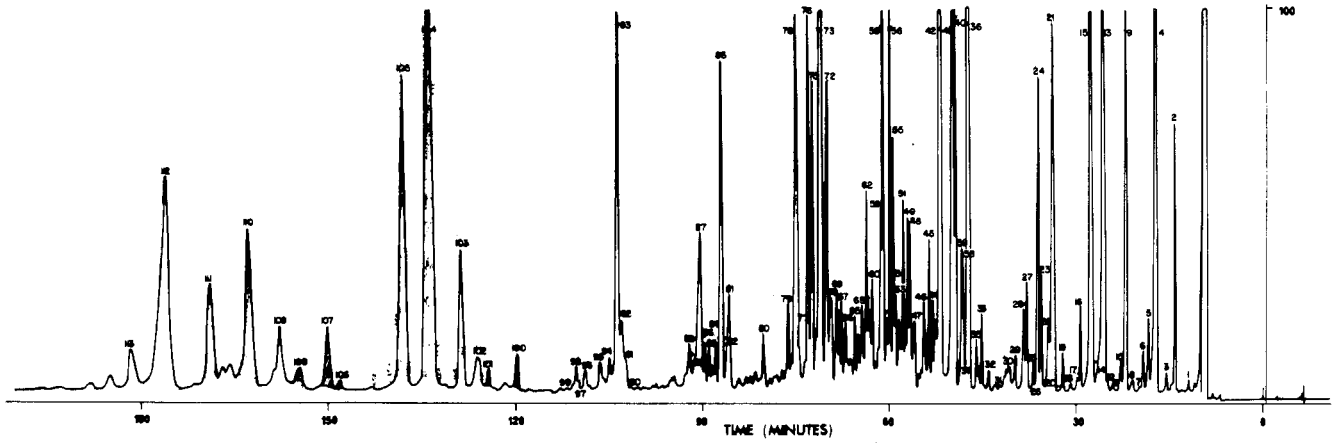

Figure 1. Gas chromatogram of Freon 11 extract obtained from the core of a 18-months old summer Beaufort Cheese: 0.75 mm i.d. × 150 m s.s. column coated with SF 96 Igepal CO 880 (95/5). Isothermal at 30 °C for 10 min, programmed 1.5 °C/min to 130 °C.

Table II. Mass Spectral Data of Sesquiterpenes Found in Beaufort Cheese

GC peak no.		M
100	81 (100), 55 (93), 41 (81), 95 (60), 69 (58), 93 (55), 67 (42), 29 (39), 82 (29), 107 (27)	206
101	105 (100), 119 (94), 161 (76), 41 (71), 93 (56), 81 (53), 204 (41), 55 (39), 91 (37), 69 (35)	204 (41)
104	69 (100), 81 (69), 41 (63), 95 (35), 55 (33), 82 (19), 67 (18), 163 (15), 123 (14), 29 (12)	206 (3)
105	69 (100), 41 (96), 93 (81), 133 (57), 79 (53), 91 (50), 81 (47), 55 (42), 105 (39), 161 (36)	204 (15)
106	69 (100), 41 (92), 82 (75), 109 (50), 55 (46), 95 (35), 67 (32), 83 (28), 123 (25), 208 (20)	208 (20)
107	93 (100), 69 (34), 41 (69), 80 (38), 81 (31), 121 (26), 55 (23), 67 (21), 95 (20), 107 (18)	204 (7)
108	69 (100), 41 (68), 81 (40), 191 (28), 95 (22), 55 (20), 135 (17), 93 (16), 69 (15), 39 (11)	206 (7)
110	109 (100), 95 (86), 96 (81), 55 (76), 81 (72), 69 (68), 41 (67), 83 (65), 165 (62)	208 (47)
111	163 (100), 41 (76), 81 (68), 55 (64), 69 (59), 107 (43), 121 (39), 93 (34), 95 (28)	206 (15)

Sulfur compounds were analyzed by a head space technique (Qvist and von Sydow, 1974) on a column made according to Jansen et al. (1971).

RESULTS AND DISCUSSION

Table I summarizes the compounds identified by the different methods. Numbers refer to the peaks illustrated in Figure 1, which shows a typical chromatogram of a Freon 11 extract from a summer cheese, and in Figure 2, which shows a chromatogram of the more volatile sulfur compounds.

Many of the positively or tentatively identified components have not been previously reported in Swiss cheese. However, most of them have already been found in other cheeses or fermented dairy products.

2-Alkanones, 2-alkanols, and esters are related to fat lipolysis, being formed by further degradation of free fatty acids. The importance of alcohols has often been underestimated as the lower homologues are relatively flavorless, but as the carbon chain increases, the flavor becomes stronger; 2-heptanol and 2-nonanol, present here in quite large quantities, have thresholds of the same order as the corresponding methyl ketones from which they are derived by reduction. The presence of esters other than methyl or ethyl should be mentioned since their absence in Swiss cheese has been pointed out by Langsrud and Reinbold (1973). Their presence here could be a direct consequence of the lengthy ripening period. Lipid oxidation can explain the presence of 1-alkanols, long-chain alkanals, alkyl hydrocarbons, and also of 1-octen-3-ol, which here has only been identified in the rind.

Others components can be considered as metabolites of the smear bacteria. This is especially true for 3-octanone and acetophenone which, already present in the bacterial suspension, are more abundant in the outer part of cheese than in the core.

The same thing happens for most of the sulfur components and particularly for methanethiol which is the most abundant. Methanethiol stands at a very high level in the bacterial suspension, the population of which mainly

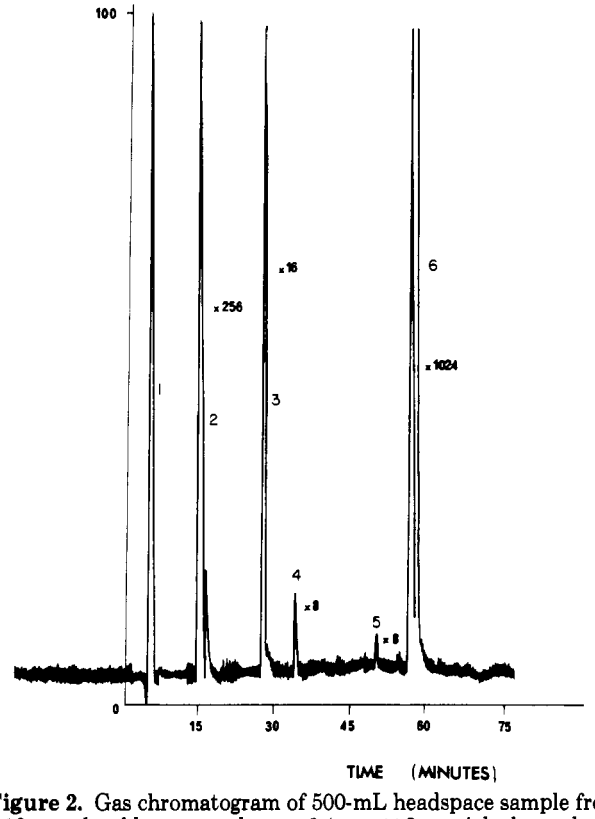

Figure 2. Gas chromatogram of 500-mL headspace sample from a 18-months old summer cheese: 6.4 mm × 2 mm i.d. glass column 5% Igepal CO 630 on Chromosorb G, AW, DMCS 80–100 mesh. Isothermal at 10 °C for 15 min programmed 4 °C/min to 110 °C. Flame photometric detector. Cheese sample, 25 g of the 5-mm thick zone taken under the rind; flask equilibration, 30 min at 30 °C.

consists of coryneform bacteria; when matured for a longer period (up to 18 months), cheeses present higher levels in the core. It can be reminded that methanethiol is not present in Swiss cheese. The variation of D.M.D.S. is similar to that of methanethiol, the former resulting from oxidation of the latter.

Methyl sulfide shows the inverse pattern, being more abundant in the core than toward the outside. Its level varies but little with the length of the ripening period. Methyl sulfide is less abundant than in Swiss cheese as it originates in Propionibacteria, the growth of which is depressed by the low ripening temperature. The presence of methanethiol acetate has been described, with its higher homologues, in surface ripened cheese (Dumont et al., 1976) but never in Swiss cheese.

The third origin of the components is to be found in the diet of the cows. This applies to monoterpenes and sesquiterpenes. The presence of monoterpenes is not unusual in itself as pinenes have been identified together with camphene and limonene in Cheddar (Liebich et al., 1970) and together with limonene in surface ripened cheese (Dumont et al., 1976). Sesquiterpenes, however, have never previously been reported in any dairy product. Mass fragmentation of these compounds is indicated in Table II but for most of them no positive identification was possible. These compounds are not present or present in much smaller quantities in cheeses made from winter milk at a period when the cows are stable-fed mainly on lowland hay; they are always present and evenly distributed in the different parts of the cheeses made from summer milk. This, together with the fact that these components have never been described in any similar type of cheeses, make the assumption of a contamination by the wooden shelves on which the cheeses lie during the ripening very unlikely. Furthermore, as the length of ripening has no effect on the level of sesquiterpenes in cheese, the assumption of a microbiological synthesis in the cheese can be eliminated. Thus, all of this gives weight to the hypothesis of an origin through the diet whether these compounds result from rumen microflora metabolism or, more likely, originate from the grass itself. In this case it does not seem that these sesquiterpenes are able to pass from the grass to the milk via the respiratory track as has been demonstrated by many authors (Honkanen et al., 1964; Gordon and Morgan, 1972; Morgan and Pereira, 1962; Shipe et al., 1962; Woods and Aurand, 1963) for very volatile components; intestinal absorption would be then involved.

The presence of sesquiterpenes in the cheeses made at a definite period of the year only gives support to the assumption already put forward, although without any demonstration, by Langsrud and Reinbold (1973) to explain, by the influence of the diet, the finding of α-pinene in Swiss cheese (Langler et al., 1967), and it shows that seasonal or geographical variation of the diet can be traced through the transformed product. Cheeses made with milk from cows on high-altitude pasture are consistently recognized by the experts and the cheese makers as having much more desirable aroma and are graded accordingly. However, that does not bring any definite evidence linking the presence of sesquiterpenes with the distinct aroma exhibited by summer cheeses. Further investigation, including addition of sesquiterpenes to winter milk and studies of the flavor properties of the resulting cheeses, is necessary to come to a definite conclusion.

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