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AROMA VOLATILES OF *CYNARA SCOLYMUS* AND *HELIANTHUS TUBEROSUS*

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Key Word Index—*Cynara scolymus*; Globe artichoke; *Helianthus tuberosus*; Jerusalem artichoke; Compositae, aroma volatiles.

Abstract—Samples of the aroma volatiles of globe artichoke and Jerusalem artichoke were obtained by well established methods and were analysed by routine GC and GC/MS. Eight sesquiterpene hydrocarbons afforded the major group of components (over 42%) in globe artichoke samples, with β-selinene (*ca* 32%) as the main constituent. Previously reported caryophyllene could not be detected. α-Cedrene was found to have globe artichoke aroma characteristics on odour evaluation of separated components at an odour port at the exit of the GC column. Jerusalem artichoke samples contained one major component (β-bisabolene, *ca* 51%) and a range of saturated long-chain hydrocarbons (*ca* 22%). The sesquiterpene presumably contributes appreciably to the characteristic flavour of Jerusalem artichoke. Both types of artichoke gave a low concentration of total volatiles.

INTRODUCTION

Until recently no detailed study had been carried out to determine the nature of the important flavour components of either the globe or Jerusalem artichokes, but in 1978 Buttery *et al.* reported the first investigation of globe artichoke [1]. However, no such work has previously been performed on Jerusalem artichoke (*Helianthus tuberosus* L.) and here we describe the first analysis of its volatile aroma components. In addition, a further examination of globe artichoke (*Cynara scolymus* L.) was undertaken and the results are also presented here.

RESULTS AND DISCUSSION

Extracts of the aroma volatiles of both globe artichoke and Jerusalem artichoke were obtained using standard procedures [2, 3]. With Jerusalem artichoke it was necessary to pool the products from four such extractions in order to obtain sufficiently concentrated samples. Extracts possessed aroma characteristics of the respective cooked artichokes, but since in both cases the residues after extraction still exhibited noticeable aroma, it cannot be claimed that complete quantitative extraction was achieved. Extracts were concentrated by low temperature–high vacuum distillation [3] and the resultant essences retained the genuine aromas of the extracts. Essences were examined by conventional GC and constituents were identified as far as possible by GC/MS, using both EI and CI techniques. Odour qualities of the separated components were assessed at a GC odour port by three assessors.

Table 1 lists the volatile components of globe artichoke, together with GC retention data, quantitative data and odour qualities of the GC peaks. Table 2 lists similar data for Jerusalem artichoke. Some general comments apply to both sets of results. In all instances where positive identities are quoted, mass spectra of sample components agree well with those in the literature [4–6] within instrumental variability. Literature [4, 7] Kováts retention indices are given for some important components, and these serve as limited supportive evidence of identity. Where no odour quality is given in the tables this means that none could be detected.

Table 1 shows that 54 main components were detected in the essence of globe artichoke, of which 28 (comprising over 89% of the sample) have been positively identified. A further four (*ca* 7.5%) were partially or tentatively characterized, leaving 22 unknown constituents (3% of the essence). Sesquiterpene hydrocarbons afforded the major group of components (over 42%) and all eight were positively identified. It is well known that mass spectra of sesquiterpene hydrocarbons are not always entirely diagnostic, but in this instance the eight spectra were quite different and agreed particularly well with the literature [5, 6]. In order to be certain, however, Kováts indices of all GC peaks of sesquiterpene hydrocarbons were measured accurately at 165° column temperature and compared with published data [7]. In all cases agreement was excellent (within ± 0.5%), thus confirming mass spectral assignments. The major sesquiterpenes of globe artichoke were thus found to be β-selinene (*ca* 32%), β-elemene (*ca* 5%) and α-cedrene (*ca* 3%). Buttery *et al.*, in their analysis of globe artichoke volatiles, detected β-selinene (40%), caryophyllene (19%) and humulene (1%) [1]. Whilst our data agree well for β-selinene and humulene (0.7%), we did not detect any caryophyllene, even though a particular search was made for this compound, which has the same Kováts index as calarene [7]. Our identification of

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Table 1. Volatile flavour components of globe artichoke (*Cynara scolymus* L.)

Peak no.	Component	R_t (min)	Kováts index (literature)*	% rel. abundance	μg/kg edible part	Odour quality
1	Unknown	1.0	—	0.2	< 0.1	—
2	Unknown	1.2	—	tr	tr	—
3	Chloroform	2.0	—	0.8	0.2	Sweetcorn
4	Unknown	2.1	—	0.3	0.1	
5	Dimethylcyclohexane	2.6	—	0.7	0.2	—
6	Unknown	3.2	—	0.1	< 0.1	—
7	Unknown	3.6	—	0.1	< 0.1	—
8	Unknown	4.0	—	0.1	< 0.1	—
9	Unknown	4.4	—	tr	tr	—
10	Unknown	4.9	—	tr	tr	—
11	Ethylcyclohexane	5.4	—	0.3	0.1	—
12	Dichloromethane	6.2	850	0.2	< 0.1	—
13	Benzene	7.0	—	tr	tr	—
14	Pentanal	8.0	1002	tr	tr	—
15	Toluene	8.7	—	0.5	0.1	Solvent-like
16	Unknown	9.1	—	tr	tr	—
17	Hexanal	9.4	1084	1.2	0.3	Sweaty
18	Unknown	10.0	—	tr	tr	Diacetyl-like, buttery
19	*m*- and/or *p*-Xylene	10.9	1150	0.1	< 0.1	—
20	Pyridine	11.4	1180	0.1	< 0.1	Rancid, burnt
21	Unknown	11.6	—	tr	tr	
22	*o*-Xylene	11.8	1191	0.2	< 0.1	Caramel, toffee-like
23	*trans*-Hex-2-enal	12.2	1207	0.8	0.2	Green grass
24	Limonene	12.6	1206	0.1	< 0.1	Sweet, fruity, floral
25	Unknown	13.4	—	tr	tr	—
26	Hexan-1-ol	13.9	1316	0.5	0.1	Green, parsley, fruity
27	Unknown	14.2	—	tr	tr	—
28	*cis*-Hex-3-en-1-ol	14.5	1351	0.1	< 0.1	Green, sweet
29	*trans*-Hex-2-en-1-ol	14.8	1368	0.9	0.2	
30	Unknown	15.2	—	0.1	< 0.1	Unpleasant
31	Terpene	15.4	—	tr	tr	—
32	2-Furfural	15.8	1449	0.1	< 0.1	Caramel, roasted
33	Unknown	16.5	—	0.1	< 0.1	—
34	Unknown	17.1	—	0.1	< 0.1	—
35	Aliphatic hydrocarbon	17.8	—	0.1	< 0.1	Sweet
36	α-Cedrene	18.2	1598	3.4	0.7	Globe artichoke
37	Longifolene	18.9	1600	1.5	0.3	Musty, mouldy
38	Calarene	19.8	1618	0.1	< 0.1	Smoky
39	β-Elemene	20.3	—	4.8	1.1	Floral, hyacinth, fragrant
40	Phenylacetaldehyde	21.3	1646	12.9	2.8	
41	Unknown	22.0	—	0.1	< 0.1	—
42	ϵ-Muurolene	23.2	1676	0.1	< 0.1	Globe artichoke
43	α-Humulene	23.8	1681	0.7	0.2	Globe artichoke, slightly peppery
44	Valencene	25.3	1726	0.3	0.1	Sweet, solvent-like
45	β-Selinene	26.2	1731	31.9	7.0	Globe artichoke, stale, dry grass, hay
46	? *cis*-Dec-3-en-1-ol	28.2	(1765)	4.3	1.0	Sweet, sickly, oily
47	Unknown	30.3	—	0.2	< 0.1	—
48	Benzyl alcohol	32.0	1822	27.1	5.9	Floral, fragrant
49	2-Phenylethanol	33.8	1859	0.2	< 0.1	Floral, fragrant
50	Unknown	35.6	—	0.3	0.1	Floral, fragrant
51	Terpene	43.7	—	3.1	0.7	—
52	Unknown	46.4	—	0.4	0.1	—
53	Unknown	49.6	—	0.2	< 0.1	—
54	Unknown	51.4	—	0.7	0.2	—

*Literature = [4, 7].
tr = trace.

Table 2. Volatile flavour components of Jerusalem artichoke (*Helianthus tuberosus* L.)

Peak no.	Component	R_t (min)	Kováts index (literature)*	% rel. abundance	μg/kg edible part	Odour quality
1	Unknown	4.9	—	0.1	0.01	—
2	Carbon tetrachloride	5.6	—	0.4	0.02	Chemical solvent
3	Unknown	6.7	—	0.1	0.01	Dry hay
4	Unknown	7.0	—	tr	tr	—
5	Benzene	8.2	—	2.8	0.14	—
6	Diacetyl	8.6	963	0.6	0.03	Diacetyl-like, buttery
7	Toluene	9.1	—	0.2	0.01	Toffee-like
8	Vinylcyclohexene	9.4	—	tr	tr	Buttery
9	Unknown	10.2	—	0.7	0.04	—
10	Hexanal	11.1	1084	0.8	0.04	Green grass, hexanal
11	*m*- and/or *p*-Xylene	11.8	1145	1.1	0.05	—
12	Unknown	12.4	—	tr	tr	Cake batter
13	Unknown	12.9	—	0.2	0.01	Sweet
14	Pentylfuran	13.2	1229	0.4	0.02	Nuts
15	Pyridine	13.7	1180	0.1	0.01	Pyridine-like
16	Hexan-1-ol	14.0	1316	0.6	0.03	Oily, fatty, hexanol
17	Anisole	14.5	1327	1.6	0.08	Sweet, fragrant
18	Unknown	15.4	—	tr	tr	Roast almonds
19	Unknown	15.6	—	0.2	0.01	Jerusalem artichoke
20	Furfural	16.2	1449	1.9	0.10	Nutty
21	Unknown	16.8	—	2.1	0.10	—
22	Unknown	17.5	—	tr	tr	—
23	Unknown	17.8	—	tr	tr	Roast almonds
24	Unknown	18.2	—	tr	tr	Roast peanuts
25	Unknown	18.5	—	0.7	0.03	Sickly, oily
26	Unknown	19.5	—	tr	tr	Fragrant, violets
27	Unknown	20.2	—	0.2	0.01	Ironing
28	Hexadecane	20.8	1600	0.3	0.02	Jerusalem artichoke
29	Propylbenzene	21.4	—	0.5	0.02	Burnt Jerusalem artichoke
30	Unknown	22.0	—	0.1	0.01	—
31	Unknown	22.6	—	0.2	0.01	Rose, geranium, fragrant
32	β-Farnesene	23.1	1678	2.5	0.13	Jasmin, fragrant
33	Heptadecane	23.8	1700	1.3	0.07	Mouldy, fatty
34	β-Bisabolene	25.0	1745	51.1	2.62	Dandelion leaves, acrid, pungent
35	Hydrocarbon	26.0	—	0.4	0.02	Sweet
36	Octadecane	27.2	1800	0.7	0.03	Mouldy, dull, meaty
37	Hydrocarbon	28.3	—	0.2	0.01	Fruity
38	Hydrocarbon	29.0	—	0.6	0.03	Apricot
39	Nonadecane	30.0	1900	2.2	0.11	Fragrant, dull
40	Hydrocarbon	32.5	—	0.8	0.04	Fruity
41	Hydrocarbon	33.6	—	1.5	0.08	Plum
42	Hydrocarbon	34.6	—	1.5	0.08	Peach
43	Eicosane	36.6	2000	3.5	0.18	Flat, dull
44	Hydrocarbon	38.0	—	1.6	0.08	Fruity, pungent
45	Hydrocarbon	40.2	—	1.4	0.07	Caramel, peach
46	Hydrocarbon	41.4	—	0.6	0.03	—
47	?C_{21} saturated hydrocarbon	44.0	—	3.8	0.20	Caramelized fruit
48	Hydrocarbon	46.0	—	tr	tr	Mouldy
49	?C_{22} saturated hydrocarbon	51.0	—	4.1	0.21	Mouldy leather
50	Hydrocarbon	52.3	—	0.3	0.02	—
51	Hydrocarbon	54.2	—	0.1	0.01	—
52	?C_{23} saturated hydrocarbon	59.0	—	5.8	0.30	Spice, sweet

*Literature = [4, 7].
tr = trace.

calarene (0.1%) was positive, the mass spectra of calarene and caryophyllene being quite different[6]. Globe artichokes from different parts of the world (possibly different cultivars) may differ to this extent, but it would be unexpected.

Other major components identified in our sample included benzyl alcohol (*ca* 27%), phenylacetaldehyde (*ca* 13%) and the tentatively characterized *cis*-dec-3-en-1-ol (*ca* 4%). The first two compounds were also detected by Buttery *et al.* but in smaller amounts (1% and 7%, respectively) [1]. Although benzyl alcohol is a common aroma volatile, it is not normally produced in such large concentrations as determined in our sample, and it may have some importance to artichoke flavour.

Buttery *et al.* [1] came to the conclusion that six of their identified compounds were particularly relevant to the aroma of cooked globe artichoke, although only one, hex-1-en-3-one, was considered to have artichoke characteristics on odour evaluation [1]. We detected only one of these six in our essence (phenylacetaldehyde), although again specific efforts were made to locate the other components and especially the hexenone. It is interesting that the higher homologue, oct-1-en-3-one, is an important constituent of mushroom volatiles and has a fresh mushroom aroma at certain concentrations [8]. This compound was also identified by Buttery *et al.* [1] in globe artichokes and they considered it to be one of the six significant components in artichoke aroma [1]. In the present work only four components, the sesquiterpenes: α-cedrene, ϵ-muurolene, α-humulene and β-selinene, were considered to have globe artichoke qualities on odour evaluation (Table 1). α-Cedrene (3.4%) is probably most important, since only traces of ϵ-muurolene were produced and the aromas of α-humulene and β-selinene were not quite so convincing. In particular, the GC peak due to the latter compound also possessed an appreciable stale dry grass quality.

The results of the analysis of Jerusalem artichoke essence are given in Table 2. Fifty-two main components were detected, of which 20 (over 72% of the sample) were positively identified. A further 15 (*ca* 23%) were partially characterized and the 17 unknown constituents comprised less than 5% of the essence. As with globe artichoke, sesquiterpene hydrocarbons were the major components (over 53%), but in this case there were only two constituents: β-farnesene (2.5%) and β-bisabolene (51.1%). The remainder of the essence was made up of a range of long-chain hydrocarbons, small amounts of common volatiles, such as benzene, xylene and furfural and the more unusual constituent, anisole (1.5%). The range of saturated, straight-chain hydrocarbons extended from hexadecane to eicosane and probably also included the C_{21}–C_{23} representatives, although molecular ions could not be detected in the mass spectra of the latter three compounds, so some doubt must exist concerning their presence in the sample. The saturated straight-chain hydrocarbons contributed nearly 22% of the sample. Evidence of a range of other hydrocarbons was also recognized in the same region of the GC trace and may represent a series of branched-chain or unsaturated homologues. However, the spectra of these components showed only alkyl fragments and no molecular ions, so they may merely represent long hydrocarbon chains attached to some other group or nucleus, although none was observed in any of these spectra.

By a considerable margin the major component, and presumably the most important, in the Jerusalem artichoke essence was β-bisabolene. However, the spectra of the major GC peak of the sample and of the other sesquiterpene peak (β-farnesene) were extremely similar—as are the spectra of authentic β-bisabolene and β-farnesene [6]. Thus considerable doubt would apply to these assignments on mass spectral evidence alone. Careful calculation of the Kováts indices of the two peaks at 165° column temperature gave values of 1678 for the minor peak and 1745 for the major peak. Accurate literature values determined under exactly the same experimental conditions are 1668 for β-farnesene and 1745.5 for β-bisabolene [7]. These data thus confirm the identities as given. β-Bisabolene is not a particularly common constituent of food volatiles, although it has been found in a wide range of plants, including carrots, citrus fruits, cinnamon, cumin, ginger, pepper and hops [9]. It would be expected that in the Jerusalem artichoke β-bisabolene would contribute appreciably to the characteristic flavour, particularly bearing in mind the identities and concentrations of other components of the essence. However, on odour evaluation of the (GC) separated components of the essence, β-bisabolene was not considered to possess characteristic Jerusalem artichoke aroma, although the described qualities are not entirely inappropriate.

Considering finally the total amounts of volatiles determined for the two vegetables, globe artichoke gave nearly 22 μg/kg whilst Jerusalem artichoke gave just over 5 μg/kg. Certainly, globe artichoke does have a stronger flavour than Jerusalem artichoke, but the difference in these two figures is relatively slight and these data do not take into account variations in odour potencies of components. However, in general terms, it can be observed that these concentrations are very low in comparison with similar data from many other foods.

EXPERIMENTAL

Artichokes were purchased fresh from local retailers as required. The 'green' variety of globe artichoke was used.

Sample preparation. (a) Globe artichoke (350 g) was chopped, mixed with H_2O (400 ml) and extracted for 3 hr in a Likens and Nickerson apparatus [2] as modified by MacLeod and Cave [3] using 2-methylbutane (25 ml) as solvent. Extracts were concd to 1.0 ml by low temp.–high vacuum distillation [3]. (b) Jerusalem artichoke (700 g), chopped in H_2O (350 ml), was similarly extracted (for 3 hr), but using trichlorofluoromethane (25 ml) as solvent. It was necessary to carry out the extraction ×4 and to pool the extracts in order to obtain a sufficiently concd sample. The extract was then further concd to 0.25 ml as before [3].

Gas chromatography. Samples were analysed by routine temp. programmed GC equipped with heated FID and a 5.5 m × 4 mm id glass column, packed with 10% Carbowax 20 M coated on 100–120 BSS mesh acid-washed Diatomite C.

Gas chromatography/mass spectrometry. Components of the essences were identified by GC/MS (both EI and CI).

Odour assessment. Aromas of separated components of the essences were assessed at an odour port following GC. An outlet splitter set at 10:1 diverted the major fraction of the eluent through a heated line to the outside of the column oven for aroma assessment by three assessors. An injection vol. of 10 μl was necessary.

Quantitative assessment. Essences were prepared in such a manner that known aliquots of artichokes were analysed. Quantitative data were derived both from the traces obtained from the TIC monitor during GC/MS and from the FID traces during routine GC. Known amounts of a selection of identified compounds (butanedione, hexanal, hexan-1-ol, phenylacetaldehyde, benzyl alcohol, anisole and hexadecane) were injected under the same analytical conditions in order to enable calculation of absolute amounts of components in the essences.

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