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VOLATILE FLAVOUR COMPONENTS OF MANGOSTEEN, *GARCINIA MANGOSTANA*

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Abstract—A representative sample of the aroma volatiles of mangosteen, a tropical fruit, was obtained using previously devised procedures. Components of the sample were identified as far as possible by GC/MS using both EIMS and CIMS. The fruit produced a relatively small quantity of aroma components (about 3 μg/kg fresh fruit), less than that obtained from similar fruits, and this partly explains its delicate flavour. The most important aroma components were hexyl acetate, *cis*-hex-3-enyl acetate and *cis*-hex-3-en-1-ol, with the two former constituents being described as having mangosteen quality on odour evaluation at an odour port during GC of the sample. Six sesquiterpenes were also identified.

INTRODUCTION

'The mangosteen is generally admitted to be one of the most attractive of tropical fruits.' [1]. It has a fugitive and delicate flavour, which is genuinely delicious but with a slightly glutinous impression. The fruit is native to Malaysia, but is widely grown in and around the Indian sub-continent. It is extremely popular locally and appeals also to the Western palate. No detailed study has yet been carried out of the nature of the volatile components responsible for the unique flavour of this fruit, and this paper describes the first such attempt.

The fruit is a berry about 3 in. in diameter produced in large numbers by a tall, but slow-growing tree. It has a tough thick red-brown or purple rind which makes up about 40–50% of the weight of the fruit. Inside, the white, edible pulp is divided into segments which contain a few large seeds. For best flavour the fruit should be consumed when fresh and perfectly ripe, which can be assessed by the firmness of the rind.

RESULTS AND DISCUSSION

An extract of mangosteen possessing the characteristic aroma of the fruit was obtained using a Likens and Nickerson apparatus [2] as modified by MacLeod and Cave [3]. The solvent used was isopentane (2-methylbutane), which has been shown previously to be suitable with similar fruits [4] and to be an efficient extractant [5]. After extraction the residue possessed no appreciable aroma. On concentration of the extract using previously described techniques [3], the resultant essence retained the genuine aroma qualities of the original extract. The essence was examined by routine temperature-programmed GLC, and constituents were then identified as far as possible by GC/MS. CIMS was useful in aiding determination of the MWs of most components, hence rendering interpretation of conventional EIMS somewhat easier.

Table 1 lists the volatile flavour components of mangosteen, together with GLC retention data, quantitative data and odour qualities of the various GLC peaks. In all instances where positive identities are given, MS of sample components agreed with those of literature spectra, within instrumental variability. All spectra have been published previously [e.g. 6, 7]. In particular, sesquiterpene spectra agreed well with those compiled by Moshonas and Lund [8]. Literature (e.g. [6, 9]) R_Is of selected important components are also included in the table. The values quoted were determined on the same stationary phase as employed in this project. These serve as limited confirmation of identity, but such retention measurements on one GLC phase are really only applicable in a negative sense, i.e. if the retention index of a suspected component is very different from that expected on the basis of the indices of positively identified components, then non-identity is proved. For example, and relevant to this work, Andersen and Falcone have shown that sesquiterpenes separated on Carbowax 20M exhibit very different R_Is at different column temperatures, and although $\Delta I/\Delta T$ approximates to 1.1 this varies with different sesquiterpenes [9]. Thus, unless one takes account of how exactly literature retention indices were determined, then their detailed predictive value is limited. The retention indices quoted in Table 1 merely confirm the general elution sequence and that the retention times are of approximately the correct order.

The quantitative data given in Table 1 show that in total only about 3 μg of aroma components were obtained per kg of fresh fruit (excluding rind). This is a very low yield and in our previous analyses of other tropical fruits using similar techniques, total amounts of aroma components obtained were about 1.2 mg/kg fresh fruit for soursop (*Anona muricata*) [4] and about 80 mg/kg for the strongly flavoured wood apple (*Feronia limonia*) [10]. These data partly explain why mangosteen flavour is so delicate and fugitive compared with some other fruits, but

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Table 1. Volatile flavour components of mangosteen fruit

Peak No.	Component	t_R (min)	Kováts index (literature)	% rel. abund.	μg/100 kg fruit	Odour quality
1	Unknown	1.2		2.56	7.53	
2	Heptane	1.5	700	1.42	4.19	
3	Branched C_8 hydrocarbon	1.7		0.21	0.63	
4	Octane	2.5	800	14.76	43.47	Rancid
5	Acetone	3.2	810	5.65	16.65	Sweet, slightly buttery
6	A dimethylcyclohexane	3.6		0.19	0.56	
7	Unknown	4.0		0.57	1.68	
8	Ethylcyclohexane	5.4		0.05	0.14	Sweaty
9	Dichloromethane	5.8		1.54	4.53	Sweaty
10	Unknown	6.8		0.05	0.14	
11	A C_6 enal	7.2		0.03	0.08	
12	Unknown	7.4		<0.01	<0.01	
13	Unknown	7.7		<0.01	<0.01	
14	Unknown	8.0		0.02	0.06	
15	A methylbutenol	8.2		4.34	12.79	Oily, linseed oil
16	Toluene	9.0		2.80	8.25	Caramel, toffee
17	Unknown	9.4		<0.01	0.01	
18	Hexanal	9.8	1084	1.24	3.64	Green, diacetyl-like
19	Unknown	10.2		0.02	0.05	Caramel
20	Unknown	10.6		<0.01	0.02	Green
21	*p*-Xylene	10.8	1140	0.07	0.20	Stale, green hay, wet leaves
22	*m*-Xylene	11.2	1147	1.16	3.43	
23	Pyridine	11.8	1180	0.04	0.13	Stale grass
24	*o*-Xylene	12.2	1191	0.52	1.54	Fruity, oily
25	*trans*-Hex-2-enal	12.5	1207	1.83	5.40	
26	Hexyl acetate	13.2	1307	7.87	23.17	Fruity, mangosteen
27	A C_5 branched enol	13.8		0.23	0.68	Fruity, caramel
28	*cis*-Hex-3-enyl acetate	14.0	1300	1.40	4.11	Mangosteen
29	Hexan-1-ol	14.2	1316	4.38	12.92	Slightly fruity
30	*cis*-Hex-3-en-1-ol	14.9	1351	27.27	80.33	Green grass, fruity, hexenol
31	Nonanal	15.7	1382	0.26	0.77	Solvent
32	Unknown	16.0		0.25	0.74	
33	Unknown	16.2		<0.01	0.01	Nuts
34	Unknown	16.6		0.15	0.43	
35	Furfural	17.0	1449	4.89	14.42	Unpleasant, caramel, metallic
36	Furfuryl methyl ketone	18.2	1491	0.87	2.57	Floral, jasmine, fragrant
37	Benzaldehyde	18.6	1502	0.01	0.03	Dry flowers
38	α-Copaene	19.4	1520	7.28	21.46	Buttery, mango
39	5-Methylfurfural	20.2	1563	1.16	3.43	Burnt
40	Unknown	21.3		0.04	0.11	Charred
41	Unknown (probably terpene)	22.1		0.03	0.08	Ironing
42	Phenylacetaldehyde	23.0	1646	1.95	5.74	Floral, hyacinth, fragrant
43	α-Terpineol	24.4	1661	0.10	0.28	Fragrant, caramel
44	Guaiene	25.2		0.07	0.20	Oily
45	Sesquiterpene (probably α-bisabolene)	26.4	(1730)	0.06	0.17	Dull fruity, fragrant
46	Valencene	28.1	1751	0.41	1.20	Caramelized orange, marmalade
47	δ-Cadinene	29.4	1761	0.39	1.14	Oily, nutty, fatty
48	γ-Cadinene (plus unknown, M = 122)	31.0	1764	1.51	4.45	Fragrant
49	Unknown	34.6		0.11	0.33	Slightly green
50	Unknown	36.1		0.04	0.13	Fruity, buttery
51	Unknown	44.3		0.27	0.80	Pine-like

they do not, of course, take into account the important factor of relative odour potencies of the flavour constituents. However, none of the identified mangosteen components has particularly low or unusual odour threshold in comparison with other typical aroma compounds.

From Table 1 it can be seen that the mangosteen essence contained 52 main components, of which 28 (comprising nearly 91% of the sample) have been positively identified with a further seven (*ca* 5%) partially

characterized. Six sesquiterpenes were present, with α-copaene being the chief representative at over 7%. All these sesquiterpenes have been identified previously in plant food systems, see e.g. [11], but from odour descriptions given in Table 1 these compounds would not appear to have particular significance with regard to the characteristic mangosteen flavour. The most important components in this respect would seem to be hexyl acetate (7.87% of the essence) and *cis*-hex-3-enyl acetate (1.40%) based on odour assessments, and *cis*-hex-3-en-1-ol (27.27%) based on the large amount produced. It is noteworthy that the two former compounds are both C_6 acetates, whilst the latter is one of the alcohols esterified. Although the other alcohol, hexan-1-ol, was also present in quite large relative amounts in the sample (4.38%), it was not considered by assessors to provide any characteristic mangosteen aroma.

All of the three compounds noted above have been found to be widely distributed in fruit aroma volatiles [11], so on the evidence presented here there would not appear to be any unique character impact compounds with regard specifically to mangosteen flavour. A mixture of these three compounds in the correct proportions and at the correct dilutions certainly did provide an aroma reminiscent of mangosteen, but it was too harsh and astringent. Presumably other compounds soften and ameliorate the sensation.

EXPERIMENTAL

Fresh, ripe mangosteen fruits were purchased in Kandy, Sri Lanka, and that day were transported by air to London to be analysed the following day.

Sample preparation. Fruit pulp (550 g) was mixed with H_2O (350 ml) and extracted for 1.5 hr in a Likens and Nickerson apparatus [2] modified as in ref. [3] using distilled (×3) 2-methylbutane (20 ml). The extraction was repeated with a fresh batch of fruit and the pooled extracts were concentrated to 0.1 ml using a low temperature–high vacuum distillation procedure [3]. The resultant essence possessed a strong aroma characteristic of the fruit.

GLC. Essences were examined by GLC using a Pye–Unicam 204 instrument equipped with heated FID. An 18 ft × 4 mm i.d. glass column packed with 10% Carbowax 20M coated on 100–120 BSS mesh acid-washed Diatomite C was used, with a carrier gas (N_2) flow-rate of 60 ml/min. The temp. programme adopted was 60° for 5 min followed by an increase at 12°/min to 180°. The detector and injection point heaters were at 250° and typically 10 μl of essence was injected. Retention times were measured from the onset of the solvent peak.

GC/MS. A Kratos MS 25 instrument was used linked on-line to a Kratos DS 50 data processing system. The same GLC conditions as described above were used but with He as carrier gas. The single-stage, all-glass jet separator was operated at 250°. EIMS: ionization potential, 70 eV; ionization current, 100 μA; source temp. 200°; accelerating voltage, 1.5 kV; resolution, 600; scan speed, 1 sec/decade (repetitive throughout run). CIMS: identical to EIMS except for the following: reagent gas, CH_4; ionization potential, 100–110 eV; emission current, 5 mA.

Quantitative assessment. Sample preparation and concentration were carried out with quantitative accuracy so that a known aliquot of the fruit sample was analysed. Quantitative data were then derived both from the trace obtained from the TIC monitor during GC/MS and from the FID trace during routine GLC. Known amounts of a selection of identified components (hexanal, hexyl acetate, *cis*-hex-3-en-1-ol and benzaldehyde) were injected under the same analytical conditions to assess the response factors of the detectors.

Odour assessment. Aromas of the sepd components of the essence were assessed at an odour port following GLC using a Pye–Unicam 104 instrument. An outlet splitter set at 10:1 diverted the major fraction of the eluent through a heated line to the outside of the oven for aroma assessment by a total of three subjects, two of whom were familiar with mangosteen flavour.

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