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Volatile Flavor Components of Beli Fruit (*Aegle marmelos*) and a Processed Product

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Representative samples of the aroma volatiles of beli—a tropical fruit—and a canned, processed product (beli cream or puree) were obtained by established procedures. Components of the essences were identified as far as possible by GC–MS using both EI and CI mass spectrometry. The major aroma component of the fruit was *cis*-linalool oxide which constituted about one-third of the total volatiles. Other important aroma compounds included alcohols and esters (saturated and unsaturated), monoterpenes, and sesquiterpenes. α-Phellandrene was the one compound described as having typical beli aroma on odor evaluation at an odor port during GC. Beli cream produced a larger total quantity of volatiles than the fruit (about 10 times) and a broader spectrum of mono- and sesquiterpenes. It was, however, lacking in a few important components. Overripe fruit contained much lesser amounts of linalool oxides and linalool and probably would not be suitable for processing purposes.

Beli (*Aegle marmelos*) is a tropical fruit native to India but commonly grown in Sri Lanka. It has always been a popular fruit with local communities due to its very pleasant and refreshing flavor, but recently it has also become an economically important commodity in Sri Lanka since it has proved possible to process the fruit to products with attractive flavor for export. The fruit is globular in shape with a smooth, hard aromatic rind. Inside is a thick mucilaginous edible pulp containing embedded seeds. The pulp is very sweet and is orange in color. It is either eaten as such or it is made into a cream (i.e., puree) or refreshing drink with sugar. To date, no detailed study has been carried out to determine the nature of the volatile aroma components responsible for the characteristic flavor of this fruit, and this paper describes the first attempt. In particular, an objective was to examine a processed, canned product (beli cream) and to compare its aroma composition with that of the fresh fruit. If any major problems or deficiencies were observed, then modifications to processing conditions could be considered in order to attempt to remedy the situation.

EXPERIMENTAL SECTION

Fresh beli fruits were transported by air from Sri Lanka such that they could be analyzed almost immediately on arrival in their ripe state. Some fruits were allowed to overripen (for about 2 weeks) before analysis. Canned beli cream (puree) was produced by the Sri Lanka Marketing Department.

Sample Preparation. Extracts (essences) of aroma components of beli fruit or cream were obtained as previously described (MacLeod and Pieris, 1981a) by using both conventional Soxhlet apparatus and the Likens and Nickerson (1964) apparatus as modified by MacLeod and Cave (1975). For the ripe fruit, 165 g of the inner pulp was used but the pulp closest to the woody rind was rejected. Similarly, 112 g of overripe fruit was extracted. Cream (175 mL) was diluted with 125 mL of water and was only extracted by means of the Likens and Nickerson apparatus. The solvent used was trichlorofluoromethane.

Sample Analysis. Concentrates were analyzed exactly as previously described (MacLeod and Pieris, 1981a), although slight variations in GC temperature programs were necessary for best resolution.

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RESULTS AND DISCUSSION

Valid aroma extracts of fresh beli fruit and canned beli cream (puree) were obtained by using previously described methods (MacLeod and Pieris, 1981a), and constituents were identified as far as possible by GC–MS. Chemical ionization mass spectrometry was useful in defining the molecular weights of many components, thus rendering interpretation of conventional electron impact spectra somewhat easier. Comparison of determined retention times of components with literature-quoted Kováts retention indexes was useful in affording some limited confirmation of mass spectral assignments. However, due to the appreciable variation in such indexes depending on the temperature of measurements and other factors, use of these values (determined on one stationary phase only) can merely be in a negative sense. In other words, if the literature retention index of a suspected component is very different from that which would be predicted from knowledge of the retention indexes of positively identified components, then the suspect identity is incorrect. Such data thus provide useful supportive, but not determinative, evidence of identity.

Table I lists the volatile flavor components of both fresh beli fruit and beli cream, together with GC retention data, quantitative data, and odor qualities of the various GC peaks. All identifications are positive by GC–MS (unless indicated by ?) and spectra of sample components agreed with those of literature spectra within instrumental variability. All spectra have been previously reported so none will be further detailed here. However, it is worth commenting that, in particular, spectra of monoterpenes and sesquiterpenes agreed well with those previously described by Ryhage and von Sydow (1963) and von Sydow (1963) (monoterpenes) and by Hirose (1967) and Moshonas and Lund (1970) (sesquiterpene hydrocarbons). Retention times quoted were measured from the onset of the solvent peak and are absolute (no internal standard was used), but agreement was good between successive runs. Literature [e.g., Andersen and Falcone (1969) and Jennings and Shibamoto (1980)] Kováts retention indexes are also given for selected important components, and it can be seen that in all instances they are of about the appropriate value and that they confirm the general elution sequence. Where no odor quality is given in Table I, this was either due to none being detected or due to a minor peak being incompletely resolved from an adjacent major peak such that no distinctly different odor could be perceived.

From Table I it can be seen that as would be expected the majority of aroma components were common to both

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Table I. Volatile Flavor Components of Fresh Beli Fruit and Beli Cream (Puree)

peak no.	component	t_R, min	Kováts index (lit.)	fruit % rel abund	fruit µg/kg of fruit	cream % rel abund	cream µg/L of cream	odor quality
1	unknown	1.4		0.49	0.15	0.004	0.015	
2	unknown	2.7		0.13	0.04	0.016	0.05	
3	acetone	4.6	810	0.89	0.27	0.014	0.05	sweet
4	ethyl acetate plus carbon tetrachloride	5.1	872	0.95	0.29	0.035	0.12	sweet, estery
5	unknown	5.6				0.02	0.07	
6	dichloromethane	5.8		2.20	0.67			buttery
7	3-methylbutanal	5.9				0.39	1.32	rancid
8	benzene	6.2		0.66	0.20			acrid
9	unknown	6.9				0.03	0.10	
10	unknown	7.4				0.008	0.03	
11	chloroform	7.9		0.26	0.08	0.003	0.01	sweet
12	1,1-dimethylprop-2-en-1-ol	8.5	~1020			4.92	16.58	candy
13	(?)pentane-2,4-dione	8.6		0.26	0.08			pleasant
14	toluene	8.8		0.52	0.16			cardboard
15	β-thujene	9.0				1.03	3.48	raspberry jam
16	(?)vinyl butanoate	9.0	1045	6.56	2.00	0.04	0.13	sweet, fruity, acetate
17	hexan-2-one	9.2	1070	0.33	0.10			cooking oil, fatty, unpleasant
18	camphene	9.8	1083	0.10	0.03			fruity, apricot
19	unknown	9.9		0.13	0.04			pleasant
20	unknown	10.0		0.10	0.03			nectarine
21	menth-2-ene	10.0				0.60	2.02	raspberry jam
22	isoamyl acetate	10.2	1110	5.12	1.56			pear drops, amyl acetate
23	*m*- or *p*-xylene	10.6	~1150	0.62	0.19	0.19	0.62	unpleasant
24	myrcene	10.9	1156			1.90	6.42	wallflowers
25	3-methylbutan-1-ol	11.0	1184	0.36	0.11			sweaty, valeric
26	α-phellandrene	11.4	1177	1.08	0.33	2.79	9.41	estery, beli
27	β-isothujene	11.6				2.08	7.02	geraniums
28	limonene	11.8	1206	0.49	0.15	17.25	58.27	sweet, floral
29	pyridine	12.1	1180	1.48	0.45			chemical lab.
30	butyl methacrylate	12.4	~1190	6.07	1.85			fatty
31	β-phellandrene	12.8	1216	0.62	0.19	2.35	7.94	fragrant, peach
32	unknown	13.2		0.69	0.21			
33	3-methylbut-2-en-1-ol	13.6	~1230	6.95	2.12	0.73	2.47	apricots
34	p-cymene	14.4	1272	1.51	0.46	0.28	0.96	estery, floral
35	α-terpinene	14.7				0.07	0.22	floral, nuts
36	*cis*-hex-3-en-1-yl acetate	14.8	1300	0.23	0.07			musty
37	(?)dimethylformamide	15.1		0.16	0.05	0.14	0.46	sweaty, fatty
38	nonanal	15.4	1382	1.51	0.46	0.07	0.26	faint musty, cardamons
39	*cis*-linalool oxide	16.6	1423	33.62	10.25	17.68	59.59	pungent, nutty, floral
40	*trans*-linalool oxide	17.3	1451	1.71	0.52	9.64	32.50	floral, musty
41	linalool	18.0	1506	0.03	0.01	5.42	18.26	lemon peel
42	unknown	18.5		0.03	0.01			cardboard
43	benzaldehyde	18.9	1502	0.03	0.01			
44	α-copaene	19.2	1520	0.07	0.02	0.05	0.18	carrots
45	a terpene	19.7				0.13	0.45	
46	(?)2-cyclohexylethyl acetate	20.1	1591	0.85	0.26	3.05	10.30	herbs, aromatic, green, floral
47	terpinen-4-ol	21.4	1628	0.89	0.27	0.11	0.36	floral, estery
48	β-elemene	21.6	~1600			0.63	2.14	nuts
49	γ-valerolactone	22.0	1617	0.03	0.01			floral
50	α-terpineol	22.0	1661			9.52	32.10	roses and nuts
51	caryophyllene	22.6	1618	1.41	0.43	13.39	45.14	aromatic, fruity, floral
52	β-farnesene	24.2	1630			0.83	2.81	sweet, floral
53	*cis*-hex-3-en-1-yl hexanoate plus ethyl benzoate	24.6	1645, 1647	1.18	0.36			sweet
54	α-humulene	25.6	1682	0.52	0.16	3.98	13.47	aromatic, floral
55	methyl phenylacetate plus γ-cadinene	27.3	1747, 1764	0.43	0.13	0.08	0.26	wallflowers
56	unknown	28.0		0.07	0.02	0.005	0.02	buttery
57	ethyl phenylacetate	29.1	1773	0.43	0.13	0.02	0.08	violets
58	octadecane	30.0	1800	0.16	0.05			
59	unknown	31.3		0.07	0.02	0.17	0.58	spicy, cloves
60	unknown	32.9		0.03	0.01			
61	benzyl alcohol	34.2	1822	1.84	0.56	0.11	0.39	floral
62	2-phenylethanol	37.0	1859	13.05	3.98			roses
63	phenylacetonitrile	40.1		1.80	0.55			
64	unknown	41.2				0.05	0.15	peaches
65	unknown	49.6		0.10	0.03	0.009	0.03	peach, clover
66	unknown	57.6		1.18	0.36	0.08	0.27	rancid

the fresh fruit and the cream, although there were some notable cases where a compound was detected in one sample only. Clearly specific efforts were made to detect any such "missing" components in a sample. In a few instances this was not possible due to a particular constituent becoming dominant and obscuring a minor component. Another reason for some qualitative differences was that the aroma components were more concentrated in the cream than in the fresh fruit, and it is possible that some components determined in the beli cream might also have been produced by the fresh fruit but were below the limits of detection (e.g, some mono- and sesquiterpenes). However, some qualitative differences must be genuine when neither of the above factors could have been operative.

The fresh fruit essence contained 54 main components of which 39 (comprising over 89% of the sample) have been positively identified with a further 4 (~8%) being partially characterized. In the latter category is a comparatively abundant constituent, peak 16 (6.56%), which was suspected to be vinyl butanoate. Although it eluted at about the correct retention time, the mass spectrum was not entirely convincing, so the identification must remain tentative. The aroma volatiles of beli cover a comparatively wide range of compound types including in particular alcohols and esters (saturated and unsaturated, aliphatic and aromatic), monoterpenes, and sesquiterpenes. The major constituent was *cis*-linalool oxide (almost certainly in the tetrahydrofuran ring form) which comprised over one-third of the essence, and this must contribute significantly to the characteristic flavor of the fruit. Other important contributors on the basis of this analysis are probably isoamyl acetate (5.12%) and 3-methylbut-2-en-1-ol (6.95%). The GC peak due to the latter possessed an appropriate odor description for beli. However, the one GC peak which was always characterised as having specifically beli aroma in all samples was that due to α-phellandrene (1.08% of the fresh fruit essence). This component can therefore reasonably be considered to be a most important contributor to the characteristic flavor, and it should be carefully retained during any processing procedure.

The total amount of aroma components produced by the fresh fruit was about 30 μg/kg. With reservations, this can be compared with figures obtained by using similar techniques for other tropical fruits. Thus soursop produced about 1.2 mg of aroma volatiles/kg of fresh fruit (MacLeod and Pieris, 1981b), the strongly flavored wood apple provided about 80 mg/kg (MacLeod and Pieris, 1981a), and only about 3 μg/kg was obtained from the very delicately flavored mangosteen (MacLeod and Pieris, 1981c). Beli fruit does indeed have a comparatively weak flavor, but these data do not, of course, take into account the relative odor potencies of the constituent aroma compounds. However, beli cream produced about 337 μg of aroma volatiles/L, and here comparison with the total volatiles from the fresh fruit is more valid. These figures suggest that the cream possessed an aroma intensity approximately 10 times that of the fresh fruit, and there is no doubt that subjectively it did have a much stronger flavor.

The detailed data for the canned beli cream in Table I show that 46 main volatile components were detected of which 32 were positively identified. These constituted over 96% of the sample, and a further four compounds (3.36%) were partially characterized. Again, one component made up the bulk of the latter group, namely, 2-cyclohexylethyl acetate (3.05%), and again, although the elution time was about right for this compound, the sample mass spectrum was not entirely convincing. As with the fresh fruit, the major aroma component of the cream was *cis*-linalool oxide (17.68%), and although in absolute terms clearly a greater amount was provided by the cream, in the more important relative terms it was less, at about half the concentration produced by the fruit. Interestingly, cream and fruit produced aproximately the same relative proportions of the linalool oxides and linalool combined. As already indicated, the cream produced a far greater proportion of monoterpenes and sesquiterpene hydrocarbons than the fruit. In particular, relatively large quantities of caryophyllene, limonene, and α-terpineol were obtained. The significant α-phellandrene, with described beli odor quality, was present in larger amounts in the cream (2.79%), and presumably it was this that at least partly ensured that the cream was, in fact, a very good representation of genuine beli flavor. However, the cream gave less 3-methylbut-2-en-1-ol and no isoamyl acetate nor butyl methacrylate, and these could be important deficiencies. The flavor of the cream certainly lacked some of the clarity and fresh notes of the fruit.

A further objective of this work was to evaluate in a commercial sense and with regard to flavor quality whether it might be possible to make use of overripe fruit for processing. Thus, a batch of the beli fruit was allowed to overripen to the stage at which it would be rejected by the average consumer. It was then analyzed as before. Detailed data are not necessary here, but in general rather more of most components was detected than had been in the fresh, ripe fruit. In particular, camphene, 3-methylbutan-1-ol, α-humulene, the phenylacetate esters, benzyl alcohol, and 2-phenylethanol were produced in much larger relative amounts. In compensation, very much lesser quantitites of the linalool oxides, linalool, and isoamyl acetate were obtained. No qualitative differences were observed. On the basis of the loss of the linalool oxides and linalool, it can be deduced that the use of overripe fruit for processing would probably be undesirable from at least a flavor point of view, although the aroma of the fruit was not particularly objectionable at the stage at which it was analyzed. Thus it would seem important, and logical, to utilize fresh, ripe beli fruit for preservation purposes.

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