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VOLATILE CONSTITUENTS AND FATTY ACID COMPOSITION OF LIPIDS IN *DURIO ZIBETHINUS*

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Abstract—The predominating flavour compounds in the fruit pulp of *Durio zibethinus* were hydrogen sulfide, ethyl hydrodisulfide and several dialkyl polysulfides, particularly $(C_2H_5)_2S_n$, where $n = 2$ or 3. Ethyl acetate, 1,1-diethoxyethane and ethyl 2-methylbutanoate contribute to an additional fruity odour note. Hydrodisulfides are probably the precursors of the dialkyl sulfides. In the pericarp and seed no volatile sulfur compounds could be detected. The fatty acid composition of the lipids in pericarp, pulp and seed depended on the origin and/or harvest season of the fruit. The main components were oleic and palmitic acids or arachidic acid together with appreciable quantities of palmitoleic, stearic, linoleic and linolenic acids.

INTRODUCTION

Durio zibethinus Murr. (Bombacaceae) is indigenous throughout Southeast Asia and in Thailand, Malaysia and Indonesia it is cultivated for its fruit (durian) [1]. The ellipsoidal-shaped fruit weighs 1–3 kg and is covered by a green to yellow-brown hard, thorny skin. The pulp (arillus) of ripe fruit releases a disagreeable, pungent smell, which is intermingled with a fruity odour note, present also in the pericarp. In spite of its unpleasant smell, the soft, yellow-white pulp is cherished as a luxury food and aphrodisiac by Southeast Asiatics. The chestnut-shaped seeds are also edible. Details of the morphology, cultivation, and utilisation are given elsewhere [1–3].

Because of their many applications, durians could make an important contribution to the beverage and food industry in the Western world. However, knowledge of the nature and content of nutrients present in the fruit and of the volatile components responsible for the characteristic odour and taste is still fragmentary and contradictory [2, 4]. General information exists on the contents of proteins, fats, carbohydrates, minerals and vitamins in the pulp or seeds [2, 5–8]. In the present investigation we have attempted to characterise the fatty acid composition of the lipids, the volatile sulfur compounds and the substances responsible for the fruity odour of individual parts of the durian.

RESULTS

Fruity odour components

From the pericarp, two major compounds were separated in equal amounts by steam distillation and identified by GC–MS and ^{1}H NMR as ethyl 2-methylbutanoate and 1,1-diethoxyethane. Both substances could also be detected together with ethyl acetate in the volatiles from the durian arillus, which for concentration were trapped on a charcoal adsorbant. None of these compounds was detected in the seed. Seasonal variations in the composition of the fruity odour components were not observed.

Sulfur-containing odour compounds

By direct headspace sampling and subsequent precipitation with cadmium ions, proof was obtained that the mature arillus releases hydrogen sulfide. From unripe fruit little or no hydrogen sulfide was released. Since no mercaptides were precipitated, thiols were either absent or of minor importance. It is almost certain that the formation of hydrogen sulfide in the ripening arillus is not the result of microbiological degradation. Tissue parts, isolated from the interior of the non-injured fruit, did not yield any microorganism growth when cultured on substrates which favour hydrogen sulfide-forming species (e.g. S-S-agar). In the pericarp only traces of hydrogen sulfide were found. Presumably these originate from the arillus since no further hydrogen sulfide was evolved after degassing. The seed contained no detectable amounts of hydrogen sulfide or thiols.

Further odorous sulfur compounds, present in the volatile arillus fraction, which had been trapped on an adsorbent, were identified spectroscopically. The predominant ^{1}H NMR signals of the total adsorbent eluate could be assigned to $C_2H_5S_n$ ($n > 1$) structures. In the direct probe MS several $R-S_n$ and $R-S_n-R'$ (R, R' = H, CH_3, C_2H_5, C_3H_7, C_4H_9) series of fragment or parent ions were recorded indicating the presence of

Table 1. Fatty acid composition of lipids (in % GLC peak area)*

Fatty acid	16 : 0	16 : 1	18 : 0	18 : 1	18 : 2	18 : 3	20 : 0	Others
Pericarp	30.9	4.2	1.8	52.8	4.2	4.0	<1	2.1
Arillus	33.9	4.9	1.0	51.2	3.0	5.1	<1	0.9
Seed	26.8	8.4	3.3	38.8	5.9	3.0	<1	13.8

* Mean values from 7 fruits, relative variations up to ±20%; origin: Chandburi/spring harvest.

dialkyl polysulfides and possibly alkyl hydropolysulfides R—S_n—H($n > 1$). The most intense ions could be attributed to the ethyl and diethyl compounds, respectively. Following GLC separation, the major peaks were identified by their R_t values and by MS as diethyl disulfide, ethyl propyl disulfide, ethyl methyl trisulfide, diethyl trisulfide, ethyl propyl trisulfide, and diethyl tetrasulfide. Diethyl disulfide and trisulfide were the main components. In the pericarp and seed no dialkyl (poly-) sulfides were detected.

The release of hydrogen sulfide from the durian arillus seems to be directly correlated to the formation of dialkyl polysulfides and also to the content of alkyl hydrodisulfides. As was observed for the predominating diethyl compounds, the amounts of diethyl disulfide and trisulfide in the arillus headspace, determined by direct headspace-GLC, as well as the generation of hydrogen sulfide, increased significantly with the state of fruit maturity, as judged by the colouring of the seed coat. In contrast, fresh unripe arillus was found to contain ethyl hydrodisulfide as a major component; its concentration, however, decreased with ripening. At full maturity, or following several weeks' storage of the fruit, little or no ethyl hydrodisulfide was present.

Fatty acid composition of lipids

Preliminary TLC investigations showed the durian fruit fatty acids to be present almost exclusively as triglycerides. The fatty acid composition was determined, after re-esterification, separately for pericarp, arillus and seed as well as according to harvest season and origin. Apart from distinct differences between harvests, the fatty acid concentrations also varied up to several per cent between the individual specimens. In Tables 1 and 2 the fatty acids identified and their average compositions are given.

Oleic and palmitic acid were the main components in all parts of fruits from the spring harvest as well as in the arillus and seed of fruits from the summer harvest. Surprisingly arachidic acid predominated in the pericarp of specimens harvested in summer, and was present to a considerable extent in the seeds. Also palmitoleic, stearic, linoleic and linolenic acids were present in higher concentrations. 12 : 0, 14 : 0, 16 : 3, 20 : 1, 20 : 3, 22 : 0, and 22 : 1 fatty acids have been identified in individual fruits in amounts less than 3%.

DISCUSSION

The odour profile of the durian was essentially related to the occurrence of hydrogen sulfide, hydrodisulfides and dialkyl polysulfides, ethyl esters and 1,1-diethoxyethane. Indole derivatives, suspected to be part of the foetid odour [2], were not detected. It is remarkable that the polysulfides of the durian arillus, as well as the fruity components, are predominantly ethyl compounds, since ethyl (poly-) sulfides are relatively rare in nature and typically occur only in lower concentrations [9–11]. Fermentation processes might have contributed in the formation of part of the observed ethyl compounds, although it appears unlikely that fermentation would account for the relative high concentration of ethylpolysulfides considering the headspace-GLC results on fresh arillus. Fermentation is mainly suggested by the occurrence of 1,1-diethoxyethane, known as a constituent of alcoholic beverages [12]. However, ethanol, which was found to be a major constituent in the fruit investigated by Baldry *et al.* [4], acetaldehyde [4] and acetic acid were not detected. Apart from the fact that the formation of 1,1-diethoxyethane from ethanol and acetaldehyde might have been favoured by acid catalysis [12], incomplete isolation of highly polar substances by the analytical procedures used cannot be excluded. Methyl-, propyl- and butyl-groups, occurring in the dialkyl (poly-) sulfides from, for example, onions, leek, garlic, or horseradish, seem to be of less importance in durians. Unsaturated alkyl residues (vinyl, propenyl, allyl), also frequently present in these plants, could not be detected.

Hydrodisulfides seem to be significant as intermediates in the biochemistry of the durian. Our investigations performed with the diethyl polysulfides suggest that the hydrogen sulfide generation, particularly

Table 2. Fatty acid composition of lipids (in % GLC peak area)*

Fatty acid	16 : 0	16 : 1	18 : 0	18 : 1	18 : 2	18 : 3	20 : 0	Others
Pericarp	14.9	1.4	5.1	17.8	7.6	4.9	33.2	15.1
Arillus	31.9	6.9	1.0	51.0	3.0	5.4	<1	0.8
Seed	23.0	3.1	1.2	41.0	11.5	5.3	9.5	5.4

* Mean values from 10 fruits, relative variations up to ±20%; origin: Prajeen Rayong/summer harvest.

in fresh and ripening fruit, is to be traced back to the synthesis of dialkylpolysulfides from hydrodisulfides. Thiols are obviously not direct precursors in the formation of dialkylpolysulfides. This is in accordance with findings by Baldry *et al.* [4] on durian fruit from Singapore although these authors found thiols as the main ingredients in fruit from Kuala Lumpur.

The occurrence of arachidic acid as an essential component in the durian pericarp and seed from Prajeen Rayong (summer harvest) is rather extraordinary. Generally this fatty acid never appears in vegetable fats in concentrations exceeding 2%. The differences in the composition of the volatiles (e.g. thiols) and fatty acids in durians that we and others [4] have found may reflect botanical variations. We suspect, however, that apart from the state of ripeness of the fruit, the harvest season, origin and the method of cultivation also influence the composition of the durian constituents.

EXPERIMENTAL

Fruit material. The durians in different states of ripeness were obtained from the Thai provinces of Chandburi (spring harvest) and Prajeen Rayong (summer harvest). The investigations were carried out on fruit which had been harvested 30 hr previously. Specimens reserved for re-examinations were stored at −40°.

Sample preparations. Odorous substances for GLC analyses were collected from the headspace of 0.5 kg of fresh fruit parts at 25° after 2 hr. Prior to GC–MS and ^{1}H NMR investigation, volatiles were adsorbed on 0.3 g charcoal (ex Merck, f.d. Gas-Chromatographie) at 25° via a N_2 stream (20 ml/min) for 48 hr and subsequently eluted with 2 ml CCl_4 (ex Merck, pro analysi), followed by 2 ml CS_2 (ex Merck, pro analysi). Steam distillation from tartaric acid soln (pH 6.5) was used to isolate volatiles from the pericarp, the distillate being taken up in pentane. Total lipids from pericarp, arillus and seeds were extracted with Et_2O, re-esterified by refluxing with 5% conc H_2SO_4 in MeOH for 30 min, and the methylated fraction extracted with hexane. H_2S and thiols in the headspace gases were determined by precipitation from aq. 0.02% $CdSO_4$. The ppt. was analysed by MS for organic residues, or, after dissolution in conc HCl, CdS was reprecipitated with synthetic H_2S for gravimetric comparison.

Chromatographic and spectroscopic measurements. Identification of all major constituents was confirmed by comparing their GLC R_t, ^{1}H NMR and MS with those of authentic samples. ^{1}H NMR: 90 MHz; amb. temp.; solvents: CCl_4 or CS_2. MS: 70 eV; source temp. 150°; direct probe *ca* 50°.

GC–MS: Coupling via jet separator; total ion current detection. GC–MS of fatty acids: 4% PEG-A on Chromosorb G-AW DMCS, 2 m × 2 mm id, 36 ml He/min, 100–250° at 8°/min, injector 250°, coupling parts 180°. GC–MS of esters, acetal and S-compounds: 3% Reoplex on Chromosorb G-AW DMCS, 3 m × 2 mm id, 30 ml He/min, 60–180° at 2–8°/min or 60° isothermal, injector 190°, coupling parts 180°.

GLC of $(C_2H_5)_2S_n$: 3% Reoplex on Chromosorb G-AW DMCS 3 m × 2 mm id, 30 ml N_2/min, 100° isothermal, injector 210°, FID 290°. 4% PEG-A on Chromosorb G-AW DMCS, 2 m × 2 mm id, 30 ml N_2/min, 50–220° at 7.5°/min, injector 250°, FID 290°. Porapak Q, 1 m × 2 mm id, 105 ml N_2/min, 180° isothermal, injector and FID 240°.

GLC of $C_2H_5S_2H$: Porapak Q, 1.5 m × 2 mm id, 30 ml N_2/min, 150° isothermal, injector and FID 190°. 3% Reoplex on Chromosorb G-AW DMCS, 3 m × 2 mm id, 22 ml N_2/min, 50° or 120° isothermal, injector 150°, FID 230°.

GLC of fatty acid Me esters: 4% PEG-A on Chromosorb G-AW DMCS, 2 m × 2 mm id, 20 ml N_2/min, 120–210° at 1–4°/min, injector and FID 280°.

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