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Essential oil chemistry of some *Mangifera indica* varieties from Kenya

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Abstract

Smelling a delightful aroma can be a very pleasurable experience with potential salutary benefits. The natural aroma of the mango plant varieties is different, implying that the chemical compositions of the components are likely to be different. In this study we focused on the analysis and identification of volatile aroma components of the leaves of six mango varieties; Ngowe, Apple, Keit, Boribo, Tommy, Atkins and Van Dyke grown in Kenya in the same agro ecological area. The hydro-distilled oil from the leaves of these mango varieties were analyzed by gas chromatograph fitted with a flame ionization detector and coupled to a mass spectrometer. It was found that the chemical profile of all the six varieties were qualitatively and quantitatively different. The oils were rich in monoterpenes (46.98%), sesquiterpene (38.17%) with minor quantities of their analogues (10.67% Trace amounts of non-terpenoid hydrocarbons and oxygenated hydrocarbons accounting for 4.19% were also identified. The major components of the different leaf oil varieties varied both qualitatively and quantitatively with δ -3-Carene being the most dominant compound in Keit (19.4%), Tommy Atkins (29.2%) and Van Dyke (17.9%). Seven compounds namely; α -pinene, camphene, β -pinene, α -copaene, β -Elemene, α -Gurjunene and α -Humulene were present in significant but varying amounts (0.3-21.9%) in all the six varieties, with β -pinene being the most dominant in Boribo (21.9%). These results differ qualitatively and quantitatively with similar reported essential oil chemical compositions of the same mango varieties from other countries. This suggests that variations in climate and soils can influence the chemical composition of mango cultivars. The variations in the essential oil compositions of the mango varieties could account for the differences in the natural aroma of the mango varieties.

Keywords: Mangifera Indica, Essential Oils, Components

1. Introduction

Mango (*Mangifera indica* L) is among the most popular and best-known tropical fruits widely grown in Kenya. Over the last decade, it is the third most important fruit in Kenya with bananas (including plantains) and pineapples being the first and second respectively in terms of total production [1] Mango is also being produced in almost every tropical country, and some subtropical regions such as Florida, Egypt, and southern Latin America [2]

Two types of mangoes are grown in Kenya, the local variety, which include; Ngowe, Dodo Boribo and Batawi and the exotic or improved variety, which include; Apple, Kent, Keit, Tommy Atkins, Van Dyke, Haden, Sabre, Sabine, Pafin, Maya, Kenston and Gesine. The latter are usually grafted on local mangoes and are grown in large scale for export market [1]. Most local varieties tend to have high fiber content, commonly referred to as "stringy", and this characteristic makes them unpopular for consumption and are usually left to grow naturally without much crop husbandry [1]. Mango varieties differ in the amount and type of flavor compounds present which is dependent on their place of origin, major and minor volatile components with the later being the key player in their aroma [3]

There is vast literature on chemical analysis of the aroma of several mango cultivars around the world [4, 5] with a wide range of compounds having been identified as esters, lactones, mono- and sesquiterpenes. Monoterpene hydrocarbons such as *cis*-ocimene, α -pinene, β -pinene, myrcene and limonene have been reported as key contributors to the aroma of the fresh fruit, depending on the variety [6, 7]. Monoterpene compounds have previously been identified in the flavor profile of Tommy Atkins [8].

The aroma is one of the significant and decisive parameters of quality in the selection of a product. Aroma compounds are present in raw foods in free volatile form and also as non-volatile precursors such as substituted cystein sulfoxides, thioglycosides, glycosides, carotenoids and cinnamic acid derivatives [9] The sugar moieties of glycosidically-bound

aroma volatiles, which have been reported in mango, are α -terpenyl- β -D-glucopyranosides, α -terpenyl-6-o-rutinosides and α -terpenyl-6-o-(α -L-arabinofuranosyl)- β -D-glucopyranosides. Aroma compounds (aglycones) can be released from glycosidically-bound compounds by enzymatic or chemical reactions during maturation, storage, industrial pretreatment/processing [10]. The different proportions of volatile components and the presence or absence of trace components often determine aroma properties [11].

In this work, we present the leaf essential oil composition of six mango varieties; Ngowe, Apple, Keit, Boribo, Tommy, Atkins and Van Dyke grown in Kenya. Prior to this study, there have been no phytochemical investigations of these varieties of Mango plant in Kenya, and this is the first report on their essential oil composition.

2. Materials and Methods

2.1. Plant Material

The Tommy Atkins, Apple, Van dyke, Boribo, Keit and Ngowe leaves of *M. indica* L. were collected from mango farms at Cheptebo, Kerio Valley in Kenya. The leaves of each variety, approximately 5 months old were picked and kept under shade for hydro-distillation while still fresh.

2.2. Extraction of Essential Oils

The leaf Essential oils of the mango varieties were extracted through hydro-distillation of the fresh leaves (750 g of each variety) using a Dean-Stark apparatus [12], with some modification. The procedure was repeated for samples that had poor oil yields to allow collection of reasonable amounts of oils. The wet extracts were dried using anhydrous Na_2SO_4 and stored in amber vials in a refrigerator.

2.3 Gas Chromatographic – Mass Spectral Analysis of oils

Qualitative and quantitative analyses of the oils were

performed using GC-FID and GC-MS. The GC-FID analysis of the oils was carried out on a GC HP-5890 II apparatus, equipped with split-less injector, attached to HP-5 column (25 m x 0.32 mm, 0.52 mm film thickness) and fitted to FID. Carrier gas (He) flow rate was 1 mL/min, split ratio 1:30, injector temperature was 250°C, detector temperature 270°C, while column temperature was linearly programmed from 40–240°C (at rate of 5°C/min). The same analytical conditions were employed for GC/MS analysis, where HP G 1800C Series II GCD system equipped with HP-5MS column (30 m x 0.25 mm, 0.25 mm film thickness) was used. Transfer line was heated at 270°C. Mass spectra were acquired in EI mode (70 eV), in m/z range 40–400 a.m.u, scan time 1.5 s with the filament solvent delay time set at 3 min. Identification of oil components was achieved on the basis of their retention indices (RI) (determined with reference to a homologous series of normal alkanes), and by comparison of their mass spectral fragmentation patterns with those reported in the literature and stored on the MS library (NIST/NBS and Wiley 275.1 database) using a computer search and literature [13, 14, 15]. For the purpose of quantitative analysis known amount of 1-heptene was added to each of the oils as an internal standard (IS). The area percent data obtained for the IS by GC-FID directly correlated with the amount of standard injected in the GC-MS equipment. From that correlation the amounts represented by the percent area of the other peaks were then easily computed.

3. Results and Discussion

The leaf essential oil composition of the six varieties of *Mangifera indica* oils is shown in the GC-MS total ion chromatograms (Figures 1-6) and the Chemical components are summarized in Table 1.

Table 1: Chemical constituents of the Mango Varieties

Peak	RI	Compound	NG	AP	KE	BO	TA	VD
1	852	3Z- Hexenol	—	0.4	—	—	—	—
2	860	1,3-dimethyl-Benzene,	—	—	—	—	—	0.9
3	936	α -pinene	5.8	10.3	2.4	10.9	24.5	18.0
4	948	Camphene	0.3	0.8	0.5	1.7	0.5	0.8
5	976	β -pinene	7.7	6.8	1.9	21.9	2.9	4.3
6	1000	δ -2-Carene	—	0.6	—	—	—	—
7	1005	α -phellandrene	—	3.7	—	—	—	—
8	1008	δ -3- Carene	—	—	19.4	—	29.2	17.9
9	1024	Limonene	—	—	1.0	1.8	—	—
10	1025	Sylvestrene	—	—	—	—	—	2.5
11	1028	β -Phellandrene	4.9	12.1	—	—	2.7	—
12	1044	β -E Ocimene	—	0.5	—	—	—	—
13	1060	Not identified	—	—	—	0.5	—	—
14	1087	Terpinolene	—	—	0.6	—	1.4	0.9
15	1090	p-Cymenene	—	0.7	—	—	—	—
16	1100	3-(4-methyl-3-pentenyl)- Furan	0.8	—	—	1.8	—	—
17	1136	trans-Pinocarveol	—	—	—	0.4	—	—
18	1150	Not identified	—	—	—	—	—	3.8
19	1176	Terpinen-4-ol	—	1.1	0.6	0.5	0.4	—
20	1184	Cryptone	2.8	—	—	—	—	—
21	1188	α -Terpineol	—	1.3	0.6	1.0	0.3	—
22	1195	Myrtenal	—	—	—	0.5	—	—
23	1300	3Z-Hexenyl valerate	—	1.1	—	—	—	—
24	1308	Not identified	—	—	—	—	—	0.8
25	1314	4-hydroxy-Cryptone	0.7	—	—	—	—	—

26	1326	Not identified	—	3.1	1	—	—	—
27	1374	α -Copaene	1.8	1.5	4.9	1.2	1.4	1.5
28	1389	β -Elemene	1.4	1.5	4.1	1.6	0.4	0.9
29	1409	α -Gurjunene	4.2	9.7	17.4	8.7	10.3	16.7
30	1417	E-Caryophyllene	—	—	—	—	2.2	3.7
31	1452	α -Humulene	3.4	2.6	2.7	2.5	1.3	3.9
32	1454	α -Patchoulene	—	—	—	1.9	—	—
33	1458	allo-Aromadendrene	—	3.1	—	2.7	—	—
34	1460	Unknown	—	—	—	0.8	—	—
35	1475	γ -Gurjunene	—	2.4	—	—	—	—
36	1478	γ -Murolene	0.9	—	3.0	—	0.6	0.7
37	1484	Germacrene D	—	1.8	5.3	—	—	0.6
38	1489	β -Selinene	2.0	—	—	1.0	3.0	9.9
39	1494	Valencene	4.3	—	—	—	—	—
40	1496	Viridiflorene	—	—	7.7	2.9	2.2	6.0
41	1500	Bicyclogermacrene	—	1.6	—	—	—	—
42	1520	δ -Cadinene	—	8.4	—	—	0.3	—
43	1521	Not identified	—	—	3.1	—	—	—
44	1523	<i>trans</i> -Calamenene	—	—	—	1.0	—	—
45	1525	Not identified	2.0	—	—	—	—	—
46	1528	<i>cis</i> -Calamenene	1.6	—	—	—	—	—
47	1577	Spathulenol	14.8	—	3.5	—	—	—
48	1602	Ledol	—	1.9	—	—	—	—
49	1608	Humulene epoxide II	—	—	—	3.3	—	—
50	1642	4-Allyloxyimino-2-carene	—	2.2	—	4.6	—	—
51	1650	Not identified	2.2	—	—	—	—	—
52	1663	Not identified	—	—	1.2	—	—	—
53	1672	Not identified	2.4	—	—	—	—	—
54	1700	Heptadecane	3.8	—	—	—	—	—
55	1768	13-hydroxy-Valencene	—	—	—	4.6	—	—
56	1774	epi-Cyclocolorenone	—	—	0.6	1.4	—	—
57	1880	Not identified	—	—	0.9	—	—	—
48	1898	Nonadecane	3.9	—	—	—	—	—
49	1925	Not identified	—	—	—	0.9	—	—
60	2000	Not identified	3.1	—	—	—	—	—
61	2100	Heneicosane	2.3	—	—	—	—	—
62	2200	Docosane	1.4	—	—	—	—	—
63	2400	Tetracosane	0.5	—	—	—	—	—

Key: NG-Ngowe; AP-Apple; KE-Keit; BO-Boribo; TA-Tommy Atkins; VD-Van Dyke
— Absent

From the table, it was established that the most abundant class of compounds from oils of the six varieties were non oxygenated monoterpenes and sesquiterpenes, which accounted for 46.98% and 38.17%, respectively, of all the identified constituents. The other classes of compounds

included oxygenated monoterpenes (3.50%), Oxygenated sesquiterpenes (7.17%), non-terpenoid hydrocarbons (2.71%) and non-terpenoid oxygenated hydrocarbons (1.48%) as summarized in Table 2.

Table 2: Summary of the Components

Class	% Composition						Total	%Total
	NG	AP	KE	BO	TA	VD		
Monoterpenes	18.7	35.5	25.8	36.7	61.2	44.4	222.3	46.98
Sesquiterpenes	19.6	29.5	45.1	20.8	21.7	43.9	180.6	38.17
oxygenated monoterpenes	3.5	4.6	1.2	6.6	0.7	0.0	16.6	3.50
Oxygenated sesquiterpenes	14.8	5.0	3.5	10.6	0.0	0.0	33.9	7.17
Non-terpenoid hydrocarbons	11.9	0.0	0.0	0.0	0.0	0.9	12.8	2.71
Non-terpenoid oxygenated hydrocarbons	0.8	1.5	0.6	4.1	0.0	0.0	7.0	1.48
Total	69.3	76.1	76.2	78.8	83.6	89.2	473.2	100.00

Key: NG-Ngowe; AP-Apple; KE-Keit; BO-Boribo; TA-Tommy Atkins; VD-Van Dyke

A total of fifty different compounds were identified in the oils of the six mango varieties. Although some compounds were common in all or some of the six varieties, there were some differences in the individual composition in each variety. In

the Ngowe oil, twenty two compounds were identified (69.3% of total oil). The main components were Spathulenol (14.8%), β -pinene (7.7%), α -pinene (5.8%) and β -Phellandrene (4.9%) as shown in figure 1 & table1.

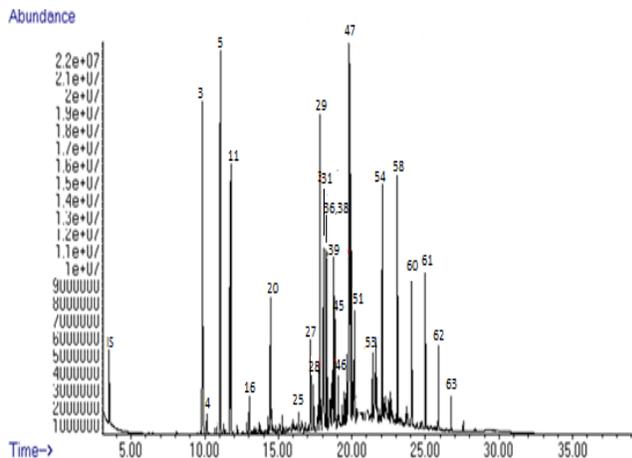


Fig 1: Representative total ion chromatogram of Ngowe variety

Twenty three compounds were identified in Apple oil, which represented 76.1 % of total oil. The major compounds in the Apple oil were β -Phellandrene (12.1%), α -pinene (10.3%), α -Gurjunene (9.7%) and δ -Cadinene (8.4%) as indicated in figure 2 & table 1.

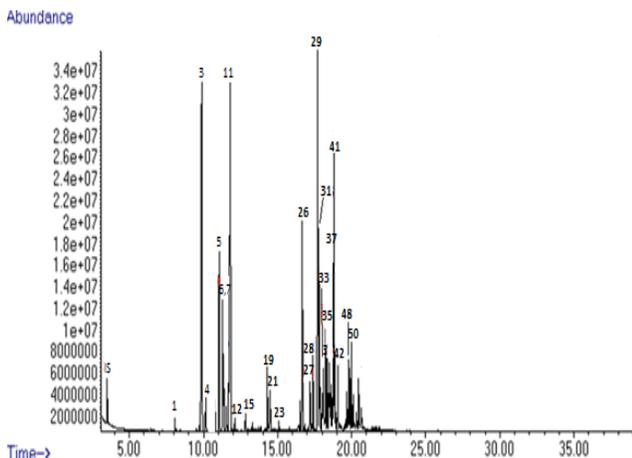


Fig 2: Representative total ion chromatogram of Apple variety

Keit had a total of seventeen compounds identified comprising 76.2% of total oil as summarized by figure 3 & table 1. The major compounds were δ -3- Carene (19.4%), α -Gurjunene (17.4%), Viridiflorene (7.7%) and Germacrene D (5.3%).

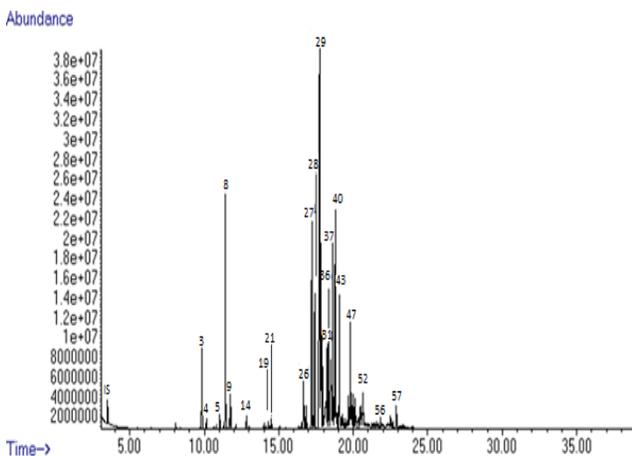


Fig 3: Representative total ion chromatogram of Keit variety

In Boribo a total of twenty three compounds were identified (78.8% of total oil). The major compounds were β -pinene (21.9%), α -pinene (10.9%), α -Gurjunene (8.7%), 4-Allyloxyimino-2-carene (4.6%) and 13-hydroxy Valencene (4.6%) as shown in figure 4 & table1.

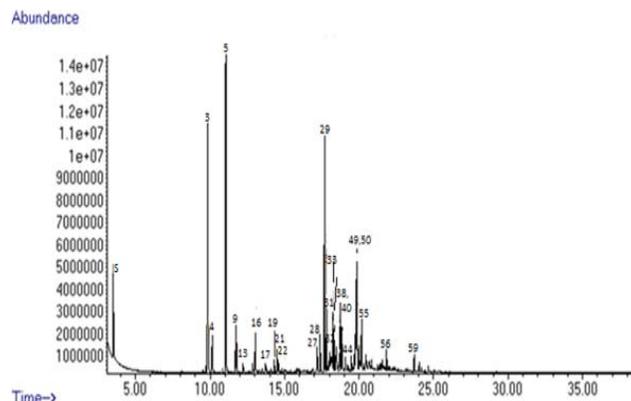


Fig 4: Representative total ion chromatogram of Boribo variety

Seventeen compounds were identified in Tommy Atkins comprising 83.6% of the total oil as indicated in figure 5 & table 1. The major compounds were δ -3- Carene (29.2%), α -pinene (24.5%), α -Gurjunene (10.3%) and β -Selinene (3.0%).

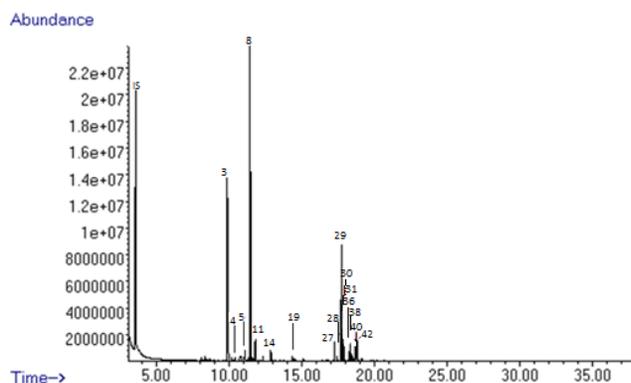


Fig 5: Representative total ion chromatogram of Tommy Atkins variety

In Van Dyke oil a total of sixteen compounds were identified which comprised 89.2% of the total oil, which are summarized in figure 6 and table1. Of these the major ones were α -pinene (18.0%), δ -3- Carene (17.9%), α -Gurjunene (16.7%) and β -Selinene (9.9%).

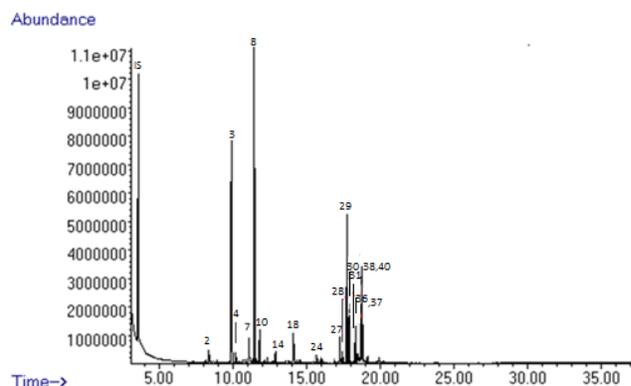


Fig 6: Representative total ion chromatogram of Van Dyke variety

Compounds present in significant but varying amounts (0.3-21.9%) in all the six varieties were α -pinene (Peak 3), Camphene (Peak 4), β -pinene (Peak 5), α -Copaene (Peak 27), β -Elemene (Peak 28), α -Gurjunene (Peak 29) and α -Humulene (Peak 31). The typical mango-like odor is due to presence of α -copaene which has also been found as a minor component in a number of fruits, including citrus, guava, litchi, and peach [5, 16, 17]. The Egyptian Mango has also been recently reported to contain α -copaene [18].

In general, the chemical profiles of all the six varieties were qualitatively and quantitatively different (Table 1). The δ -3-carene, which was identified in Keit, Tommy Atkins and Van Dyke as a major compound, has also been reported previously as a major leaf oil constituent of mango [19, 20]. It has been found to be among other important terpenes contributing to mango flavor [21-24]. Similar results were also reported in cultivars from Sao Paulo [25] Cuba [26], Venezuela [25], Brazil [27] Colombia [28] and Indian cultivar [29].

Non-terpenoid compounds, the aliphatic compounds and their esters were also detected in the Kenyan varieties in trace quantities and especially in the hydro-distilled Ngowe variety leaf oil. These compounds have been reported as the dominant aroma principles in different fruit cultivars from Cuba though obtained by solvent extraction [30].

There are a lot of qualitative differences between the Kenyan Mango leaf oils reported in this paper and that reported from other countries. The African mango in Senegal had a sesquiterpene, eremophilene as the major constituent [22]. Two Indian mango fruit oils are characterized by β -ocimene and 2, 5-dimethyl-4-hydroxyl-3(2H)-furanone [31], α -pinene, caryophyllene oxide and humulene oxide [32]. Srilankan cultivar is dominated by β -ocimene and terpinolene [6, 31], the Egyptian cultivar by myrcene and limonene [33], the Brazilian cultivars by terpinolene [27], and Florida cultivar by terpinolene and ethyl butyrate [16]. These differences could be attributed to variations in climate and soil type.

4. Conclusions

The leaf essential oils compositions of the six *Mangifera indica* varieties are mainly rich in monoterpenes. The major chemical constituents in almost all the varieties except in Keit and Ngowe where they are not major are α -Pinene and α -gurjunene, respectively. In the leaf oils of Keit, Tommy Atkins and Van Dyke varieties δ -3-carene is the predominant chemical constituent; while Boribo leaf oil is an α - and β -Pinene chemotype. These major chemical constituents of the mango leaf oils contribute to the characteristic natural aroma of the leaves of the six varieties of *Mangifera indica*.

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