

Volatile Flavor Constituents of Fruits from Southern Africa: Mobola Plum (*Parinari curatellifolia*)

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The volatile flavor components of Mobola plum (*Parinari curatellifolia*), a native fruit of Southern Africa, have been isolated by a vacuum headspace concentration method. The concentrate was analyzed by hyphenated gas chromatographic techniques, including gas chromatography (GC)/mass spectrometry (MS) and GC/Fourier transform infrared (FTIR), together with other GC-coupled detection devices for the specific and selective detection of nitrogen- and sulfur-containing compounds. A total of 88 components were identified. Of these compounds, 12 contain nitrogen, including 2-aminobenzaldehyde and phenylacetaldoxime, which are detected for the first time in an edible fruit. In addition, two unusual nitrated compounds have been identified, including optically active (2-nitrobutyl)benzene, which is a new natural product. Quantitative and sensory data of the new compounds are provided.

KEYWORDS: Mobola plum flavor; *Parinari*; chrysobalanaceae; vacuum headspace method; GC/MS; nitro compounds

INTRODUCTION

The Mobola plum tree, *Parinari curatellifolia* Planchon ex Benth. (Chrysobalanaceae) is a large evergreen tree, which grows up to 13 m high. It is distributed along the eastern coast of South Africa and extends into the Limpopo Province. It is also found in the southern parts of Zimbabwe and is reported to grow in parts of Mozambique and Malawi. The oval (50 mm × 25 mm), russet-yellow, pitted fruits have a yellow flesh with a pleasant taste. Wild Mobola plum, or sand apple, is consumed by local people, who eat it fresh or prepared as a syrup (1). In many parts of Southern Africa, a beer is brewed from this fruit. Because the flavor of Mobola plum has not been studied so far, we report herein the study of the volatile fraction, using a sampling procedure of proven efficacy and a combination of hyphenated gas chromatographic techniques for the identification of individual components: gas chromatography/mass spectrometry (GC/MS), gas chromatography with Fourier transform infrared (GC/FTIR) detection, gas chromatography with pulsed flame photometric detection (GC/PFPD), and gas chromatography with nitrogen chemiluminescence detection (GC/NCD).

MATERIALS AND METHODS

Materials. Fresh ripe fruits were collected in October 2002 from wild-growing trees near Thohoyandu (Venda), South Africa.

Sample Preparation. The method similar to vacuum headspace (2) was used with some modifications. It involved a 4 L round bottom flask fitted with a mechanical stirrer. The aqueous distillate was precooled in a descending condenser with circulating water at 4° C, before being condensed in two successive cooling traps (dry ice–acetone). A total of 2576 g of fruit pulp (pH 6.2) was placed in the flask with 257 μ L of a 0.1% solution (w/vol) of veratrole (internal standard, 0.1 ppm), in analytical grade methylene dichloride (CH₂Cl₂). Subsequently, a vacuum was applied during 5 h (5–10 mbar) so that the internal temperature was constantly maintained at 20–23 °C. At the end of the sampling period, the aqueous distillates were pooled (ca. 500 g) and extracted with pentane/CH₂Cl₂ (51/49, w/w), and the solvent was evaporated to a final volume of ca. 50 μ L.

Quantitation. The quantitative results shown in Table 1 were determined based on the response factors of all ingredients being equal to 1 for the total extraction procedure, except in the case of 2-phenylethanol, since its content is far outside the concentration range of all of the other constituents. Its approximate concentration was determined by carrying out a model liquid/liquid extraction of a known amount of analyte with the same solvent system. The recovery rate of selected nitrogen-containing compounds during the total isolation process was determined by carrying out model experiments; phenylacetoneitrile (1.05 mg), 2-aminobenzaldehyde (0.232 mg), phenylacetaldoxime (0.752 mg), (2-nitroethyl)benzene (1.0 mg), and (2-nitrobutyl)benzene (0.942 mg) in 2.5 L of water at pH 6.2 were submitted to vacuum hydrodistillation for 2 h. Then, 0.670 mg of veratrole was added to the aqueous distillate (ca. 440 g) prior to extraction and workup as above. In a separate experiment, similar amounts of the five compounds were added in water (300 mL) containing a known amount of veratrole, and extraction was carried out as above. Recovery rates were calculated in taking into account the GC/FID response factors of the five analytes.

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Table 1. Volatile Compounds Identified in *Parinari* Fruit Flavor

compound	RI ^a	C ^b	compound	RI ^a	C ^b
esters					
methyl butyrate	315	47	isobutyl butyrate	554	tr
methyl isovalerate	411	17	butyl acetate	412	73
methyl pentanoate	423	43	butyl propionate	507	130
methyl hexanoate	523	26	butyl butyrate	595	403
methyl benzoate	688	tr	butyl 2-methylbutyrate	648	tr
ethyl acetate	200	110	butyl 3-methylbutyrate	650	59
ethyl propionate	300	292	butyl pentanoate	693	127
ethyl butyrate	400	1148	butyl hexanoate	793	tr
ethyl pentanoate	500	1407	butyl benzoate	962	tr
ethyl 2-methylbutyrate	448	88	butyl anthranilate	1213	tr
ethyl 2-methylpentanoate ^e	538	58	3-methylbutyl acetate	474	tr
ethyl hexanoate	600	433	3-methylbutyl propionate	571	112
ethyl octanoate	800	tr	3-methylbutyl butyrate	660	128
ethyl decanoate	1000	tr	3-methylbutyl anthranilate ^d	1277	tr
ethyl dodecanoate	1200	tr	benzyl benzoate	1350	10
ethyl crotonate	427	24	phenylethyl acetate	848	80
ethyl (<i>E</i>)-2-methyl-2-butenate	539	tr	phenylethyl propionate	945	174
ethyl 2-methyl-2-pentenoate	630	tr	phenylethyl butyrate	1031	987
ethyl benzoate	760	53	phenylethyl isobutyrate	996	11
ethyl phenylacetate	836	13	phenylethyl 2-methylbutyrate	1098	tr
ethyl anthranilate	1005	tr	phenylethyl 3-methylbutyrate	1100	790
diethyl phthalate ^c	1168	tr	phenylethyl pentanoate	1140	135
propyl acetate	310	38	phenylethyl (<i>E</i>)-2-methyl-2-butenate	1178	tr
propyl propionate	413	74	phenylethyl 4-methylpentanoate	1165	10
propyl isobutyrate	445	114	phenylethyl hexanoate	1233	tr
propyl 2-methylbutyrate	548	21	phenylethyl benzoate	1445	28
propyl 3-methylbutyrate	553	115	phenylethyl phenylacetate	1508	tr
propyl benzoate	860	17	3-(acetyloxy)-2-butanone	474	35
propyl anthranilate	1127	tr	3-(butanoxyloxy)-2-butanone	658	tr
alcohols					
1-butanol	238	180	1-octen-3-ol	583	17
3-methyl-1-butanol	319	77	α -terpineol	793	32
1-hexanol	466	55	2-phenylethanol	700	\approx 12 600
(<i>Z</i>)-3-hexenol	446	tr			
phenols					
2-methoxy-4-methylphenol (creosol)	781	tr	vanillin	983	tr
eugenol	949	30			
carbonyls					
(<i>E</i>)-2-hexenal	436	tr	1-phenyl-2-butanone	816	tr
benzaldehyde	543	tr	benzophenone	1217	tr
phenylacetaldehyde	630	tr	dibenzyl ketone	1344	tr
miscellaneous N and S compounds					
benzyl cyanide	719	620	quinoline	817	tr
(2-nitroethyl)benzene	866	460	benzothiazole	802	tr
(2-nitrobutyl)benzene	999	67	methyl 3-(methylthio)propionate	612	17
<i>syn</i> -phenylacetaldoxime	848	54	ethyl 2-(methylthio)acetate ^f	573	tr
<i>anti</i> -phenylacetaldoxime	865		ethyl 3-(methylthio)propionate	689	tr
2-aminobenzaldehyde	798	18	propyl 3-(methylthio)propionate	788	tr

^a Retention indices calculated relative to ethyl esters of normal chain aliphatic acids (4). ^b Approximate concentrations in $\mu\text{g}/\text{kg}$ of fresh fruit; concentrations below 10 $\mu\text{g}/\text{kg}$ are noted as tr (trace). ^c Analytical artifact. ^d Tentative identification: MS [m/z (%): 65 (33), 92 (42), 119 (100), 120 (46), 137 (51), 207 (34). ^e MS [m/z (%): 43 (75), 55 (13), 71 (55), 74 (52), 87 (12), 99 (28), 102 (100), 115 (12), 129 (1), 144 (<1). ^f Identified by GC/PFPD only.

GC/FTIR Spectroscopy. For GC/FTIR analyses, an IRD II (Bio-Rad, Cambridge, MA) equipped with a liquid nitrogen-cooled wide-band MCT detector ($4000\text{--}750\text{ cm}^{-1}$) and coupled to an Agilent 6890 gas chromatograph (Agilent, Palo Alto, CA) was used. The gas chromatograph was equipped with a CP-Sil 5CB column, $50\text{ m} \times 0.32\text{ mm ID}$, $d_f = 0.4\text{ }\mu\text{m}$ (Varian, Les Ulis, France) and operated in splitless mode (injected volume, $1\text{ }\mu\text{L}$); the injector temperature was $250\text{ }^\circ\text{C}$; the constant flow rate of the helium was $1\text{ mL}/\text{min}$. The oven temperature program was $60\text{--}280\text{ }^\circ\text{C}$ at $2\text{ }^\circ\text{C}/\text{min}$ and was held at $280\text{ }^\circ\text{C}$ for 35 min. The end of the column was connected to the inlet of the light pipe ($120\text{ mm} \times 1\text{ mm}$), heated at $280\text{ }^\circ\text{C}$ using a transfer line heated at $290\text{ }^\circ\text{C}$. Makeup gas (nitrogen, 5 psi) was added to both GC/FTIR interfaces to maintain chromatographic resolution. Gram-Schmidt chromatograms were processed with Grams/32 IRD software (Galactic, Salem, MA).

GC/MS. A Hewlett-Packard (Palo Alto, CA) 5890 series II gas chromatograph was used, equipped with a CP-Sil 5CB column, 50 m

$\times 0.32\text{ mm ID}$, $d_f = 0.4\text{ }\mu\text{m}$ (Varian), and coupled to a 5972 quadrupole mass selective detector (Hewlett-Packard). The column was operated at $1\text{ mL}/\text{min}$ helium constant flow; the temperatures of the injector and transfer line were 250 and $280\text{ }^\circ\text{C}$, respectively. The oven temperature program was $65\text{ }^\circ\text{C}$ isothermal for 10 min, raised at $5\text{ }^\circ\text{C}/\text{min}$ to $280\text{ }^\circ\text{C}$, and then isothermal at $280\text{ }^\circ\text{C}$ for 30 min.

Chiroselective GC. The chiral separation was carried out at $110\text{ }^\circ\text{C}$ (isothermal) with a custom-made capillary column ($10\text{ m} \times 0.25\text{ mm}$, $d_f = 0.25\text{ }\mu\text{m}$) coated with 2,3-diacetoxy-6-*t*-butyldimethylsilyl- β -cyclodextrin at 50% in OV 1701.

Analysis of Sulfur-Containing Compounds. Selective detection of sulfur compounds was carried out with an Agilent 5890A gas chromatograph, equipped with a split/splitless injector (injected volume, $1\text{ }\mu\text{L}$ in splitless mode), and the injector temperature was $250\text{ }^\circ\text{C}$. Separations were performed using the same type of column and flow rate as for the GC/MS experiments. The oven temperature program was $60\text{--}280\text{ }^\circ\text{C}$ at $2\text{ }^\circ\text{C}/\text{min}$ and was held at $280\text{ }^\circ\text{C}$ for 20 min. At the

end of the capillary column, a silica Y-splitter was used to send 20% of the flow to a flame ionization detector (temperature, 280 °C) and 80% of the flow to a model 5380 pulsed flame photometric detector (OI Analytical, College Station, TX). The detector temperature was 250 °C; the voltage was 600 V; the sulfur gate was 6–24.9 ms; and the detector trigger was 800 mV. The gas flows to the detector were 11.5 mL/min of H₂, 12 mL/min air–2, and 10 mL/min air–1. The signals were processed with HP ChemStation software, and sulfur compounds were identified by their Kovats indices calculated with respect to linear methyl thioesters, which have been shown to be well-correlated with those of normal chain ethyl esters (3), and comparison with an in-house database.

Nitrogen-Containing Compounds Analysis. Nitrogen-containing compounds were analyzed with a chemiluminescence nitrogen detector (7090 Series from Antek, Houston, TX), fitted to an Agilent 6890 gas chromatograph). The nitrogen detector was fed with H₂ (250 mL/min) and O₂ (5 mL/min). The chromatograph was fitted with a DB-1 column, 10 m × 0.18 mm ID, *d_f* = 0.4 μm (Agilent). The column was operated at 1.5 mL/min helium constant flow, and the temperature of the injector was 250 °C. The oven temperature program was 40 °C isothermal for 1 min, then raised at 40 °C/min to 260 °C, and held at that temperature for 0.5 min. To allow further confirmation of identifications, the system was coupled in parallel with a Pegasus time-of-flight mass spectrometer (Leco, St. Joseph, MI), operating with a 50 spectra/s acquisition rate (35–355 amu).

NMR Analyses. ¹H NMR and ¹³C spectra of synthetic samples were obtained at 400 and 100.6 MHz, respectively, on a Bruker DPX400 instrument, with chloroform as the internal standard.

Component Identification. Retention indexes were calculated vs linear aliphatic acid ethyl esters (4), injected in the same chromatographic conditions. Identifications were made by comparing MS and retention data recorded from authentic reference compounds. Unless otherwise specified hereafter, all reference compounds are commercially available (Sigma-Aldrich, Saint Quentin Fallavier, France). 3-(Acetyloxy)-2-butanone and 3-(butanoyloxy)-2-butanone were obtained from Berjé (Bloomfield, NJ) and Northville Labs (Northville, MI), respectively. Ethyl 2-(methylthio)acetate was obtained from Janssen (Titusville, NJ). A number of compounds were prepared for the purpose of this study by standard or published synthetic procedures: propyl 2-methyl- and 3-methylbutyrates were prepared by reacting the corresponding acid chlorides with 1-propanol. Ethyl 2-methyl-2-pentanoate and phenylethyl pentanoate and phenylethyl 4-methylpentanoate were similarly prepared from the corresponding acid chlorides and the suitable commercially available alcohols. The acid chlorides were prepared from the commercial acids and redistilled thionyl chloride. 2-Aminobenzaldehyde was prepared from 2-nitrobenzaldehyde (Aldrich) by catalytic hydrogenation (5); (2-nitrophenyl)ethane was prepared by reduction of (2-nitroethyl)benzene with NaBH₄ (6); the latter was prepared by aldol condensation of nitromethane with benzaldehyde (7); phenylacetaldoxime (F. 104–106°) was prepared by oximation (8) of freshly distilled phenylacetaldehyde (Aldrich). (2-Nitrobutyl)benzene was synthesized by condensing lithiated 1-nitropropane with benzyl bromide at –90 °C, in 55% yield (9). CAS RN 61668-44-8. MS [*m/z* (%): 39 (9), 51 (7), 65 (13), 77 (7), 91 (100), 117 (32), 132 (34), 179 (<1)]. ¹H NMR: δ 7.36–7.18 (m, 5 H, Ar protons), 4.66 (dddd, *J*₁ = 9.3 Hz, *J*₂ = 8.5 Hz, *J*₃ = 7.5 Hz, *J*₄ = 5.8 Hz, 1 H, CHNO₂), 3.29 (dd, *J*₁ = 14.2 Hz, *J*₂ = 8.5 Hz, 1 H, PhCHHCHNO₂), 3.06 (dd, *J*₁ = 14.2 Hz, *J*₂ = 5.8 Hz, 1 H, PhCHHCHNO₂), 2.05 (ddt, *J*₁ = 11.8 Hz, *J*₂ = 9.3 Hz, *J*₃ = 7.4 Hz, 1 H, CH₂CHHCHNO₂), 1.87 (ddt, *J*₁ = 11.8 Hz, *J*₂ = 7.5 Hz, *J*₃ = 7.4 Hz, 1 H, CH₂CHHCHNO₂), 1.01 (t, *J* = 7.4 Hz, 3H, CH₃); these values differ significantly from the published ones (10). ¹³C NMR: δ 135.6 (s), 128.80 (2d), 128.77 (2d), 127.3 (d), 91.8 (d), 40.1 (t), 27.2 (t), 10.6 (q). FTIR (gas phase): ν (cm⁻¹) 1563 and 1368 (C–NO₂).

RESULTS AND DISCUSSION

2-Phenylethanol is by far the main component of the volatile fraction of Mobola plum (12–15 ppm in the fresh fruit), and the bulk of its esters represents about 25% of the remaining part (Table 1). This accounts for the floral character of the

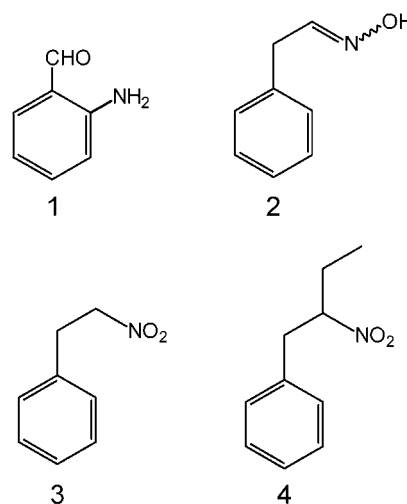


Figure 1. Structures of 2-aminobenzaldehyde (1), phenylacetaldoxime (2), (2-nitroethyl)benzene (3), and (2-nitrobutyl)benzene (4).

flavor, which otherwise is dominated by the typical fruity note provided by various ethyl esters, which themselves represent the major part within the ester category. Among these, ethyl 2-methylpentanoate is unusual in a fruit flavor: as of today, it has been reported only in the volatile fraction of durian (10). However, it is a product of commerce in the fragrance industry with an odor described as “a high impact fresh, fruity-green note, evocative of ripe apple skin” (Manzanate, a trade name of Quest International). While (3-acetyloxy)-2-butanone (so-called acetoin acetate) has been identified in green and ripened pineapple (11), both the acetate and the corresponding butyrate reported herein in Mobola plum had also been detected previously in banana fruit (12). The identification of nitrogen-containing compounds is noteworthy. While esters of 2-aminobenzoic acid (anthranilic acid) have been found in a few fruits only, 2-aminobenzaldehyde (1) (Figure 1) is reported herein for the first time in a natural food, although its application in fruit flavor compounding has been patented (13). It had been found previously only in the headspace of some flowers (14), where it is biosynthesized from indole (15). Likewise, phenylacetaldoxime (2) (Figure 1), also a constituent of certain flower headspaces (14), has not been found so far in any foodstuff. The amount of 2 given in Table 1 refers to the sum of *syn*- and *anti*-configured isomers, taking into account their possible interconversion during the GC analysis (16). Indeed, the assignment of aldoxime geometrical isomers by standard GC is not easy and has not been addressed to date. In the present case, using gas phase GC/FTIR, we propose that *syn*-2 (minor; IR: 962 and 1255 cm⁻¹) is eluted before *anti*-2 (major; IR: 885 and 1304 cm⁻¹) on a nonpolar stationary phase. Nitro compounds are very unusual in foods, although (2-nitroethyl)benzene (3) (Figure 1), along with other aliphatic nitro compounds, was detected in the volatile fraction of tomato (17). Nitro phellandrenes have been found in angelica root essential oil (18). (2-Nitrobutyl)benzene (4) (Figure 1) is a new natural product. Its molecular weight (179) was determined by positive CI/MS, using ammonia as a reactant gas, which makes the interpretation of the EI mass spectrum straightforward, due to the loss of 47 mass units from the parent ion and due to the presence of a base peak at *m/z* 91. Further evidence was provided by the IR spectrum, which shows a striking similarity with that of (2-nitroethyl)benzene (3). Final confirmation of the structure was provided by direct GC/MS comparison with a synthetic reference sample (9). Using an appropriate chiral phase, baseline GC separation of the two enantiomers of 3 can

be achieved. In using the same column type and GC/MS in selected ion mode (ion m/z 91), it was possible to observe that **3** occurs in the fruit extract in ca. 50% enantiomeric excess (*ee*). However, the enantiomer assignment of this scalemic mixture and the determination of the *ee* recovery rate during the extraction procedure require an authentic sample prepared by enantioselective means; further work in this direction is in progress and will be reported elsewhere. The biogenesis of (2-nitroethyl)benzene (**3**), as well as its congeners, 2-phenylethanol, phenylacetaldoxime, and phenylacetone, is related to phenylalanine, whereas the direct formation of (2-nitrobutyl)benzene (**4**) from any amino acid precursor is unlikely, although (2-nitroethyl)benzene is itself a putative intermediate. The odor of **3** is described as primarily floral, green, with geranium, tomato, and oily undertones, with an odor threshold of 2 ppb in water (17). The odor of **4** is sweet, fruity, and berrylike. When tasted at 1 ppm in water, the flavor is rosy and lycheelike, whereas at 10 ppm, the flavor is spicy, carrot seed, and cuminalike with green and woody undertones. Because the recovery rate of phenylacetaldoxime had previously been shown to be dependent on the isolation procedure (19), we decided to undertake a specific investigation on this item and selected other nitrogen-containing compounds identified in the present study. The recovery rates of phenylacetone, 2-aminobenzaldehyde (**1**), phenylacetaldoxime (**2**), (2-nitroethyl)benzene (**3**), and (2-nitrobutyl)benzene (**4**) during the vacuum hydrodistillation step were 68, 25, 4, 72, and 115%, respectively, while the recovery rates of all five compounds during the extraction step only were 94–116%. These results suggest that the organoleptic contribution of these compounds in the fruit, especially **1** and **2**, might be significant. Indeed, while the flavor of **1** is similar to that of ethyl anthranilate when tasted at 3 ppm, the odor of phenylacetaldoxime (**2**) is reminiscent of phenylacetaldehyde with orange blossom notes, but its flavor is insignificant when tasted at 10 ppm or lower.

At least 12 sulfur-containing compounds were selectively detected using a PFPD. The three main components are ethyl- (major), methyl-, and propyl 3-(methylthio)propionate. Their presence was subsequently confirmed in carrying out a selective search by GC/MS.

In summary, the volatile compounds identified in Mobola plum make an interesting blend, which suggests original applications in flavor compounding. Further results concerning other fruits originating from the same area will be reported in forthcoming papers.

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