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Study on the volatile constituents of *Solanum nigrum* var. *virginicum* L. from Nigeria

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ABSTRACT

Essential oil obtained from the hydrodistilled leaves of Solanum nigrum var. virginicum L. from Nigeria was characterised by means of gas chromatography (GC) and gas chromatography coupled with mass spectrometry (GC-MS). Thirty-seven volatile constituents accounting for 97.6% of the total oil contents were identified from the oil sample. The oil was highly composed of sesquiterpene compounds (70.8% hydrocarbon content and 10.2% oxygenated counterpart), but low in monoterpene (0.7% hydrocarbon and 1.2% oxygenated). Fatty acids were also present in appreciable quantity (14.1%). Germacrene D (14.8%), pentadecanal (11.4%), β-elemene (10.1%), α-bulnesene (7.9%), δ-cadinene (6.0%), β-caryophyllene (6.5%) and α-copaene (5.5%) were the major components of the oil. Comparative compositional analysis of the constituents of known studied Solanum species was also evaluated.

Keywords: *Solanum nigrum* var. *virginicum*; terpenes; germacrene D; pentadecanal; β-elemene; chemical forms

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INTRODUCTION

Essential oils are odouriferous mixtures of complex compounds. Research on the chemical composition and biological activities of essential oils different from Nigeria [1-3] and other parts of the world have been documented [4, 5]. *Solanum nigrum L.* var *virginicum* (syn: *Solanum ptycanthum* Dunal ex DC) Solanaceae, is a fairly common herb or short-lived perennial shrub known as 'Black Nightshade'. It could grow up to 120 cm with the ovate to heart-shaped wavy leaves measuring about 75 cm long and 2-5 cm wide. The flowers have petals with greenish to whitish colour and surrounded by bright yellow anthers. The plants native to India and America but found in almost all parts of Africa [6]. Extracts of *S. nigrum* have shown anti-tumour and neuro-pharmacological properties as well as antioxidant and cancer chemo-protective matter [7-9]. The leaves and seeds (berries) are used in Nigeria as vegetable in soup [10]. Besides being used for human consumption, the leaves serve as fodder and browse for domestic herbivorous animals. The plant is used for the treatment of boils and gonorrhea but toxic to man.

The berries especially when unripe were reported to contain poisonous solanocapsine and other alkaloids, that are fatal to man and animals [11, 12]. *S. nigrum* and its varieties have shown pharmacological properties [13, 14]. The phytochemical analysis of *S. nigrum* revealed that the plant have potential to reduce blood pressure while its saponins may prevent cancer [15]. The plant contained an abundance of linoleic acid which gives the oil the nutritional and dietetic properties [16].

The present report is a result of our investigation into volatile constituents of *S. nigrum* var. *virginicum*. The authors are aware of literature information on the oil constituents of some Solanum species from Nigeria [17, 18] and

elsewhere [19, 20], but the essential oil constituents of any parts of *S. nigrum* var. *virginicum* have not been the subject of chemical analysis, as a justification for the present study.

MATERIALS AND METHODS

***Plant Material*:** Aerial parts of the plant were collected from swampy area at Ibiye phase II along Badagry Expressway, Lagos, on April 15, 2009. Botanical identification was performed at the Herbarium Headquarters, Forestry Institute of Nigeria (FRIN), Ibadan, Nigeria, where voucher specimen (FHI 108421) has been deposited for future reference.

Isolation of the Essential Oil: Aliquots (350 g) of the air-dried and pulverized plant sample were subjected to hydrodistillation for 3h using a Clevenger-type apparatus in accordance with the British Pharmacopoeia specification [21] to produce a pale yellow essential oil.

Analysis of the oil sample: GC analysis was accomplished with a HP-5890 Series II instrument equipped with a HP-Wax and HP-capillary columns (both 30 m x 0.25 mm, 0.25 µm film thickness), working with the following temperature program: 60 ^{0}C for 10 min, rising at 5 ^{0}C/ min to 220 ^{0}C. The injector and detector temperatures were maintained at 250 ^{0}C; carrier gas nitrogen (2 mL/min); detector dual, FID; split ratio 1:30. The volume injected was 0.5 µL. The relative proportions of the oil constituents were percentages obtained by FID peak-area normalization without the use of response factor.

GC-EIMS analysis was performed with a Varian CP-3800 gas-chromatograph equipped with a HP-5 capillary column (30 m x 0.25 mm; film thickness 0.25 µm) and a Varian Saturn 2000 ion trapmass detector. Analytical conditions: injector and transfer line temperature 220 ^{0}C and 240 ^{0}C respectively; oven temperature programmed from 60^0- 240 ^{0}C at 3 ^{0}C/min; carrier gas was helium at a flow rate of 1 mL/min.; injection of 0.2 µL (10% hexane solution); split ratio 1:30. Mass spectra were recorded at 70 eV. The acquisition mass range was 30-300 m/z at a scan rate of 1 scan/sec.

Identification of the Constituents: Identification of the constituents was based on comparison of the retention times with those of authentic samples, comparing their linear retention indices (LRI) relative to the series of n hydrocarbons, and on computer matching against commercially available spectral [22]. Further identifications were also made possible by the use of homemade library mass spectra built up from pure substances and components of known oils and MS literature data [23]. Moreover, the molecular weights of all the identified substances were confirmed by GC-CIMS, using MeOH as CI ionizing gas.

RESULTS AND DISCUSSION

Essential oil from the aerial parts of *S. nigrum* var. *virginicum* was obtained by hydrodistillation in a yield of 0.56% (v/w), on a dry weight basis. Table 1 displays the result of the GC-MS analysis. Thirty-seven volatile constituents accounting for 97.6% of the total oil contents were identified from the oil sample. It could be observed that the oil was highly composed of sesquiterpene compounds (70.8% hydrocarbon content and 10.2% oxygenated counterpart), but low in monoterpene (0.7% hydrocarbon and 1.2% oxygenated). Fatty acids were also present in appreciable quantity (14.1%) represented mainly by pentadecanal (11.4%). Germacrene D (14.8%), pentadecanal (11.4%), β-elemene (10.1%), α-bulnesene (7.9%), δ-cadinene (6.0%), β-caryophyllene (6.5%) and α-copaene (5.5%) were the major components of the oil. Other components obtained in significant amount included α-humulene (3.8%) α-selinene (3.7%) β- selinene (2.9%), selin-11-en-4α-ol (2.8%), hexahydrofarnesylacetone (2.8%) and germacrene B (2.3%).

There are literature reports on the essential constituents of some *Solanum* species but not that of *S. nigrum* var. *virginicum*. The volatile oils, obtained by hydrodistillation parts of *S. erianthum*, *S. macranthum*, and *S. torvum* from Nigeria have been reported [17, 18]. *S. erianthum* essential oils were characterized by the abundance of α-terpinolene (17.8%), α-phellandrene (17.5%), p-cymeme (15.7%) and β-pinene (11.7%) in the leaves; α-humulene (23.1%), humulene epoxide II (20. 0%), caryophyllene oxide (16.5%), methyl salicylate (11.8%) and β-caryophyllene (10.9%) in the fruits [17]. Another investigation [18] showed the oil of *S. erianthum* comprised mainly of α-humulene (46.6%), β-caryophyllene (20.6%), germacrene D (4.8%), humulene epoxide II (4.4%) and caryophyllene oxide (4.0%). The leaf oil of *S. macranthum* consisted of (*E*)-phytol (29.0%), pentadecanal (28.1%), pentadecane (7.7%) and ethyl palmitate (5.7%) while the fruit counterpart had α-humulene (36.5%), (*E*)-caryophyllene (17.8%), ethyl palmitate (9.4%), and methyl salicylate (8.2%) as major compounds [17]. However, (*E*)-phytol acetate (38.7%), pentadecanal (25.3%) and (*E*)-geranyl acetone (5.0%) is the main constituents of *S.*

torvum [18]. A recent report from India identified 9,12-Octadecadienoic acid (*Z, Z*)-, methyl ester (14.3 %), cedrandiol, 8s, 14- (13.2 %) and caryophyllene (11.8 %) as main compounds of fruit oil of *S. erainthum* [19].

A report showed that the leaf oil of *S. aculeastrum* comprised mainly of n-nonane (12.4%) and o-phthalic acid (11.8%) while the berries had undecane (21.7%), tetradecane (10.8%) and tridecane (10.0%) as major compounds [20]. Both oils contained relatively fewer terpenoid compounds. From the of peelings of lulo fruit, *S. vestissimum*, were identified methyl 3-hydroxyhexanoate, γ-hexalactone, benzyl alcohol, hexadecanoic acid, (*Z*)-hex-2-enyl acetate, (*E*)-hex-2-en-1-ol, (*Z*)-hex-3-en-1-ol, (*Z*)-isoeugenol, vanillin and 3-hydroxy-7-8-didehydro-β-ionone were found to be the major constituents [24]

The major constituents of the essential oil obtained by hydrodistillation of unripe berries of the shrub of *S. pseudocapsicum* from South Africa [25] were determined to be decane (41.06%), undecane (29.26%), α-thujone(6.06%), phytol (5.95%) and L-camphor (3.08%). Sesquiterpenes were less represented. Moreover, *trans*-carophyllene (23.2%), trans-2-pentadecene (22.6%), germacrene D (12.2%) and bicyclogermacrene were the main compounds of the volatile oil from the leaves of *S. bicolor* [26]. *Trans*- and *cis*-caryophyllene, α-ylangene, α-copaene, β-bourbonene, β-elemene, (*Z*)-β-farnesene, aromadenrene, β-bisabolene, α-humulene, α-elemene, α-cadinene and δ- cadinene were the major terpenoid compounds identified by dynamic gas extraction from the scent of the leaves of potato *S. tuberosum* [27, 28].

Recent reports have shown the oil of *S. spirale* comprised mainly of (*E*)-phytol (48.10%), n-hexadecanoic acid (7.34%), β-selinene (3.67%), α-selinene (2.74%), octadecanoic acid (2.12%) and hexahydrofarnesyl acetone (2.00%) [29]. The fruit of *S. betaceum* from Panama [30] was studied and the constituents reported as follows: golden-yellow variety comprised mainly of methyl hexanoate (8.4%), α-terpineol (12.7%), ethyl octanoate (7.1%), 1, 8-cineole (5.6%) and ethyl hexanoate (5.6%) while the redish-purple variety had an abundance of naphthalene (22.9%), α-phellandrene-8-ol (11.4%), n-nonanal (9.0%), decanal (6.0%) and ethyl octanal (5.4%).

Table 1: Percentage composition of essential oils of Nigerian grown *S. nigrum* var. *virginicum*

Constituents	Percent (%)	LRI[a]	Constituents	Percent (%)	LRI[a]
α-Pinene	0.4	910	α-Humulene	3.8	1458
Sabinene	0.3	950	γ-Muurolene	1.1	1478
2-Pentyl furan	0.1	969	Germacrene D	14.8	1483
Decane	Tr	972	β-Selinene	2.9	1486
α-Phellandrene	Tr	1008	α-Selinene	3.7	1498
Limonene	Tr	1034	α-Muurolene	0.7	1502
1,8-Cineole	0.6	1037	α-Bulnesene	7.9	1506
Phenylacetaldehyde	Tr	1048	*trans*-γ-Cadinene	1.0	1515
n-Undecane	0.4	1100	δ-Cadinene	6.0	1525
4-Terpineol	0.3	1181	α-Cadinene	Tr	1538
α-Terpineol	0.3	1193	α-Calacorene	Tr	1543
δ-Elemene	0.5	1343	Germacrene B	2.3	1557
α-Cubebene	1.8	1354	Spathulenol	0.7	1578
Cyclosativene	0.3	1373	Caryophyllene oxide	0.9	1583
α-Copaene	5.5	1378	*n*-Hexadecane	0.6	1600
β-Cubebene	1.4	1392	Tetradecanal	1.7	1614
β-Elemene	10.1	1394	1-*epi*-Cubenol	1.0	1631
n-Tetradecane	Tr	1400	*epi*-α-Cadinol	1.7	1640
Methyl eugenol	Tr	1409	τ-Muurolol	0.3	1650
β-Caryophyllene	6.5	1421	Selin-11-en-4-α-ol	2.8	1657
β-Gurjunene	0.3	1430	Pentadecanal	11.4	1719
trans-α-Bergamotene	0.2	1439	Hexahydrofarnesylacetone	2.8	1848
α-Himachalene	Tr	1454	Abietatriene	0.5	2054
Total				**97.6**	
Monoterpene hydrocarbons				**0.7**	
Oxygenated monoterpenes				**1.2**	
Sesquiterpene hydrocarbons				**70.8**	
Oxygenated sesquiterpenes				**10.2**	
Aromatic compounds				**0.1**	
Fatty acids				**14.6**	

Retention indices on HP-5 MS capillary column; Tr, trace amount (< 0.1%)

It could be seen that each species has its own compositional pattern and are quite different from others. Table 2 shows the major volatile constituents of some studied *Solanum* species. Therefore, the volatile constituents of *Solanum* species studied so far can be distinguished into chemical forms namely; (i) oil with abundance of monoterpene hydrocarbons as seen in *S. erianthum* (leaves) [17]; (ii) oils with abundance of sesquiterpene hydrocarbon as exemplified by *S. erianthum* (fruits and leaves) [17, 18], *S. macranthum* (fruits) [17], *S. tuberosum*

[27, 28], *S. nigrum* var. *virginicum* (this study) and *S. bicolor* [26]; (iii) oils with abundance of oxygenated monoterpenes and fatty acids as seen in *S. betaceum* (fruits) [30]; (iv) oils which are rich in fatty acids represented by *S. macranthum* (leaves) [17], *S. aculeastrum* [20] and *S. pseudocapsicum* (berries) [25]; (v) oils rich in diterpenoids and fatty acids e.g. *S. torvun* (leaves) [18] and *S. spirale* (leaves) [29]; and (vi) oil with significant proportion of non-ubiquitous terpenoids such as aliphatic alcohol, esters and lactones common to *S. vestissimum*.

Table 2: Major constituents of some studied volatile oils of *Solanum* species

Species/Plant Parts	Major constituents	References
S. erianthum (leaves)	α-terpinolene, α-phellandrene, p-cymene, β-pinene	17
S. erianthum (fruits)	α-humulene, humelene epoxide, caryophyllene oxide, methyl salicylate, β-caryophyllene	17
S. erianthum (leaves)	α-humulene, β-caryophyllene, germacrene D, humulene epoxide II, caryophyllene oxide	18
S. macranthum (leaves)	(*E*)-phytol, pentadecanal, pentadecane, ethyl palmitate	17
S. macranthum (fruits)	α-humelene, (*E*)-caryophyllene, ethyl palmitate, methyl salicylate	17
S. torvum (leaves)	(*E*)-phytol acetate, pentadecanal, (*E*)-geranyl acetone	18
S. erainthum (fruit)	9,12-Octadecadienoic acid (*Z, Z*)-, methyl ester, cedran-diol, 8s, 14, caryophyllene	19
S. aculeastrum (leaves)	n-nonane, o-phthalic acid	20
S. aculeastrum (berries)	undecane, teteradecane, tridecane	20
S. vestissimum (fruit peelings)	methyl-3-hydroxylhexanoate, γ-hexalactone, benzyl alcohol, hexadecanoic acid, (*Z*)-hex-2-enylacetate, (*E*)-hex-2-en-1-ol, (*Z*)-hex-3-en-1-ol, (*Z*)- isoeugenol vanillin, 3-hydroxyl-7-8-didehydro-β-ionone	24
S. pseudocapsicum (berries)	decane, undecane, α-thujone, phytol, *L*-camphor	25
S. bicolor (leaves)	*trans*-caryophyllene, *trans*-2-pentadacene, germacrene D, bicyclogermecrene, caryophyllene oxide	26
S. tuberosum (leaves)	*trans*- and *cis*-caryophyllene, α-ylangene, α-copaene, β-bourbonene, β-elemene, (*Z*)-β-farnesene, aromadenrene, β-bisabolene, α-humulene, α-elemene, γ-cadinene, δ-cadinene	27, 28
S. nigrum var. *virginicum* (leaves)	germacrene D, pentadecanal, β-elemene, α-bulnesene, δ-cadinene, β-caryophyllene, α-copaene	Present study
S. spirale (leaves)	(*E*)-phytol, n-hexadecanoic acid, β-selinene, α-selinene, octadecanoic acid, hexahydrofarnesyl acetone	29
S. betaceum (fruit); golden-yellow variety	methyl hexanoate, α-terpineol, ethyl octanoate, 1, 8-cineole, ethyl hexanoate	30
S. betaceum (fruit); redish-purple variety	naphthalene, α-phellandrene-8-ol, n-nonanal, decanal, ethyl octanal	30

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