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Chemical constituents of leaf essential oils of two varieties of *Caesalpinia pulcherrima Linn* growing in north central Nigeria

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ABSTRACT

Pulverized leaves of red and yellow varieties of *Caesalpina pulcherrima* yielded 0.50 and 0.52% v/w of essential oils on hydrodistillation. GC and GC-MS analyses of the oils revealed the presence of fifty eight and fifty three compounds in the oil of red and yellow varieties respectively. Percentage compositions of oxygenated monoterpenes in the oil of red and yellow varieties were 70.4 and 85.1%. Sesquiterpenes constituted 28.8% of the leaf oil of red variety, while 5.1% of the oil of yellow variety was sesquiterpenes. The principal constituents of the oil of red variety were; γ-terpinene (44.4%), germacrene B (14.3%), myrcene (5.6%), allo-ocimene (5.9%), β-caryophylene (5.1%) and α-pinene (4.2%). Major compounds identified in the oil of yellow variety were; citronellal (58.0%), geranial (17.5%), β-caryophylene (5.1%), linalool (2.5%) and α-terpineol (2.3%). With the abundance of γ-terpinene and citronellal in the oils of red and yellow varieties, the oils are of γ-terpinene and citronellal chemotypes respectively.

Introduction

Caesalpinia pulcherrima Linn (family fabaceae) is a leguminous perennial shrub widely grown in Nigeria as ornamental plant. It is commonly known as Eko-omode by Yorubas, Waken Bature by Hausas and Nwayi/Nwoke Ibem by Igbos[1]. In India, leaves of *C. pulcherrima* are traditionally used as purgative, tonic, antipyretic and emmenagogue. While roots extracts are used in the treatments of convulsions, intermittent fevers, lung and skin diseases [2]. In the Amazon rain forest, the juice from the leaves and flowers are used for the treatments of fever and sores while the seeds are used to cure bad cough, breathing difficulty and chest pain [3]. The root extracts is also known to induce abortion in the first trimester of pregnancy [4]. In Eastern Himalaya, the flowers, leave-sap, and other parts are used to treat inflammations, earache, muscular and rheumatic pain and various cardiovascular diseases [5]. Biological activities such as antimicrobial [6], anticonvulsant [7], anti-ulcer [8], anti-inflammatory [9] antithemintic[10] and analgesic[11] properties of the plants extracts, justify its use in traditional medicine.

Phytochemical investigations of the plant revealed the presence of caesalpin-type diterpenoids; sitosterol, pulcherrimin, lupeol, lupeol acetate, myricetin, quercetin and rutin. Other classes of secondary metabolites such as flavonoids, carotenoids, glycosides, peltogynoids, phenols and steroids were also detected in the plant [12-13].

Earlier, work on flower essential oil of Nigerian grown *C.pulcherrima* , revealed the predominance of α-phellandrene, p-cymene and α-terpinene in the oil [14]. Meanwhile, red and yellow varieties of *C.pulcherrima* exist in Nigeria and interestingly, the phenotypic variation may affect the composition pattern of the oils obtainable from the plants as it affect the constituents of rhizome oils of two varieties of *Cyperus articulatus* grown in Nigeria [15]. It is on the basis of this that we investigate the leaf oils of red and yellow varieties of *Caesalpinia pulcherrima* growing in North-central Nigeria.

Materials and Methods

Plant Materials

Fresh leaves of red and yellow variety of *Caesalpinia. Pulcherrima* were collected from Ilorin Kwara State, Nigeria. Identification of the plants was done at the herbarium of Plant Biology Department of University of Ilorin, Nigeria where voucher specimens were deposited.

Oil Isolation

Fresh pulverized leaves of red and yellow varieties of *C. pulcherrima*. (500g) were separately hydrodistilled for 3 hr. in Clevenger- type apparatus designed according to the British Pharmacopoeia Specifications [16]. The resulting oil was collected and preserved in sealed vials and stored under refrigeration until analysis.

Gas Chromatography (GC) Analysis

GC analysis was performed on Orion micromat 412 double focusing gas chromatography system fitted with two capillary columns coated with CP-Sil 5 and CP-Sil 19 (fused silica, 25µm x 0.25mm, 0.15µm film thickness) and flame ionization detector (FID). The volume injected was 0.2mL and the split ratio was 1:30. Oven temperature was programmed from 50^0C -230^0C at 5^0C/min, using hydrogen as carrier gas. Injection and detector temperatures were maintained at 200^0C and 250^0C respectively. Qualitative data were obtained by electronic integration of FID area percent without the use of correction factor.

Gas Chromatography-Mass Spectrometry (GC-MS)

A Hewlett-Packard HP 5890 GC with a VG analytical 70-250s double focusing mass spectrometer was used. Helium was used as the carrier gas at 1.2ml/min. The MS operating conditions were ionization voltage 70ev, ion source 230^0C. The

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GC was fitted with a 25m x 0.25mm, fused silica capillary column coated with CP-Sil 5. The film thickness was 0.15µm. The GC operating conditions were identical with those of GC analyses. The MS data were acquired and processed by on-line desktop computer equipped with disk memory. The identification of the components was based on the comparison of retention indices (determined relative to the retention times of series of n-alkanes) and mass spectra with those of authentic samples and with data from literature [17, 18, and 19].

Results and Discussion

Pulverized leaves of red and yellow variety of *Ceasalpinia. Pulcherrima* yielded 0.50% and 0.52% v/w of essential oils on hydrodistillation.

Table 1 shows the retention indices, relative percentages and the identities of the constituents of the oils. A total of 57 and 53 compounds representing 99.0 and 98.5% of the leaf oils of the red and yellow varieties were identified from their mass spectra. Hydrocarbon monoterpenoids constituted 70.4 and 90.8% of the oil of red and yellow varieties respectively. Percentage composition of sesquiterpenoids in the oils of red and yellow varieties were; 28.6 and 7.7%.

The oil of the red variety was characterized by the abundance of γ-terpinene (44.4%), germacrene B (14.3%), allo-ocimene (5.9%), myrcene (5.6%) farnescene (5.3%), β-caryophyllene (5.1%) α-pinene (4.2%) and germacrene D (4.0%). Other components identified in significant quantities were; β-pinene (1.8%), α-thujene (1.7%) and camphene (1.1%). The principal constituents of the leaf oil of yellow variety were; citronellal (58.0%), geranial (17.5%) and β-caryophyllene (5.1%). Nerol (2.9%), linalool (2.5%), α-terpineol (2.3%), limonene (1.5%) and β-pinene (1.2%) were also detected in appreciable proportions. With the predominance of γ-terpinene and citronellal in the oil of red and yellow varieties, the oils are of γ-terpinene and citronellal chemotypes respectively.

Qualitatively, the composition patterns of the oils were similar with respect to some of the predominant constituents of the oils. For instance, γ-terpinene, β-pinene, α-pinene, allo-ocimene, trans-β-fanascene and myrcene that predominates the oil of red variety were also found in the oil of yellow variety but, in lower proportions.

On the other hand, citronellal, geranial, that predominates the oil of yellow variety were not detected in significant quantities in the oil of red variety. Meanwhile, β-caryophyllene existed in the same proportions in the oils. Further more, germacrene B and germacrene D that were detected in appreciable proportions in the oil of red variety were not found in the oil of yellow variety. However, benzaldehyde, citral, neryl acetate, α-selinene, that were detected in trace amounts in the oil of red variety were completely absent in the oil of yellow variety. On the other hand, p-cymene that was detected in significant proportion in the oil of yellow variety was not found in the oil of red variety. The variations in some of the constituents of the oils may be due to varietal difference of the plant.

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Table 1: Chemical Composition (%) of the leaf oils of two varieties of *Caesalpinia Pulcherrima*

compound[a]	R1[b]	Red Variety	Yellow Variety
α-pinene	933	4.8	0.9
camphene	946	1.1	0.4
benzalaldehyde	955	tr	-
sabinene	971	tr	tr
1-octen-3-ol	974	tr	1.0
β-pinene	980	7.4	1.2
myrcene	990	5.6	tr
α- phellandrene	1005	tr	tr
α- terpinene	1020	tr	tr
P- cymene	1026	-	0.6
limonene	1027	tr	1.5
benzyl alcohol	1028	tr	tr
1,8 – cineole	1029	tr	tr
cis-ocimene	1035	tr	tr
trans-β-ocimene	1045	tr	tr
2,6-dimethyl -5-heptanal	1055	tr	1.6
γ-terpinene	1057	44.4	0.4
isoartemisia Ketone	1062	tr	tr
terpinolene	1087	tr	tr
linalool	1098	tr	2.5
allo-ocimene	1142	5.9	tr
citronellal	1150	tr	58.0
borneol	1162	tr	tr
terpinen -4 –ol	1175	tr	tr
α- terpinol	1190	tr	2.3
citronellol	1226	tr	tr
nerol	1230	tr	2.9
ascaridole	1237	tr	tr
neral	1238	tr	tr
citral	1240	tr	-
linalylacetate	1255	tr	0.9
geranial	1270	tr	17.5
borneol acetate	1285	tr	0.1
α- tepinenyl acetate	1348	tr	0.2
neryl acetate	1363	tr	-
α- copaene	1375	tr	tr
geranyl acetate	1382	tr	0.7
cyperene	1398	tr	tr
α- gurjunene	1409	tr	tr
β- caryophyllene	1423	5.1	5.1
α- bergamotene	1436	tr	tr
aromadendrene	1438	tr	tr
α- selinene	1448	tr	-
ethyl cinnamate	1460	tr	tr
humulene	1461	tr	tr
germacrene D	1479	4.0	-
β- selinene	1485	tr	tr
valencene	1491	tr	tr
germacrene B	1494	14.3	-
γ- murolene	1499	tr	tr
α-bisabolene	1504	tr	tr
β- bisabolene	1509	tr	tr
trans-β-farnesene	1523	5.2	tr
viridiflorol	1589	tr	tr
α- bisabolol	1683	tr	tr
aristolone	1763	tr	tr
TOTAL		99.0	98.5

[a]Compound are listed in order of elution from silica capillary column coated on CP-Sil 5; [b]retention indices on fused silica capillary column coated with CP-Sil 5; t= trace (<0.1%).