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Chemical composition of the wood and leaf oils from the "Clanwilliam Cedar" (*Widdringtonia cedarbergensis* J.A. Marsh): A critically endangered species

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Abstract

Widdringtonia is the only genus of the 16 genera of Cupressaceae present in South Africa. This genus is represented by three species in South Africa; *W. nodiflora*, *W. schwarzii* and *W. cedarbergensis* (= *W. juniperoides*) and the latter listed as critically endangered. Cedarwood oil (generally obtained from *Juniperus* species) is widely used as a fragrance material in several consumer products, however, no data has been published on the volatiles of the Clanwilliam cedar (*W. cedarbergensis*) native to South Africa. The essential oil composition of the wood and leaf oil isolated by hydro-distillation were analysed by GC–MS. The two oils were distinctly different. Twenty compounds representing 93.8% of the total oil were identified in the leaf oil which was dominated by terpinen-4-ol (36.0%), sabinene (19.2%), γ-terpinene (10.4%), α-terpinene (5.5%) and myrcene (5.5%). Twenty six compounds representing 89.5% of the total were identified in the wood oil with the predominance of thujopsene (47.1%), α-cedrol (10.7%), widdrol (8.5%) and cuparene (4.0%).
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Keywords: Essential oil; Sabinene; Terpinen-4-ol; Thujopsene; *Widdringtonia cedarbergensis*; Widdrol; α-Cedrol; γ-Terpinene

1. Introduction

The genus *Widdringtonia* belongs to the Cupressaceae (cypress family) of which the name is derived from the well known conifer botanist Edward Widdrington. The cypress family is represented by 16 genera with one genus (*Widdringtonia*) present in southern Africa more precisely in South Africa and Malawi (Farjon, 2005). There are four species of *Widdringtonia*, all native to southern Africa. Three of these species are native to South Africa (*W. nodiflora*, *W. schwarzii* and *W. cedarbergensis*) and *Widdringtonia whytei* is native to Malawi. *Widdringtonia cedarbergensis* J.A. Marsh generally known as "Clanwilliam Cedar, Cape Cedar, sederboom or Clanwilliam cypress" is an evergreen tree usually 5–7 m tall but could reach a height of 20 m (Fig. 1). Today, this plant is critically endangered due to loss of habitat, unsustainable harvesting and recurrent veld fires. This species is facing an extremely high risk of extinction in the wild and for this reason it has been placed on the Red Data List of South African Plants (Farjon, 2005; Mustart et al., 1995; Pauw and Linder, 1997). The tree is renowned for its valuable timber and used for construction and furniture and has been used to treat several ailments such as gout, rheumatism, oedematous swellings.

The heartwood of *Widdringtonia cedarbergensis* is pungently aromatic and produces oil which may have various applications. However, the chemical composition of this oil has not been investigated. Cedarwood oil produced by various species is used as an exclusive ingredient in several consumer products. While Texas cedarwood is mostly used as feedstock for the production of some compounds such as cedrol, cedryl

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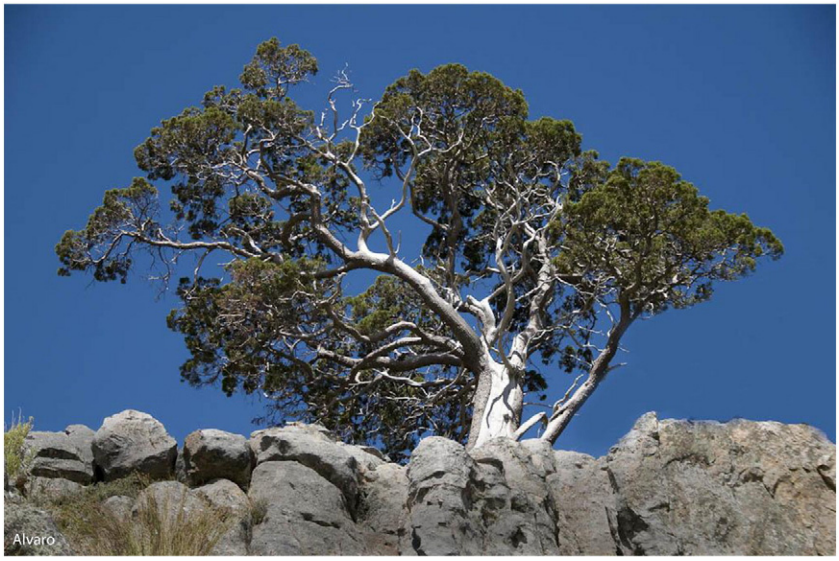

Fig. 1. The Clanwilliam cedar in habitat.

methyl ether, acetyl cedrene, Virginia cedarwood is used in cosmetic formulations, soaps, perfumes, aftershave lotions (FAO, 1995; Schreiber, 1996). It was also noted that cedarwood oil is used in combination with other substances as a homeopathic remedy and marketed as a vaporizing ointment for skin application. We here provide the first analysis of this iconic species which occurs at an altitude of 2000 m on the Cedarberg Mountains and compare the essential oil composition with some commercial cedarwood oils.

2. Materials and methods

2.1. Plant material

After obtaining a collecting permit from Cape Nature Conservation the leaves and wood of *Widdringtonia cedarbergensis* were collected near Driehoek (S 32 25.508 E 19 08.810, 1136 m) in the Cedarberg region (Western Cape) of South Africa. The oil was isolated by hydro-distillation using the Clevenger type apparatus for 3 h from the fresh plant material. The oils were then stored at 7 °C until analysis.

2.2. Gas chromatography coupled to mass spectrometry (GC–MS)

The oil was analysed by GC–MS (Agilent 6890 N GC system coupled directly to a 5973 MS). A volume of 1 µl was injected using a split ratio (200:1) with an autosampler at 24.79 psi and an inlet temperature of 250 °C. The GC system equipped with a HP-Innowax polyethylene glycol column 60 m × 250 µm i.d. × 0.25 µm film thickness was used. The ion source operates by electron ionization and the GC–MS interface temperature was 260 °C. The oven temperature program was 60 °C for the first 10 min, rising to 220 °C at a rate of 4 °C/min and held for 10 min and then rising to 240 °C at a rate of 1 °C/min. Helium was used as carrier gas at a constant flow of 1.2 ml/min. Spectra were obtained on electron impact at 70 eV, scanning from 35 to 550 m/z. The percentage composition of the individual components were obtained from electronic integration measurements using flame ionization detection (FID). *n*-Alkanes were used as reference points in the calculation of relative retention indices (RRI). The identification of the compounds was carried out using NIST®, Mass Finder® and Flavour® and the Başer Library of Essential Oil Constituents by comparing mass spectra and retention indices (Viljoen et al., 2008).

3. Results

The essential oil yields of the wood and leaves were 0.85 and 0.10%, respectively (Table 1). The oils isolated from the leaves and wood of *Widdringtonia cedarbergensis* are distinctly different and no common compounds could be identified in the two oils (Table 1). Twenty compounds were identified from the leaves representing 93.8% of the total oil. The major constituent include terpinen-4-ol (36%), sabinene (19.2%), γ-terpinene (10.4%), α-terpinene (5.5%) and myrcene (5.5%) (Table 1). In the wood oil the major compounds include thujopsene (= widdrene) (47.1%), α-cedrol (10.7%), widdrol (8.5%) and cuparene (4.0%) (Table 1). The chemical structures of these four compounds are presented in Fig. 2. The composition of *W. cedarbergensis* oil is qualitatively comparable to other cedarwood oils such as Virginia cedarwood (*Juniperus virginiana*), Texas cedarwood (*Juniperus ashei* or *J. mexicana*) and Mulanje cedarwood (*W. whytei*) (Table 2), however β-funebrene, thujopsenal, mayurone, α-cedral and α-bisabolol found in the Clanwilliam cedarwood (*W. cedarbergensis*) oil could not be identified in Mulanje cedarwood (*W. whytei*) native to Malawi.

Table 1
Essential oil composition of cedarwood and leaves oil obtained by hydro-distillation and analysed by GC–MS.

RRI	Compounds	*Widdringtonia cedarbergensis* (leaves)	*Widdringtonia cedarbergensis* (wood)
1016	α-pinene	1.9	–
1019	α-thujene	2.0	–
1057	Camphene	–	–
1104	β-pinene	0.2	–
1117	Sabinene	19.2	–
1159	Myrcene	5.5	–
1193	α-terpinene	5.5	–
1194	Limonene	2.8	–
1203	β-phellandrene	0.5	–
1242	γ-terpinene	10.4	–
1270	*p*-cymene	0.3	–
1281	Terpinolene	3.9	–
1527	Isolongifolene	–	0.2
1540	β-cubebene	0.8	–
1546	Linalool	0.1	–
1554	α-longipinene	–	0.2
1572	α-cedrene	–	0.5
1580	α-barbatene	–	tr
1601	β-cedrene	–	0.4
1602	Terpinen-4-ol	36.0	–
1606	β-funebrene	–	1.0
1627	*cis-p*-menth-2-en-1-ol	1.1	–
1629	Thujopsene (widdrene)	–	47.1
1647	*allo*-aromadendrene	–	0.3
1657	β-barbatene	–	0.2
1682	*trans*-piperitol	0.3	–
1682	Selina-4,11-diene	–	0.1
1692	β-chamigrene	–	0.6
1701	α-terpineol	1.4	–
1739	Pseudowiddrene	–	0.7
1741	Bicyclogermacrene	0.8	
1744	α-cuprenene	–	1.3
1763	Thujopsadiene	–	1.8
1763	δ-cadinene	0.3	–
1778	*ar*-curcumene	–	0.1
1790	β-cuprenene	–	0.9
1836	Cuparene	–	4.0
1841	Dehydro-β-ionone	–	0.2
1938	8,9-dehydroneolongifolene	–	0.3
2118	α-cedrol	–	10.7
2169	Widdrol	–	8.5
2180	3-thujopsanone	–	1.1
2201	α-cadinol	0.8	–
2220	α-cedrenal	–	0.5
2223	α-bisabolol	–	3.0
2326	Thujopsenal	–	3.2
2457	Mayurone	–	2.6
Total		93.8	89.5

tr: trace amount (<0.05%); –: not detected; RRI: relative retention indices.

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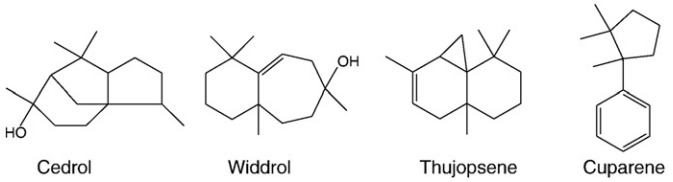

Fig. 2. Chemical structures of the major constituents of Clanwilliam cedarwood oil.

Table 2
Comparison between cedarwood oil obtained from different species.

Major compounds	*W. cedarbergensis* (South Africa)	*W. whytei* (Malawi)	*J. ashei* or *J. mexicana* (USA)	*J. virginiana* (USA)	*T. plicata* (USA)
α-cedrene	0.5	2.0	1.8	27.2	–
Thujopsene	47.1	31.9	60.4	27.6	–
α-cedrol	10.7	*ca* 13.0	19.0	15.8	–
Widdrol	8.5	*ca* 5	1.1	1.0	–
Cuparene	4.0	3.8	–	–	–
Methyl thujate	–	–	–	–	65
Thujic acid	–	–	–	–	25

Sources: Lawrence, 1993; Mookherjee and Wilson, 1996; Green et al., 1988.

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