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TERPENOIDS AND POLYACETYLENIC ESTERS OF THE ESSENTIAL OIL OF *ERIGERON NAUDINI*

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Key Word Index—*Erigeron naudini*; Compositae; terpenes; polyacetylenic methyl esters; geranium essential oil adulteration.

The essential oil of *Erigeron naudini* (Bonnet) Bonnier, common name 'millefeuille', may be an adulterant of the geranium oil *Pelargonium graveolens* L'Her, which is one of the major resources of Reunion Island [1]. In order to protect the latter's production we have undertaken a study of the composition of the essential oil of *E. naudini* with the purpose of identifying at least one major, characteristic constituent which would be revealing in the event of fraud on geranium oil.

The essential oil of *E. naudini* was obtained with an average yield of 0.2% by hydrodistillation of the whole plant during 3 hr in a still usually used for geranium distillation. The monoterpenic hydrocarbons, which represent approximately 50% of the essential oil, were separated almost entirely by fractional distillation; limonene was the major constituent. The distillation residue was then separated into two parts by Si gel chromatography; the hydrocarbons were eluted with hexane and the more polar constituents with AcOMe, then with MeOH. The fraction composed only of hydrocarbons, the majority being sesquiterpenic, was analysed by GC–MS (WCOT column, 40 m, Carbowax 20M).

We can propose a structure for only 14 of the sixty or so sesquiterpenic hydrocarbons present in this fraction, and we cannot vouch for ten of those by simple examination of

Table 1. Compounds identified in the essential oil of *E. naudini*

Hydrocarbons

α-pinene*	α-cubebene†	α-muurolene†
β-pinene*	α-copaene†	β-bisabolene*
myrcene*	β-bourbonene†	β-curcumene†
limonene*	β-elemene*	Ar-circumene†
(E) β-ocimene*	caryophyllene*	*cis*-calamenene†
n-tridecane*	calarene (β-gurjunene)*	*trans*-calamenene†
allo-ocimene‡	α-humulene†	calacorene†

Alcohols

linalol*	geraniol*
1-terpinene-4-ol*	nerolidol*
α-terpineol*	α-cadinol‡
citronellol*	spathulenol*

Various

perillene†		
α-terpenyl acetate*		
acetylenic ester (1)‡	*cis*	$Me-CH_2-CH_2-C\equiv C-C\equiv C-CH=CH-COOMe$
acetylenic ester (2)‡ ('matricaria ester')	*cis, cis*	$Me-CH=CH-C\equiv C-C\equiv C-CH=CH-COOMe$

*Constituents identified by direct comparison with a genuine sample.

†Constituents for which we propose a tentative identification based only on the examination of MS and retention data.

‡Constituents isolated by preparative GC whose spectral data (NMR, IR, MS) are identical to those already published.

the MS and the retention data (Table 1). The percentage content of polyacetylenic compounds **1** and **2** in the essential oil of *E. naudini* was very high (35–40%), as in all *Erigeron* species. Therefore both esters **1** and **2** may testify to the accidental or fraudulent presence of the essential oil of *E. naudini* in geranium essential oil. Indeed, the IR spectrum of the latter, when pure, presents no absorption band at 2200–2220 cm^{-1}, the area where the very intense sharp absorption band of the acetylenic bond is usually found.

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TERPENOIDS FROM THE SEED OF *THUJOPSIS DOLABRATA*

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Key Word Index — *Thujopsis dolabrata* var. *hondae*; Cupressaceae; seed; mono-, sesqui-, and diterpenes; sabinene; hedycaryol.

Abstract—Sabinene and hedycaryol were found to be the main components of the seed oil of *Thujopsis dolabrata*. Nine mono- and three sesquiterpenes were also isolated from the distilled, neutral oil. Hedycaryol rearranged to elemol during GLC at higher temperatures. The distillation residue contained *n*-paraffins, eight diterpenes, sitosterol, and *trans*-communic acid and isocupressic acid.

INTRODUCTION

Although terpenoid constituents of woods, barks, and leaves of conifer species have been investigated by many workers, very few studies appear to have been reported on those of seeds. It is well known that considerable differences in chemical constituents between woods, barks, and leaves exist. Therefore, it seemed to be of interest from a biogenetic viewpoint to examine components of seeds.

Thujopsis dolabrata Sieb. et Zucc. var. *hondae* Makino (Cupressaceae) is one of the most valuable trees endemic to Japan. The wood contains predominantly sesquiterpenes, such as thujopsene, cedrol [1], γ-cuparenol, α-, β-costal, β-elemenal, mayurone, widdrol, elemol, sesquibenihiol, sesquibenihidiol and selinadiol [2] together with various tropolones [3, 4] and phenols [5], while the leaf oil is composed of monoterpenes, such as *d*-sabinene, borneol, sabinol, and dipentene [6], together with a small amount of the diterpene hydrocarbons, dolabradiene, hibaene, and ar-abietatriene [7].

In a previous paper [8], we described the isolation of a new diterpene glycoside and two lignans from the ether extract of the seed. This paper deals with terpenoid components from the *n*-hexane extract.

RESULTS AND DISCUSSION

α-Pinene, sabinene, β-myrcene, sabinyl acetate, terpinen-4-ol, α-terpinyl acetate, β-eudesmol and elemol were isolated and identified by their IR and NMR spectra. Small amounts of limonene, β-phellandrene, *p*-cymene, terpinolene, and cuparene were identified by GC–MS (Table 1).