Pergamon

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ISOPRENE RELATED ESTERS, SIGNIFICANT COMPONENTS OF *PANDANUS TECTORIUS*

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Key Word Index—*Pandanus tectorius*; Pandanaceae; 3-methyl-3-buten-1-yl acetate; 3-methyl-3-buten-1-yl cinnamate; 3-methyl-2-buten-1-yl acetate; 3-methyl-2-buten-1-yl cinnamate.

Abstract—Isopentenyl and dimethylallyl acetates and cinnamates have been found in large amounts in an essential oil obtained from the ripe fruit of *Pandanus tectorius*, their identification has been confirmed by synthesis. This is the first time that these esters, apart from one, have been found in the plant kingdom and, generally speaking, that monoterpene precursors predominate in an essential oil. Copyright © 1996 Published by Elsevier Science Ltd

INTRODUCTION

Pandanus is a complex paleotropical genus comprising probably 600–700 species; *P. tectorius* Parkinson can be discriminated from the closely related *P. odoratissimus* by few botanical characteristics and by nearly distinct geographical distributions; the former is more eastern in distribution (Polynesia, Micronesia, Melanesia, Australia) while the latter is more western (Malaysia, Sri Lanka, India) [1]. *P. tectorius* or 'fara', after the coconut tree, is a most useful plant to the Polynesian inhabitants of Tropical Pacific Islands [2]. It is used for many purposes: the fruit 'fara' or the staminate inflorescence 'hinano' are excellent for manufacturing scented oil, 'monoi fara' or 'monoi hinano' which are appreciated as ointments. In traditional medicine, Polynesians used the fruit or root sap to treat several diseases [3].

The volatile compounds of species belonging to the genus *Pandanus* have been rarely described in literature. The essential oil from the leaf of *P. latifolius* contains mainly sesquiterpene hydrocarbons (6–42%) accompanied by linalool (6%) [4]. Ethyl formate and 3-methyl-1-butanal have been found in leaves of *P. odoratissimus* [5] whereas phenylethyl alcohol and its methyl ether and acetate have been found to predominate in the oil obtained from flowers of the same species [6]. The main fragrant component of *P. amaryllifolius* leaves has been found to be 2-acetyl-1-pyrrolin [7]. The only papers related to the chemical constituents of the species *P. tectorius* deal with non-volatile compounds: fatty acids, sterols [8, 9] and amino acids [10].

We present here the results of the analysis of an oil sample obtained by hydrodistillation of yellow ripe fruit of *P. tectorius* collected in Haumi, Island of Moorea (French Polynesia).

RESULTS AND DISCUSSION

Among the 24 compounds found above 0.1% in the volatile extract of the fruit of *P. tectorius*, 20 were compounds usually encountered in essential oils and their identification was performed directly by capillary GC and GC-mass spectrometry (Table 1).

Examination of the mass spectra of the four other constituents, representing roughly 40% of the mixture, suggested the presence of isopentenyl and dimethylallyl/acetates (**1a–2a**) and cinnamates (**1b–2b**).

These components were synthesized by esterification of the two corresponding alcohols, 3-methyl-3-buten-1-ol, (**1**) and 3-methyl-2-buten-1-ol (**2**) with either acetic acid anhydride or (E) cinnamyl chloride; the retention indices and mass spectra of the chemically synthesized compounds were found to be identical to those of the natural compounds.

Compound **2a** has been found in small amounts ($< 1\%$) in *Cananga odorata* oils [11, 12] and in *Pimenta haitiensis* oils [13] along with the isoprene related alcohols **1** and **2**; furthermore, these two latter components have been detected in *Narcissus* [14]. However, the three other esters (**1a**, **1b** and **2b**) have never been identified so far in the plant kingdom, nor described; only cinnamate derivatives, in the form of ferulates and caffeate esters, have been reported in polar buds and propolis [15, 16]. Finally, in the genus *Pandanus*, the isoprene type structure was detected only in *P. odoratissimus* in the form of the non ethylenic aldehyde.

Molecules with the isoprene type structure are situated at an early stage along the biosynthetic pathway of terpenoids, just after (3R) mevalonic acid. Their occurence in high yields in the essential oil of *P. tectorius* constitutes a rare and very interesting observation in the biological and chemotaxonomical fields.

Table 1. Identified constituents and approximate percentage in the essential oil of the fruit of *P. tectorius*

Component	Percentage*	RI†
3-Methyl-3-buten-1-yl acetate	10.1	878
3-Methyl-2-buten-1-yl acetate	4.7	915
Camphene	0.1	958
(*Z*)-β-Ocimene	0.1	1032
(*E*)-β-Ocimene	0.1	1039
Linalool	1.9	1097
Benzyl acetate	0.2	1151
α-Terpineol	0.3	1189
2-Phenylethyl acetate	2.9	1250
Geraniol	1.0	1252
Bornyl acetate	0.2	1284
Eugenol	0.1	1352
Neryl acetate	0.1	1359
Phenylacetonitrile	0.2	1365
Geranyl acetate	27.5	1381
β-Caryophyllene	0.4	1419
Cinnamyl acetate	5.2	1440
α-Humulene	0.1	1453
Ethyl cinnamate	10.2	1461
$C_{15}H_{24}$	1.8	1504
Epoxycaryophyllene	0.2	1574
3-Methyl-3-buten-1-yl cinnamate	17.1	1747
3-Methyl-2-buten-1-yl cinnamate	4.5	1792
Farnesyl acetate	0.9	1834

*Area percentage.

†Linear retention indices on DB-5 column.

Futhermore, the isopentenyl esters are much more abundant than the dimethylallyl derivatives: 10.1 *vs* 4.7 for the acetates and 17.1 *vs* 4.5 for the cinnamates. Thus it would seem that the isopentenyl alcohol is esterified faster than it is isomerized to dimethylallyl alcohol.

EXPERIMENTAL

Material. Ripe fruits of *P. tectorius* were collected in Haumi, Moorea Island (Society Islands) in June 1992. Batches (400 g) of plant material were submitted to hydrodistillation; the oil possessing the strong characteristic odour of the fruit was obtained in 0.02% (w/w) mean yield and was analysed by GC and GC-MS.

Capillary GC. GC analysis was performed on a Varian GC 3400 (FID) fitted with two fused silica capillary columns (30 m × 0.32 mm i.d. coated with DB-5 and 30 m × 0.32 mm i.d. coated with DB-Wax: J & W Scientific California), using the following experimental conditions: Temp. programme 80–200° at 2° min^{-1} with a final hold time of 30 min; injector temp. 180°, detector temp. 250°, carrier gas UHP He at a flow rate of 0.8 ml min^{-1}.

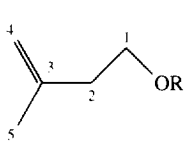
GC-MS. The sample was then analysed by GC-MS using a Hewlett Packard capillary GC-quadrupole MS system (model 5970), operating at 70 eV and fitted with a 25 m × 0.23 mm fused-silica column coated with DB-1; temp. was programmed as follows: 60° (1 min), 60–180° (3° min^{-1}). He was used as carrier gas at a flow rate of 0.9 ml min^{-1}.

3-Methyl-3-buten-1-yl acetate (**1a**) *and 3-methyl-2-buten-1-yl acetate* (**2a**). These were obtained from the corresponding alcohols (0.03 mol) by acetylation, at room temp. with Ac_2O (5 ml) catalysed by *N,N*-dimethylamino-4-pyridine (50 mg). After 1 hr, the remaining Ac_2O was hydrolysed by addtn of aq 5% $NaHCO_3$ soln (12 ml); the mixture was then extracted (×3) with Et_2O, giving the acetates, after drying and evapn of the solvent, in 80% yield.

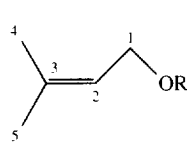
Compound **1a**. MS *m/z* (rel. int.): 43 (100), 68 (62), 67 (35), 39 (14), 41 (13), 53 (12), 73 (5), 128 (1); ^1H NMR. (250 MHz, $CDCl_3$): δ 1.69 (3H, *s*, CH_3-5), 1.97 (3H, *s*, CH_3-CO), 2.28 (2H, *t*, CH_2-2, *J* = 6.9 Hz), 4.11 (2H, *t*, CH_2-1, *J* = 6.9 Hz), 4.61 (1H, *s*, CH_2-4) and 4.74 (1H, *s*, CH_2-4).

Compound **2a**. MS *m/z* (rel. int.): 43 (100), 68 (77), 67 (63), 41 (53), 69 (38), 71 (26), 53 (25), 39 (22), 86 (22), 128 (4); ^1H NMR (250 MHz, $CDCl_3$): δ 1.65 (3H, *s*, CH_3), 1.71 (3H, *s*, CH_3), 1.98 (3H, *s*, CH_3-CO), 4.49 (2H, *d*, CH_2-1, *J* = 7.0 Hz), 5.28 (1H, *t*, CH-2, *J* = 7.0 Hz).

3-Methyl-3-buten-1-yl cinnamate (**1b**) *and 3-methyl-2-buten-1-yl cinnamate* (**2b**). These were obtained from the corresponding alcohols (0.025 moles) by esterification with cinnamoyl chloride (0.028 moles) catalysed by *N,N*-diethylamino-4-pyridine (122 mg). Addition of acid chloride, dissolved in 10 ml Et_2O was made at 0°; the mixture was stirred at room temp. for 2 hr, then treated according to the same procedure as described previously. Finally, product isolation was performed by CC on silica gel 60 (Merck, 70–230 mesh ASTM) eluted with a hexane–Et_2O gradient (yield 60%).



1 R = H
1a R = CO–CH_3
1b R = CO–CH = CH–C_6H_5



2 R = H
2a R = CO–CH_3
2b R = CO–CH = CH–C_6H_5

Compound **1b**. MS *m/z* (rel. int.): 131 (100), 148 (50), 103 (41), 147 (38), 68 (29), 76 (26), 216 (4) $[M]^+$; ^1H NMR (250 MHz, $CDCl_3$): δ 1.75 (3H, *s*, CH_3-5), 2.38 (2H, *t*, CH_2-2, $J=6.7$ Hz), 4.30 (2H, *t*, CH_2-1, $J=6.7$ Hz), 4.76 (1H, *s*, CH_2-4), 4.80 (1H, *s*, CH_2-4), 6.40 (1H, *d*, =CH-CO, $J=16.0$ Hz), 7.37 and 7.48 (5H, phenyl), 7.68 (1H, *d*, CH vinyl, $J=16.0$ Hz).

Compound **2b**. MS *m/z* (rel. int.): 131 (100), 69 (52), 147 (50), 103 (43), 41 (34), 77 (33), 171 (32), 216 (11) $[M]^+$; ^1H NMR (250 MHz, $CDCl_3$): δ 1.79 (3H, *s*, CH_3), 1.83 (3H, *s*, CH_3), 4.75 (2H, *d*, CH_2-1, $J=7.1$ Hz), 5.47 (1H, *t*, CH-2, $J=7.1$ Hz), 6.50 (1H, *d*, =CH–CO, $J=16.0$ Hz), 7.41 and 7.55 (5H, phenyl), 7.75 (1H, *d*, CH vinyl, $J=16.0$ Hz).

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