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Apodophyllone and isotorquatone, two arenic ketones from *Eucalyptus apodophylla*☆

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Abstract

The essential oil of *Eucalyptus apodophylla* exploited in Burkina Faso consists mainly in monoterpenes (53.7–66.9%) and sesquiterpenes (9.0–10.0%). It is characterized by important amounts (15.2–32.9%) of arenic ketones belonging to the series of torquatone and of jensenone. Among them, two new structures, apodophyllone and isotorquatone, were clearly identified by ^1H and ^{13}C NMR. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Eucalyptus apodophylla Blakely & Jacobs ex Blakely (‘whitebark’) is classified in *Eucalyptus*, subgenus Symphyomyrtus, section Exsertaria (Pryor & Johnson, 1971). This smallish tree (up to 18 m high) native to the north coastal region of Australia is characterized by the even whiteness of the newly exposed bark and the absent (or very short) leaf stalks in all phases of leaf development (Boland, Brophy, & House, 1991). This species has been introduced for reafforestation in Burkina Faso in 1963, along with other species as *E. camaldulensis* or *E. alba* and these Eucalyptus plantations are exploited for wood production. Up to now, the leaves are waste material in this exploitation and the purpose of this study was to determine their oil yield and chemical composition in order to select the species that might show potential for essential oil production.

To our knowledge, the only results relative to the leaf essential oil of *E. apodophylla* concern a species collected in Australia (Boland et al., 1991). The authors mention the presence of two major components (alpha-pinene and limonene) in the leaf essential oil (respectively, 37.2 and 31.4% of whole oil).

We present here the results of the analysis of two oil samples obtained by hydrodistillation of leaves of *E. apodophylla* trees growing at Dinderesso (Bobo Dioulasso area, Burkina Faso). The compositions of these oils are quite different from the one previously described; furthermore, we have isolated and characterized two novel structures analogous to torquatone, an arenic ketone which is commonly found in Eucalyptus essential oil as well as the corresponding series of constituents related to jensenone.

2. Results and discussion

Among the 32 compounds found above 0.1% in the volatile extracts of leaves of *E. apodophylla*, 25 were

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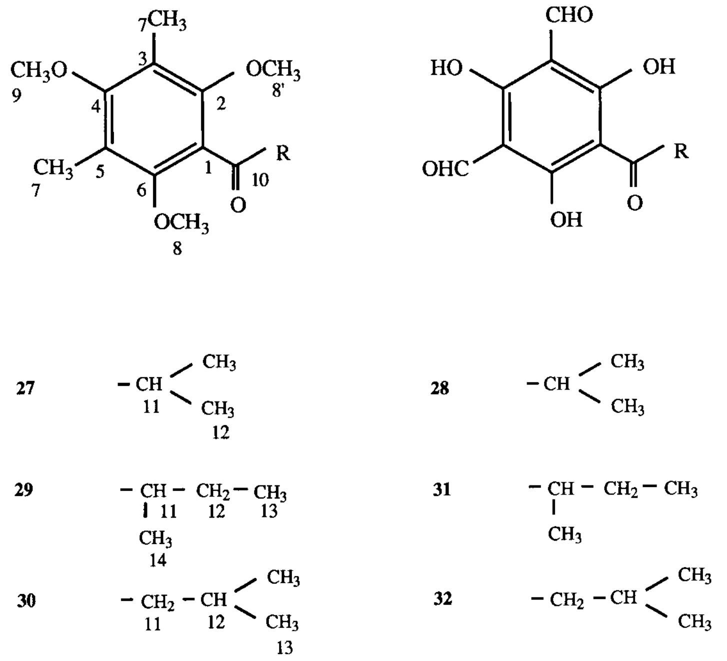

terpenoids usually encountered in essential oils and their identification was performed directly by capillary GC and GC–mass spectrometry (Table 1), with the exception of an oxygenated sesquiterpene (**24**, $C_{15}H_{26}O$). In this chemical class, the monocyclic structures predominate, principally represented by three monoterpene hydrocarbons (43–51% of the whole oil), limonene (**7**) and *p*-cymene (**6**), abundant in the two samples, and phellandrenes (alpha + beta, **5**,**8**) which were only found in sample 1. Among the sesquiterpenes, bicyclogermacrene (**20**) predominates in the same sample (5.7%). This compound, common in Eucalyptus oil, was found to be the major volatile constituent (65.6%) of leaves of *E. incerata* Brooker&Hopper (Bignell, Dunlop, & Brophy, 1998).

The two oils contained six other constituents (**27**–**32**) characterized by linear retention indices higher than 1680 on OV 101. Examination of their mass spectra indicated two series of different structures, related, respectively, to torquatone **30** (2,4,6-trimethoxy-3,5-dimethyl-1-(3-methylbutyroyl)-benzene) (Bignell & Dunlop, 1994) and jensenone **32** (4,6-diformyl-2-isopentanoylphloroglucinol) (Boland, Brophy, & Fookes, 1992), representing altogether more than 30% of the sample 1 and only 15.2% of the sample 2.

The mass spectral data of the components **27** and **29** correspond to those of two structures, reported for the first time in 1996 in four Eucalyptus species belonging to subgenus Symphyomyrtus and named components A and B by the authors (Bignell, Dunlop, Brophy, & Jackson, 1996). Since then, the same components were found in other species classified in the subgenera Symphyomyrtus (Bignell, Dunlop, Brophy, & Jackson, 1996) or Monocalyptus (Bignell, Dunlop, Brophy, & Fookes, 1997), but still in minor amounts.

Owing to the high content of the compounds **27** and **29** in our samples, we could purify them by silica gel column chromatography and elucidate their structures (which were found to be related to that of torquatone) on the basis of their ^{1}H and ^{13}C NMR data (Table 2). The ^{1}H NMR spectrum of **27** showed the presence of an isopropyl alkyl group (in agreement with the structure which was tentatively proposed for the component A (Bignell et al., 1996)). A C_4 alkyl group had been proposed for compound B (Bignell et al., 1996); our results indicate clearly 1-methylpropyl substituent in **29**. Accounting for their structures and their botanical source, we suggest the names apodophyllone and isotorquatone be adopted for compounds **27** and **29**.

The three other constituents (**28**, **31** and **32**), which are characterized by similar spectral data, with a major ion at m/z 209, may be related to jensenone (Boland et al., 1992), this proposal being supported by their high polarity (low R_f in TLC). Jensenone was identified in the steam volatile oil of *Eucalyptus jensenii*, which belongs to subgenus Symphyomyrtus (its closest relatives are considered to be *E. crebra* F. Muell., *E cullenii* Cambage and *E. staigeriana* F. Muell. ex F. M. Bail) and later in minor amounts in the essential oil of another Myrtaceae, *Choricarpia leptopetala* (Brophy, Goldsack, & Forster, 1994). The component the most abundant in this series (**32**) could be identified as jensenone, with an alkyl group (isobutyl) identical with that

Table 1
Identified constituents and approximate percentage in the leaf essential oil of *Eucalyptus apodophylla*. **24**: $M=222$: m/z (rel. int.): 163 (80), 149 (32), 109 (31), 107 (100), 91 (35), 81 (46), 69 (30), 59 (50), 43 (60)

No.	Component	Percentage[a] sample 1	Percentage[a] sample 2	RI[b]
1	α-thujene	0.8	–	928
2	α-pinene	3.5	7.7	936
3	β-pinene	0.2	1.1	976
4	myrcene	0.4	0.2	987
5	α-phellandrene	16.5	–	1002
6	p-cymene	9.7	18.3	1014
7	limonene	15.5	33.0	1019
8	β-phellandrene	1.6	–	1020
9	γ-terpinene	1.1	–	1055
10	terpinolene	1.5	0.2	1083
11	cryptone	0.2	–	1156
12	terpineol-4	1.2	2.3	1168
13	α-terpineol	0.7	2.3	1180
14	carvone	0.3	0.7	1223
15	piperitone	0.5	1.1	1235
16	β-caryophyllene	0.2	–	1420
17	aromadendrene	0.5	1.5	1442
18	*allo*-aromadendrene	0.4	0.7	1462
19	germacrene D	0.2	–	1483
20	bicyclogermacrene	5.7	0.2	1496
21	δ-cadinene	0.1	–	1517
22	spathulenol	0.7	2.4	1569
23	globulol	1.0	1.5	1580
24	$C_{15}H_{26}$ 0	0.7	1.1	1587
25	γ-eudesmol	0.2	1.1	1625
26	β-eudesmol	0.2	0.5	1645
27	apodophyllone	5.2	3.9	1685
28	component C	0.2	0.5	1741
29	isotorquatone	11.5	5.8	1777
30	torquatone	11.0	4.0	1791
31	component D	1.0	0.2	1818
32	jensenone	4.0	0.8	1839

[a] Area percentage.

[b] Linear retention indices on OV 101 column.

of torquatone. According to their relative retention indices and their mass spectral characteristics, it is more than likely that the two others (**28**, component C and **31**, component D) are, respectively, characterized by the same alkyl groups as apodophyllone (isopropyl) and isotorquatone (1-methylpropyl). This hypothesis

Table 2
NMR data ($CDCl_3$; δ, ppm) for apodophyllone (**27**), isotorquatone (**29**) and torquatone (**30**)

H or C	**27**		**29**		**30**	
1		127.96		127.50		127.49
2,6		159.22		159.25		159.20
3,5		121.18		121.24		121.30
4		154.15		153.89		154.04
7,7′	2.104 s	9.58	2.101 s	9.63	2.108 s	9.63
8,8′	3.827 s	62.03	3.833 s	62.73	3.825 s	62.82
9	3.860 s	60.41	3.855 s	60.41	3.868 s	60.41
10		210.06		209.54		205.53
11	2.965 h(6.95)	42.70	2.820 m	49.50	2.610 d (6.75)	54.48
12	1.080 d (6.95)	18.35		25.42	2.184 m	24.28
12′			1.732 ddq (13.65, 7.40, 6.80)			
12″			1.326 ddq (13.65, 7.42, 7.40)			
13			0.939 t (7.40)	12.01	0.911 d (6.63)	22.02
14			1.060 d (7.60)	15.46		

should be corroborated by further investigations on essential oils containing larger amounts of these constituents.

Finally, the chemical composition of the essential oil obtained from *E. apodophylla* growing in Burkina Faso is very different from the one previously described. Furthermore, high contents of torquatone, jensenone and their analogous structures have been found for the first time, to our knowledge, in a species belonging to the section Exsertaria (subgenus Symphyomyrtus). Our results agree with previous comments about a wide distribution of torquatone (Bignell & Dunlop, 1994) in Eucalyptus oils and allow the extension of this hypothesis to jensenone.

3. Experimental

3.1. Material

Leaves of *Eucalyptus apodophylla* were collected in the arboretum of Dinderesso (located 15 km from Bobo-Dioulasso, Burkina Faso), respectively, in August and September 1994, for samples 1 and 2. The botanical identification of the material collected was carried out by Dr. Diallo (Centre National de la Recherche Scientifique et Technologique).

Batches (200 g) of plant material were submitted to hydrodistillation; the oils were obtained in 0.5% (w/w) mean yield and were analysed by GC and GC–MS.

3.2. Capillary GC

The oil samples were analysed on a Shimatzu GC 14A with flame ionization detectors fitted with two fused silica capillary columns (25 m × 0.25 mm i.d. coated with OV 101 and 25 m × 0.22 mm i.d. coated with Carbowax 20 M). Temp. programme, 50–200°C at 5°C/min; injector temp., 220°C; detector temp., 250°C; carrier gas N_2, 0.8 ml/min. The linear retention indices of the components were determined relatively to the retention times of a series of *n*-alkanes and the percentage compositions were obtained from electronic integration measurements without taking into account relative response factors.

3.3. GC–MS

The essential oils were analysed using a Hewlett Packard capillary GC–quadrupole MS system ((Model 5970) fitted with a 25 m × 0.25 mm i.d. fused silica column coated with DB 1. Temp. programme, 60°C (1 min), 60–250°C at 5°C/min. Helium was used as the carrier gas at a flow rate of 0.9 ml/min; the mass spectrometer was operated at 70 eV.

Except for the compounds **27**–**32**, the identification of the usual constituents was based on a comparison of their retention indices and their mass spectra with literature data (Adams, 1989).

3.4. Isolation

Apodophyllone (**27**) and isotorquatone (**29**) were isolated by CC of sample 1 on silica gel 60 (Merck, 70–230 mesh ASTM) eluted with a pentane–Et_2O gradient. ^1H and ^{13}C NMR were taken at 400 MHz ($CDCl_3$) and the corresponding data are given in Table 2.

3.5. MS data

27 (apodophyllone), *m*/*z* (rel. int.): 266 (8) [M^+], 224 (11), 223 (100), 208 (3), 193 (5), 165 (6), 43 (3).
28 (component C), *m*/*z* (rel. int.): 252 (13) [M^+], 210 (10), 209 (100), 43 (5).
29 (isotorquatone), *m*/*z* (rel. int.): 280 (6) [M^+], 224 (15), 223 (100), 208 (2), 193 (3), 165 (7), 41 (5).
30 (torquatone), *m*/*z* (rel. int.): 280 (14) [M^+], 224 (15), 223 (100), 208 (3) 196 (5), 193 (4), 165 (6), 41 (4).
31 (component D), *m*/*z* (rel. int.): 266 (10) [M^+], 223 (2), 210 (10), 209 (100), 166 (4), 55 (2), 41 (3).
32 (jensenone), *m*/*z* (rel. int.): 266 (15) [M^+], 251 (6), 235 (5), 210 (10), 209 (100), 182 (4), 166 (5), 43 (3), 41 (3).

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