

TRITERPENOID, COUMARIN AND QUINONE CONSTITUENTS OF ELEVEN *DIOSPYROS* SPECIES (EBENACEAE)*

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Key Word Index—*Diospyros*; Ebenaceae; triterpenoids; sitosterol; scopoletin; naphthaquinones; chemotaxonomy.

Abstract—From the bark and/or timber extracts of *Diospyros hirsuta*, *D. moonii*, *D. quaesita*, *D. spinescens*, *D. thwaitesii* and *D. walkeri*, the following compounds have been isolated; lupeol, betulin, betulinic acid sitosterol, taraxerol, taraxerone, ursolic acid, oleanolic acid scopoletin, plumbagin, elliptinone, diospyrin and diosindigo A. TLC examination of the bark and timber extract of *D. acuta*, *D. chaetocarpa*, *D. oblongifolia*, *D. oppositifolia* and *D. rheophytica* is reported. Lupeol betulin, oleanolic acid and sitosterol have been isolated from the fruit of *D. oblongifolia*.

INTRODUCTION

The Ebenaceae are mainly found in the tropics and subtropics. According to Hegnauer [1], it consists of seven genera, namely *Diospyros*, *Euclea*, *Maba*, *Onotheca*, *Rhapidanthe*, *Royena* and *Tetracelis*. However, at present most botanists consider that it is composed of the three genera *Diospyros*, *Euclea* and *Lassiocarpa* [2]. Thus *Maba*, *Rhapidanthe*, *Royena* and *Tetracelis* are included under *Diospyros* and *Onotheca* is included as a monotypic family [2].

The bark, timber, roots and mesocarp of over forty species of *Diospyros* have been investigated [2–15] and several naphthaquinones, naphthols, sitosterol and triterpenes isolated. The latter are mainly in the lupene series and occur in high yields.

In a recent taxonomic revision, Kostermans [16] recorded 32 species of *Diospyros* for Sri Lanka of which 21 are regarded as endemic to the island. Most of them are large trees and some (such as ebony) are in demand as timber. A large number of the endemic species are confined to the fast dwindling lowland rain forests of the Southern and Sabaragamuwa Provinces of Sri Lanka. The present paper describes the chemical investigation of eleven such endemic *Diospyros* taxa, namely *D. hirsuta* L.f., *D. moonii* Thw., *D. quaesita* Thw., *D. spinescens* Kosterm., *D. thwaitesii* Bedd., *D. walkeri* (Wight) Guerke, *D. acuta* Thw., *D. chaetocarpa* Kosterm., [*Maba ovalifolia* (Thw.) Hiern pp.], *D. oblongifolia* (Thw.) Kosterm., [*Maba oblongifolia* (Thw.) Hiern pp.], *D. oppositifolia* Thw. and *D. rheophytica* Kosterm. *D. quaesita* is well known for the quality of the timber known as Calamander or King Ebony. Furniture made from the timber of this tree is so highly ranked that this tree was exploited to near extinction during the period of the

Dutch occupation of Sri Lanka. The leaves of this plant are reported to be used as a cure for asthma.

RESULTS AND DISCUSSION

Table 1 summarizes the compounds isolated from the eleven *Diospyros* species. The results obtained in this study as well as published data [15] indicate that besides the widely distributed sitosterol, triterpenes of the lupene series, i.e. lupeol, betulin and betulinic acid are good taxonomic markers of the genus *Diospyros*.

Maba was considered to be a genus distinct from *Diospyros* on the basis of sepal and petal number, but at present, most botanists agree that this generic distinction is not justified and hence all species of *Maba* have been transferred to *Diospyros*. Chemotaxonomic data obtained in this study support the view that *Maba* species should be included in *Diospyros*.

Morphologically, the endemic *D. spinescens* shows striking similarity to *D. montana* Roxb. [1], found both in Sri Lanka and South India. The present study shows that the chemistry of the two species is very similar; perhaps they represent only two distinct ecotypes of one species.

Although *Diospyros* is considered as a rich source of naphthaquinones, the present study showed their occurrence in the bark and timber of only four species. The quinone content decreases from *D. walkeri*, through *D. spinescens* and *D. hirsuta* to *D. moonii*.

EXPERIMENTAL

The plant material was obtained in Sri Lanka as indicated below: *D. hirsuta*—Gilimale; *D. moonii*, *D. thwaitesii*, *D. oppositifolia*, *D. oblongifolia*, *D. acuta*, *D. chaetocarpa* and *D. walkeri*—Kanneliya (wet lowland forest), *D. rheophytica*—Mahiyangana, *D. spinescens*—Cheddikulam, and *D. quaesita*—Kottawa. Mps are uncorr. The bark and timber (in some instances the roots, fruits and leaves as well) of the endemic *Diospyros* taxa were separately ground. The powdered bark was extracted with cold CHCl₃ in the dark, followed by hot MeOH. The timber was extracted with light petrol (bp 60–80°), C₆H₆

* Part 31 in the series 'Chemical Investigation of Ceylonese Plants'. For part 30 see Bandaranayake, W. M., Karunanayake, S., Sotheeswaran, S. and Sultanbawa, M. U. S. (1978) *Phytochemistry* (in press).

§ Spec. var.; diagnoses to be published.

Table 1. Compounds isolated from *Diospyros* species (percentage yield/dry wt)

	Sitosterol	Lupeol	Betulin	Betulinic acid	Taraxerol	Taraxerone
<i>Diospyros hirsuta</i> L.f.						
bark		0.003	0.2	0.01		
timber	0.015		0.11	0.04	0.016	
leaves	0.12	0.07				
fruits	0.015		0.008	0.002	0.05	
roots*	0.012	0.03				
<i>D. moonii</i> Thw.						
bark	0.007	0.483				0.044
timber	0.010	0.068	0.056	0.008		
roots*	0.007	0.50				0.039
<i>D. quaesita</i> Thw.						
bark	0.001	0.30	0.37	0.21		0.0012
timber	0.0007	0.0006	0.048	0.22		
<i>D. spinescens</i> Kosterm						
bark	0.0004	0.016	0.162	0.432		
timber	0.0006	0.003	0.091	0.021		
<i>D. thwaitesii</i> Bedd.						
bark	0.006	0.51				0.03
timber	0.0035	0.015	0.055	0.048		0.003
roots*	0.003	0.11				0.01
<i>D. walkeri</i> (Wight) Guerke						
bark	0.01	0.38	0.08			
timber		0.07	0.029	0.1		
<i>D. acuta</i> Thw.						
bark*	0.01	0.32				0.05
timber*	0.008	0.013				0.008
<i>D. oblongifolia</i> Thw. Kosterm.						
bark*	0.023	0.42				0.062
timber*	0.004	0.02				0.003
<i>D. oblongifolia</i> Thw. Kosterm.						
bark*	0.001	0.5				0.081
timber*	0.0041	0.011				0.002
fruits	0.017	0.44	0.1			
<i>D. oppositifolia</i> Thw.						
bark*	0.003	0.28				0.004
timber*	0.043	0.0004				0.0001
<i>D. rheophytica</i> Kosterm.						
bark*	0.007	0.65				0.04
timber	0.006	0.01				0.002

* Compounds estimated by TLC

and MeOH. The different extracts were subjected to column chromatography and prep TLC. The 7 triterpenoids, sitosterol, scopoletin and the 4 naphthaquinones were identified by comparison with authentic samples (TLC, mp, mmp and in some cases optical rotation UV and/or MS) and by preparation of derivatives [17–19].

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Ursolic acid	Oleanolic acid	Scopoletin	Plumbagin	Elliptinone	Diospyrin	Diosindigo A
						0.0006
0.01						0.0001
						0.0003
	0.002					0.0001
		0.001				
					0.65 0.04	
			0.12 0.518	0.01		
		0.123				
	1.12					

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