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COUMARINS FROM *OLEA AFRICANA* AND *OLEA CAPENSIS*

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Key Word Index—*Olea africana; Olea capensis*; Oleaceae; coumarins; esculetin; scopoletin; isoscopoletin; scoparone.

Abstract—Esculetin and scopoletin were isolated from the bark of *Olea africana* while isoscopoletin and scoparone were isolated from the bark of *Olea capensis*. The distribution of these coumarins in *Olea* species from South Africa is described.

The bark of *Olea europaea* L. was found to contain new lignans, i.e. 1-acetoxypinoresinol and related compounds [1, 2]. During an investigation of the bark constituents, esculetin (6,7-dihydroxycoumarin) was isolated [3]. Previously, the occurrence of coumarins in Oleaceae was only known in *Fraxinus* species [4]. The present paper describes the isolation of coumarins from South African *Olea* species, *Olea africana* and *Olea capensis* L. *Olea africana*, recently reclassified as *Olea europaea* L. subsp. *africana* (Mill.) P. S. Green [5], is not found outside Southern Africa [6].

Esculetin (**1**) and scopoletin (**2**) were isolated from the bark of *Olea africana* and identified by direct comparison with respective authentic samples. Isoscopoletin (**3**) and scoparone (esculetin dimethyl ether, **4**) were isolated from the bark of *Olea capensis* and identified by direct comparison with respective authentic samples. This represents the first report of esculetin methyl ethers **2**, **3** and **4** in Oleaceae.

In addition, the distribution of these coumarins in *Olea woodiana* Knobl. and *Olea exasperata* Jacq. was examined by comparison with that in *O. europaea*, *O. africana* and *O. capensis*. These species have sometimes been confused with *Olea africana* [6, 7]. Identification of coumarins was determined by co-chromatography with authentic standards in two solvent systems, benzene–EtOAc (1:1) and $CHCl_3$–EtOAc (1:1), on silica gel TLC plates. The results are as shown in Table 1. It is noteworthy that esculetin (**1**) is the major coumarin in all the species examined except *Olea capensis*.

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EXPERIMENTAL

All mps are uncorr. The ^1H NMR spectra were run on a 90 MHz instrument in DMSO-d_6 with TMS as int. standard. MS were obtained by a direct inlet system.

Plant materials. The plant materials collected were: *Olea africana* in August 1982 at Kirstenbosch Botanic Garden and in October 1982 at Bloemfontein; *Olea capensis* in August and November 1982 at Kirstenbosch Botanic Garden; *Olea woodiana* and *Olea exasperata* in August 1982 at Kirstenbosch Botanic Garden. Specimens from which samples for coumarin analysis were taken are lodged at the Herbarium of Higashi Nippon Gakuen University.

Isolation of esculetin (**1**) *and scopoletin* (**2**). Dry powdered bark (1.0 kg) of *Olea africana* was extracted × 3 with MeOH. The concd extract plus H_2O was extracted with Et_2O. The Et_2O extract was chromatographed on a silica gel column with a $CHCl_3$–EtOAc gradient. The fractions were monitored by TLC

Table 1. Distribution of hydroxycoumarins in *Olea* barks

	Esculetin (1)	Scopoletin (2)	Isoscopoletin (3)	Scoparone (4)
Olea europaea	+ + +	(+)		
Olea africana (*Olea europaea* subsp. *africana*)	+ + +	+ +	(+)	
Olea capensis	(+)	(+)	+ + +	+ +
Olea woodiana	+ + +	(+)		
Olea exasperata	+ + +	(+)		

+ + + = Major compound present; + + = present; (+) = minor trace detected.

developed with benzene–EtOAc (1:1). The fractions showing a TLC spot at R_f 0.26 in UV light were concd to afford **1** (94.4 mg). Recrystallization from MeOH gave pale yellow prisms, mp 272–274°. (Found: $[M]^+$ at m/z 178.0259; $C_9H_6O_4$ requires: 178.0265.) IR ν_{max}^{KBr} cm^{-1}: 3175 (OH), 1665 (CO), 1610 (C=C), 1565 (aromatic C=C). UV λ_{max}^{EtOH} nm (log ε): 230.0 (4.13), 258.0 (3.72), 262.0 (3.71) sh, 300.7 (3.76), 351.6 (4.06). ^1H NMR: δ6.14 (1H, *d*, *J* = 10 Hz, H-3), 6.73 (1H, *s*, H-8), 6.96 (1H, *s*, H-5), 7.81 (1H, *d*, *J* = 10 Hz, H-4). The fractions showing a TLC spot at R_f 0.41 were concd to afford **2** (32.9 mg). Recrystallization from MeOH gave colorless needles, mp 205–207°. (Found: $[M]^+$ at m/z 192.0418; $C_{10}H_8O_4$ requires: 192.0421.) IR ν_{max}^{KBr} cm^{-1}: 3300 (OH), 1670 (CO), 1615 (C=C), 1595, 1550, 1490 (aromatic C=C). UV λ_{max}^{EtOH} nm (log ε): 229.2 (4.18), 253.7 (3.71), 260.0 (3.68) sh, 298.8 (3.74), 346.5 (4.12). ^1H NMR: δ3.80 (3H, *s*, MeO), 6.17 (1H, *d*, *J* = 10 Hz, H-3), 6.74 (1H, *s*, H-8), 7.14 (1H, *s*, H-5), 7.83 (1H, *d*, *J* = 10 Hz, H-4).

Isolation of isoscopoletin (**3**) *and scoparone* (**4**). Dry powdered bark (110 g) of *Olea capensis* was treated in the same manner as for that of *Olea africana*. The fractions showing a TLC spot at R_f 0.48 were concd to afford **3** (491.4 mg). Recrystallization from MeOH gave pale yellow needles, mp 187–190°. (Found: $[M]^+$ at m/z 192.0408; $C_{10}H_8O_4$ requires: 192.0421.) IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1695 (CO), 1624 (C=C), 1565, 1515 (aromatic C=C). UV λ_{max}^{EtOH} nm (log ε): 230.5 (4.20), 254.5 (3.75), 259.0 (3.74) sh, 296.1 (3.78), 347.6 (4.01). ^1H NMR: δ3.91 (3H, *s*, MeO), 6.16 (1H, *d*, *J* = 10 Hz, H-3), 6.75 (1H, *s*, H-8), 6.89 (1H, *s*, H-5), 7.55 (1H, *d*, *J* = 10 Hz, H-4). The fractions showing a TLC spot at R_f 0.56 were concd to afford **4** (15 mg). Recrystallization from MeOH gave colorless needles, mp 145–146°. (Found: $[M]^+$ at m/z 206.0573; $C_{11}H_{10}O_4$ requires: 206.0577). IR ν_{max}^{KBr} cm^{-1}: 1710 (CO), 1620 (C=C), 1565, 1515 (aromatic C=C). UV λ_{max}^{EtOH} nm (log ε): 230.4 (4.05), 250.5 (3.57) sh, 257.5 (3.53) sh, 288.5 (3.58) sh, 294.6 (3.60), 343.0 (3.78). ^1H NMR: δ3.77, 3.83 (6H, each *s*, 2 × MeO), 6.23 (1H, *d*, *J* = 10 Hz, H-3), 6.99 (1H, *s*, H-8), 7.18 (1H, *s*, H-5), 7.87 (1H, *d*, *J* = 10 Hz, H-4). These compounds were identical with authentic samples in all respects.

Coumarin analysis of Olea *species*. The bark (10 g each) of *Olea* species were respectively extracted with MeOH. The concd extract plus H_2O was extracted with Et_2O. The Et_2O extract was examined by TLC using pre-coated TLC plates silica gel 60 F_{254} (Merck) in two solvent systems, benzene–EtOAc (1:1) and $CHCl_3$–EtOAc (1:1). The coumarins appeared under UV (254 nm) as a dark absorbing spot and under UV (360 nm) as a bright fluorescent spot.

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