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TWO CHEMICALLY DISTINCT GROUPS OF *CALOPHYLLUM* SPECIES FROM SRI LANKA

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Key Word Index—*Calophyllum* species; Guttiferae; (+)-*cis*-dihydroinophyllolide; inophyllum A; (−)-*trans*-dihydroinophyllolide; soulattrolide; calozeylanic acid.

Abstract—The leaf extracts of *Calophyllum moonii* and *C. walkeri* were investigated. The former contained neoflavonoids whereas the latter had calozeylanic acid. Distribution of natural products in the leaf extracts of seven *Calophyllum* species has been reviewed and the existence of two chemically distinct groups in *Calophyllum* species has been recognized.

INTRODUCTION

Nine endemic *Calophyllum* species are recorded in Sri Lanka. They are: *C. bracteatum* Thw., *C. calaba* L., *C. cordato-oblongum* Thw., *C. cuneifolium* Thw., *C. lankaensis* Kosterm (= *C. zeylanicum* Kosterm.), *C. moonii* (= *C. soulattri* Burm f.), *C. thwaitesii* Planch and Triana, *C. trapezifolium* Thw. and *C. walkeri* Wight. We have reported [1–3] the chemical investigation of the bark and leaves of a few *Calophyllum* species. In this paper we report on the leaf extractives of two species, namely, *C. moonii* and *C. walkeri*. These, and our previous results, indicate the existence of two chemically distinct groups of *Calophyllum* species.

RESULTS AND DISCUSSION

The hot petrol extracts of the leaves of *C. moonii* when chromatographed over silica gel and eluted with petrol–EtOAc gave (i) a sitosterol ester which on hydrolysis with potassium hydroxide gave sitosterol and (ii) D:A-friedo-oleanan-3-one (friedelin). Two neoflavonoids were eluted next and have been characterized as (+)-*cis*-dihydroiniphyllolide (**1**) [4] and (−)-*trans*-dihydroinophyllolide (**2**) [5].

It appeared from the data given in the Experimental that **1** is a neoflavonoid and is probably (+)-*cis*-dihydroinophyllolide (inophyllum A). The following decoupling studies to confirm the stereochemistry at C-11 and C-10 were carried out on this neoflavonoid. Irradiation at δ_H 1.16 caused the multiplet at δ_H 2.27 to collapse to a double-doublet ($J = 3.46$ and 5.19 Hz) and irradiation at δ_H 1.43 caused the multiplet at δ_H 4.43 to collapse to a doublet ($J = 3.46$ Hz). The complete chemical shift data are given in Fig. 1. These results confirm that the neoflavonoid is identical to inophyllum A (**1**) characterized by Kawazu *et al.* [4, 6]. The data for **1** suggest that H-10–H-11 is *gauche* ($J = 3.46$ Hz) and that H-11–H-12 is probably *gauche* ($J = 5.19$ Hz). Thus the C-10 methyl and the hydroxyl are pseudo-equatorial and the C-11 methyl is pseudo-axial.

The second neoflavonoid isolated had M_r (mass spectrum), mass spectral fragmentation pattern, IR and UV spectra all identical to **1**. However, the $[\alpha]_D$ value was negative and the ^{1}H NMR spectrum was slightly different to that of **1**. Irradiation at δ_H 1.18 resulted in the multiplet at δ_H 1.80 collapsing to a double doublet ($J = 3.46$ and 10.30 Hz). Irradiation at δ_H 1.45 resulted in the multiplet at δ_H 4.31 collapsing to a doublet ($J = 10.30$ Hz). The neoflavonoid is thus identified as soulattrolide (**2**) and it exists in a conformation in which both methyl groups at C-10 and C-11 are pseudo-equatorial and the hydroxyl group at C-12 is pseudo-axial. This leads to a *gauche* arrangement of H-11 and H-12 and $J = 3.46$ Hz and a *trans* arrangement of H-10 and H-11 with ($J = 10.30$ Hz). The ^{1}H NMR chemical shifts of **2** are given in Fig. 1. This is the second report of the neoflavonoid **1** and **2**. The next compound isolated from the *C. moonii* leaf extract was identified as apetalactone (**3**) [1].

The hot petrol extractives of the leaves of *C. walkeri*, when separated on a column of silica gel, gave D:A-friedo-oleanan-3-one (friedelin), 28-hydroxy-D:A-friedo-oleanan-3-one(canophyllol) and an acid mixture. The major component of the latter was found to be calozeylanic acid (**4**) [7]. We characterized this acid (**4**) earlier [1] from the leaf extracts of two other *Calophyllum* species, namely, *C. lankaensis* and *C. thwaitesii*. These results are summarized in Table 1.

All the *Calophyllum* species examined had triterpenoids containing the friedo-oleanane skeleton in their leaf extracts. Two major groups of *Calophyllum* species thus emerge. One group (*C. cordato-oblongum* and *C. moonii*) contain neoflavonoids while the other group contain acids in their leaf extracts. Amongst the acid containing group all, except *C. calaba*, had the same acid, calozeylanic acid

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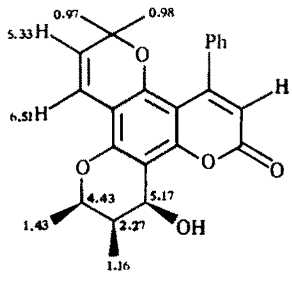

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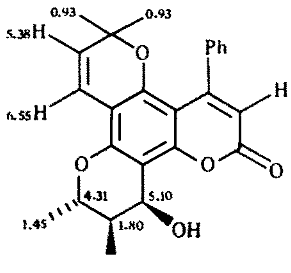

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Fig. 1. ^{1}H NMR chemical shifts [δ(ppm)] of **1** and **2**.

(**4**). Calozeylanic acid (**4**) would appear to be the biogenetic precursor of chapelieric acid (**7**) found in the leaf extract of *C. calaba*.

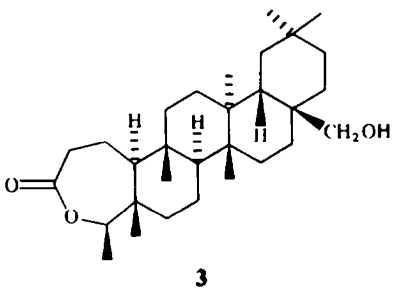
EXPERIMENTAL

Plants were collected at the Kanneliya rain forest in the South of Sri Lanka.

Calophyllum moonii Sun dried milled leaves (4 kg) gave 72 g of hot petrol extract. This was chromatographed over silica gel and elution with petrol–EtOAc gave: sitosterol ester (0.07%) which on hydrolysis (KOH–MeOH) gave sitosterol, mp 137°, lit. [8] 140°; $[\alpha]_D = -38°$, lit. [8] $-35°$. D:A-Friedooleanan-3-one(friedelin) (0.025%), mp 264–265° lit. [3] 265°; $[\alpha]_D = -22.5°$ ($CHCl_3$), lit. [3] $-22.5°$. (+)-*cis*-Dihydroinophyllolide (inophyllum A) (**1**) (0.03%), mp 193–195°, lit. [6] 200°; $[\alpha]_D = +68.8°$ ($CHCl_3$), lit. [6] +43°; IR ν_{max}^{KBr} cm^{-1}: 3400, 2680–2820, 1710, 1635, 1590, 1445, 1380, 1350, 1150, 850, 770, 700; ^{1}H NMR ($CDCl_3$): δ7.30 (5H, *m*, ArH), 6.51 (1H, *d*, $J = 9.90$ Hz), 5.96 (1H, *s*), 5.33 (1H, *d*, $J = 9.90$ Hz), 5.17 (1H, *d*, $J = 5.19$ Hz), 4.43 (1H, *m*, $J = 3.46$ Hz and 6.92 Hz), 2.27 (1H, *m*, $J = 5.19$ and 3.46 Hz), 1.43 (3H, *d*, $J = 6.92$ Hz), 1.16 (3H, *d*, $J = 7.20$ Hz), 0.98 (3H, *s*, Me) and 0.97 (3H, *s*, Me); MS *m/z*: 404 $[M]^+$ (25%), 389 (100), 386 (1), 371 (4), 333 (50). Oxidation of **1** with CrO_3–pyridine at room temp. gave a product which was purified by prep. TLC to give the oxidized product, mp 155°, lit [6] 149–151°; $[\alpha]_D = +65.5°$ ($CHCl_3$), lit. [6] +70°; ^{1}H NMR ($CDCl_3$): δ7.40 (5H, *m*, ArH), 6.58 (1H, *d*, $J = 9.90$ Hz), 6.01 (1H, *s*), 5.42 (1H, *d*, $J = 9.90$ Hz), 4.75 (1H, *m*), 2.60 (1H, *m*), 1.43 (3H, *d*, $J = 7.0$ Hz), 1.16 (3H, *d*, $J = 9.0$ Hz), 0.95 (6H, *s*). (−) *trans*-Dihydroinophyllolide (soulattrolide) (**2**) (0.003%), mp 198–200°, lit. [5] 201–202°; $[\alpha]_D = -21.8°$ ($CHCl_3$), lit. [5] $-29.6°$; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3100–3500,

Table 1. Distribution of natural products in the leaf extracts of *Calophyllum* species

Species	Triterpenoids	Coumarins	Acids
C. calaba	Friedelin Friedelan-3β-ol Canophyllal Canophyllol Friedelan-3β,28-diol	—	Canophyllic acid (**5**) *cis*-Chapelieric acid (**6**) Chapelieric acid (**7**)
C. cordatooblongum	Friedelin Canophyllol	Cordatolide-A (**8**) Cordatolide-B (**9**) Oblongulide (**10**)	—
C. lankaensis	Friedelin Canophyllol Canophyllal Apetalactone (**3**)	—	Calozeylanic acid (**4**) Thwaitesic acid (**11**) *iso*-Thwaitesic acid (**12**)
C. moonii	Friedelin Apetalactone (**3**)	(+)-*cis*-Dihydroinophyllolide (**1**) (−)-*trans*-Dihydroinophyllolide (**2**)	—
C. thwaitesii	Friedelin Canophyllol Apetalactone (**3**)	—	Calozeylanic acid (**4**) Thwaitesic acid (**11**)
C. trapezifolium	Friedelin Canophyllol	—	Calozeylanic acid (**4**)
C. walkeri	Friedelin Canophyllol	—	Calozeylanic acid (**4**)



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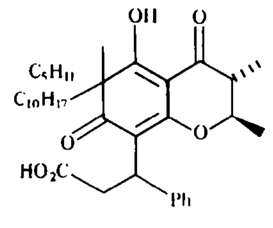

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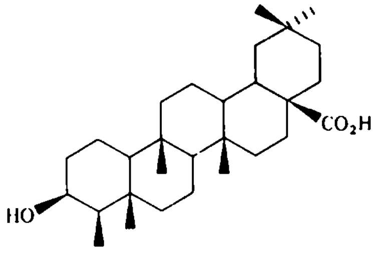

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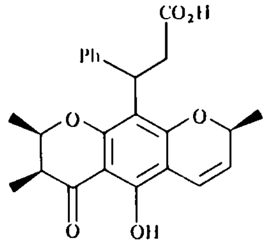

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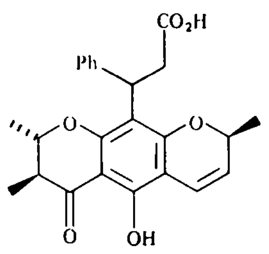

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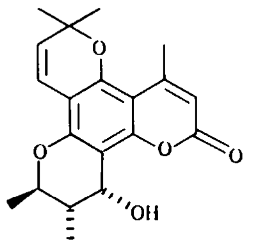
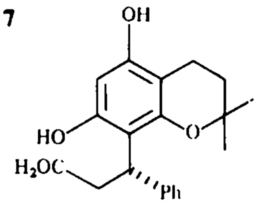


8 α−OH
9 β−OH



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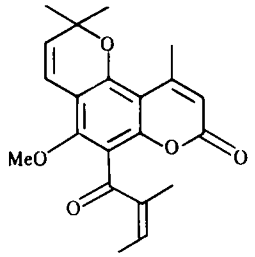

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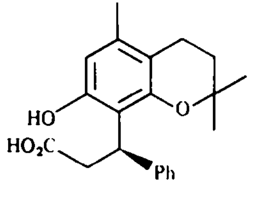

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1370, 1140, 910, 870; ¹H NMR ($CDCl_3$): δ7.40 (5H, *m*, ArH), 6.55 (1H, *d*, *J* = 10.0 Hz), 5.96 (1H, *s*), 5.38 (1H, *d*, *J* = 10.0 Hz), 5.10 (1H, *d*, *J* = 3.46 Hz), 4.31 (1H, *m*, *J* = 6.29 and 10.30 Hz), 2.8 (1H, OH), 1.80 (1H, *m*, *J* = 3.46, 6.77 and 10.30 Hz), 1.45 (3H, *d*, *J* = 6.30 Hz), 1.18 (3H, *d*, *J* = 6.77), 0.93 (6H, *s*, 2 × Me); MS *m/z*: 404 $[M]^+$ (20%), 389 (50), 386 (40), 371 (100), 105 (2), 77 (5). Apetalactone (**3**) 0.01%), mp 330–332°, lit. [1] 335°; $[\alpha]_D$ = +33.0° ($CHCl_3$) lit. [1] +37°, identical with authentic sample (mmp).

Calophyllum walkeri. Leaves (2 kg) gave 25 g of hot petrol extract. This on CC over silica gel gave: D:A-friedo-oleanan-one(friedelin) (0.01%) mp 262°, lit. [3] 265°; $[\alpha]_D$ = −25.5° ($CHCl_3$), lit. [3], −22.5°. 28-Hydroxy-D:A-friedooleanan-3-one (canophyllol) (0.015%), mp 280°, lit. [3] 280–282°; $[\alpha]_D$ = −20°

($CHCl_3$), lit. [3] −21°. Calozeylanic acid (**4**), (0.5%), $[\alpha]_D$ = +14° ($CHCl_3$), lit. [7] +12.6°; MS *m/z*: 562 $[M]^+$ (10%), 494 (30), 476 (24), 450 (15), 439 (20), 413 (15), 407 (25), 354 (25), 353 (100), 351 (25) and 345 (12); identical with authentic sample (IR, ^1H NMR, TLC).

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