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TRITERPENES OF SOME SPECIES OF FLACOURTIACEAE*

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The Flacourtiaceae is well known for its characteristic medicinal oils obtained from their seed kernals. Chaulmoogra oil [1] from *Hydnocarpus kurzii* (King) Warb (formerly called *Taraktogenos kurzii* King) has been used for a very long time for the treatment of skin diseases and especially for leprosy [2] and as an ointment for tuberculosis patients [3]. Therapeutically effective oils have also been obtained from *H. venenata* Gaertn. [4] *H. wightianus* Blume [5] and *H. anthelmintica* Pierre [6]. Hegnauer [7] has discussed the characteristic fatty acids, isolated from this family. Other compounds characterised include mangiferin from *Flacourtia indica* (Burm. f.) Merr [8], *Aphloia madagascariensis* [9] and *A. theiformis* (Vahl) Benn. [10] and friedelin from *Scolopia crenata* Clos. [2].

We have recently reported the presence of mangostin in the bark of *Hydnocarpus octandra* Thw. and *H. venenata* Gaertn. [11] and described several new triterpenoids containing the friedelane skeleton in *H. octandra* [12] and *Trichadenia zeylanica* Thw. [13]. As a continuation of these studies, the triterpenoids of the bark and wood of *H. venenata*, *Erythrospermum zeylanicum* (Gaertn) Alston, *Casearia thwaitesii* Briq., *Scolopia schreberi* J. F. Gmel and *Chlorocarpa pentachista* Alston have now been investigated. The results are shown in Table 1.

Although *H. octandra* [12] gave 7 new triterpenes having the friedelane skeleton with 29-Me or 26-Me transformed, no friedelane derivatives have been isolated from *H. venenata*. *H. octandra* and *Trichadenia zeylanica* [13] are rare endemic trees of the wet lowland forests of Sri Lanka while *H. venenata* is found growing along streams and rivers in the mixed deciduous forests of the dry zone. Habitat differences may be one of the factors that account for the total absence of friedelane derivatives from *H. venenata*. On a chemical basis these two species of *Hydnocarpus* are very different and thus a taxonomic reappraisal is indicated [14]. There are some intergeneric chemical links (Table 1) between the *Hydnocarpus*, *Erythrosperumum*, *Casearia* and *Scolopia* but *Chlorocarpa* seems to stand apart in having cycloartenol and cycloartenone [15] as the only triterpenoid constituents.

EXPERIMENTAL

Bark and timber of each species were separately extracted with different solvents. The extracts were then separated on a Si gel column and the isolated compounds identified with authentic samples by mmp, IR and TLC comparison. Mp's were determined on a Kofler hot stage. Petrol refers to light petroleum bp 60–80°.

Erythrospermum zeylanicum. Collection was from Morapitiya in Kalutara district. The bark (2.6 kg) gave (a) petrol extract (4.7 g, 0.18%) (b) rectified spirit extract (14.3 g, 0.55%). The timber (3.5 g) gave (a) petrol extract (2.7 g, 0.08%) (b) rectified spirit extract (14.3 g, 0.40%). The bark extract (4.7 g) was chromatographed on Si gel (160.g) and eluted with C_6H_6–petrol (2:3), C_6H_6 and C_6H_6–$CHCl_3$ (1:1) to give friedelin mp 263–4°, $(\alpha)_D^{27}$ – 23.4° (lit. [16] mp 266°, $[\alpha]_D$ – 23.1°); sitosterol mp 136–7° (lit. [17] mp 136–37°); betulinic acid mp 300–1°, $[\alpha]_D^{27}$ + 12.1° (lit. [18] mp 361–8°, $[\alpha]_D$ + 8°); ursolic acid mp 283–4°, $[\alpha]_D^{27}$ + 67.1° (lit. [19] mp 283–4°, $[\alpha]_D$ + 65.9°). Separation of the timber extract (2.7 g) gave only sitosterol (0.21 g).

Casearia thwaitesii. Collection was from the Montane forest bordering Horton Plains in Nuwara Eliya District. The bark (1.0 kg) gave (a) petrol extract (5.1 g, 0.51%) (b) MeOH extract (230 g, 23%). The timber (2.2 kg) gave (a) petrol extract (1.3 g, 0.06%) (b) MeOH extract (370 g, 17.0%). The bark petrol extract (5.0 g) on chromatographic separation using Et_2O–petrol mixtures gave β-amyrin mp 198–9° $[\alpha]_D^{27}$ + 89.3° (lit. [20], mp 200°, $[\alpha]_D$ + 88°), sitosterol mp 136–7°. The timber extract (1.2 g) on similar separation gave β-amyrin and sitosterol.

Scolopia schreberi. Collection was from Pallegama in Matale District. The bark (2.25 kg) gave (a) petrol extract (6.2 g, 0.27%) (b) MeOH extract (70 g, 3.1%). The timber (4.2 kg) gave (a) petrol mixtures gave β-amyrin mp 198–9° $[\alpha]_D^{27}$ + 89.3° (lit. The bark petrol extract (6.2 g) was shaken with petrol (100 ml) at room temp. Petrol soln gave a gum (2.6 g, 0.12%) and a solid residue (3.6 g, 0.15%). This solid (1.6 g) was separated on Si gel (75 g) using C_6H_6–petrol mixture to give friedelin mp 264–5°, epifriedelinol mp 280–1°, $(\alpha)_D^{27}$ + 25° (lit. [21], mp 283–5°, $[\alpha]_D$ + 24°) and β-amyrin mp 199–200°. The petrol-soluble fraction was separated to give only sitosterol. Timber petrol extract on similar separation gave friedelin, β-amyrin and sitosterol.

Chlorocarpa pentachista. Collection was made near Bakiella in the Amparai District. The bark (0.4 kg) gave (a) petrol extract (2.1 g, 0.52%) (b) MeOH extract (15 g, 3.7%). The timber

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Table 1. Amount of triterpenes (% dry weight) in Flacourtiaceae species

	Hydnocarpus venenata	**Erythrospermum zeylanicum*	**Casearia thwaitesii*	**Scolopia schreberi*	**Chlorocarpa pentachista*
Acetyl-betulinic acid	B 0.003	—	—	—	—
	T —	—	—	—	—
Acetyl-ursolic acid	B 0.005	—	—	—	—
	T —	—	—	—	—
β-Amyrin	—	—	B 0.025	B 0.001	—
	—	—	T 0.009	—	—
Betulinic acid	B 0.006	B 0.011	—	—	—
	T —	—	—	—	—
Betulonic acid	B 0.004	—	—	—	—
	T —	—	—	—	—
Cycloartenol	—	—	—	—	B 0.015
	—	—	—	—	T 0.0005
Cycloartenone	—	—	—	—	B 0.002
	—	—	—	—	T 0.0002
Epifriedelinol	—	—	—	B 0.017	—
	T —	—	—	—	—
Friedelin	—	B 0.004	—	B 0.010	—
	—	—	—	T 0.002	—
Ursolic acid	B 0.003	B 0.002	—	—	—
	T —	—	—	—	—
Sitosterol	B 0.008	B 0.008	B 0.021	B 0.020	B 0.032
	T 0.034	T 0.006	T 0.006	T 0.003	T 0.001

*Endemic species. B = Bark; T = Timber.

(2.0 kg) gave (a) petrol extract (2.3 g, 0.078%) (b) MeOH extract (55 g, 1.5%). The bark petrol extract (2.1 g) on separation on Si gel (95 g) with $CHCl_3$–petrol mixture gave cycloartenone mp 107–8°, $[\alpha]_D^{27}$ + 23.0° (lit. [22], mp 109°, $[\alpha]_D$ + 24°), cycloartenol mp 110–11°, $[\alpha]_D^{27}$ + 55.2° (lit. [22] mp 114°, $[\alpha]_D$ + 54°) and sitosterol mp 136–7°. The same 3 compounds were separated from the timber petrol extract.

Hydnocarpus venenata. Collection was from Naula in the Matale District. Bark (4.6 g) gave (a) Petrol extract (28.6 g, 0.62%), (b) MeOH extract (550 g, 11.9%). Timber (5.0 g) gave (a) petrol extract (11.9 g, 0.23%) (b) MeOH extract (104 g, 2.0%). The petrol extract (28.6 g) was triturated with petrol (400 ml) and filtered to give a grey solid A (2.1 g). Filtrate was concd and separated on a column to give (i) with petrol an oil (6.2 g) Density 0.9471 g cm^{-1} at 26° n_D^{26} 1.473, I_2 number 103.4. It contained several TLC spots and was not further investigated, (ii) C_6H_6, a white solid (1.2 g), (iii) $CHCl_3$–C_6H_6 (1:1) a greyish solid (1.9 g); (iv) $CHCl_3$, a grey solid (1.6 g), (v) Me_2CO, a solid (3.2 g). Fraction (ii) on separation on a column with Et_2O–petrol mixture gave acetylbetulinic acid mp 280° (lit. [23] mp 289°), acetylursolic acid mp 289–90° (lit. [19] mp 289–90°) and sitosterol mp 136–37°. Fraction (iv) (0.250 g) on PLC separation with MeOH–$CHCl_3$ (1:49) gave betulonic acid mp 257–8° (lit. [24] mp 258–60°). $[\alpha]_D^{26}$ + 14.0° (lit. [24] + 12.3°). Grey solid A on separation on a column with $CHCl_3$–C_6H_6 mixture gave betulinic acid mp 300–2°, ursolic acid mp 283–4°. The timber extract (11.9 g) was dissolved in petrol (20 ml) and allowed to crystallise. Sitosterol (1.7 g) was obtained.

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REFERENCES

1. Power, F. B. (1915) *Am. J. Pharm.* **87**, 493.
2. Kiang, P. C. (1923) *China Med. J.* **37**, 142.
3. Govindachari, T. R., Jadhir, S. J., Joshi, B. S., Kamat, V. N., Mohamed, P. A., Patenker, P. L., Prakash, D., Rane, D. F. and Viswanath, N. (1969) *Indian J. Chem.* 308.
4. Ghosh, S. (1920) *Indian J. Med. Res.* **6**, 211.
5. Nair, N. D. and Xavier, N. S. (1954) *Indian Soap J.* **19**, 225.
6. Adrians, L. (1965) *Inst. Roy. Colonial Belge Sec. Sci. Nat. ed. Med.* **15**, 87.
7. Hegnauer, (1966) *Chemotaxonomie der Pflanzen* Band 4 p. 164. Birkhauser Verlag Basel.
8. Bate-Smith, E. C. (1963) *J. Linn. Soc. (Botany)* **88**, 144.
9. Billet, D., Massicot, J., Mercier, C., Anker, D., Mastchenco, A. and Meuizer, M. C. (1965) *Bull. Soc. Chim, France* 3006.
10. Parris, R. R. and Etchepare, E. (1964) *Compte. Rend.* **258**, 5277.
11. Gunasekera, S. P., Sultanbawa, M. U. S. and Balasubramaniam, S. (1973) *Phytochemistry* **12**, 232.
12. Gunaskera, S. P. and Sultanbawa, M. U. S. (1973) *Chem. Ind.* 790; *idem. J. Chem. Soc. Perkin I* in press.
13. Gunasekera, S. P. and Sultanbawa, M. U. S. (1973) *Tetrahedron Letters* 2837; *J. Chem. Soc. Perkin I* in press.
14. Corner, E. J. H. (1976) *The seeds of Dicotyledons Vol. I* p. 143. Cambridge University Press, Cambridge.
15. Pavanasasivam, G. and Sultanbawa, M. U. S. (1973) *Phytochemistry* **12**, 2725.
16. Arthur, H. R., Lee, C. M. and Ma, C. N. (1956) *J. Chem. Soc.* 1461.
17. Heilbron, I. (ed) (1965) *Dictionary of Organic compounds* p. 2902. Oxford University Press, Oxford.
18. Robertson, A., Soliman, G. and Owen, E. C. (1939) *J. Chem. Soc.* 1267.
19. Ewens, E. S. and Spring, F. S. (1943) *J. Chem. Soc.* 523.
20. Mathew, A. G. and Lakshiminarayan, S. (1969) *Phytochemistry* **11**, 507.
21. McLean, J., Rettie, G. H. and Spring, F. S. (1958) *Chem. Ind.* 1515.
22. Barton, D. H. R. (1951) *J. Chem. Soc.* 1444.
23. Ruzicka, L. and Christie, L. (1938) *Helv. Chim. Acta* **21**, 1706.
24. Lehn, J. M. and Ourisson, G. (1962) *Bull. Soc. Chim. France.* 1133.