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TRITERPENES FROM *GYMNOSPORIA EMARGINATA**

DHARMASSREE B. T. WIJERATNE†, VIJAYA KUMAR†§, M. UVAIS S. SULTANBAWA†
and SINNATHAMBY BALASUBRAMANIAM‡

†Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka; ‡Department of Botany, University of Peradeniya, Peradeniya, Sri Lanka

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Key Word Index—*Gymnosporia emarginata*; Celastraceae; triterpenes; quinone-methides; dulcitol; sitosterol; chemotaxonomy.

Abstract—Triterpene quinone-methides, lupenone, β-amyrin, dulcitol, and sitosterol have been isolated from the timber, root and leaf extracts of *Gymnosporia emarginata*. Their chemotaxonomic significance is discussed.

INTRODUCTION

Gymnosporia emarginata is a shrub growing in the dry zone of Sri Lanka. Oleananes and lupanes have been isolated from the stem bark of *G. emarginata* [2] while triterpene quinone-methides, oleananes, lupanes and long-chain hydrocarbons have been reported from *G. rothiana* [3], *G. ovata* [4], *G. wallichiana* [5, 6] and *G. montana* [7]. We now report a systematic chemical examination of the root bark, root, leaves and timber of *G. emarginata*.

RESULTS AND DISCUSSION

The root bark, root, leaves and timber of *G. emarginata* were separately extracted with hot benzene and hot methanol. The extracts were separated into their chemical constituents by column and prep. TLC.

As previously found in stem extracts [2], β-amyrin was found to be the main component, with sitosterol being an important component of root, leaf and timber benzene extracts. This is true for all *Gymnosporia* species studied so far [3–7] and appears to be of chemotaxonomic significance since β-amyrin has also been reported from *Celastrus* and *Maytenus* species [8, 9]. *Celastrus*, *Maytenus* and *Gymnosporia* belong to the tribe Celastreae of the subfamily Celastroideae [10]. β-Amyrin has not been isolated from other tribes or subfamilies of the Celastraceae.

Lupenone, previously identified as a constituent of the stem bark of *G. emarginata* [2], in the present study was also found in the root. Oxolupane derivatives have been isolated from the stem bark of both *G. emarginata* [2] and *G. wallichiana* [5, 6]. According to Ding [11], the distinction between the genera *Gymnosporia* and *Maytenus* on the basis of spiny branchlets in *Gymnosporia* appears to be artificial and several *Gymnosporia* species have been transferred to *Maytenus*. The presence of oxygenated lupanes in some *Gymnosporia* species supports such a revision of the genus *Gymnosporia*.

The quinone-methide, pristimerin, present in the root, and dulcitol found in the stem and leaves, are characteristic constituents of members of the Celastraceae [11]. In the present investigation of *G. emarginata* dulcitol was isolated from all plant parts including leaf, root, root bark and timber. Pristimerin is accompanied in the roots of *G. emarginata* by tingenone and iguesterin.

EXPERIMENTAL

Gymnosporia emarginata (Willd.) Hook. f. ex. Thw. was collected in Amaduwa near Hambantota, Sri Lanka. Mps are uncorr. Identity of compounds was established by mp, mmp, TLC, and IR. Prep. TLC was carried out with 1 mm thick Kieselgel 60 $PF_{254+366}$ plates. ^1H NMR spectra were measured at 60 MHz. Optical rotations were carried out at 27° in $CHCl_3$ soln.

Extraction of plant material. Root bark (125 g), root (1 kg), leaves (360 g), timber (1.5 kg) and stem bark (1 kg) were separately extracted with hot C_6H_6 and MeOH. They gave 7.5, 15.2, 12.5, 10.5 and 22.0 g of C_6H_6 extracts and 5.2, 12.8, 8.2, 6.8 and 26.5 g of MeOH extracts, respectively.

Separation of root bark extracts. (a) C_6H_6 *extract.* Chromatography of the C_6H_6 extract (7.5 g) on Si gel (160 g) gave, on elution with $CHCl_3$: β-amyrin (0.2 g), colourless needles from petrol, mp 196–197°, $[\alpha]_D$ +88° (*c* 2.5), (lit. [12] mp 197–197.5°, $[\alpha]_D$ +88°) and sitosterol (38 mg), colourless needles from MeOH, mp 136–137°, $[\alpha]_D$ −34° (*c* 2.0), (lit. [12] mp 136–137°, $[\alpha]_D$ −35°). Further elution with $CHCl_3$–MeOH (99:1) gave iguesterin (200 mg), orange amorphous solid, $[\alpha]_D$ −99° (*c* 2.0), (lit. [7] mp 196–197°, [13] $[\alpha]_D$ −99°) and pristimerin (2.0 g), orange needles from MeOH, mp 213–214°, $[\alpha]_D$ −164° (*c* 1.0), (lit. [13] mp 214–217°). Elution with $CHCl_3$–MeOH (19:1) followed by prep. TLC (Et_2O–petrol, 2:1) on work-up gave tingenone, orange needles from MeOH, mp 200° (d), (lit. [7] mp 155–158°).

(b) MeOH *extract.* The MeOH extract (2 g) was acetylated at 100° with Ac_2O–pyridine and the product crystallized from MeOH as colourless cubes of dulcitol acetate (380 mg):

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§Author to whom correspondence should be addressed.

mp 162–164°, (lit. [14] mp 162–164°). ^{1}H NMR δ 2.0–2.1 (3*s*, OAc), 3.85 (2H, *dd*, J = 12 and 8 Hz, C$\underline{H}_2$), 4.33 (2H, *dd*, J = 12 and 5 Hz, C$\underline{H}_2$), 5.2–5.4 (4H, 2 overlapping *m*, $W_{1/2}$ = 12 and 2 Hz, C$\underline{H}$).

Separation of root extracts. (a) C_6H_6 *extract.* Chromatography of the C_6H_6 extract (15.2 g) on Si gel (350 g) gave on elution with petrol–$CHCl_3$ (1:1):lup-20(29)-en-3-one, colourless needles from EtOH, mp 169–170°, $[\alpha]_D$ +62° (*c* 2.5), (lit. [12] 170°, $[\alpha]_D$ +63.5°). Elution with $CHCl_3$ gave β-amyrin (2.25 g) and sitosterol (90 mg), while $CHCl_3$–MeOH (99:1) followed by prep. TLC ($CHCl_3$–MeOH, 99:1) gave iguesterin (110 mg) and pristimerin (1.1 g). Elution with $CHCl_3$–MeOH (19:1) followed by prep. TLC (Et_2O–petrol, 2:1) gave tingenone (10 mg).

(b) MeOH *extract.* The MeOH extract (2 g) gave on acetylation and crystallization, dulcitol acetate (368 mg).

Separation of leaf extracts. (a) C_6H_6 *extract.* Chromatography of the C_6H_6 extract (12.5 g) on Si gel (260 g) gave on elution with $CHCl_3$ followed by prep. TLC ($CHCl_3$ × 1) β-amyrin (300 mg) and sitosterol (70 mg).

(b) MeOH *extract.* The MeOH extract (2 g) gave on acetylation and crystallization, dulcitol acetate (980 mg).

Separation of timber extracts. (a) C_6H_6 *extract.* Chromatography of the C_6H_6 extract (10.5 g) on Si gel (250 g) gave β-amyrin (420 mg) and sitosterol (100 mg) on elution with $CHCl_3$.

(b) MeOH *extract.* The MeOH extract (2 g) gave on acetylation and crystallization, dulcitol acetate (200 mg).

Separation of stem bark MeOH *extract.* The extract (2 g) gave on acetylation and crystallization, dulcitol acetate (0.6 g).

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REFERENCES

1. Weeratunga, G., Kumar, V., Sultanbawa, M. U. S. and Balasubramaniam, S. (1982) *J. Chem. Soc. Perkin Trans.* 1 (in press).
2. Wijeratne, D. B. T., Kumar, V. and Sultanbawa, M. U. S. (1981) *J. Chem. Soc. Perkin Trans.* 1 2724.
3. Govindachari, T. R., Mohammed, P. A. and Parthasarathy, P. C. (1970) *Indian J. Chem.* **8**, 395.
4. Desai, H. K., Gawad, D. H., Govindachari, T. R., Joshi, B. S., Kamat, V. N., Modi, J. D., Parthasarathy, P. C., Patankar, S. J., Sidhaya, A. R. and Viswanathan, N. (1971) *Indian J. Chem.* **9**, 611.
5. Kulshreshtha, D. K. (1977) *Phytochemistry* **16**, 1783.
6. Kulshreshtha, D. K. (1979) *Phytochemistry* **18**, 1239.
7. Joshi, K. C., Singh, P. and Singhi, C. L. (1981) *Planta Med.* **43**, 89.
8. Bruning, R. and Wagner, H. (1978) *Phytochemistry* **17**, 1821.
9. Abraham, D. J., Trojanek, J., Munzing, H. P., Fong, H. H. S. and Farnsworth, N. R. (1971) *J. Pharm. Sci.* **60**, 1085.
10. Engler, A. (1964) *Syllabus der Pflanzenfamilien* Vol. 2, p. 293. Gebruder Brontraeger, Berlin.
11. Ding H. (1962) *Flora Malesiana* Series I, Vol. 6, pp. 227–291.
12. Heilbron, S. I. and Bunbury, H. M. (1953) *Dictionary of Organic Compounds.* Eyre & Spottiswoode, London.
13. Gonzalez, A. G., Francisco, C. G., Freire, R., Hernandez, R., Salazar, J. A. and Suarez, E. (1975) *Phytochemistry* **14**, 1067.
14. Anjaneyulu, A. S. R. and Rao, M. N. (1980) *Phytochemistry* **19**, 1163.