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ANTHOCYANINS OF CORNACEAE, *CORNUS CANADENSIS*

C. T. DU, P. L. WANG and F. J. FRANCIS

Department of Food Science and Nutrition, University of Massachusetts, Amherst, MA 01002, U.S.A.

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Key Word Index—*Cornus canadensis*; Cornaceae; pelargonidin and cyanidin 3-robinobiosides.

Plant and source. Cornus canadensis, collected from Acadia National Park ground, Maine, U.S.A. *Uses.* Ornamental. *Previous work on anthocyanins of Cornaceae.*[1,2] *Plant parts examined.* The ripe berries were extracted with 1% methanolic HCl and purified as previously described.[1,2] Examination of the purified pigment extract on *n*-BuOH-formic-H_2O (20:5:12, upper) chromatograms showed the presence of four major orange colored anthocyanins and other minor pigments. Identifications were based on results of partial and complete acid hydrolysis, H_2O_2 oxidation, UV and visible spectra, and comparison of the pigments and their hydrolysis products with authentic markers. The major anthocyanins were identified as the 3-glucoside, 3-galactoside, 3-rutinoside and 3-robinobioside of pelargonidin. The minor and trace pigments were the 3-glucoside, 3-galactoside, 3-rutinoside, 3-robinobioside of cyanidin and 3-sophoroside of pelargonidin. This is the first reported co-occurrence of these closely related glucose and galactose containing glycosides of pelargonidin and cyanidin in the same plant source.

Acknowledgements—The authors are grateful to Dr. J. B. Harborne for providing pelargonidin 3-sophoroside as a pigment marker.

[1] DU, C. T. and FRANCIS, F. J. (1973) *Hort. Sci.* **8**, 29.
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BETULINIC ACID IN THE DILLENIACEAE AND A REVIEW OF ITS NATURAL DISTRIBUTION*

G. PAVANASASIVAM and M. U. S. SULTANBAWA

Department of Chemistry, University of Sri Lanka, Peradeniya Campus Peradeniya, Sri Lanka

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Key Word Index—*Dillenia*; *Wormia*; *Acrotrema* spp.; Dilleniaceae; betulinic acid; triterpene acid.

Dillenia indica L. was investigated by Bhattacharjee and Chatterjee[1] and the occurrence of 0·75% betulinic acid in the bark was observed. As a part of a study on Ceylonese Plants.

* Part IX in the series "Chemical Investigation of Ceylonese Plants".

[1] BHATTACHARJEE, S. R. and CHATTERJEE, A. (1962) *J. Indian Chem. Soc.* **39**, 276.

the extractives of five plants of the Dilleniaceae: *D. indica* L., *D. retusa* Thw., *Wormia triquetra* Rottb., *W. burbidgei* and *Acrotrema uniflorum* Hook., have been sudied. Betulinic acid was readily separated by crystallization from methanol of the benzene extracts or by silica gel chromatography and characterized by comparison of m.m.p., IR, NMR and MS with an authentic sample. The amounts isolated from the different parts of each plant are given in Table 1.

TABLE 1. AMOUNT OF BETULINIC ACID (% OF DRY WT)

	Bark	Timber	Pericarp	Fruit	Whole plant	Flower centre
D. indica L.	1·3	0·25	1·9	—	—	—
**D. retusa* Thunb.	0·8	0·13	—	1·6	—	—
**W. triquetra* Rottb.	1·6	0·15	—	1·0	—	0·45
W. burbidgei	2·4	—	—	—	—	—
**A. uniflorum* Hook.	—	—	—	—	0·12	—

* Endemic species.

The amount in the bark is greater than in the timber and the amount in the pericarp or fruit is even greater than that in the bark in *Dillenia*. The presence of considerable amounts of betulinic acid in the five species suggests that betulinic acid may be a chemotaxonomic marker for the family. Table 2 lists the reported isolations of betulinic acid in other plant species with yields, wherever available; it occurs mainly in tree species which are valuable for timber purposes. It should be noted that over 1% betulinic acid has been reported in 11 other species besides the 4 species in this report.

TABLE 2. DISTRIBUTION AND YIELD OF BETULINIC ACID

Family	Genus and species	% Yield	Part	Reference
Alangiaceae	*Alangium lamarckii* Lam.	—	seeds	2
Apocynaceae	*Alyxia buxifolia* R.Br.	0·8	leaves	3
Akaniaceae	*Akania luceus* Hook f.	0·02	bark	4
Avicenniaceae	*Avicennia marina* L.	0·30	bark	5
Balanopaceae	*Balanops australiana* F. muell.	0·009	bark	6
Betulaceae	*Betula pendula* Roth.	0·21	bark	7
Cactaceae	*Lemaireocereus griseus*	2·0	whole plant	8
	L. hystrix	0·04	whole plant	9
	L. quevedonis	—	whole plant	8
	L. stellatus	0·38	whole plant	10
	Machaerocereus gummosus	0·40	whole plant	10
Cornaceae	*Cornus florida* Hook.	2·00	bark	11
Dilleniaceae	*Dillenia indica* L.	0·75	bark	1
Dipterocarpaceae	*Dipterocarpus hispidus* Thw.	0·014	bark	12
Ebenaceae	*Diospyros buxifolia* Hiern.	—	—	13
	D. discolour	0·05	fruit	14
	D. derra	—	—	13
	D. hirsuta L.f.	0·01	bark	15
		0·013	timber	15
		0·02	fresh fruit	15
	D. kaki L.	—	calyx	16
		—	leaves	17

TABLE 2.—*cont.*

Family	Genus and species	% Yield	Part	Reference
	D. lotus L.	—	—	13
	D. melanoxylon Roxb.	0·01	timber	14
	D. morrisiana Hause	—	—	18
	D. perigrina	2·5	bark	14
		—	seeds	19
	D. tomentosa Poir.	—	—	13
Ericaceae	*Arbutus menziesii* Pursh.	2·0	—	20
	Rhododendron grande Wight.	—	bark	21
	R. arboreum Sm.	—	bark	22
Euphorbiaceae	*Biscofia javanica* Blume.	—	bark	23
Flacourtiaceae	*Hydnocarpus venenata* Gaertn.	0·006	bark	12
Gentianaceae	*Menyanthes trifoliata* Neck.	0·1	rhizome	24
Guttiferae	*Calophyllum apetalum* Willd.	—	trunk bark	25
	C. bracteatum Thw.	0·003	timber	26
	Caraipa densiflora Mart.	—	trunk wood	27
	C. grandifolia Mart.	—	trunk wood	28
	Clusia sp.	—	timber	29
	Kayea stylosa Thw.	0·01	bark	30
Labiatae	*Anisomeles malabarica* R.Br.	0·01	whole plant	31
Leguminosae	*Melanoxylon brauna*	—	soft wood	32
Loranthaceae	*Nuytsia floribunda* R.Br.	1·70	stem and leaves	3
Myrtaceae	*Eugenia fruticosa* Roxb.	—	stem bark	33
	E. jambolana Lam.	0·17	bark	34
	E. wallichii Wight.	—	stem bark	33
	Leptospermum ericoides A.	—	bark	35
	L. scoparium Forst.	0·50	bark	36
	Metrosideros excelsa Soland.	0·10	flowers	37
	Syncarpia laurifolia Tenore	1·2	bark	38
Platanaceae	*Platanus acerifolia* Willd.	1·8	bark	39
	P. occidentalis L.	1·75	bark	40
	P. orientalis L.	—	rind	41
	P. vulgaris Spach.	—	heart wood	42
Punicaceae	*Punica granatum* L.	—	bark and leaves	43
Rhamnaceae	*Ceanothus americanus* L.	0·02	root bark	44
	Discaria longispina Miers	—	—	45
	Zizyphus vulgaris Lamark. var *Spinosus* Bunge.	—	seeds	46
Sapotaceae	*Madhuca neriifolia* Thw.	0·03	bark	47
Scophulariaceae	*Bacopa monieri* Vettst.	0·11	—	48
	Gratifolia officianalis L.	0·25	—	49
Ternstroemiaceae	*Ternstromia merriliana* Jack.	2·0	bark	50
Theaceae	*Eurya acuminata* DC	1·8	bark	51
Verbenaceae	*Tectona grandis* L.f. (Teak)	1·0	timber	52

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EXPERIMENTAL

The plants were collected as follows: *Wormia triquetra* Rottb. and *Dillenia retusa* Thunb. from Kanneliya forest; *D. indica* L. from Hanguranketa, Kandy; *Acrotrema uniflorum* Hook. from Ratnapura; *W. burbidgei* and fruits of *W. triquetra* Rottb. from Botanical Gardens, Peradeniya. The plant material was extracted with petrol. (60–80°) C_6H_6 and MeOH. The methanol extract was re-extraced with EtOAc. The benzene extract was repeatedly crystallized from methanol to give pure betulinic acid. Alternatively, it was separated from a silica gel column m.p. 283° $[\alpha]_D^{27}$ +14° ($CHCl_3$) (lit.[53] m.p. 306–310°, $[\alpha]_D$ +9°). It was shown to be identical with an authentic sample by m.m.p., IR and TLC comparison. It gave a methyl ester with ethereal CH_2N_2 m.p. 225° (lit.[10] 221–223°) which was converted into acetyl methyl betulinate with Ac_2O and pyridine. m.p. 202° $[\alpha]_D$ +20° ($CHCl_3$) (lit.[10] m.p. 201–206° $[\alpha]_D$ +19°). It was shown to be identical with an authentic sample by m.m.p., TLC and IR comparison.

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TERPENOID AND OTHER CONSTITUENTS OF *HERNANDIA VOYRONI* AND *ANTHOCLEISTA AMPLEXICAULIS**

NIKOLAUS WEBER

Department of Pharmacology, University of Heidelberg, D-6900 Heidelberg 1, BRD

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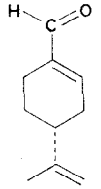
Key Word Index—*Hernandia voyroni*, Hernandiaceae; *Anthocleista amplexicaulis*; Loganiaceae; terpenoids; (+)-perillaldehyde; swertiamarin; (+)-bornesitol

Plant sources. H. voyroni Jum. (Hernandiaceae), *A. amplexicaulis* (Loganiaceae). R. Pernet[1] has identified perillaldehyde as a constituent of the oil obtained from *H. peltata* Meissn. He also investigated extracts obtained from *H. voyroni*, whose alkaloid contents he estimated to be 0·5%, and in addition isolated 2·9% of an oil with camphor-like smell. We have further examined this oil and we have isolated (+)-perillaldehyde (**1**) from this species. Derivatives of **1** (oxime, semicarbazone) were prepared and compared with authenitic samples.

Swertiamarin (**2**) and (+)-bornesitol (**3**) were isolated from *A. amplexicaulis*, tetraacetyl- and dihydrotetraacetyl-**2** were prepared, spectroscopically investigated and compared with authentic specimens. **2** has previously been isolated from *A. procera*.[2] **3** was transformed into its pentaacetyl derivative and the constitution of this product was elucidated by NMR spectroscopy. **3** has been previously found in *Sarcocephalus diderichii* (Rubiaceae).[3]



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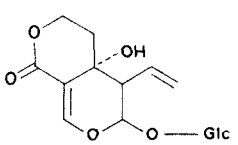

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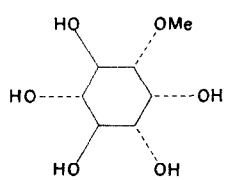

(3)

* Part 4 in the series "Plants from Madagascar"; for part 1, see SCHLITTLER, E. and WEBER, N. (1972) *Lloydia* **35**, 181. Part 2, see SCHITTLER, E. and WEBER, N. (1972) *Helv. Chim. Acta* **55**, 2061. Part 3, see WEBER, N. (1973) *Chem. Ber.* **106**, 3769.

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