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SHORT COMMUNICATION

THE OCCURRENCE OF LUNULARIC AND ABSCISIC ACIDS IN PLANTS

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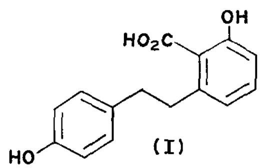
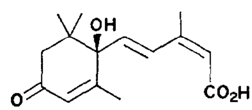
Abstract—The natural dihydrostilbene growth inhibitor of liverworts, lunularic acid, is shown to be of general occurrence in the algae. It could not be detected in mosses or pteridophytes and is not generally distributed in higher plants. The chemotaxonomic and phylogenetic significance of the mutually exclusive occurrence of lunularic acid and abscisic acid in these groups of plants is discussed.

LUNULARIC acid (I), a natural dihydrostilbene growth inhibitor first isolated and characterized from the liverwort *Lunularia cruciata*,[1] has been shown to be present without exception in all liverworts examined.[2] The inability to detect the ubiquitous growth inhibitor of higher plants, abscisic acid (II),[3] in liverworts, together with the observation that abscisic acid can mimic the growth inhibitory effect of lunularic acid when applied to *L. cruciata*, has prompted the suggestion that lunularic acid may be the biological equivalent of abscisic acid in this lower group of plants.[2] The potential phylogenetic and chemotaxonomic significance of the occurrence of lunularic acid in liverworts and also in algae but not in mosses, pteridophytes or (with one exception) higher plants, has been referred to briefly[4] and this paper records the details of these investigations.



(I)



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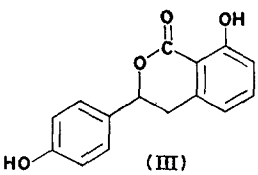

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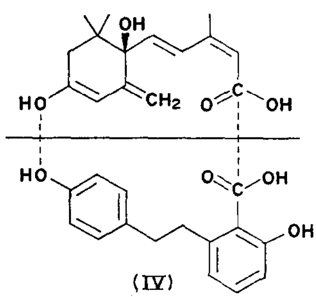

(IV)

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[1] I. F. M. VALIO, R. S. BURDEN and W. W. SCHWABE, *Nature, Lond.* **223**, 1176 (1969).
[2] R. J. PRYCE, *Planta* **97**, 354 (1971).
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[4] R. J. PRYCE, *Phytochem.* **10**, 2679 (1971).

Lunularic acid was extracted from plant material and detected by TLC and GLC as previously described.[2] All liverworts and all fresh water and marine algae examined contained lunularic acid (Table 1). Samples of the fresh water algae were obtained from axenic cultures. All other plants referred to in this paper were collected from their natural habitat. None of the mosses and pteridophytes examined (Table 2) have been found to contain any detectable lunularic acid (limit of detection 1 part in 10^8 fresh tissue).

TABLE 1. ALGAE AND LIVERWORTS IN WHICH LUNULARIC ACID HAS BEEN DETECTED

Algae* Class	Order	Species	Liverworts (Hepaticae)† Order	Species
Blue–green (Cyanophyceae)	Hormogonales	*Anabena* sp.	Marchantiales	*Conocephalum conicum*
				Lunularia cruicata
Diatoms (Bacillariophyceae)	Pennales	*Navicula* sp.		*Marchantia alpestris*[5]
				Marchantia polymorpha
				Riccia fluitans
Brown (Phaeophyceae)	Fucales	*Ascophyllum nodosum*		
		Fucus ceranoides		
Red (Rhodophyceae)	Gigartinales	*Chondrus crispus*	Metzgeriales	*Pellia epiphylia*
	Ceramiales	*Polysiphonia urceolata*		*Pellia endiviifolia*
			Jungermanniales	*Lophocolea cuspidata*
Yellow-green (Xanthophyceae)	Heterotrichales	*Tribonema* sp.		*Solenostoma triste*
				Solenostoma crenulatum
Green (Chlorophyceae)	Volvocales	*Chlamydomonas* sp.		
	Chlorococcales	*Chlorella* sp.		
	Ulvales	*Ulva lactuca*		

* Lunularic acid present in algae at *ca.* 1 μg/g fr. wt.
† Lunularic acid present in liverworts at 1–300 μg/g fr. wt.

The biosynthetic pathway to lunularic acid in *L. cruciata* probably involves hydrangenol (III) as an intermediate.[4] Although there is no evidence for the co-occurrence of these two compounds in *L. cruciata*, lunularic acid does exist along with hydrangenol in leaves of the garden hydrangea, *Hydrangea macrophylla*. However, no lunularic acid nor hydrangenol could be detected in leaves of other members of the *Saxifragales* (Table 2). The only fungus examined, the domestic mushroom (*Agaricus bispora*) also contained no lunularic acid.

TABLE 2. MOSSES PTERIDOPHYTES AND ANGIOSPERMS IN WHICH NO LUNULARIC ACID HAS BEEN DETECTED

Mosses (*Musci*) Order	Species	Pteridophytes Class	Order	Species	Angiosperms Order	Species
Sphagnales	*Sphagnum fimbriatum*	Ferns (Filicinae)	Filicales	*Polypodium vulgare*	*Saxifragales*	*Bergenia cordifolia*
						Hydrangea quercifolia
Polytrichales	*Polytrichum formosum*	Horsetails (Equisetinae)	Equisetales	*Equisetum arvense*		*Kalanchoe blossfeldiana*
Dicranales	*Leucobryum glaucum*	Lycopods (Lycopodinae)	Selaginallales	*Selaginella kraussiana*		*Pileostegia viburnioides*
Eubryales	*Mnium hornum*					*Ribes nigrum*
Hyponbryales	*Hypnum cupressiforme*					

[5] S. HUNECK and R. J. PRYCE, *Z. Naturf.* **26**, 738 (1971).

The results in Tables 1 and 2 suggest that lunularic acid could act as an effective chemotaxonomic marker substance for the bryophytes, since liverworts contain readily detectable amounts of lunularic acid and mosses contain none.

As referred to above abscisic acid is of general occurrence in higher plants and it is also known to occur in pteridophytes and mosses.[6] Abscisic acid, however, has not been found in liverworts[2] or algae.[6] An apparently mutually exclusive situation therefore seems to be associated with the occurrence of these two growth inhibitory substances, lunularic acid and abscisic acid. This observation may be of some phylogenetic significance since lunularic acid is only found amongst the more primitive green plants, algae and liverworts, and abscisic acid is found in mosses and all higher plants. Although the active plant growth inhibitory agent, lunularic acid or abscisic acid, may have changed during evolution its site of action may have remained essentially unchanged. Two facts support this hypothesis: firstly, both lunularic and abscisic acid promote dormancy and inhibit growth in both liverworts and higher plants,[2,7,8] and secondly, a structural similarity exists between lunularic and abscisic acids. This is indicated by (IV) which shows the enol form of the carbonyl group of abscisic acid and demonstrates the similar relative positions of the unsaturated carboxyl-enolic hydroxyl of abscisic acid to that of the unsaturated carboxyl-phenolic hydroxyl of lunularic acid.

The ability of abscisic acid to mimic the growth inhibitory effect of lunularic acid may not be confined to liverworts for it can also imitate the growth inhibitory effect of an uncharacterized acidic inhibitory substance from the marine brown alga *Eklonia radiata*.[9] At the present time it is impossible to say whether or not the inhibitory substance from *E. radiata* and other(s) reported to occur in the marine brown alga *Fucus vesiculosus*[10,11] are identical with lunularic acid.

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[6] R. W. P. Hiron, Personal communication of unpublished results.
[7] I. F. M. Valio and W. W. Schwabe, *J. Exptl Bot.* **21**, 138 (1970).
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Key Word Index—Algae; liverworts; mosses; bryophytes; pteridophytes; Angiosperms; phylogeny; chemotaxonomy; lunularic acid; abscisic acid.