Phytochemistry, 1975, Vol. 14, pp. 195–197. Pergamon Press. Printed in England.

OCCURRENCE OF SHIKIMIC AND QUINIC ACIDS IN ANGIOSPERMS

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(*Received* 19 *May* 1974)

Key Word Index—Angiosperms; quinic acid; shikimic acid; alicyclic acid metabolism; chemotaxonomy.

Abstract—Leaves of 83 angiosperms have been made surveyed for quinic and shikimic acids. The quinic acid content was higher in woody dicotyledons than in herbaceous dicotyledons or in the monocotyledons, substantiating the view that its presence may be correlated with the lignification in plants.

INTRODUCTION

A preliminary report [1, 2] from this laboratory on the occurrence of quinic acid in the lower cormophytes has clearly shown that it is only found in the ferns, suggesting that it is particularly characteristic of the vascular plants. However, the literature on its occurrence in monocotyledons is scanty, although its distribution in gymnosperms and some dicotyledons has been investigated [3,4].

Present study was undertaken to determine the occurrence of quinic and the related shikimic acid in angiosperms, especially in monocotyledonous plants.

RESULTS AND DISCUSSION

The results are presented in Tables 1–3. They show (Table 1) that quinic is actually present in a large number of monocotyledons, although the concentration is low. This contrasts with the acid patterns in gymnosperms and ferns, where high concentrations are present. Similar results were obtained from herbaceous dicotyledons in which the ratio of quinic to shikimic is about 3·2 (Table 2). This similarity is to be expected, since monocotyledons are also predominantly herbaceous.

These results confirm that there is a correlation between the quinic acid content and lignification [4]. In woody dicotyledons, the alicyclic acid pattern was quite different from herbaceous plants and was similar to that of gymnosperms; the ratio of quinic to shikimic was high (average 13·8) (Table 3).

Table 1. Alicyclic acid contents (mg/g fr. wt) in monocotyledons

Plant source	Shikimic	Quinic
Orchidaceae		
Calanthe discolor Lindl.	0	0
Cannaceae		
Canna generalis Bailey	0·11	0·04
Zingiberaceae		
Zingiber officinale Rosc.	trace	0
Z. mioga Rosc.	trace	trace
Iridaceae		
Gladiolus gandavensis Van Houtt.	0	0
Iris pseudacorus L.	0·14	0·43
Dioscoreaceae		
Dioscorea japonica Thunb.	0·08	0·09
Amaryllidaceae		
Crinum asiaticum L. var. *japonicum* Baker	0	0
Agave americana L. var. *variegata* Nicholson	0	0
Zephyranthes candida Herb.	0	0
Liliaceae		
Rohdea japonica Roth	trace	0·03
Scilla chinensis Benth.	trace	0
Aloe arborescens Mill. var. *natalensis* Berger	0	0·03
Liriope graminifolia Baker	0·11	0·06
Cordyline terminalis Kunth	trace	0·01
Sansevieria trifasciata Prain	0	0
Allium tuberosum Rottl.	0	0
Chlorophytum comosum Baker	trace	0·01
Aspidistra elatior Blume	0·01	0·24
Yucca recurvifolia Salisb.	0	0·04
Pontederiaceae		
Eichhornia crassipes Solms	0·42	trace
Commelinaceae		
Commelina communis L.	0·28	0·01
Rhoeo discolor Hance	trace	0
Kniphofia uvaria Hook.	0·05	0·01
Zebrina pendula Schnizl.	0	0
Bromeliaceae		
Ananas comosus Merr.	0	trace

Table 1. *Continued*

Plant source	Shikimic	Quinic
Araceae		
Richardia africana Kunth	0	0·01
Colocasia antiquorum Schott var. *esculenta* Engl.	trace	0
Palmae		
Trachycarpus excelsus H. Wendl.	0·05	0·51
Rhapis humilis Blume	0·12	0·67
Cyperaceae		
Cyperus microiria Steud.	0·02	0·01
Gramineae		
Miscanthus sinensis Anderss.	0·03	0·29
Coix lacryma-jobi L.	0·06	0·07
Oryza sativa L.	0·02	0·04
Setaria viridis Beauv.	trace	0·01
Digitaria adscendens Henr.	0·01	0·02
Pleioblastus Chino Makino	0·04	0·03

Table 2. Alicyclic acid contents (mg/g fr. wt) in herbaceous dicotyledons

Plant source	Shikimic	Quinic
Compositae		
Helianthus tuberosus L.	trace	0·07
Taraxacum albidum Dahlst.	0	0
Plantaginaceae		
Plantago asiatica L.	0	0
Gesneriaceae		
Saintpaulia ionantha Wendl.	0	0
Solanaceae		
Petunia hybrida Hort.	0	0
Convolvulaceae		
Pharbitis nil Choisy	0	0·13
Primulaceae		
Primula sieboldi E. Morr.	0	0
Begoniaceae		
Begonia evansiana Andr.	0	0
Violaceae		
Viola tricolor L.	0	0
Euphorbiaceae		
Ricinus communis L.	0·18	0·32
Oxalidaceae		
Oxalis corniculata L.	0	0·05
Leguminosae		
Arachis hypogaea L.	0·01	0·05
Trifolium repens L.	0	0·03
Rosaceae		
Fragaria chiloensis Duch. var *ananassa* Bailey	0·04	1·38
Saxifragaceae		
Saxifraga stolonifera Meerb.	0·62	1·34
Crassulaceae		
Kalanchoe blossfeldiana von Poelln.	0	trace
Sedum kamtschaticum Hort.	trace	0·02
Cruciferae		
Brassica oleracea L. var. *acephala* DC.	0	0·32
Hesperis matronalis L.	trace	0·19
Papaveraceae		
Macreya cordata R. Br.	0·41	0·20

Table 2. *Continued*

Plant source	Shikimic	Quinic
Nymphaeaceae		
Nymphaea tetragona Georgi var. *angusta* Casp. subvar. *orientalis* Casp.	0·22	0·25
Nyctaginaceae		
Mirabilis Jalapa L.	0	0
Chenopodiaceae		
Spinacia oleracea L.	0	0

Table 3. Alicyclic acid contents (mg/g fr. wt) in woody dicotyledons

Plant source	Shikimic	Quinic
Caprifoliaceae		
Viburnum awabuki K. Koch	0·06	2·40
Rubiaceae		
Gardenia jasminoides Ellis f. *grandiflora* Makino	0·06	1·43
Oleaceae		
Jasminum officinale L. var. *grandiflorum* Kobuski	trace	0·03
Osmanthus ilicifolius Mouill.	0·01	0·73
Forsythia suspensa Vahl	0·01	0·06
Ligustrum japonicum Thunb.	0·01	0·06
Ericaceae		
Rhododendron mucronatum G. Don	0·08	2·05
R. Metternichii Sieb. et Zucc.	0·03	8·28
Araliaceae		
Fatsia japonica Decne. et Planch.	0·39	9·60
Hedera rhombea Bean	0·30	0·78
Thymelaeaceae		
Daphne odora Thunb.	0	0·10
Aquifoliaceae		
Ilex integra Thunb.	0·01	0·67
Euphorbiaceae		
Daphniphyllum macropodum Miq.	0·03	2·88
Leguminosae		
Cytisus scoparius Link	0·03	0·03
Rosaceae		
Prunus yedoensis Matsum.	0·01	0·10
Rosa multiflora Thunb.	0·36	2·52
Platanaceae		
Platanus orientalis L.	1·93	8·00
Saxifragaceae		
Hydrangea macrophylla Ser. var. *Otaksa* Makino	0·11	1·37
Berberidaceae		
Mahonia japonica DC.	0·01	1·37
Moraceae		
Ficus elastica Roxb.	0·02	0·58
Morus bombycis Koidz.	0·02	0·27
Fagaceae		
Quercus acutissima Carruth.	0·16	8·10
Salicaceae		
Salix babylonica L.	0·03	0·02

Table 4. Average amounts (mg/g fr. wt) of alicyclic acids in angiosperms

	Numbers of species tested	Shikimic acid	Quinic acid	Ratio Quinic:shikimic
Monocots	37	0·04	0·07	1·8
Dicots				
Woody	23	0·16	2·21	13·8
Herb	23	0·06	0·19	3·2

These results are summarized in Table 4. The following trends are clear: shikimic and quinic acids occur singly or together in most species, irrespective of their contents; and herbaceous plants have low concentrations, while woody plants are rich in these acids.

EXPERIMENTAL

Plant materials. Leaves were collected in the campus of Tokyo Metropolitan University in Aug and Sept 1973, at which time the content of alicyclic acids was reasonably stable.

Isolation and determination of alicyclic acids. Usually 10–20 g of fr. leaves were extracted 3 × with 100 ml of hot 80% aq. EtOH. The combined extract was conc *in vacuo*, the remaining residue dissolved in hot H_2O, and insoluble materials filtered off. The aq. sol was passed through a column of Amberlite IR 120 (H^+ form), which was then washed thoroughly with H_2O. The effluent was applied to a column of Amberlite IRA 410 (acetate form). The organic acids adsorbed to the resin were then eluted with 2 N HOAc; the eluate was conc *in vacuo*, and the concentrate dissolved in a small amount of H_2O. The organic acid fraction thus obtained was streaked as a line on Whatman No. 1 paper, which was developed with *sec*–BuOH–EtOAc–HOAc–HCOOH–H_2O (35:35:8:2:20). The bands corresponding to shikimic (R_f 0·51) and quinic (R_f 0·30) were cut out, and the acids were extracted with 50% aq. EtOH and H_2O, successively. The amounts were determined spectrophotometrically, by the methods described previously [2].

Acknowledgements—The authors thank Dr. M. Ono of Makino Herbarium, Tokyo Metropolitan University for providing plant materials and also Prof. M. Hasegawa for his criticism.

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