ranosyl-β-D-arabinopyranoside (1 → 4 linkage).

Acknowledgements—T. J. V. thanks the C.S.I.R., New Delhi, for a research fellowship and Dr. Gowri Shanker, Head, Horticulture Department, Allahabad Agr. Inst., for providing the plant material.

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Phytochemistry, 1979, Vol. 18, pp. 1767–1768. © Pergamon Press Ltd. Printed in England.

PARALLELISM IN HILL ACTIVITY AND ANTHOCYANIDIN CONTENT IN *EUPHORBIA PULCHERRIMA*

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(*Received* 9 *March* 1979)

Key Word Index—*Euphorbia pulcherrima*; Euphobiaceae; Hill activity; anthocyanidin; chlorophyll.

Abstract—Pigment compositions and Hill activities of red-leafy bracts, red-green leaves and green leaves of *E. pulcherrima* were studied. Interestingly enough, the chloroplasts from anthocyanidin-containing leaves are intrinsically more active than those from green leaves.

The inflorescence of *Euphorbia pulcherrima* Willd. ex Klotzsch (poinsettia) has an involucre of bright red-leafy bracts and some red-green foliage below, besides the usual green leaves. It was of interest to find whether the red bracts contain chlorophylls besides the obvious anthocyanins and if so, whether they are photosynthetically active. Hence, comparative studies on Hill activities, anthocyanidins and chlorophyll compositions of three types of fully expanded foliage, i.e. the red-leafy bracts, red-green leaves and green leaves, were undertaken.

The comparative Hill activity and pigment compositions are shown in Table 1. It is remarkable that on the basis of Hill activity, the most active chloroplasts are those from the red bracts. Thus, the Hill activity of the green leaf is 132.6 μM DCPIP reduced/mg chl./hr and while the activity of the chloroplasts from red-green leaves is about 7% higher, that of red-leafy bracts is about 60% higher.

The red bracts contain maximal anthocyanidin, the red-green leaves lower amounts and in green leaves anthocyanidins could not be detected. In the red-leafy bracts and red-green leaves there are two anthocyanidins, cyanidin and pelargonidin, and the relative amount of cyanidin in both is about twice that of pelargonidin. The total chlorophyll content of the green leaves is 2.15 mg/g fr.wt and those of the red-green leaves and leafy bracts are much lower. The chlorophyll b/a ratio is *ca* 0.5 in the green and red-green leaves and in the leafy bract it is *ca* 0.3, indicating the existence of a proper pigment system. The association of higher anthocyanin content with higher Hill activity in leaves is noteworthy.

These results indicate that the red-leafy bracts, although completely pigmented like petals, are capable of photosynthesizing and fulfilling, at least partly, their nutrient requirement. Photosynthetic activity also in the red-purple coloured leaves of the 14 cultivars of *Coleus* has been reported [1]. Such work and the novel association of higher Hill activity with the occurrence of anthocyanins reported here and the reports of the presence of flavonoid glycosides in chloroplasts [2] show that such unconventional systems as anthocyanin-containing leaves can be used for photosynthetic studies. Such an approach will not only lead to a better understanding of the possible role of different pigments in the bio-utilization of solar energy, but also a better appraisal of the role of flavonoids customarily overlooked as secondary.

Table 1. Hill activity and pigment composition of the leafy-bract and different leaf types of *Euphorbia pulcherrima*

Leaf type	Hill activity μM DCPIP reduced/mg chlorophyll/hr	Chlorophylls (mg/g fr. wt) a	b	Total	Anthocyanidin Cyanidin *A* 535/g fr. wt	Pelargonidin *A* 520/g fr. wt	Total *A* 525/g fr. wt
Red-leafy bract	210.0	0.025	0.007	0.07	0.13	0.05	0.89
Red-green leaf	139.8	0.311	0.115	0.77	0.08	0.04	0.54
Green leaf	132.6	0.803	0.476	2.15	*	*	*

* Not detected in our method.

EXPERIMENTAL

Anthocyanidin extraction and chromatography were done by the method of ref. [3]. Total anthocyanidin estimations were made by measuring A_{525} in MeOH–HCl (99:1) with a final vol. of 20 ml/g fr. wt. The extract was concd to dryness, redissolved in 1 ml MeOH–HCl/g fr. wt and 0.1 ml subjected to PC in formic solvent (conc HCl–HCO_2H–H_2O, 2:5:3) and Forestal solvent (conc. HCl–HOAc–H_2O, 3:30:10). The fractionated anthocyanidins were eluted, made up to 10 ml with MeOH–HCl and quan-

titatively estimated by measuring A at their respective λ_{max}. Identifications were based on R_fs, colour in visible light, colour in UV light and λ_{max}. Two anthocyanidins, cyanidin (R_fs 0.22 in formic, 0.49 in Forestal. λ_{max} 535 nm) and pelargonidin (R_fs 0.33 in formic and 0.68 in Forestal, λ_{max} 520), were identified in red-leafy bracts and red-green leaves. Total chlorophyll, Chl.a and Chl.b were quantitatively extracted and estimated spectrophotometrically [4–6]. Chloroplast isolation and Hill activity measurements are based on an earlier method developed in our laboratory [7, 8].

Acknowledgements—Thanks are due to Dr. Y. S. Murty, Head of our Department, for constant encouragement and to the C.S.I.R. for the award of Junior Research Fellow to V.S.

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Phytochemistry, 1979, Vol. 18, pp. 1768–1769. © Pergamon Press Ltd. Printed in England.

A NEW QUINOLINE ALKALOID FROM *RUTA GRAVEOLENS**

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(*Received* 22 *February* 1979)

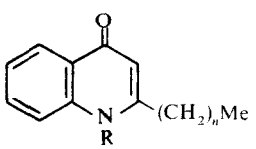
Key Word Index—*Ruta graveolens*; Rutaceae; quinoline alkaloids; 1-methyl-2-*n*-nonyl-4-quinolone.

4-Quinolones containing long alkyl chains in the 2-position (pseudans) were first obtained from micro-organisms, but in recent years pseudans have also been isolated from rutaceous species. The 2-alkyl-1-methyl-4-quinolones (**1**; R = Me, n = 10, 12 or 14), for example, were shown to be constituents of *Evodia rutaecarpa* [1], whereas the 4-quinolones (**1**; R = H, n = 10–13) lacking an *N*-methyl group were obtained as an unresolved mixture from the roots of *Ruta graveolens* [2]. We now report the isolation of a new alkaloid, 1-methyl-2-*n*-nonyl-4-quinolone (**2**) from the aerial parts of *Ruta graveolens*.

Extraction of the leaves, shoots and flowers of *R. graveolens* and chromatography of the acid-soluble portion resulted in the identification of the furoquinoline alkaloids dictamnine, γ-fagarine, kokusaginine and skimmianine, which have been isolated previously from the plant [3]. The more polar fraction contained the 2-aryl-*N*-methyl-4-quinolone, graveoline, also a known constituent [4].

A new alkaloid, 1-methyl-2-*n*-nonyl-4-quinolone (**2**), was shown to be a minor component of the graveoline fraction, and its structure was established by spectroscopy. The UV spectrum in neutral and in acid solution was consistent with that of a 4-quinolone unsubstituted in the homocyclic ring; this was confirmed by IR absorption at 1618 cm^{-1} (4-quinolone carbonyl) and by the ^1H NMR resonance at δ 8.45, characteristic of an aromatic proton at C-5 deshielded by a 4-quinolone carbonyl group (cf. graveoline). The ^1H NMR spectrum also confirmed the presence of an *N*-methyl group, a proton at C-3 and an alkyl chain at C-2. Although elemental analysis and the mass of the molecular ion formed in the mass spectrometer showed that the alkaloid contained a C_9H_{19} substituent, the complete structure of

* Part 18 in the series "Quinoline Alkaloids". For Part 17 see Grundon, M. F. and James, K. J. (1979) *J. Chem. Soc. Perkin Trans.* 1 (in press).



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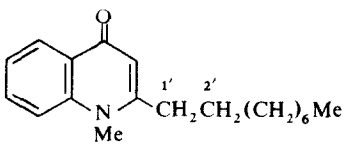

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