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QUERCETAGETIN AND PATULETIN IN *ERIOCAULON**

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Abstract—The yellow flavonol quercetagetin has been identified in the hydrolysates of leaves of six *Eriocaulon* species. Two other quercetagetin derivatives were isolated from *E. brownianum*: the 6-methyl ether, patuletin, and a more highly methylated compound. These results constitute the first record in the monocotyledons of flavonols bearing an extra 6-hydroxyl (or methoxyl) substituent.

INTRODUCTION

THE SINGLE European species of *Eriocaulon* in the monocotyledonous family Eriocaulaceae is the pipewort, *E. septangulare* With., which only grows in the United Kingdom in watery places in Skye and western Ireland. Analysis of the acid hydrolysate of the leaves of this plant during a survey for phenolic constituents[1] indicated the presence of a flavonoid aglycone with an unusually low R_f (0·25) in Forestal solvent, appearing dark brown in u.v. light, becoming bright yellow in ammonia in visible light. The properties did not fit any of the three common flavonols but agreed with those of the relatively rare compounds, quercetagetin (I, $R_1=OH$, $R_2=H$) and gossypetin (I, $R_1=H$, $R_2=OH$), two isomeric compounds which cannot be distinguished by R_f and colour alone.[2,3] Since neither of these substances has previously been reported in the monocotyledons, a more detailed examination of the flavonoids of *Eriocaulon* was carried out. According to Hegnauer,[4] chemical data on this genus and family are singularly lacking.

RESULTS

The rare flavonol constituent was isolated from the leaves of both *Eriocaulon septangulare* and *E. brownianum* Mart. (see below) and identified unambiguously as quercetagetin (I, $R_1=OH$, $R_2=H$) by direct comparison with authentic material. It was clearly distinguished from gossypetin by its failure to respond to the sodium acetate test and by its different spectral properties.[2,3] A survey of fresh and herbarium leaf samples of *Eriocaulon* showed

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[1] E. C. BATE-SMITH, *J. Linn. Soc.* (*Botany*) **60**, 325 (1968).
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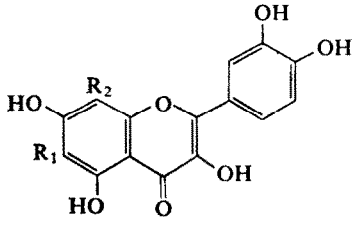
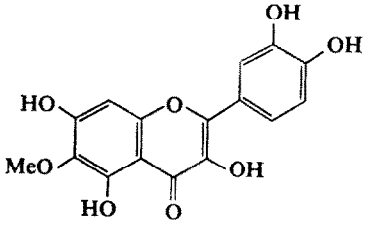
[3] J. B. HARBORNE, *Phytochem.* **8**, 177 (1969).
[4] R. HEGNAUER, *Chemotaxonomie der Pflanzen*, Vol. II, Birkhauser Verlag, Basel (1963).

that it also occurs in four other species. It was previously reported[1] in *E. nilagirense* Steud. as well as in *E. septangulare*, and has now been found in the fresh leaves of *E. decangulare* L. (airmailed from the United States) and in fresh leaves of *E. brownianum* Mart., *E. sexangulare* L. and *E. wightianum* Mart. studied in Ceylon; it was not present in *E. truncatum* Ham. (also studied in Ceylon).

Analyses of dried material gave more irregular results. Thus, quercetagetin was detected in the leaves of some, but not all, herbarium specimens of *E. decangulare* and *E. septangulare* but could not be found in twelve other species, including *E. wightianum* and *E. nilagirense*, fresh material of which were both positive. In specimens of these last species brought from Ceylon in a semi-dry condition, the quercetagetin content was much reduced. It is evident, therefore, that quercetagetin is easily lost during the drying process and failure to detect it in herbarium specimens is no guarantee of its absence from the fresh plant. This contrasts with previous studies which have indicated that the majority of flavonoid constituents are remarkably persistent in herbarium material;[5,6] the difficulty in this case is probably due to the facts that the plants have a high moisture content (i.e. they cannot be dried quickly) and that the quercetagetin content is relatively low.



Quercetagetin (I) $R_1 = OH, R_2 = H$
Gossypetin (I) $R_1 = H, R_2 = OH$



Patuletin (II)

Quercetagetin was accompanied in at least one of the six positively reacting species by a more abundant second flavonol, with the R_f of isorhamnetin (0·53) in Forestal but with a bright yellow-brown, instead of yellow, colour in u.v. light. This was isolated in crystalline form from *E. brownianum* and identified as patuletin (II), the 6-methyl ether of quercetagetin, by direct comparison with material from *Tagetes patula* (Compositae), the first known plant source.[7] The Compositae is, in fact, the only family in which quercetagetin and patuletin have previously been found together to any extent (both in *Hymenoxys* and *Tagetes*) and the remarkable similarity in flavonoid pattern between the Eriocaulaceae and the Compositae thus revealed has been further strengthened by the discovery of a more highly *O*-methylated quercetagetin in *E. brownianum* inflorescences. This compound, erioflavonol, has not yet been fully identified but its properties (see Experimental) indicate that it contains three or more *O*-methyl groups and thus belongs to a group of highly methoxylated flavonols like centaureidin, jaceidin and polycladin which are particularly characteristic of the Compositae.

Patuletin was also detected, without quercetagetin, in leaves of *E. truncatum*. The presence of quercetin as a minor constituent of *E. brownianum* leaves was also noted during these studies.

[5] E. C. BATE-SMITH, *Phytochem.* **3**, 623 (1964).
[6] J. B. HARBORNE, in *Progress in Phytochemistry* (edited by L. REINHOLD and Y. LIWSCHITZ), Vol. I, Interscience, London (1968).
[7] L. R. ROW and T. R. SESHADRI, *Proc. Indian Acad. Sci.* **23A**, 140 (1946).

DISCUSSION

Because of the failure of herbarium leaf tests, it is not yet clear how widely quercetagetin is distributed in *Eriocaulon*, a genus reputed to contain over 150 species but which more conservative estimates might limit to 25–30 species. It has, however, been found in six of seven species examined as fresh material and its presence in Asian, European and American species represents a striking homogeneity of the genus without regard to geographical distribution, reinforcing the distinctive morphology of the *Eriocaulon* inflorescence.

The discovery of quercetagetin and patuletin in *Eriocaulon* represents the first record in the monocotyledons of flavonols bearing an extra hydroxyl in the 6 or 8 position. Such substances have been found in no less than nine dicotyledonous families, in most of which they contribute to yellow flower colour.[3] In the dicotyledons, these yellow flavonols undoubtedly have phyletic significance. The same may be true in the monocotyledons since, very recently,[8] the presence of gossypetin and a compound which may be 6-hydroxykaempferol have been noted in the Restionaceae (*Restio*), a family often linked phyletically with the Eriocaulaceae (see e.g. Cronquist[9]). Of similar significance is the recent report of a chalcone, okanin, related to gossypetin in the Cyperaceae (*Kyllinga*).[10] Further studies of flavonoid patterns in these and neighbouring families are in progress and may be expected to yield other sources of these interesting flavonoids.

EXPERIMENTAL

Plant Material

Fresh plants of *Eriocaulon septangulare* were collected by Mrs. C. W. Murray from Sligachan lochan, Isle of Skye, in October 1968 and supplied to both authors. Fresh plants of *Eriocaulon* species indigenous to Ceylon were examined by one of us (E. C. B-S.) in Ceylon and material of Ceylonese and U.S. plants were kindly supplied by Dr. E. M. Chenery and by Dr. P. B. Tomlinson respectively. Leaf samples from herbarium specimens were obtained from the herbaria of the Universities of Liverpool and Cambridge, by kind permission of the Professor of Botany and Keeper, respectively.

Flavonoid Identifications

Quercetagetin was identified in the leaf hydrolysates by co-chromatography with authentic material, isolated from *Tagetes*, in five solvents, and by its characteristic spectral properties.[2,3] It was distinguished from gossypetin by these properties and by its failure to respond to the "gossypetone" or sodium acetate colour tests. Patuletin was similarly identified by direct chromatographic and spectral comparison,[11] with material isolated from *Tagetes patula*. It was obtained as pale yellow needles (from aqu. EtOH) and further characterized by m.p. 264–266° and mixed m.p. 264–266° (lit.[7] m.p. 262–264°), by demethylation to quercetagetin and by reductive cleavage.

Properties of Erioflavonol

The new quercetagetin methyl ether was separated by paper chromatography from the acid hydrolysate of *E. brownianum* inflorescences. It was pale yellow on paper in visible light, dark brown in u.v. light a colour unchanged by NH_3 treatment. It had λ_{max}^{EtOH} 276, 336; λ_{max}^{EtONa} 278, 330, 400; λ_{max}^{NaOAc} 277, 294, 375; $\lambda_{max}^{NaOAc-H_3BO_3}$ 276, 366; and $\lambda_{max}^{AlCl_3}$ 284, 308, 359 nm. On demethylation with pyridinium chloride, it gave quercetagetin and an intermediate methyl ether similar in colour. This intermediate had λ_{max}^{EtOH} 288, 340; λ_{max}^{EtONa} 294, 331, 389; λ_{max}^{NaOAc} 291, 356; $\lambda_{max}^{NaOAc-H_3BO_3}$ 292, 348; and $\lambda_{max}^{AlCl_3}$ 305, 366 nm. R_f values (× 100) for erioflavonol, the demethylation intermediate, patuletin and quercetagetin were respectively: 89, 75, 63, 44 in BAW; 85, 69, 60, 19 in PhOH; and 82, 60, 53, 30 in Forestal. Erioflavonol shows a larger hypsochromic shift in its neutral spectrum (long wavelength band: 30 nm) when compared with quercetagetin than any of the known partial methyl ethers and therefore appears to be a new compound. Further structural studies are in progress.

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[8] J. B. HARBORNE and H. T. CLIFFORD, unpublished results.
[9] A. CRONQUIST, *Evolution and Classification of Flowering Plants*, Nelson, London (1968).
[10] H. J. CLIFFORD and J. B. HARBORNE, *Phytochem.* **8**, 123 (1969).
[11] J. B. HARBORNE, *Phytochem.* **4**, 647 (1965).