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ISOFRAXIDIN IN *ERICA* FLOWERS

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Key Word Index—*Erica* species; Ericaceae; 6,8-dimethoxy-7-hydroxycoumarin; isofraxidin.

In connection with a broad biochemical systematic programme on simple phenols in *Erica*, the dominant component of the heath ecosystem of NW Spain, a compound was isolated from *E. cinerea* [1] and *E. vagans* [2]. On the basis of spectral data it was tentatively identified as a 6,7- or 7,8-alkylhydroxycoumarin but its structure was not fully elucidated [2]. The occurrence in *Erica* species of a coumarin different to scopoletin and esculetin prompted us to reinvestigate these plants.

We readily found in *E. cinerea* the reported compound which proved to be stable to acid. The blue fluorescence in UV light turning to very bright green on fuming with ammonia was characteristic of a dimethoxy-hydroxy substitution as found in the sinapoyl moiety. The compound showed UV maxima in MeOH at 259 (*sh*), 305 (*sh*), 338 nm shifting to 268, 399 nm after basification, but the spectrum was unaffected by adding $AlCl_3$. Finally, the compound cochromatographed with isofraxidin (6,8-dimethoxy-7-hydroxycoumarin) in 14 solvents. The NMR spectrum (80 MHz, $CDCl_3$) of the unknown exhibited a three-proton singlet at 3.8 ppm (—OMe attached to a benzene nucleus). The mass spectrum showed peaks at *m/e* (%) 222(M^+; 35.7), 207 (9.2), 194 (5.3) and 179 (5.6) consistent with the fragmentation pattern of authentic isofraxidin.

Isofraxidin has been reported in *Achillea filipendulina* [3] and several *Artemisia* species (Compositae) [4–7], in *Fraxinus excelsior* and *F. japonica* (Oleaceae) [4] and in *Eleutherococcus senticosus* (Araliaceae) [4]. To our knowledge this is the first report of its occurrence in Ericaceae. Its distribution is by no means general in the family or in the genus. In fact, isofraxidin was not detected in *Daboecia cantabrica* (Huds.) K. Koch, *E. arborea* L., *E. australis* L. and *E. umbellata* L. in full agreement with previous surveys in these species [8–10]. That isofraxidin may be an artifact is unlikely, since the compound was also isolated from an ethanolic extract of *E. vagans*.

EXPERIMENTAL

The plants were collected in June and September 1976. Flowers of *D. cantabrica* and the mentioned *Erica* species were homogenised with warm MeOH and the homogenate shaken *ca* 18 hr. After filtration, the extraction was repeated for 3 consecutive 24hr periods. The filtrates were combined, concd *in vacuo* and the residue taken up in H_2O and extracted 3 × with Et_2O. The ether soln was separated into neutral and phenolic fractions by extraction with 5% $NaHCO_3$ (3 ×). The aq. extract was acidified to pH 2–3 and back-extracted with Et_2O (3 ×). The ether fraction was dried and chromatographed on Whatman 3 mm paper in toluene–HOAc–H_2O (4:1·5) (over-run for 13 hr). The chromatograms were observed in UV light and a strong blue fluorescent band (R_f 0.58–0.77) eluted with MeOH and successively chromatographed with H_2O (over-run for 9 hr, R_f 0.22–0.32) and *iso*-PrOH–NH_3–H_2O (10:1:1) (over-run for 26 hr; R_f 0.29–0.47). The eluted compound proved to be pure and was characterized as isofraxidin by NMR, MS and UV spectroscopy, co-chromatography and chromogenic reaction with diazotised sulfanilic acid.

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REFERENCES

1. Ballester, A. (1971) Ph.D. Thesis, Universidad de Santiago de Compostela.
2. Arines, J (1973) Ph.D. Thesis, Universidad de Santiago de Compostela.
3. Sham'Yanov, I D., Mallabaev, A. and Sidyakin, G P. (1974) *Khim. Prir. Soedin.* 784
4. Pimenov, M. G. (1971) *List of Coumarin-bearing Plants*, Isdat. Nauka, Leningrad.
5. Danielak, R. and Borkowski, B. (1970) *Diss. Pharm. Pharmacol.* **22**, 231.
6. González, A. G., Estévez-Reyes, R. and Herrera, J (1975) *Ann. Quím.* **71**, 437.
7. Yusupov, M. I. and Sidyakin, G. P. (1975) *Khim. Prir. Soedin.* 91.
8. Alonso, J. L. (1969) M.Sc. Dissertation, Universidad de Santiago de Compostela
9. Carballeira, A. (1973) M.Sc. Dissertation, Universidad de Santiago de Compostela.
10. Salas, M. C. (1968) Ph.D. Thesis, Universidad de Santiago de Compostela.