

sitosterol; the Et₂O concentrate gave quercetagenin (a flavanol of rare occurrence often misidentified) [6] (identified by R_f , λ_{\max} , colour reactions, specific test with NaOAc and confirmed by direct comparison with an authentic compound), kaempferol, apigenin and luteolin (λ_{\max} , U.V. fluorescence and co-PC with authentic samples). EtOAc extract yielded 4 flavone glycosides (separated by adsorption over Si gel and elution with moist EtOAc and EtOAc-MeOH mix.) identified as kaempferol-3-rutinoside, apigenin-7-rutinoside, apigenin-7-glucuronide and luteolin-7-glucuronide (λ_{\max} , products of hydrolysis and co- R_f with authentic samples).

Plant. *Gmelina asiatica* L. (voucher specimen No. 2/74 deposited at JIPMER). *Uses.* Medicinal [1,2]. *Previous work.* Sitosterol and a yellowish orange colouring matter from seed oil [1].

Present work. On the flavones of leaves, flowers and fruits. Examination of the leaves, flowers and fruits of *G. asiatica* on similar lines as *G. arborea* revealed the same flavonoid pattern except for the overall low concentration of the pigments. The yellow colour of flowers and ripe fruits was mainly due to carotenoids. The presence of quercetagenin was confirmed in this case as above; the yellow-

orange pigment (reported earlier [1]) was non-phenolic in nature and could not be identified.

Comment. The presence of the 6-hydroxyflavonol, quercetagenin, in *G. arborea* and *G. asiatica* of the Verbenaceae is significant from the point of molecular taxonomy since it is of rare occurrence, being confined mainly to the Compositae [6] and to a lesser extent in the Leguminosae [7]. However, the methyl ethers of quercetagenin (casticin and artemetin) have been reported in *Vitex* sp. of the Verbenaceae [8,9].

REFERENCES

1. Anon (1956) *Wealth of India. Raw Materials*, Vol. IV, pp. 154-156, C.S.I.R., New Delhi.
2. Chopra, R. N., Nayar, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 126, C.S.I.R., New Delhi.
3. Rao, D. V., Rao, E. V. and Viswanatham, N. (1967) *Curr. Sci.* **36**, 71.
4. Rao, D. V. and Rao, E. V. (1970) *Indian J. Pharm.* **32**, 140.
5. Desai, H. K. *et al.* (1973) *Indian J. Chem.* **11**, 840.
6. Harborne J. B. (1969) *Phytochemistry*, **8**, 177.
7. Harborne, J. B. (1971) in *Chemotaxonomy of the Leguminosae* (Harborne, J. B., Boulter, D. and Turner, B. L., eds.), p. 31. Academic Press, London.
8. Harborne, J. B. (1967) *Comparative Biochemistry of Flavonoids*, p. 216. Academic Press, New York.
9. Nair, A. G. R., Ramesh, P. and Subramanian, S. S. (Unpublished data).

Phytochemistry, 1975, Vol. 14, pp. 1136-1137. Pergamon Press. Printed in England.

6-HYDROXYKYNURENIC ACID FROM *THAPSIA VILLOSA*

JESÚS MÉNDEZ and ANTONIO MASA

C.S.I.C., Santiago de Compostela, Spain

(Received 29 October 1974)

Key Word Index—*Thapsia villosa*; Umbelliferae; quinoline; 6-hydroxykynurenic acid.

Plant. *Thapsia villosa* L. Voucher sample No. 4779 Department of Botany Herbarium, University of Salamanca, Spain. *Source.* Umbels and fruits from Ortigueira and Muros (Coruña), respectively. *Previous work.* Flavonoids in leaves [1] and fruits [2]. Absence of myristicin in two *Thapsia* spp [3].

During an examination of *T. villosa* for coumarins, we isolated a compound showing a pink

fluorescence in UV light, changing to yellow when fumed with NH₃. The compound proved not to be the coumarin cichoriin, which exhibits similar fluorescence, and was identified as 6-hydroxykynurenic acid, which was first found in higher plants in 1968 [4].

The occurrence of this quinoline derivative in the Umbelliferae, an evolved family, accords with the findings of a small-scale survey showing a pre-

ponderance in the more phylogenetically advanced dicotyledons and its absence in species belonging to four monocotyledonous families [4]. In contrast to a previous report [4], the content of 6-hydroxykynurenic acid was high in inflorescence and fruits and was not detected in leaf and root tissue. Neither the metabolic role nor the biosynthetic pathway for 6-hydroxykynurenic acid, a typical product of the mammalian, avian and bacterial tryptophan catabolism, have been fully clarified in higher plants [5].

EXPERIMENTAL

Powdered air-dried fruits (400 g) and homogenized inflorescences (1200 g, fr. wt) collected in July were extracted 3 × MeOH at room temp. Filtrates were concentrated, and the residues continuously extracted overnight with Et₂O. Concentrated extracts were chromatographed on Whatman 3MM paper with *n*-BuOH–C₆H₆–C₅H₅N–H₂O (10:2:6:3). The band fluorescing pink in UV (*R_f* 0.19) was eluted with warm MeOH and re-chromatographed on Si gel TLC plates with *n*-BuOH–

C₅H₅N–H₂O (14:3:3) (*R_f* 0.68). The compound was identified with authentic material by PC and TLC using several solvent systems, and by UV-spectroscopy (neutral, alkaline and acidic media) and fluorimetry. Methylation overnight with CH₃N₂ gave the blue fluorescent dimethyl derivative whose identity with an authentic sample was confirmed by PC, TLC and UV.

Acknowledgements—We are indebted to Dr. P. K. Macnicol, CSIRO, Canberra, for authentic material, Dr. D. J. Austin, Rothamsted Experimental Station, Harpenden, for corrections of the English text, and Drs. R. Alvarez, University of Santiago de Compostela, and B. Casaseca, University of Salamanca, for identification of the plant.

REFERENCES

1. Crowden, R. K., Harborne, J. B. and Heywood, V. H. (1969) *Phytochemistry* **8**, 1963.
2. Harborne, J. B. and Williams, C. A. (1972) *Phytochemistry* **11**, 1741.
3. Harborne, J. B., Heywood, V. H. and Williams, C. A. (1969) *Phytochemistry* **8**, 1729.
4. Macnicol, P. K. (1968) *Biochem. J.* **107**, 473.
5. Slaytor, M., Copeland, L. and Macnicol, P. K. (1968) *Phytochemistry* **7**, 1779.

Phytochemistry, 1975, Vol. 14, pp. 1137–1138. Pergamon Press. Printed in England.

NEW CHROMONES FROM *PEUCEDANUM OSTHRUTHIUM**

J. REISCH, S. A. KHALED, K. SZENDREI and I. NOVÁK

Institute for Pharmaceutical Chemistry, Westfalian Wilhelm-University Münster, F.R.G.;
Institute of Pharmacognosy, Medical University, Szeged, Ungarn

(Received 27 October 1974)

Key Word Index—*Peucedanum osthruthium*; Umbelliferae; chromones; peucenin; peucenin-7-methyl ether; hamaudol acetate.

Plant. *Peucedanum osthruthium* (L.) Koch (syn. *Imperatoria osthruthium* L.) Umbelliferae roots collected in South Tyrol (Italy).† **Uses.** Medicinal—*Radix Imperatoriae* [1]. **Previous work**—see previous papers [2, 3].

Present work. Dried roots (440 g) were extracted with C₆H₆. The residue from the C₆H₆ extract was chromatographed over a Si gel column and

afforded, beside several coumarins and peucenin [2], fractions containing peucenin-type compounds (violet colour reaction with FeCl₃, yellow coloration with conc. H₂SO₄). Further purification on Si gel preparative layers (System: C₆H₆–EtOAc 9:1) afforded three crystalline products: peucenin (1) mp 209–212°, (lit. 210–211° [4]), peucenin-7-*O*-methyl ether (2)—osthol mixture, mp 106–109°, and a third chromone, mp 134–135°, to which structure 3 can be attributed on the basis of spectral data.

The identification of the peucenin-7-*O*-methyl ether was based upon the polarity, UV-, IR- and

* Part 49 in the series "Natural Product Chemistry", for Part 48 see Reisch, J., Rozsá, Zs., Szendrei, K. and Körösi, J. (1974) *Phytochemistry* (in press).

† We wish to thank Mr. Felix Augscheller, St. Martin, South Tyrol for collecting the roots.