

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

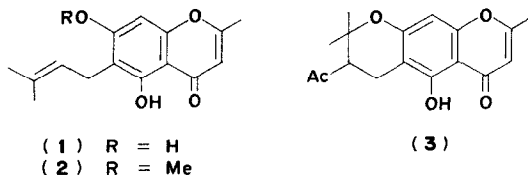
afforded, beside several coumarins and peucenin [2], fractions containing peucenin-type compounds (violet colour reaction with FeCl₃, yellow coloration with conc. H₂SO₄). Further purification on Si gel preparative layers (System: C₆H₆–EtOAc 9:1) afforded three crystalline products: peucenin (1) mp 209–212°, (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.

the MS of its mixture with osthol. The identity was proved by direct comparison with authentic material.



Compound **3** is optically active $[\alpha]_D^{30} -34.1^\circ$ (589), -31.6° (578), -34.1° (546), -49.4° (436) and -55.7° (405) (c 0.79) and has a molecular weight of 318 (from mass spectrum), $C_{17}H_{18}O_6$. Its UV-spectrum, especially the high intensity of the band at 258 nm characterizes it as a chromone derivative [5], $\lambda_{(max)}^{MeOH}$ 250 sh, 258, 268 sh, 294 nm, $\log \epsilon$ 4.35, 4.33, 4.20, 3.95). In its IR spectrum two $C=O$ bands are present at 1750 and 1670 cm^{-1} . The latter is due to the conjugated chromone carbonyl group, the former can be attributed to an ester $C=O$ group on the non-chromone part of the molecule. NMR ($CDCl_3$, TMS as internal reference δ ppm) 1.4 (6H, s, 2 Me at C-8), 2.1 (3H, s, $MeCOO$ at C-7), 2.4 (3H, s, Me at C-2), 2.9 (2H, m, CH_2 at

C-6), 5.2 (1H, m, CH at C-7), 6.05 (1H, s, $CH=$ at C-3), 6.4 (1H, s, H at C-10) and 13.0 (1H, s, O-H $\cdots O=$ at C-5). MS: M^+ (6%), 258 (22%), $M-60$, (100%, $M-60-15$). The parent alcohol hamaudol was isolated by Nitta [6] from roots of *Angelica japonica*. An ester described as hamaudol-7-*O*-acetate having a mp $127-128^\circ$ was isolated from *Xanthogalum sachokianum* by Sokolova and Pimenov [7, 8] and its spectroscopic properties are comparable to those described above.

REFERENCES

1. Hörhammer, L., Wagner, H. and Heydwiller, D. (1969) *Phytochemistry* **8**, 1605.
2. Khaled, S. A., Szendrei, K., Reisch, J. and Novák, I. (1975) *Phytochemistry* (in press).
3. Reisch, J., Khaled, S. A., Szendrei, K. and Novák, I. (1975) *Phytochemistry* (in press).
4. Bolleter, A., Eiter, K. and Schmid, H. (1951) *Helv. Chim. Acta* **34**, 186.
5. McCabe, P. H., McCrinde, R. and Murray, B. D. H. (1967) *J. Chem. Soc., C*, 145.
6. Nitta, A. (1965) *J. Pharm. Soc. Japan* **85**, 55.
7. Ssavina, A. A., Perelsson, M. E., Ban'kovskij, A. I. and Nikonov, G. K. (1970) *Khim. Prir. Ssoed.* **4**, 411.
8. Sokolova, A. I. and Pimenov, M. G. (1970) *Khim. Prir. Ssoed.* **4**, 468.

Phytochemistry, 1975, Vol. 14, pp. 1138-1139. Pergamon Press. Printed in England.

ELLAGIC ACIDS FROM VOCHYSIACEAE*

DIRCEU DE BARROS CORRÊA, ELSE BIRCHAL,
JOÃO E. VALE AGUILAR and OTTO R. GOTTLIEB†

Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Belo Horizonte, Brasil

(Received 10 September 1974)

Key Word Index—*Erismia calcaratum*; *Salvertia convallariodora*; *Vochysia acuminata*; *V. tyrsoides*; Vochysiaceae; ellagic acids.

The Vochysiaceae include only five south American genera, namely *Callisthene*, *Erismia*, *Qualea*, *Salvertia* and *Vochysia*. Ellagic acids were found in *E. calcaratum* (Link) Warm. (1b, 1c), *S. convallariodora* St. Hil. (1b, 1d, 1e, 1f), *V. acuminata* Bongard (1a, 1b) and *V. tyrsoides* Pohl (1b, 1d). The last named species contains additionally physcion and

2,6-dimethoxy-1,4-benzoquinone. These and the ellagic acids of known natural occurrence 1a, 1b, 1d were identified by comparison of their physical and spectral data with published data, preparation of derivatives and interconversions. 3,3',4'-Tri-*O*-methyl-4'-*O*-rutinosylellagic acid (1c) was hydrolyzed to rhamnose, glucose and 1b. The PMR spectrum of its hexaacetate contained the characteristic signals of the hexa-*O*-acetylrutinosyl group [1]. A product, isolated in small amount, was shown by MS to be an *O*-methyl-*O*,*O*-methyl-

* Part I in the proposed series "The Chemistry of Brazilian Vochysiaceae". Sponsored by Conselho Nacional de Pesquisas, Brasil.

† Instituto de Química, Universidade de São Paulo, Brasil.