

furanocoumarins isoimperatorin, bergapten and isooxypeucedanin were isolated and identified by m.p., IR and NMR spectra.

Furthermore, a crystalline mixture of isomers of oxypeucedanin, ( $[\alpha]_D^{20} -10.1^\circ$  ( $\text{CHCl}_3$ )), was obtained (ca. 1% yield). Recrystallizations from  $\text{CHCl}_3$ -ether afforded the pure compounds (*R,S*)-oxypeucedanin, m.p.  $140.5-142^\circ$  and (*S*)-(-)-oxypeucedanin, m.p.  $103-104^\circ$ ,  $[\alpha]_D^{20} -14.0^\circ$  (*c* 0.9,  $\text{CHCl}_3$ ), which was identical with synthetic material (m.p.  $101.5-102.5^\circ$ ,  $[\alpha]_D^{24.0} -13.5^\circ$ ). For (*R*)-(+)-oxypeucedanin Ghoshal *et al.*<sup>4</sup> reported m.p.  $104-105^\circ$  and  $[\alpha]_D^{30} +20.1^\circ$ .

(*R,S*)-Oxypeucedanin has been isolated from some 20 umbellifer species (see Nielsen<sup>5</sup>), (*R*)-(+)-oxypeucedanin (prangolarin) from 3.<sup>5</sup> To our knowledge (*S*)-(-)-oxypeucedanin has not previously been obtained from natural sources. In one case, the isolation of both (*R*)-(+)- and (*R,S*)-oxypeucedanin was reported.<sup>4</sup>

*Acknowledgements*—Thanks are due to the Danish Natural Science Research Council for placing an NMR spectrometer at the disposal of this laboratory, and to the Botanic Garden, University of Copenhagen, for supplying the plant material

<sup>3</sup> B. E. NIELSEN and J. LEMMICH, *Acta Chem. Scand.* **23**, 962 (1969).

<sup>4</sup> C. R. GHOSHAL, S. SEN, S. S. GUPTA and A. CHATTERJEE, *Chem. & Ind.* 1430 (1963).

<sup>5</sup> B. E. NIELSEN, *Dansk Tidsskr. Farm.* **44**, 111 (1970).

---

Phytochemistry, 1971, Vol. 10, pp. 3334 to 3335. Pergamon Press. Printed in England.

## VALERIANACEAE

### ISOLATION OF ACTINIDINE FROM *VALERIANA OFFICINALIS*

R. D. JOHNSON and G. R. WALLER

Department of Biochemistry, Agricultural Experiment Station,  
Oklahoma State University, Stillwater, Oklahoma 74074, U.S.A.

(Received 14 April 1971)

*Plant. Valeriana officinalis.*

*Source.* Dried roots obtained from the Laboratorium voor Plantenbiochemie, Rijks Universiteit, Gent, Belgium.

*Uses.* Possesses cat-attractant properties,<sup>1,2</sup> which may, in part, be due to actinidine.<sup>2</sup>

*Previous work.* In an earlier paper on *Valeriana officinalis* alkaloids by Torssell and Wahlberg,<sup>1</sup> two new actinidine-like alkaloids were isolated and their structures determined. Franck<sup>3</sup> identified 8-methoxy-actinidine from *Valeriana officinalis*, and Gross *et al.*,<sup>4</sup> identified actinidine as well as confirmed the presence of the major alkaloid discovered by Torssell and Wahlberg in *Valeriana officinalis*. This communication confirms the presence of actinidine in *Valeriana officinalis*.

*Isolation of alkaloids.* The alkaloids were isolated from dried roots of *Valeriana officinalis* by  $\text{CHCl}_3$ -MeOH preceded by an  $\text{Et}_2\text{O}$  extraction, and followed by a 10% HCl extraction,

<sup>1</sup> K. TORSELL and K. WAHLBERG, *Acta Chem. Scand.* **21**, 53 (1967).

<sup>2</sup> T. SAKAN, A. FUYINO, F. MURAI, Y. BUTSUGAN and A. SUZUI, *Bull. Chem. Soc. Japan* **32**, 315 (1959).

<sup>3</sup> B. FRANCK, *Abh. Dtsch. Akad. Wiss. Berlin*. In press.

<sup>4</sup> D. GROSS, G. EDNER and H. R. SCHUTTE, *Arch. Pharmaz.* **304**, 20 (1971).

according to the method of Torssell and Wahlberg.<sup>1</sup> Column chromatography first on silicic acid and next on neutral alumina yielded a purified alkaloid fraction.

**Actinidine.** TLC of the purified alkaloid fraction, or of the  $\text{CHCl}_3$ -MeOH extract on silica gel HF in  $\text{CHCl}_3$ -MeOH (5:1), or in EtOAc-*iso*-PrOH- $\text{NH}_4\text{OH}$ , (45:35:20), yielded several Dragendorff's positive bands. Preparative TLC of the Dragendorff's positive band with the highest  $R_f$ , in hexane-acetone- $\text{Et}_2\text{NH}$  (4:1:1), yielded a purified Dragendorff's positive band with the same retention time as that of authentic actinidine. GLC on a 3.6 m  $\times$  6 mm glass column, packed with 15% Carbowax 20 M on Anakrom ABS, using a modified Barber-Colman Model 5000 gas chromatograph<sup>5</sup> equipped with a hydrogen flame detector, yielded a symmetrical peak with the same retention time as that of authentic actinidine. Co-chromatography with authentic actinidine confirmed the identification. Mass spectra of the isolated compound was very similar to that of authentic actinidine. Major fragment ions found in the mass spectrum of this compound were  $M^+$  147,  $m/e$  132 [ $M-\text{CH}_3$ ],  $m/e$  117 [ $M-\text{CH}_3-\text{CH}_3$ ] and a metastable ion at  $m/e$  103.8 confirming the transition  $m/e$  132,  $m/e$  117 + 15, which agrees with the published mass spectrum by Auda *et al.*<sup>6</sup>

**Mass spectra.** The prototype<sup>5</sup> of the LKB-9000 gas chromatograph-mass spectrometer, (LKB Instruments Incorporated, Rockville, Maryland), was used. The instrument was operated at 70 eV, 3.5 kV accelerating voltage, 20  $\mu\text{A}$  trap current, 290° ion source temp., 160° column temp. and a helium flow rate of 20 ml min.

**Acknowledgements**—We thank Dr. C. F. Van Sumere for the dried *V. officinalis* roots, Dr. Takeo Sakan for a sample of authentic actinidine, and W. Springstube and J. Marshall for technical assistance.

<sup>5</sup> G. R. WALLER, *Proc. Okla. Acad. Sci.* **47**, 295 (1968).

<sup>6</sup> H. AUDA, G. R. WALLER and E. J. EISENBRAUN, *J. Biol. Chem.* **242**, 4157 (1967).

---

Phytochemistry, 1971, Vol. 10, pp 3335 to 3339. Pergamon Press. Printed in England.

## ZINGIBERACEAE

### FLAVONOLS AND QUINONES IN STEMS OF *AFRAMOMUM GIGANTEUM*

GIOVANNI VIDARI, PAOLA VITA FINZI and MARIA DE BERNARDI

Istituto di Chimica Organica, Università di Pavia, Italia

(Received 21 April 1971)

**Abstract**—Three rare naturally occurring flavonol 3-methyl ethers have been isolated from stems of *Aframomum giganteum*: kaempferol 3,7,4'-trimethyl ether, quercetin 3,7,4'-trimethyl ether (ayanin) and quercetin 3,7,3',4'-tetramethyl ether (retusine). The following compounds have also been isolated: chrysophanol, physcion, 2,6-dimethoxybenzoquinone and  $\beta$ -sitosterol. Phytochemical aspects of the flavonoids occurring in the Zingiberaceae are discussed.

## INTRODUCTION

*Aframomum giganteum* K. Schum. (syn. *Amomum giganteum* Oliv. and Hanb., Zingiberaceae), grows in the tropical zone of Central Africa. The plant reaches a height of 5–6 m and all the