Phytochemistry, 1975, Vol. 14, pp. 594–595. Pergamon Press. Printed in England.

VOMIFOLIOL IN *CROTON* AND *PALICOUREA* SPECIES

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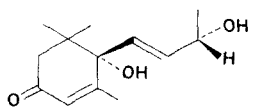
(*Received* 18 *June* 1974)

Key Word Index—*Palicourea alpina*: Rubiaceae; *Croton lobatus*; *Croton trinitatis*; Euphorbiaceae; vomifoliol (blumenol A).

Vomifoliol was first reported from *Rauwolfia vomitoria* Afz. (Apocynaceae) [1] and more recently from *Croton sparsiflorus* Morong, (Euphorbiaceae) [2]. We now report its isolation from *Palicourea alpina* (Sw.) DC, *Croton lobatus* L. and *Croton trinitatis* Millsp. From its m.p. and spectral data (IR, NMR, CD, UV) it appears certain that this compound is identical with blumenol A isolated from *Podocarpus blumei* Endl (Podocarpaceae) [3]. Since the stereochemistry of the latter compound has been established as shown in structure **1** [4, 5] the same applies for vomifoliol, and the name vomifoliol should have priority.



(**1**)

This report serves to show that vomifoliol is more widely distributed than previously recognised, and like S-(+)-abscisic acid may have biological significance. This theory is now being actively tested. *Palicourea alpina* has not been previously investigated, but other *Palicourea* species have been reported to contain alkaloids of undetermined structures [6], *N*-methyltyramine [7], uncharacterised acids [8] and monofluoroacetic acid [9–11], while *Croton* species have yielded a variety of natural products [12–18].

* Voucher No. 31, 130, The Herbarium, Botany Department, University of the West Indies, Jamaica.

† Voucher No. 27, 340, Herbarium, Botany Department, University of the West Indies, Jamaica.

‡ Voucher No. 27, 339, The Herbarium, Botany Department, University of the West Indies, Kingston 7, Jamaica.

EXPERIMENTAL

Extraction of Palicourea alpina and separation of vomifoliol. 3·5 kg of dried and powdered plant material (leaves, twigs and some bark*) collected from Hardwar Gap, St. Andrew, Jamaica, in July 1973 was percolated with 2% tartaric acid until the extract gave no precipitate with Mayers reagent (42 l.). The extract was conen under red press to 2 l. and kept at 0° overnight. The non-alkaloidal salts were filtered off and the filtrate adjusted to pH 8 (NH_4OH) and continuously extracted with $CHCl_3$ to yield on evaporation 9·8 g of yellow–brown material. This was separated in a semi-automatic countercurrent apparatus with $CHCl_3$ (stationary phase) and 0·062 M phosphate buffer (pH 6·08) with 100 transfers. Tubes 40–75 contained 794 mg of a mixture of 5 compounds. PLC on silica plates using first $CHCl_3$–MeOH (12:1) followed by AcOEt then AcOEt–$CHCl_3$ (6:1) afforded 39 mg of vomifoliol. Recrystallisation from light petrol–EtOAc yielded colourless needles, m.p. 112–114°. This was identical (m.p., m.m.p., R_f, NMR, IR) with an authentic sample of vomifoliol.

Croton lobatus. Powdered material (3·3 kg, stem and leaves)† which was collected from the Lusignan Backlands of the East Coast, Demerara, Guyana, in 1969, was extracted with 2% tartaric acid as outlined above and yielded 4·6 g of a crude product. This was separated into phenolic (1·38 g) and non-phenolic fractions using 5% NaOH. The former was chromatographed on Grade II–III alumina using $CHCl_3$–MeOH of graded polarity. 54 fractions (25 ml each) were collected, and PLC of fractions 2–6 on silica yielded 46 mg of vomifoliol: $[\alpha]_D$ +177·8 (*c* 1·59 in $CHCl_3$), CD (acetonitrile) 340 *sh* ($\Delta\epsilon$ −0·50), 327 (−0·64) 315 *sh* (−0·54), 242 (+9·67), UV. λ_{max}^{EtOH} 237 (log ϵ 4·05), NMR ($CDCl_3$) showed signals at δ 1·07, 1·01 (*s*, 3H each; gem dimethyls), 1·28 (*d*, 3H, *J* 6·3 Hz, sec. methyl), 1·91 (*d*, 3H, *J* 1·3 Hz, vinylic Me), 2·30 (*s*, 1H), 2·36 (*s*, 1H), exchangeable protons at δ 2·64 and 2·86; 1 proton at 4·4 (*m*, C<u>H</u>OH and 3 olefinic protons between 5·82–5·92. (Found: C, 68·53; H, 9·23; O, 22·09. Calc. for $C_{13}H_{20}O_3$: C, 69·61; H, 8·99; O, 21·40%).

Croton trinitatis Millsp. Powdered stem and leaves (1·57 kg) collected in March 1971 from the Triumph Backlands of the East Coast, Demerara, Guyana‡ was extracted as outlined above to yield 4·9 g of crude material. Separation on silica plates using $CHCl_3$–AcOEt as solvent yielded 52 mg of vomifoliol. Acetylation with Ac_2O–pyridine yielded the monoacetate, IR, 3410 (OH), 1740 (acetate), 1650 (enone) cm^{-1}. NMR showed signals at δ 1·00 and 1·07 (*s*, 3H each), 1·31 (*d*, 3H, *J* 6·3 Hz), 1·86 (*d*, 3H, *J* 1·2 Hz), 2·03 (*s*, 3H, acetate), 5·35 (*m*, 1H), 5·73–5·85 (3H) and an exchangeable proton at *ca.* δ 2·30.

Acknowledgements—We thank Professor Günther Snatzke, Ruhr University, for determining CD data on vomifoliol samples and also drawing our attention to the similarity of data for 'blumenol A' and vomifoliol. We thank Professor Koji Nakanishi, Columbia University, for unpublished data on compounds related to vomifoliol and we also thank Dr. R. S. Kapil, Central Drug Research Institute, Lucknow, India, for a sample of vomifoliol and copies of NMR, IR and UV spectra of vomifoliol and vomifoliol acetate.

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Phytochemistry, 1975, Vol. 14, pp. 595–596. Pergamon Press. Printed in England.

ESSENTIAL OIL OF *SAURURUS CERNUUS**

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(*Received* 12 *July* 1974)

Key Word Index—*Saururus cernuus*; Saururaceae; Essential oil; GLC; GC–MS; Terpenoids.

Plant. Saururus cernuus L. *Source.* S. B. Penick Co. (No. LLC 765). Voucher specimen is kept in the Herbarium of the School of Pharmacy, University of the Pacific (SCA-0725). *Uses.* Variety of folklore medicinal uses [1–4]. *Previous work.* On the absence of Alkaloids [5], on the Protein and Carbohydrate content of the plant grown in sites of different fertilities [6]. *Plant part examined.* Aerial parts.

Present work. The steam-distilled essential oil from the aerial parts showed the presence of 26 components on GLC, of which 16 were identified by means of spectral data, (IR, NMR and GC–MS) retention times and peak enhancement. The analytical data shows that the oil is rich in sesquiterpenoid compounds (57%).

EXPERIMENTAL

Isolation of essential oil. Dried powdered aerial parts (10 mesh powder, 300 g) upon steam-distillation for 48 hr yielded 1·0 ml (0·3% v/w) of yellow oil.

Gas chromatography. GLC separations were carried out on 1·8 m × 6 mm i.d. stainless steel column with 3% OV-17 on chromosorb-HP and a thermal conductivity detector.

GC–MS. Was on a 1·8 m × 6 mm i.d. glass column filled with 3% OV-17 on Gaschrom-Q and an FID; The GC–MS interphase was at 245° and the separator at 235°; MS were recorded at 80 ev.

Collection of GC peaks. Individual components from the GC were trapped at room temp. in 5 in. long glass capillaries cut out from disposable pipettes. The micro samples (1–3 μl) thus collected were used to record IR and NMR spectra, and the identifications were confirmed by comparison.

* Part IV in the series *Saururaceae*. For Part III see *Phytochemistry* **10**, 3331 (1971).