easily demonstrated by physical methods. The PMR spectrum displayed the aldehyde proton at 9·40δ whereas the quaternary methyl group appeared at 1·11δ. A methyl group at 1·89δ long-ranged coupled with a vinylic proton at 5·49δ indicated the migration of the exocyclic double bond as shown. In the mass spectrum its parent peak at *m/e* 246 supported its molecular formula, and fragments at *m/e* 218 ($M^+ - 28$) and *m/e* 217 ($M^+ - 29$) confirmed the presence of an aldehyde function. The IR spectrum was in good agreement with the proposed rearrangement. The aldehyde group gave absorptions at 1724 and 2720 cm^{-1} whereas the typical exocyclic double bond absorption at ~890 cm^{-1} was absent.

Other structural modifications of eremanthine have been achieved and will be reported elsewhere. The name eremanthine for **1** has historical precedence over vanillosmin so that the latter name should no longer be used.

EXPERIMENTAL

Mp's are uncorrected. IR spectra were run as KBr pellets; NMR spectra of $CDCl_3$ solutions with internal TMS. Mass spectra were obtained at 70 eV. Silica gel GF_{254} and PF_{254} were used for TLC and preparative TLC respectively.

Eremanthine (**1**). Was obtained as previously described [1]. ^{13}C NMR spectrum [25·2 MHz, $CDCl_3$, 12·5%; obtained under proton noise decoupling conditions and δ values (ppm) are relative to TMS ($\delta = 0$)] 169·88, 150·25, 140·40, 138·04, 121·07, 119·25, 110·86, 83·24, 52·68, 47·11, 45·34, 30·56, 29·70, 29·22, 27·87.

9,14-Dibromoeremanthine-4,10-ether (**2**). Eremanthine (100 mg, 0·435 mmol) was dissolved in a mixture of dioxane (8 ml) and water (2 ml) and the solution cooled to ~0–4°. *N*-Bromosuccinimide (160 mg, 0·87 mmol) was added and the reaction mixture stirred for 30 min at ~0–4°. The resulting solution was partitioned between $CHCl_3$ (30 ml) and H_2O (20 ml) and the H_2O extract further partitioned with $CHCl_3$ (3 × 20 ml). The combined organic extracts were concentrated *in vacuo* and the residue was purified by preparative TLC using hexane–EtOAc (4:1) as eluant. The main product (**2**, R_f 0·60) was eluted giving 64 mg; mp 130° dec., (Found: C, 44·47; H, 4·56; Br, 39·15. Requires: C, 44·33; H, 4·43; Br, 39·40); ν_{max} 1754 (*s*), 1656 (*w*), 1150 (*s*) cm^{-1}; PMR (100 MHz) δ 6·19 and 5·45 (1 each, *d* *J* 3·5 Hz, C_{11}–CH_2), 4·23 (1, *t*, *J* 3 Hz, C_9–H), 3·94 (1, *dd*, *J* 2, 11 Hz, C_6–H), 3·55 (2, *s*, C_4–CH_2Br), 1·57 (3, *s*, C_{10}–Me); MS (*m/e*): 404, 406, 408 (1:2:1, M^+, 4%), 325, 327 (1:1, 18%), 298, 300 (1:1, 33%).

Reaction of eremanthine-9,10-epoxide (**3**) *with* BF_3–Et_2O. Epoxide (**3**) [1] (100 mg, 0·48 mmol) was dissolved in C_6H_6 (4 ml) and recently distilled BF_3–Et_2O (0·2 ml, 0·816 mmol) added. After 2 hr at room temp. the mixture was partitioned between EtOAc (25 ml) and H_2O (25 ml). The organic layer was washed with H_2O (2 × 25 ml), concentrated *in vacuo* and the residue purified by preparative TLC using hexane–EtOAc (7:3) as eluant. The main product (**5**, R_f 0·38) was eluted giving 45 mg; mp 104–105°; ν_{max} 2720 (*w*), 1754 (*s*), 1724 (*s*), 1653 (*w*) cm^{-1}; PMR (100 MHz) δ 9·40 (1, *s*, C_{10}–CHO), 6·10 and 5·45 (1 each, *d*, *J* 3·5 Hz, C_{11}–CH_2), 5·49 (1, *m*, C_3–H), 3·51 (1, *t*, *J* 11 Hz, C_6–H), 1·89 (3, *m*, C_4–Me), 1·11 (3, *s*, C_{10}–Me); MS (*m/e*): 246 (M^+, 15%), 228 (10%), 218 (17%), 217 (30%), 80 (100%).

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3. A sample of vanillosmin was supplied by Dr. P. Gariboldi to Dr. W. Vichnewski who passed the sample on to one of us. Dr. Vichnewski had independently realized the possible identity of vanillosmin and eremanthine since the latter also occurs in *Vanillosmopsis erythropappa*, (1972) *J. Pharm. Pharmac.*, **24**, 853.
4. The optical rotation given previously (ref. [1]) $[\alpha]_D^{29} = -59°$ (*c*, 1·0, $CHCl_3$) is not correct. A new determination gave $[\alpha]_D^{23} = -111·7°$ (*c*, 1·0, $CHCl_3$), in good agreement with $[\alpha]_D^{20} = -110°$ reported in ref. [2].

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A GENERAL METHOD FOR VOMIFOLIOL DETECTION

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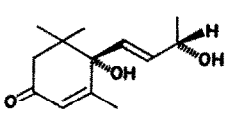
Key Word Index—Vomifoliol; screening procedure; chromatography; role.

Vomifoliol (**1**) has so far been reported as being present in four plant families [1] and has also been shown to occur as the β-glucoside, roseoside, in *Vinca rosea* [2]. Vomifoliol is as active and as rapid acting as abscisic acid on stomatal aperture in epidermal strips from *Eichhornia crassipes* (Mart) Solms [3,4]. These results, taken in conjuction with its lack of activity in the area of growth, as attested to by several assay methods [4,5] is part of the strong evidence being accumulated that vomifoliol plays an important role as an endogenous regulator of stomatal aperture. Because of this, it is important to be able to detect the presence of vomifoliol in a routine manner, as a means of providing evidence of its wide distribution in vasular plants.



(**1**)

Earlier reported methods [1,6] all relied on the separation of sufficient material for the usual physical and

spectroscopic identification (mp IR, NMR, CD, UV and MS). We now report a method which is capable of detecting vomifoliol quantitatively, even at low concentrations. The method involves a MeOH extraction of the plant material in a Soxhlet and the separation of the mixture so obtained on an alumina column using solvent mixtures of graded and increasing polarity. PLC is then used to further purify fractions which might contain vomifoliol as judged by TLC monitoring. Identification is made by TLC comparison with natural or synthetic [7,8] vomifoliol in three solvent systems and then finally confirmed by a GLC method. This method has so far been tested on six different plants which have previously not been screened for vomifoliol.

Leaves and stems of *Croton linearis* Jacq. (Euphorbiaceae), *Blighia sapida* Konig (Sapindaceae), *Murraya paniculata* (L) Jack (Rutaceae) and *Eichhornia crassipes* (Mart) Solms (Pontederiaceae) have been shown to contain vomifoliol. The bark of *Gliricidia sepium* (Papilionaceae) and the fruit of *Persea americana* Mill (Lauraceae) were shown to be negative.* A typical procedure is given in the experimental for material from *Blighia sapida*. In the case of the avacado pears (*Persea americana*) an additional defatting stage, using petrol (40–60°) was carried out in the Soxhlet extractor prior to the MeOH extraction.

EXPERIMENTAL

Blighia sapida, dried milled leaves and twigs (120 g) was extracted in a Soxhlet continuously with 700 ml MeOH until no further colouring material was extracted (3 days). Solvent removal yielded 9 g of crude material. This was placed on a Grade II–III Al_2O_3 column, (4 × 45 cm) in a minimum of MeOH and then eluted with pure solvents and solvent mixtures (C_6H_6–EtOAc–MeOH) of increasing polarity. Seven 1l fractions were collected as follows: *1*, C_6H_6; *2*, C_6H_6–EtOAc (9:1); *3*, C_6H_6–EtOAc (1:1); *4*, EtOAc; *5*, EtOAc–MeOH (1:1); *6*, EtOAc–MeOH (1:4) and *7*, MeOH. With the aid of TLC (Kiselgel 0·05–0·2 mm, 70–325 mesh) and using $CHCl_3$–EtOAc (1:6) as the developing solvent, fractions *5*, *6* and *7* were shown to contain material with similar R_f values to vomifoliol (R_f = 0·35) and were combined (1·8 g). This material was further purified by PLC on silica using the solvent system $CHCl_3$–EtOAc (1:6). Two additional TLC solvent systems, $CHCl_3$–EtOAc (1:1) (R_f = 0·23) and EtOAc–MeOH (5:1) (R_f = 0·64) were used to verify the presence of vomifoliol with the aid of an authentic marker. On TLC plates, appeared as a bright purple florescent spot under UV light (254 nm). Location was confirmed either by its reaction to iodine vapour (brown spot) or by spraying with a 2% aq: solution of 2,4-dinitrophenylhydrazine containing 4% conc. H_2SO_4, (orange spot). Further confirmation was by way of a GLC study of the PLC purified materials. In a typical run a 2 m × 3 mm, 3% SE-30 column was used with He at 30 ml/min; runs were isothermal at 170°, with injection port temperature of 250°, and detection (FID) temperature of 270°. Sample size varied from 0·2–2·0 μl with EtOAc as solvent and identity confirmed with synthetic vomifoliol as marker . In preliminary experiments it was shown that other naturally occurring compounds such as farnesol [9], geraniol and abscisic acid (ABA) could be efficiently separated from vomifoliol by this GLC system: (R_t) for these compounds: geraniol, 2 min; *cis-trans*-farnesol, 10 min; *trans-trans*-farnesol, 11 min; vomifoliol, 13 min; ABA > 20 min.

*All plant material was identified by the Herbarium, Botany Department, U.W.I., Jamaica.

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TWO NEW TOXINS FROM THE LATEX OF *EUPHORBIA POISONII*

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Key Word Index—diterpenes; irritants; *Euphorbia poisonii*; Euphorbiaceae.

The latex of *Euphorbia poisonii*, known as "Tinya" (Hausa), has been used in West Africa as an arrow fish poison [1]. It produces lesions of the skin in both man and livestock which are susceptible to secondary infections. It also causes inflammation of the mucus membranes of the nose, mouth and eyes and in chronic exposure leads to blindness. A biological screen of Nigerian succulent species [1] suggested that on mouse skin the inflammation produced, although acute initially, did not persist for up to 24 h as is normally the case for diterpene