élevée) est inattendue étant donné que seul son isomère, la gentisine, a été identifiée dans les racines des espèces voisines [7].

Identification. Gentiopicrine: $[\alpha]_D^{25}$ (MeOH) = −195°, R_f [5], UV, IR, RMN du dérivé acétylé [6]. *Amarogentine*: comparaison avec un échantillon authentique (R_f, F, $[\alpha]_D^{25}$ (MeOH) = −114°, UV, IR). *Amaropanine*: comparaison avec un échantillon authentique (R_f, $[\alpha]_D^{25}$ (MeOH) = −102°, UV). *Isogentisine*: comparaison avec un échantillon authentique (R_f, F, UV, IR, RMN du dérivé acétylé).

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ABSOLUTE STEREOCHEMISTRY OF EREMANTHINE, A SCHISTOSOMICIDAL SESQUITERPENE LACTONE FROM *EREMANTHUS ELAEAGNUS**

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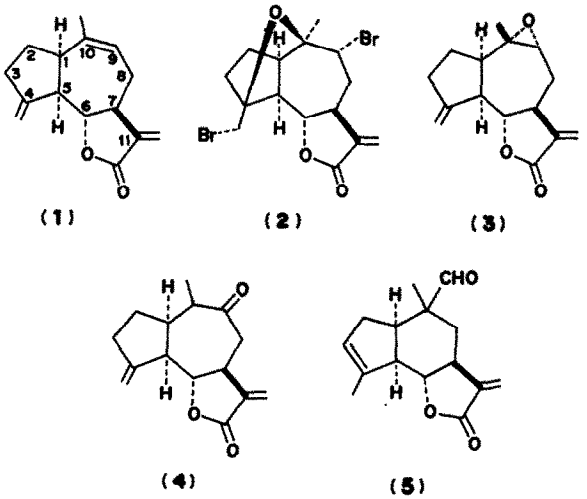
Key Word Index—*Eremanthus elaeagnus*; Compositae; sesquiterpene lactone; eremanthine; vanillosmin.

A previous report from this laboratory [1] dealt with the structural elucidation of eremanthine (**1**), the principal active constituent responsible for the prophylactic action of the heartwood oil from *Eremanthus elaeagnus* Sch. Bip. against the human parasite *Schistosoma mansoni*. The only structural feature not resolved in that work was the absolute configuration at C-1. More recently, it was demonstrated that vanillosmin, isolated from *Vanillosmopsis erythropappa*, also had structure **1** [2]. In this latter case however, the absolute configurations at both C-1 and C-5 were elucidated and shown to be both *R* as depicted.



That both eremanthine and vanillosmin could in fact be the same compound and possess a 1,5-*cis*-fused bicyclo [5.3.0] decane skeleton was suggested by the formation of the dibromoether **2** when eremanthine was treated with *N*-bromosuccinimide in dioxane containing 20% water. Analysis of the mass spectrum of **2** revealed the presence of parent peaks at 404, 406 and 408 (1:2:1) showing that **2** is derived from **1** by addition of two atoms of bromine and one atom of oxygen. In the PMR spectrum, the methyl group appeared at 1·57δ whereas a triplet at 4·23δ and a singlet at 3·55δ were assigned to C_9–H and C_4–CH_2– respectively. In the IR spectrum the absence of bands which could be attributed to an OH group further supported the proposed structure. Inspection of a Dreiding Model of **2** clearly indicates that formation of an ether linkage between the 4 and 10 positions is possible only if the 5 and 7 membered rings are *cis*-fused.

Analysis of a sample of vanillosmin [3] served to confirm its identity with eremanthine. Thus, a mixed mp determination showed no depression when compared with either sample; their chromatographic properties were the same; their optical rotations were in reasonable agreement [4] and more importantly their IR, PMR and ^{13}C NMR spectra were superimposable.

It had been reported [1] that reaction of epoxide **3** with BF_3-etherate gave the ketone **4**. Reinvestigation of this reaction showed this structural assignment to be incorrect. Under the reaction conditions reported, the main product is the aldehyde **5**. The structure of **5** could be

* Part 1 in the series *Chemical Transformations of Abundant Natural Products*.

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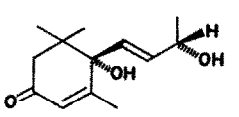
Key Word Index—Vomifoliol; screening procedure; chromatography; role.

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