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TWO ACYCLIC MONOTERPENE DIOLS FROM *CINNAMOMUM CAMPHORA*

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Key Word Index—*Cinnamomum camphora*; Lauraceae; acyclic monoterpenediols; 3,7-dimethylocta-1,7-dien-3,6-diol; 3,7-dimethylocta-1,5-dien-3,7-diol.

Plant. Linalool tree, one of five forms of *Cinnamomum camphora* Sieb. (camphor tree), classified according to the major component of leaf oil [1]. *Source*: The garden of Ehime University, Matsuyama-si, Japan: Uses. The leaves and small twings are steam-distilled to obtain an oil, called "Ho-oil", in Japan.

Previous work. Non-volatile sesquiterpenoids in the leaves [2].

Present work. The Me_2CO-extract of the fresh leaves was extracted with *n*-hexane. The hexane was evaporated *in vacuo*, and the residue steam-distilled. The essential oil produced (yield 2%, n_D 1·4608, $[\alpha]_D$ −14·06, major component (−) linalool *ca* 80%) was distilled under red. pres. (~55° 0·4 mm Hg) and the residue chromatographed on a column of Si gel with *n*-hexane–EtOAc (1:1) to give 3 fractions. The last fraction was further purified by means of preparative TLC on Si gel to give [1] and [2]. [1]: $C_{10}H_{18}O_2$, oil, n_D 1·4859, IR (cm^{-1}) 3330 (OH) 995, 920 ($CH{=}CH_2$) 895 ($=CH_2$), NMR (δ, ppm) 1·22 (3H, s, CH_3), 1·68 (3H, *s*, CH_3–C=C), 3·92 (1H, *m*, –CHOH–) 3·92 (2H, *m*, disappears when added with D_2O, OH), 4·6 ~ 5·3 (4H, *m*, CH_2=C<, CH_2=CH–), 5·62 ~ 5·98 (1H, *d*, *d*, *J* 10, 17 Hz, CH_2=CH–■). Monoacetate: oil, $[\alpha]_D$ −7·7, IR (cm^{-1}) 3450 (OH), 1740, 1240 (acetate), NMR (δ, ppm) 1·22 (3H, *s*, CH_3–), 1·71 (3H, *s*, CH_3–C=C), 2·00 (3H, *s*, CH_3CO), 2·50 (1H, *m*, OH), 4·8 ~ 5·3 (5H, *m*, CH_2=C<, CH_2=CH–, –CHOAC), 5·95 ~ 5·68 (1H, *d*, *d*, *J* 10, 18 Hz, CH_2=CH–) [2]: $C_{10}H_{18}O_2$, oil, n_D 1·4818, IR (cm^{-1}) 3330 (OH), NMR (δ, ppm) 1·22 (*s*) 1·26 (*s*) (9H, CH_3–) 3·54 (2H, *m*, disappears when added with D_2O, OH), 4·90 ~ 6·00 (3H, ABX, J_1 10, J_2 17, J_{gem} 2 Hz, ■–CH=CH_2) 5·5 ~ 5·62 (2H, *m*, –CH=CH–). These data for **1** and **2** correspond to 3,7-dimethylocta-1,7-dien-3,6-diol and 3,7-dimethylocta-1,5-dien-3,7-diol respectively, which were prepared by photosensitized oxidation of (−) linalool [3]. Neither compound has been found previously in nature.

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SECOIRIDOIDES ET XANTHONES DE *GENTIANA BURSERI**

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Key Word Index—*Gentiana burseri*; Gentianaceae; secoiridoids; gentiopicrin; amarogentin; amaropanin; xanthone; isogentisin; chemotaxonomy.

Plante et provenance. Gentiana burseri Lapeyr., Pyrénées orientales, France. Dans deux récentes communications [1,2], nous avons décrit six *C*-glucosides flavoniques isolés à partir des feuilles de *G. burseri* et constaté l'absence de xanthones dans ces organes. Le présent travail a trait à l'identification des principes amers de cette même espèce dans les feuilles et dans les racines. Le matériel végétal frais a été extrait à froid au MeOH. Après concentration de la liqueur d'extraction et addition de H_2O, on extrait successivement par $CHCl_3$, AcOEt et BuOH. Les fractions BuOH des feuilles et des racines, chromatographiées sur colonne d'alumine neutre (Me_2CO 50% [3]) fournissent la gentiopricrine (400 mg pour 200 g de feuilles/250 mg pour 200 g de racines). La CC de silice de l'extrait AcOEt des racines ($CHCl_3$–MeOH, détails voir [4]) conduit à l'amarogentine (10 mg pour 200 g de racines). Enfin l'extrait au $CHCl_3$ des racines, après concentration, fournit l'isogentisine qui cristallise (80 mg pour 200 g de racines). Le filtrat, chromatographié sur silice ($CHCl_3$–MeOH [4]) donne l'amaropanine (2 mg pour 200 g de racines).

Comme c'est le cas pour toutes les gentianes étudiées, les racines de *G. burseri* contiennent la gentiopicrine et l'amarogentine. En revanche, l'amaropanine n'a été identifiée jusqu'à présent que dans les racines d'autres espèces de la section *Coelanthe* (*G. pannonica, purpurea, punctata*) [5]. Quant à l'isogentisine, sa présence (en concentration

* Partie 12 de la série *Contribution à la Phytochimie du genre* Gentiana. Pour la partie 11, voir [1].

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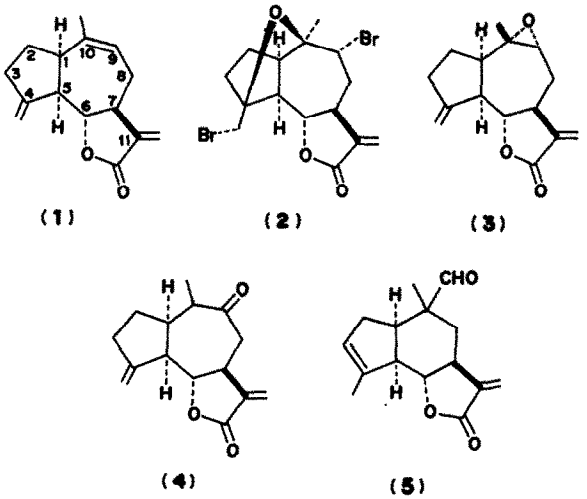
Key Word Index—*Eremanthus elaeagnus*; Compositae; sesquiterpene lactone; eremanthine; vanillosmin.

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

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