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TERPENOIDS ISOLATED FROM *WIGANDIA KUNTHII**

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Key Word Index -*Wigandia kunthii*; Hydrophyllaceae; farnesylhydroquinone; benzocyclodecadiene, wigandol.

INTRODUCTION

Several plants belonging to the Hydrophyllaceae are known to cause allergic contact dermatitis [1, 2]. This led us to examine the constituents of *Wigandia kunthii* Choisy, collected in the valley of Mexico.

RESULTS AND DISCUSSION

The extract of aerial parts (leaves and flowers) of *Wigandia kunthii* afforded farnesol and the known flavonoids, 5,4′-dihydroxy-7-methoxyflavone (**1**) and 5,-4′-dihydroxy-6, 7-dimethoxyflavone (**2**). In addition, two new terpenoids, farnesylhydroquinone (**3**) and wigandol (**6**) were isolated. Compound **3** was a colourless oil, $C_{21}H_{30}O_2$ (M^+ at *m/e* 314). Its IR spectrum demonstrated the presence of OH groups (3400 cm^{-1}) and isolated double bonds (1660 cm^{-1}), the presence of the former groups being confirmed by the production of a diacetate (**4**) upon treatment with Ac_2O and pyridine. Its UV spectrum showed λ_{max}^{MeOH} 293 nm (ε = 3768) and was almost identical to that of prenylhydroquinone [3], $\lambda_{max}^{Et_2O}$ 295 nm (ε = 4100). The presence of a 1,2,4-substituted benzene ring was confirmed by the signal in the ^1H NMR spectrum ($CDCl_3$) of **3** between δ 6.5 and 6.73 (3H), the spectrum in this region was identical to that of alliodorin (**5**) [4].

The stereochemistry of the double bond at C-2, C-3 was established as *trans* by comparing the ^1H NMR spectra of compound **3** and its acetate (**4**) which showed an upfield shift of the C-3 methyl of 0.08 ppm (δ 1.75–1.67) [5]. Finally, the ^1H NMR spectrum of compound **3** was identical to that of the compound synthesized by condensation of hydroquinone with *trans–trans*-farnesol, thus establishing the *trans–trans* configuration of the two double bonds of the natural farnesylhydroquinone (**3**).

Wigandol (**6**) (mp 163–165°), $C_{18}H_{22}O_3$ (M^+ at *m/e* 286) showed bands in the IR spectrum at 3450, 1765 and 1650 cm^{-1} for an OH group, one AcO group and isolated double bonds, respectively. Acetylation of **6** with Ac_2O–pyridine gave the acetate (**7**), mp 141–142°, which showed a new signal in the ^1H NMR spectrum at δ 2.3 corresponding to the acetyl group.

The UV spectrum of **6** indicated the presence of a benzene ring (λ_{max}^{EtOH} 283 nm). This was tetrasubstituted because the ^1H NMR spectrum of wigandol (**6**) showed an AB system at δ 6.4 (1 H, *d*, *J* = 8 Hz) and 6.67 (1 H, *d*, *J* = 8 Hz), characteristic of two aromatic protons in the *ortho* position. Furthermore the ^1H NMR spectrum ($CDCl_3$) showed two signals at 3.3 (2 H, *d*, *J* = 7 Hz) and 3.25 (2 H, *br s*) which correspond to two methylene groups between two double bonds. The presence of a *trans–trans*-1,5-diene in wigandol was established by obtaining the Cope rearrangement product **8** by pyrolysis of the diacetate (**7**). The ^1H NMR spectrum of compound **8** exhibited signals at δ 6.88 (2 H, *s*), 5.94 (1 H, *dd*, *J* = 11, 17 Hz, $CH{=}CH_2$), 4.97 (1 H, *dd*, *J* = 1.5, 11Hz, *cis* $-CH{=}CH_2$), 4.89 (1H, *dd*, *J* = 1.5, 17, *trans* $CH{=}CH_2$), 4.88 and 4.78 (each 1 H, *br s*, $-C{=}CH_2$), 2.29 (6 H, *s*, —Ac), 1.77 (3 H, *s*, =CR—Me), 1.13 (3 H, *s*, tertiary Me). The chemical shift for the tertiary Me in compound **8** is identical to that of cordiachrome C [6] suggesting that **8** possessed the same *cis*- stereochemistry.

The position of the acetoxy group in **6** was established at C-1′ due to the downfield shift of the ^1H NMR resonance of the C-8 methylene when this was acetylated (δ 3.26–3.42).

The isolation of wigandol (**6**) is of particular interest, since it is probably the precursor of the cordiachromes recently isolated by Thomson [6].

EXPERIMENTAL

Mps were determined on a Kofler block and are uncorr. Analysis was determined by Dr. F. Pascher, Germany.

Isolation of farnesylhydroquinone (**3**) *and wigandol* (**6**). *Wigandia kunthii* Choisy was collected in the campus of the UNAM (México, D.F.) in February 1979. Voucher specimen Gomez-10 is on deposit at the Herbario Nacional of the UNAM (MEXU). Leaves and flowers (750 g) of the plant were extracted with $CHCl_3$ under reflux and the resulting extract (20 g) was dissolved in petrol–C_6H_6 (1:1) and cooled. The 5,4′-dihydroxy-6, 7-dimethoxyflavone (**2**) pptd out from the soln as a solid (50 mg), mp 264–266° (lit. 255–257°) [7]. The later extract was chromatographed on a Si gel column and from the fractions eluted with petrol–C_6H_6 (1:1) after purification by TLC, 5,4′-dihydroxy-7-methoxyflavone (**1**), farnesol, farnesylhydroquinone (**3**) and wigandol (**6**) were isolated. The 5,4′-dihydroxy-7-methoxyflavone (**1**) (Genkwanin) was a solid (317 mg), mp 293–294° (lit. 285–287°) [8] and its diacetate, mp 197° (lit. 204°) [8].

Farnesylhydroquinone (**3**). Colourless oil (153 mg). IR ν_{max}^{film} cm^{-1}: 3400, 1660, 1600, 860 and 810. ^1H NMR (100 MHz $CDCl_3$): δ 1.60 (6 H, *s*, C-7 and C-11 Me groups), 1.67 (3 H, *s*, C-11 Me group *cis*), 1.75 (3 H, *s*, C-3 Me group), 1.95–2.2 (8 H, *m*), 3.29 (2 H, *d*, *J* = 7 Hz, (C-1), 5.1 (2 H, *m*, C-6 and C-10), 5.3 (1 H, *br t*, *J* = 7 Hz, C-2). MS, 70 eV, *m/e*: 314 (M^+); 245

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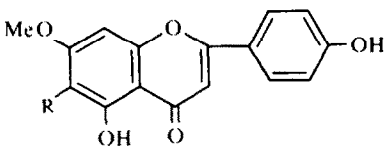

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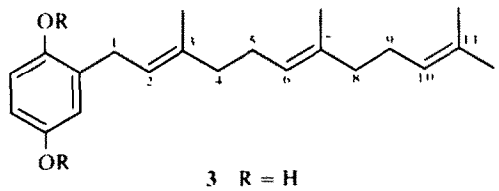

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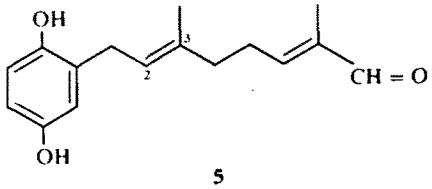

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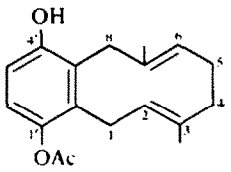

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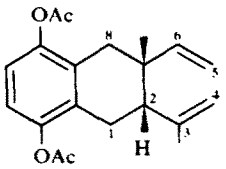

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$(M^+ - C_6H_9)$, 177 $(M^+ - C_{10}H_{17})$, 123 $(C_7H_7O_2^+)$, 109, 81, 69, 43, 41 (100).

Wigandol (**6**). Yield 76 mg, mp 163–165°; ^{1}H NMR (100 MHz, $CDCl_3$): δ 1.57 (3 H, *s*, C-7 Me), 1.76 (3 H, *s*, C-3 Me), 2.28 (3 H, *s*, Ac), 3.26 (2 H, *br s*, C-8), 3.33 (2 H, *d*, J = 7 Hz, C-1), 5.16 (2 H, *m*, C-2, C-6), 6.48 and 6.67 (2 H, *d*, J = 8 Hz, aromatic protons). MS, 70 eV, *m/e* (rel. int.): 286 (M^+, 6.5), 244 ($M^+ - 42$, 33), 123 (12), 69 (47), 55 (33), 43 (75), 41 (100).

Farnesylhydroquinone acetate (**4**). Colourless oil, UV λ_{max}^{EtOH} nm (ε): 211 (15 351), 263 (777); IR ν_{max}^{film} cm^{-1}: 1765, 1500. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.58 (6 H, *br s*), 1.67 (6 H, *br s*), 2.21 (3 H, *s*, Ac), 2.23 (3 H, *s*, Ac), 3.18 (2 H, *d*, J = 7 Hz), 5.0–5.3 (3 H, *m*), 6.85–7.0 (3 *H*, *m*). MS, 70 eV, *m/e*: 398 (M^+), 355 ($M^+ - 43$), 177, 152, 138, 123, 69 43 (100).

Wigandol acetate (**7**). Mp 141–142°; UV λ_{max}^{MeOH} nm (ε): 212 (18 742); IR ν_{max}^{film} cm^{-1}: 1765, 1200, 1180. ^{1}H NMR (100 MHz, $CDCl_3$): δ 1.54 (3 H, *s*, C-7 Me), 1.76 (3 H, *s*, *C*-3 Me), 2.28 (3 H, *s*, Ac), 2.3 (3 H, *s*, Ac), 3.29 (2 H, *d*, J = 7 Hz, C-1), 3.42 (2 H, *br s*, C-8), 5.0–5.3 (2 H, *m*, C-2, C-6), 6.9 (2 H, *s*, aromatic protons). MS, 70 eV, *m/e*: 328 (M^+), 286 ($M^+ - 42$], 244 ($M^+ - 42 - 42$), 43 (100). (Found: C, 72.40; H, 7.36; O, 19.51. $C_{20}H_{24}O_4$ requires: C, 73.14; H, 7.37; O, 19.49%).

Pyrolysis of **7**. Wigandol acetate (**7**) (60 mg) was heated for 15 min under high vacuum at 190° in a sublimation tube to give **8** as a crystalline solid. Mp 97–99°. UV λ_{max}^{EtOH} nm (ε): 212 (9768); IR $\nu_{max}^{CDCl_3}$ cm^{-1}: 1765, 1650, 890 MS, 70 eV, *m/e* 328 (M^+), 286 ($M^+ - 42$), 244 [$M^+ - 42 - 42$], 43 (100).

Synthesis of farnesylhydroquinone (**3**). A mixture of 5.6 g *trans*-*trans*-farensol, 2.8 g hydroquinone and 20 ml 1% aq. oxalic acid was heated at 85–90° with stirring for 2 hr. The mixture was extracted twice with EtOAc and chromatographed on a Si gel column. The synthetic compound **3** was obtained in the fractions eluted with heptane–$CHCl_3$ (1:1). UV, ^{1}H NMR and IR spectra were identical to those of the natural compound.

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