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AN ANTHRAQUINONE FROM THE ROOTS OF *DIGITALIS DAVISIANA**

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Key Word Index—*Digitalis davisiana*; Scrophulariaceae; anthraquinones.

Abstract—A new anthraquinone, 1-hydroxy-2-hydroxymethyl-8-methoxyanthraquinone, was isolated from the root of *Digitalis davisiana*.

In the course of our investigations on the anthraquinones and flavones in Turkish *Digitalis* species, we have detected eleven anthraquinone pigments (D_1–D_{11}) in the ethanol extract of the roots of *Digitalis davisiana* Heyw. Most of these were present in trace amounts and only four could be isolated in very poor yield. By direct comparison (mmp, TLC, IR) with authentic samples D_1, D_2 and D_4 were identified as 1,5-dihydroxy-3-methylanthraquinone (ziganein) [1], 1-hydroxy-8-methoxy-2-methylanthraquinone [2] and 5-hydroxy-1-methoxy-3-methylanthraquinone [1], respectively.

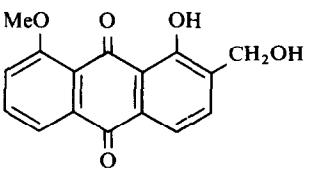
The fourth compound, D_{11}, $C_{16}H_{12}O_5$, was different from all known *Digitalis* anthraquinones by TLC comparison. The IR spectrum showed free and chelated carbonyl absorption at 1665 and 1629 cm^{-1}. From the ^1H NMR spectrum the pigment contained a methoxyl group, a hydroxymethyl group, and a *peri*-hydroxyl group, and five aromatic protons, none of which were isolated. According to these data, D_{11} must be a monomethyl ether of ω-hydroxy-isochrysophanol and therefore a new compound. To confirm this we prepared 1-hydroxy-2-hydroxymethyl-8-methoxyanthraquinone (**1**) by hydroxymethylation [3–5] of 1-hydroxy-8-methoxyanthraquinone with formaldehyde and dithionite (cf. ref. [6]). Direct comparison (mmp, TLC, IR) of the synthetic sample with the natural pigment showed that they were identical.

With the isolation of this new quinone from the root of *D. davisiana*, the number of *Digitalis* anthraquinones is now thirty-one [7].

EXPERIMENTAL

The plant material was collected in July 1978 near Alanya in Turkey. (A voucher specimen (ISTE 26331) is kept at the Herbarium, Faculty of Pharmacy, University of Istanbul, Istanbul, Turkey.) Dried and coarsely powdered roots (1.25 kg) were percolated with 96% EtOH. After removal of solvent the aq. residue was extracted successively with petrol (bp 50–70°). C_6H_6 and Et_2O. The C_6H_6 extract was transferred to a column of acidic Si gel and eluted with the same solvent. TLC monitoring revealed the presence of eleven pigments (D_1–D_{11}). Four of them were obtained in pure and crystalline state by prep. TLC on Si gel and/or polyamide column chromatography: D_1 = 4.2 mg, D_2 = 2 mg, D_4 = 3 mg and D_{11} = 8 mg. Compound D_{11}: orange needles, mp 216–217°; UV λ_{max}^{MeOH} nm (log ε): 257 (4.30), 275 sh (4.00), 415 (3.93); IR ν_{CO} 1669, 1629 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.08 (2H, *d*, $-C\underline{H}_2OH$), 4.85 (1H, *s*, $-CH_2O\underline{H}$), 7.25–8.00 (5H, *m*, ArH), 13.32 (1H, *s*, –OH); MS (Found: M^+ 284.0684, $C_{16}H_{12}O_5$ requires M, 284.0681) *m/z* (rel. int.): 284 (100), 269 (71), 255 (20), 240 (7), 152 (8).

1-Hydroxy-2-hydroxymethyl-8-methoxyanthraquinone (**1**). 1-Hydroxy-8-methoxyanthraquinone (50 mg) was dissolved in 0.5 M NaOH (30 ml), and $Na_2S_2O_4$ (50 mg) and 30% formalin (0.5 ml) were added under N_2. The reaction mixture was kept for 30 min at room temp., acidified and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O to remove the acid and dried over Na_2SO_4. After evapn the residue was purified by prep. TLC on Si gel (petrol–C_6H_6, 1:1) to give orange needles, mp 217° (36 mg from MeOH) identical with D_{11}.



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REFERENCES

1. Imre, S., Öztunç, A. and Büyüktimkin, N. (1974) *Phytochemistry* **13**, 681.
2. Imre, S. (1973) *Z. Naturforsch. Teil C* **28**, 436.
3. Marschalk, C., Koenig, F. and Ouroussoff, N. (1936) *Bull. Soc. Chim. Fr.* 1545.
4. Imre, S. and Ersoy, L. (1978) *Liebigs Ann. Chem.* 2018.
5. Bredereck, K., Metwally, S. A., Koch, E. and Weckmann, R. (1975) *Liebigs Ann. Chem.* 972.
6. Brew, E. J. C. and Thomson, R. H. (1971) *J. Chem. Soc. C* 2007.
7. Imre, S., Sar, S. and Thomson, R. H. (1976) *Phytochemistry* **15**, 317.

*Part 12 in the series "Flavone and Anthraquinone Pigments from *Digitalis* sp.". For Part 11 see Imre, S., Sar, S. and Thomson, R. H. (1976) *Phytochemistry* **15**, 317.