The occurence of geissoschizol was so far described only in *Rauwolfia vomitoria*[2] and *Aspidosperma oblongum*.[3] The remaining alkaloids were already reported to be constituents of *Peschiera affinis*[5] and *Peschiera lundii*.[6]

[5] Weisbach, J A, Raffauf, R F, Ribeiro, O, Macko, E and Douglas, B (1963) *J Pharm Sci* **52**, 350

[6] Hwang, B, Weisbach, J A, Douglas, D, Raffauf, R, Cava, M P and Bessho, K (1969) *J Org Chem* **34**, 412

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(−)-*cis*-CHRYSANTHENOL *O*-β-D-GLUCOPYRANOSIDE. A NEW MONOTERPENE GLUCOSIDE FROM *DICORIA CANESCENS*

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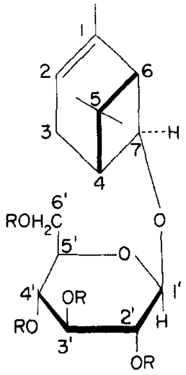
We report the isolation and structure determination of the first glucoside of (−)-*cis*-chrysanthenol. Chloroform extracts from air-dried and ground *Dicoria canescens* collected in Arizona, August 1970, afforded in 0·21% yielded the new glucoside, $C_{16}H_{26}O_6$, m p. 136–137°. The evidence presented below established that the compound is (−)-*cis*-chrysanthenol *O*-β-D-glucopyranoside (**1**)



(1) R = H
(2) R = Ac

β-Glucosidase hydrolysis of the new glucoside afforded the known (−)-*cis*-chrysanthenol,[1] indicating a C_1'-β anomeric configuration. This result was consistent with the

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[1] Pinhey, J T and Southwell, I A (1971) *Australian J Chem* **24**, 1311

large (8·0 cps) coupling constant of the C_1' anomeric proton signal.[2] The sugar obtained by acid hydrolysis of the glucoside was shown to be glucose by glc of the trimethylsilyl ether. It was evident from NMR data for both the glucoside and its tetraacetate that a glucopyranoside was present. Therefore, the new glucoside is (−)-*cis*-chrysanthenol *O*-*β*-D-glucopyranoside (**1**).

EXPERIMENTAL

Isolation of (−)-cis-*chrysanthenol* O-*β*-D-*glucopyranoside* (**1**) *from* Dicoria canescens. Dried and ground plant material (405 g) of *Dicoria canescens* collected August 1970 5 miles west of Dateland on Hwy. 80, Yuma Co., Arizona was extracted with $CHCl_3$ and worked-up in the usual way,[3] yielded of crude syrup 22 g. The crude syrup was chromatographed over a silica gel column (800 g) packed in $CHCl_3$. Elution with $CHCl_3$–MeOH (9:1) in 150 ml fractions yielded in fractions 12–17, 3·10 g of a glassy material. Recrystallization of the crude syrup with EtOH yielded 1·90 g of crude crystals which afforded 0·81 g of pure **1** after recrystallization from EtOAc. m.p.* 136–137°, $[\alpha]_D^{23}$ −42·2 (*c* 0·74, MeOH) (Found: C, 61·05; H, 8·33. $C_{16}H_{26}O_6$ requires: C, 61·12; H, 8·34%); IR (Nujol) 3300 cm^{-1} (OH). NMR (acetone-d_6): 5·21 (*m*, 1H) for 2-H, 4·45 (*br. d*, *J* 7 Hz, 1H) for 1′-H, 3·90–3·20 (*m*, 5H) for 2′, 3′, 4′, 5′, 6′-H, 1·65 (*dd*, *J* 3, 1·5 Hz, 3H) for 1-Me, 1·52 and 0·89 (*s*, 3H for each) for two 5-tert. Me.

Acetylation of **1** *to give* **2**. The crude acetate (pyridine–Ac_2O) was purified by recrystallization from isopropyl ether with small amounts of EtOAc giving the tetraacetate (**2**) as needles, m.p. 127·5–128·5° (Found: C, 59·63; H, 7·12. $C_{24}H_{34}O_{10}$ requires: C, 59·74; H, 7·10%). IR (Nujol), 1750 cm^{-1} (C=O), 1230 (acetyl). NMR (CCl_4), 5·19 (*m*, 1H) for 2-H, 5·08–4·80 (*m*, 3H) for 2′, 3′, 4′-H, 4·46 (*br. d*, *J* 8 Hz, 1H) for 1′-H, 4·20–3·90 (*m*, 2H) for 6′-H, 3·82 (*s*, 1H) for 7-H, 3·70–3·40 (*m*, 1H) for 5′-H, 2·07, 2·03 and 2·00 (*s*, total 12H) for acetyl-Me, 1·68 (*dd*, *J* 3, 1·5 Hz, 3H) for 1-Me, 1·37 and 0·89 (*s*, 3H for each) for two 5-tert. Me.

Enzymatic hydrolysis of **1** *to* (−)-cis-*chrysanthenol*. A solution of 70 mg of **1** in 2 ml of 0·01 M NaOAc buffered with HOAc to pH 4·50 was added to 15 mg of emulsin[4] (*β*-glucosidase); the resultant solution was allowed to stand at 34° for 19 hr. The mixture was extracted with 2 ml of Et_2O and the extract was dried with Na_2SO_4. The ether was evaporated under N_2 to leave a yellowish oil which yielded after vacuum distillation *ca* 20 mg of colourless oil. Gas chromatographic analysis gave only a single peak (1·5%, SE-30 glass column 3 mm × 2·1 m, FID, carrier N_2 0·8 kg/cm^2, 100°, t_R 5′20″); GC–MS: M^+ 137, 121, 109, 91, 85, 83 and 81. The material was identical with authentic (−)-*cis*-chrysanthenol[5] by NMR and IR. ORD gave a single (−) cotton effect curve between 600–310 nm (*c* 5·28, $CHCl_3$).

Acid hydrolysis of **1** *and identification of the glucose moiety*. A soln of 90 mg of **1** in 4 ml of MeOH was mixed with 4 ml of 0·1 N H_2SO_4, the resultant solution was kept at 100° for 1 hr. The soln was conc *in vacuo* to *ca* 3 ml and washed with $CHCl_3$ (2 × 3 ml). The aq. layer was neutralized and filtered. The aq. filtrate which was conc to dryness yielded a thick syrup which was extracted with hot MeOH. The MeOH extract yielded a clear syrup (32 mg). To a soln of the syrup in 0·5 ml of dry-pyridine was added 0·5 ml of $(Me)_3SiCl$ and 0·5 ml of $[(Me)_3Si]_2NH$. After stirring 5 min, the solution was evaporated to dryness. The residue was dissolved in dry CCl_4, the solution was filtered and the filter was washed with additional CCl_4. The filtrate (plus washings) was gas chromatographed and found to contain 1,2,3,4,6-penta-*O*-trimethylsilyl-D-glucopyranose by co-gas chromatographic analysis with an authentic sample. Gas chromatographic conditions: Shimadzu GC-3BF, FID, carrier N_2 0·8 kg/cm^2 (5%, SE-30 glass column 3 mm × 2·1 m, 185°) t_R, *α*-epimer 4′25″, *β*-epimer 7′20″; (5%, DEGS, glass column 3 mm × 1·5 m, 140°) t_R, *α*-epimer 4′55″, *β*-epimer 7′55″.

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* All m.ps. are uncorrected. NMR spectra were recorded on a Hitachi R-20B (60 MHz) spectrometer at 35°. Values are given in ppm (*δ*-scale) relative to TMS as an internal standard.

[2] Lemieux, R. U. *et al.*, established that in penta-*O*-acetyl-D-glucopyranose the anomeric proton shows a coupling constant of about 8 cps in the *β* epimer while the *α* epimer shows a smaller coupling constant of 3·2 cps (Lemieux, R. U., Kullnig, R. K., Bernstein, H. J. and Schneider, W. G. (1958) *J. Am. Chem. Soc.* **80**, 6098).

[3] Yoshioka, H., Mabry, T. J. and Higo, A. (1969) *J. Org. Chem.* **34**, 3697.

[4] Purchased from Calbiochem., California, U.S.A.

[5] We thank Dr. J. T. Pinhey, Department of Organic Chemistry, University of Sydney, N.S.W., Australia for NMR and IR spectra of (−)-*cis*-chrysanthenol.