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PAUCIN, A SESQUITERPENE LACTONE GLUCOSIDE

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As part of a chemical investigation of the genus Baileya (Compositae; tribe Heleniae), we have examined collections of B. pauciradiata Harv. and Gray and B. pleniradiata Cov., desert herbs common to Southern California and Arizona. Paucin (I), a new pseudoguaianolide, was isolated in about 0.04% yield from both species and was found to be a β-D-glucoside. This paper reports on the structure of paucin, the first sesquiterpene lactone glucoside.

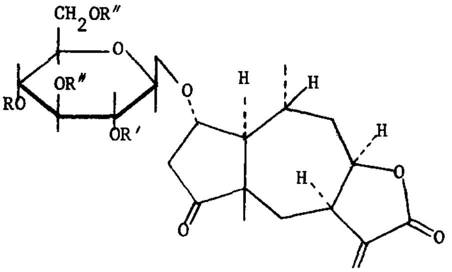
Paucin, m.p. 178-9°, $[\alpha]^{25}_{D}$ + 51.7, has the molecular formula $C_{23}H_{32}O_{10}\cdot H_2O$. The highest ion in the mass spectrum obtained with consistency is at m/e 246.12598 (calc. for $C_{15}H_{18}O_3$, m/e 246.12559;cf. IV). Paucin shows λ_{max} 207 mμ (log ε 3.98) and infrared peaks (nujol) at 3600-3200 (OH), 1750 (γ lactone), 1738 (cyclopentanone), 1720 (OAc), and 1660 cm^{-1} (double bond). The NMR spectrum and a positive Zimmerman test are in accordance with I.

The reaction of paucin with acetic anhydride in pyridine or with isopropenyl acetate and TsOH yields triacetylpaucin (II), $C_{29}H_{38}O_{13}$, m.p. 241-3°, showing no hydroxyl absorption in the infrared ($CHCl_3$). The mass spectrum of II confirms the molecular formula (molecular ion at m/e 594.23071; calc. for $C_{29}H_{38}O_{13}$, m/e 594.23099) and gives convincing evidence for the presence of a tetraacetyl glucoside moiety, with peaks of high intensity at m/e 347, 331, 271, 229, 211, 169, 157, 115, 109, and 73.[2] The NMR spectrum (in pyridine) of triacetylpaucin (II) reveals the presence of four acetyl groups (δ 1.96, 9 protons; δ 2.02, 3 protons). The most striking feature in the NMR spectrum of II is that the signal for the C-10 methyl group, appearing at δ 1.50 in paucin (pyridine), has shifted upfield to δ 1.10. This high degree of shielding is consistent with the stereochemistry at C-10 and C-2 shown in II.

The reaction of paucin with 5% H_2SO_4 yields glucose, identified by thin-layer and paper chromatography and by the preparation of D-glucose phenylosazone.

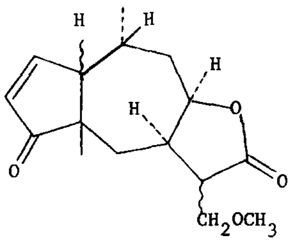
Methanolic potassium carbonate hydrolysis of paucin gives the methoxy derivative III, m.p. 154-8°, which shows infrared absorption at 1750 cm^{-1} (γ lactone), 1712 cm^{-1}, and 1570 cm^{-1} (cyclopentenone). The mass spectrum displays a molecular ion at m/e 278 and a peak of high intensity at m/e 246 ($M-CH_3OH$), along with the corresponding metastable ion for that transition. The mass spectrum of III and that of paucin at values below m/e = 246 are nearly identical.

The reaction of paucin in DMF with barium oxide yields aromatin (IV), m.p. 165-6°, a sesquiterpene lactone of known structure and stereochemistry, isolated earlier from Helenium aromatin Hook.[3] The aromatin obtained from paucin had a specific rotation and an infrared spectrum identical with that of an authentic sample and the mixed melting point was not depressed.[4] The mass spectra of I, III, and IV are essentially identical at m/e values below 246.

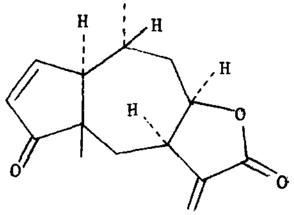


I R or R' = Ac, R'' = H

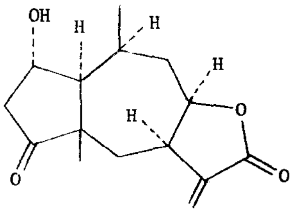
II R = R' = R'' = Ac



III



IV



V

The ORD curve of paucin displays a positive Cotton effect (a = + 53.6) and is nearly superimposable on the ORD curve of burrodin (V)^5 (a = + 55.4). A C-2 α-substituent in <u>trans</u>-fused pseudoguaianolides is pseudoequatorial and on an octant diagram lies partly in a positive and partly in a negative quadrant. Therefore, the acetylglucose moiety in paucin must be α and equatorial as is the hydroxyl group in burrodin.

The position of the acetyl group on the glucose portion of paucin has not yet been established, but it is at position 2′ or 4′, for paucin consumes but one mole of HIO_4 when oxidized with a two-fold molar excess of the reagent.

Paucin is hydrolyzed by β-glucosidase and is therefore a β-glucoside. Elemental analyses and quantitative acetyl determinations of paucin and triacetylpaucin are in agreement with the proposed structures.

References

1. Contribution No. 2349 from the Department of Chemistry, U.C.L.A.

2. H. Budzikiewicz, C. Djerassi, and D. Williams, <u>Structure Elucidation of Natural Products by Mass Spectrometry</u>. Vol. II, Holden-Day, Inc., San Francisco, 1964, Ch. 27; T. C. Smale and E. C. Waight, <u>Chem. Comm.</u>, <u>1966</u>, 680.

3. J. Romo, P. Joseph-Nathan, and F. Diaz, <u>Tetrahedron</u>, <u>20</u>, 79 (1964).

4. We thank Dr. Romo for a specimen of aromatin.

5. T. A. Geissman and S. Matsueda, <u>Phytochemistry</u>, <u>1968</u>, 1613.