

SESQUITERPENE LACTONES. CONSTITUENTS OF *BAILEYA* SPECIES

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Abstract—Examination of three species of *Baileya* (Compositae) has disclosed the presence of two new sesquiterpene lactones: baileyin (VI) and plenolin(VII). The seven lactones so far found in the genus represent a closely allied group of compounds whose structures suggest their biosynthetic interrelationships.

INTRODUCTION

EXAMINATION of three closely allied species of *Baileya*—*B. pleniradiata*, *B. multiradiata* and *B. pauciradiata*—has disclosed the presence in these plants of a number of sesquiterpene lactones. These are of special interest because they include representatives of several structural classes: germacranolides, guaianolides and pseudoguaianolides. The structures of these compounds provide a revealing glimpse of biosynthetic relationships between the members of a group of related substances.

Earlier communications have described the isolation from *Baileya* and structure determination of paucin (I),² a sesquiterpene lactone glucoside, and of radiatin (II) and pleniradin (III).³

Baileya is a genus of the tribe Helenieae, family Compositae. The species *multiradiata* and *pleniradiata* ("desert marigold") form showy stands, abundant in the south-western deserts in Arizona and California. *B. pauciradiata*, with less conspicuous inflorescence, occurs in similar localities.⁴ Preliminary examination of several specimens showed that these plants are rich in compounds of the sesquiterpene lactone class and, in view of the extensive investigations that have been carried out on members of the tribe Helenieae,⁵ a systematic study of these plants was undertaken.

RESULTS AND DISCUSSION

A total of seven sesquiterpene lactones have been isolated from the three species of *Baileya* and their structures established. A prominent constituent of two collections of BM and BPL was fastigilin C (IV), previously found in *Gaillardia fastigiata* Greene.⁶ Another lactone,

¹ Contribution No. 2416 from the Department of Chemistry, UCLA.

² T. G. WADDELL and T. A. GEISSMAN, *Tetrahedron Letters* 515 (1969).

³ A. YOSHITAKE and T. A. GEISSMAN, *Phytochem.*, **8**, 1753 (1969).

⁴ The specimens used in this study are represented by UCLA herbarium voucher numbers RJB-61167-BR (*B. multiradiata*); TGW-41368-4-1-IY, 41368-4-1-III JT, RJB-67358-9367-BP, and TAG-42068-BLV (*B. pleniradiata*); and TGW-41368-4-1-IIY (*B. pauciradiata*). For convenience, these species will be referred to in this account by the abbreviations BM, BPL and BPC, respectively.

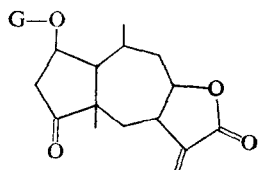
⁵ For a partial summary, see W. HERZ, in *Recent Advances in Phytochemistry* (edited by T. J. MABRY, R. E. ALSTON and V. C. RONECKLES), p. 229, Appleton-Century-Crofts, New York (1968).

⁶ W. HERZ, S. RAJAPPA, S. K. ROY, J. J. SCHMID and R. J. MIRRINGTON, *Tetrahedron* **22**, 1907 (1966).

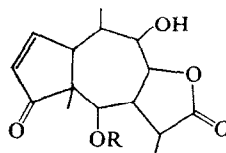
present in a very small amount, was baileyolin (V), isomeric with fastigilin A, the spectral properties of which were found to be essentially identical with those of fastigilin A,⁶ but which was not this compound. It is believed that baileyolin and fastigilin A are stereoisomers at one or more of the numerous possible sites, but the nature and location of the differences are not yet known.

Baileyin (VI), $C_{15}H_{20}O_4$, was isolated in 0.002 per cent yield from BM and 0.005 per cent yield from BPL. It has a bitter taste and melts to an amber glass at 189° . Its i.r. spectrum shows the presence of a γ -lactone (1765 cm^{-1}), a hydroxyl group (3580 cm^{-1}) and a carbon-carbon double bond ($1650\text{--}1665\text{ cm}^{-1}$). No other carbonyl absorption is seen in the i.r. spectrum. The mass spectrum shows the expected molecular ion (m/e 264), and an intense peak at 246 (M-18), for which the appropriate metastable ion (229) is seen. The u.v. spectrum shows only the end absorption characteristic of the α -methylene- γ -lactone.

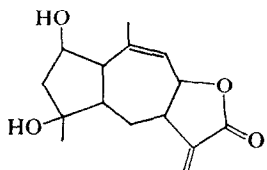
The NMR spectrum is in accord with the structure (VI). The two protons of the α -methylene group appear as doublets ($J=3\text{ Hz}$) at δ 5.87 and 6.20, and the methyl group sat C-10 and C-4 are seen, respectively, as a doublet ($J=1\text{ Hz}$) at δ 1.80 and a singlet at 1.08.



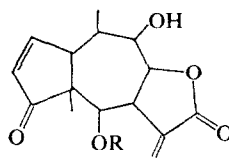
(I) Paucin; G = mono-O-acetylglucosyl



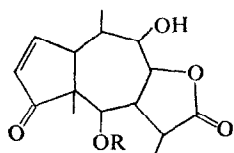
(II) Radiatin
R = $-\text{COC}(\text{CH}_3)=\text{CH}_2$



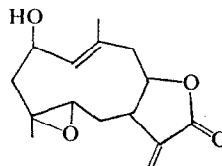
(III) Pleniradin



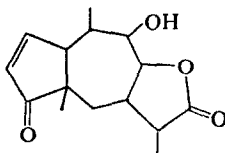
(IV) Fastigilin C
R = $\text{COCH}=\text{C}(\text{Me})_2$



(V) Baileyolin
R = $\text{COC}(\text{CH}_3)=\text{CHCH}_3$
(angelyl)



(VI) Baileyin



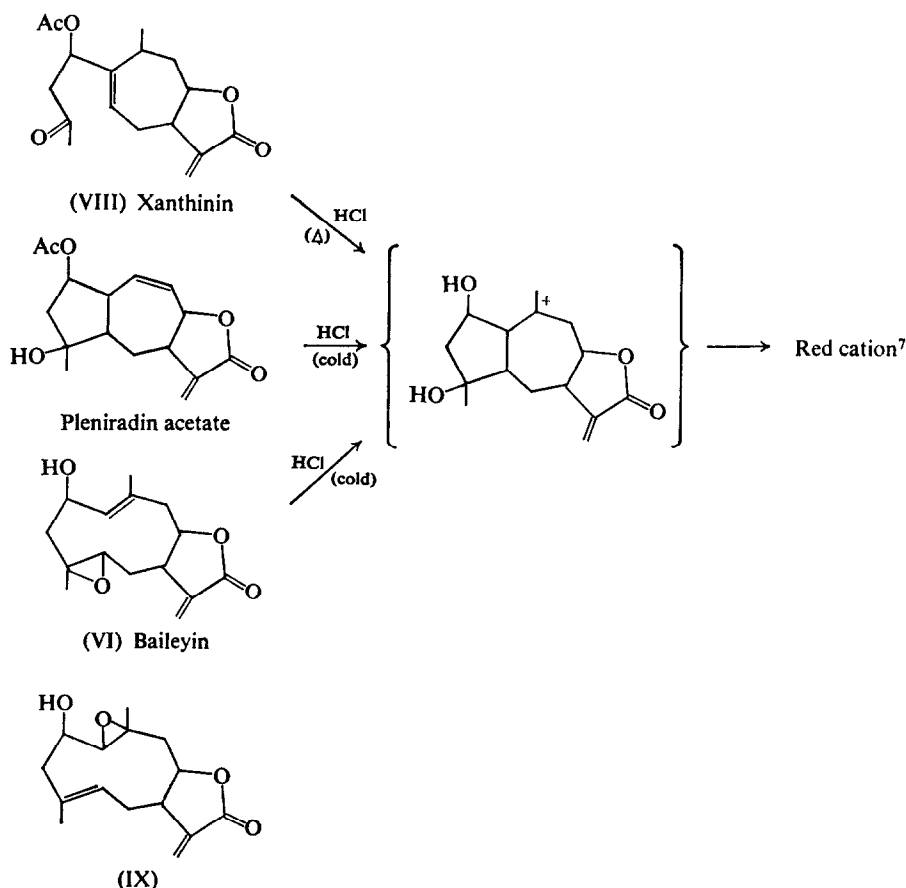
(VII) Plenolin

The vinyl proton at C-1 appears as a broadened doublet ($J=10$ Hz) at δ 5.39, and that at C-5 as a quartet at δ 2.06 ($J=10, 1.5$ Hz). The signals for the protons at C-2 and C-8 are not separated in the spectrum of baileyin, but, as described below, can be seen in the spectrum of the acetate. The NMR spectrum of the acetate of baileyin shows the proton at C-2 of the CH-OAc group as a broadened triplet ($J=9, 10, 3$) at δ 5.40, now separated from the C-8 proton, which is seen as an octet ($J=9, 10, 3$) at δ 4.11.

The formation of a monoacetate and the absence in the latter of hydroxyl absorption led to the conclusion that the fourth oxygen atom of baileyin was in an ether linkage, a conclusion supported by the position and pattern of the NMR signal for the C-5 proton, which is seen in the spectrum of the acetate as a quartet ($J=10, 1$ Hz) at δ 2.55.

Catalytic hydrogenation of baileyin yielded a mixture of two relatively nonpolar compounds (by TLC). The high R_f of these products compared with that of baileyin and the absence of hydroxyl absorption in the i.r. spectrum indicated that hydrogenolysis of the C-2 hydroxyl group had occurred, and that the hydroxyl group of baileyin is allylic.

Treatment of an ethanol solution of baileyin with cold, concentrated hydrochloric acid results in the immediate formation of a wine-red solution. The color so produced is identical with that formed when xanthinin (VIII) is heated in ethanol-hydrochloric acid, and with the



⁷ The intermediate cation is formulated in an arbitrary way, for the position of the positive charge and the sequence in which the hydroxyl groups are eliminated cannot be specified.

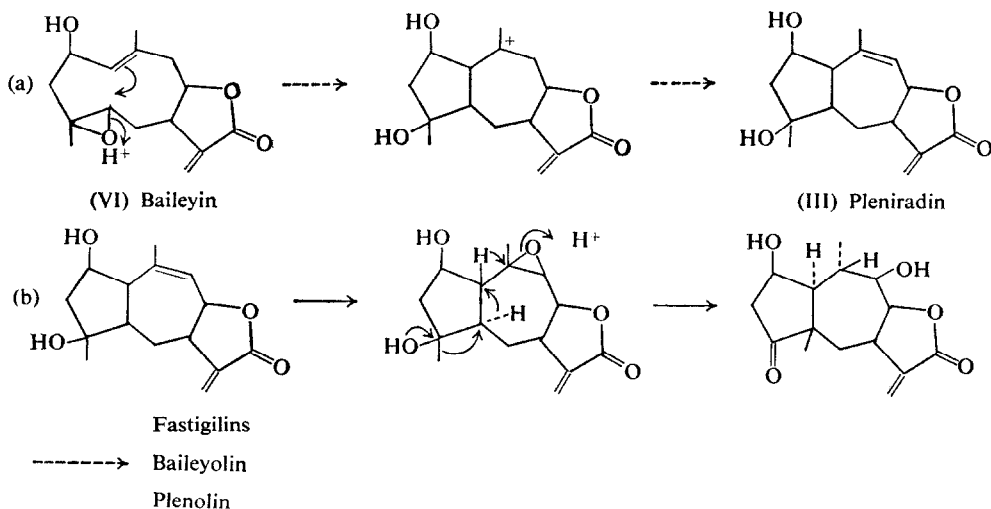
color formed when pleniradin (III) acetate is treated with hydrochloric acid. The absorption spectra of the colored solutions formed from these three compounds all show an identical maximum at 542 nm but differ somewhat at lower wavelength regions of the spectra. The interpretation of these results affords strong support for the structure (VI) assigned to baileyin, for it is apparent from the following formulation that the acid-catalyzed transformations of these three compounds can lead to a common intermediate from which the colored cation is formed.⁸

An alternative formulation (IX) for baileyin could accommodate the color reaction, but can be discarded on the basis of the NMR spectrum described above. In particular, the signal for the C-1 (vinyl) proton of (the acetate of) structure (VI) is a doublet ($J=11$ Hz), clearly coupled to the C-2 proton of the CH -Ac group, which is seen as an octet with coupling constants of 11 ($J_{1,2}$), 9 ($J_{2,3a}$) and 2 ($J_{2,3b}$) Hz. These features establish the presence of the grouping,



in the structure, as shown in VI.

The close structural relationship between baileyin and its companion, pleniradin, is suggestive of their participation in the biosynthetic process. A simple acid-catalyzed process can be visualized as the manner in which baileyin leads to pleniradin. Moreover, the further transformations that lead to the co-occurring plenolin (see below) and the fastigilins can be supposed to represent subsequent events in a common pathway:



The formation of paucin by a pathway similar to that shown in (b) requires only that the migration of the C-4 methyl group occurs by the agency of protonation of the C-9/10 double bond rather than by epoxidation and acid-catalyzed opening. It is relevant to these proposals that gaillardin has been found to have C-1 $H\beta$,⁹ and paucin has C-10 $CH_3\alpha$.

⁸ The question of the nature of the red cation is under investigation and will be the subject of a later communication; see also Ref. 3.

⁹ T. A. DULLFORCE, G. A. SIM, D. N. J. WHITE, J. E. KELSEY and S. M. KUPCHAN, *Tetrahedron Letters* 973 (1969).

A closely related compound, plenolin, $C_{15}H_{20}O_4$, was isolated in 0.0003 per cent yield from BPL. Although too little plenolin was obtained to permit detailed chemical investigation, the assignment of the structure VII can be made with confidence from the characteristic spectral data. The presence of a hydroxyl group (3485 cm^{-1}), a γ -lactone (1750 cm^{-1}) and a cyclopentenone grouping ($1710, 1580\text{ cm}^{-1}$) can be deduced from the i.r. spectrum. The mass spectrum shows a molecular ion (264) and has peaks at M-18 (m/e 246), M-28 (236) and M-18-15 (231), along with the corresponding metastable ions. The presence of the cyclopentenone is confirmed by the u.v. spectrum (225 nm , $\log \epsilon$ 3.97), and by the NMR spectrum, in which the protons at C-2 and C-3 are seen as the characteristic doublets of doublets at δ 7.65 ($J=5.5, 2\text{ Hz}$) and 6.10 ($J=5.5, 3.5\text{ Hz}$). Plenolin lacks the α -methylene group on the lactone ring, and is the corresponding α -methyl- γ -lactone. Three-proton methyl group signals are seen at δ 1.29 (C-11 methyl, d, $J=7\text{ Hz}$), 1.05 (C-10 methyl, d, $J=7\text{ Hz}$), and 1.10 (C-5 methyl, s). The protons at the CH-O positions of the lactone (at C-8) and the hydroxyl group (at C-9) are found as one-proton signals; the first of these is a broad triplet at δ 4.98, the second a triplet at 3.30. The coupling of these protons is clearly revealed by the coupling constant ($J=5\text{ Hz}$) shown by both signals. These features of the NMR spectrum are in complete accord with the pseudoguaianolide structure (VII) assigned, and serve to establish both the C-8 position of lactone closure and the C-9 position of the hydroxyl group. It will be seen that the principal features of the structure of plenolin are in accord with those of the co-occurring fastigilins (IV), radiatin (II) and baileyolin (V), except for the absence in plenolin of a C-6 hydroxyl group. This suggests that plenolin lies at an earlier point in the biosynthetic pathway (and, indeed, can be simply derived from pleniradin, via baileyin, as described above), and further suggests that hydroxylation at C-6 is an event that occurs late in the synthetic process.

The partial stereochemistry of plenolin has been established by a study of the circular dichroism. The CD curve of plenolin reveals a negative Cotton effect for the $n \rightarrow \pi^*$ transition of the α, β -unsaturated ketone, with $[\theta]_{322} = -5210$. The position, sign and amplitude of this Cotton effect are the same as those of bigelovin,¹⁰ aromaticin,¹¹ ambrosin¹² and helenalin,¹³ compounds having the *trans*-ring fusion at C-1/C-5. In the steroid series, androst-15-ene-3 β -ol-17-one, with a *trans* fusion at C-13/C-14, shows a negative Cotton effect at 320 nm for the $n \rightarrow \pi^*$ transition of the cyclopentenone. Its *cis*-fused isomer (at C-13/C-14) shows a positive Cotton effect for the same transition. Plenolin thus has a *trans*-fused cyclopentenone-cycloheptane system.

The stereochemistry of the lactone ring in baileyin can be assigned as *trans* on the basis of two observations. Application of CD measurements to baileyin indicate this stereochemistry for baileyin exhibits a positive Cotton effect, with $[\theta]_{255} = +1550$, in agreement with the finding that *trans*-fused C-7/C-8 lactones in guaianolides and pseudoguaianolides show positive Cotton effects for the $n \rightarrow \pi^*$ transition of the lactone carbonyl group.¹⁴ However, since these rules cannot be applied with confidence to germacranolides because of conformational uncertainties, this result is not definitive. An examination of the NMR signal for the lactone proton (at C-8) in baileyin acetate does provide positive evidence for the *trans*-fusion of the lactone. The following figures (Table 1) show the comparisons between

¹⁰ W. HERZ and U. V. LANKSHINIKAUTHAM, *Tetrahedron* **21**, 1711 (1965).

¹¹ J. ROMO, P. JOSEPH-NATHAN and F. DIAZ, *Tetrahedron* **20**, 79 (1964).

¹² M. T. EMERSON, W. HERZ, C. N. CAUGHLAN and R. W. WITTERS, *Tetrahedron Letters* 6151 (1966).

¹³ M. T. EMERSON, C. N. CAUGHLAN and W. HERZ, *Tetrahedron Letters* 621 (1964).

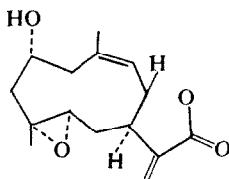
¹⁴ T. G. WADDELL, W. STÖCKLIN and T. A. GEISSMAN, *Tetrahedron Letters* 1313 (1969).

the NMR signals for the C-8 proton in baileyin acetate, aromaticin (*trans*-fused lactone) and aromatin (*cis*-fused lactone):

TABLE 1

Compound	C-8 H	<i>J</i> , Hz	Band width, Hz
Baileyin acetate	Octet	9, 10, 3	25
Aromaticin	Octet	10, 12, 3	28
Aromatin	Broad, multiplet	—	43

These comparisons, coupled with the CD data, indicate that baileyin possesses C-7 α H/C-8 β H. When it is recalled that pleniradin possesses an α -oriented hydroxyl group at C-2 and that, on biogenetic grounds, the C-4 methyl group is β -oriented, the complete stereochemistry of baileyin can be represented as follows:



Paucin, a principal constituent of BPC and also isolated from one collection of BPL, has been described.² The evidence for its structure (I), given in brief form in the earlier report, will not be described in detail here, but the account of the experimental work performed in its study is presented in this paper.

A major constituent of BPL, a non-crystallized glucoside so far identified only as BP II, is still of unknown constitution. It is an α -methylene- γ -lactone which yields glucose, identified by chromatographic methods, when hydrolyzed with dilute sulfuric acid. No crystalline derivatives of BP II have been prepared and no structure can be proposed. It is of interest that when thin-layer chromatograms containing BP II (which forms a single spot) are sprayed with sulfuric acid, a bright purple spot appears. This behavior indicates that BP II is not a pseudoguaianolide similar to paucin or radiatin, but may be a glucoside having the principal structural features of pleniradin or baileyin, both of which give this color reaction with strong acid. Further study of BP II is continuing.

Distribution of Lactonic Constituents in Baileya

Seven separate collections of the three *Baileya* species were examined in the course of this work. In Table 2 are listed the results of these studies; it will be noted that the lactonic composition does not define the species, for different populations of the same species show different constituents.¹⁵

¹⁵ The differences between BM and BPL are subtle, but recognizable. We are grateful for assistance in the botanical identifications from Mr. David Verity and Dr. M. Mathias, Botany Department, UCLA; and Mr. R. J. Barr, Tucson, Arizona, who provided those specimens identified by "R. J. B."

TABLE 2

Plant	Voucher No.	Location	Date collected	Components isolated
<i>B. pleniradiata</i>	TAG-522	Yuma, Ariz.	March 1964	Baileyolin Fastigilin C
<i>B. pleniradiata</i>	TGW-41368-4-1-IY	Yuma, Ariz.	April 1968	Paucin Baileyin Plenolin
	TGW-41368-4-1-III-JT	Joshua Tree, Calif.	April 1968	
	TAG-42068-BLV	Lucerne Valley, Calif.	April 1968	
<i>B. pleniradiata</i>	RJB-67358-9367-BP	Cochise Co., Ariz.	Sept. 1967	Pleniradin Radiatin
<i>B. pleniradiata</i>	RJB-61167-BR	Tucson, Ariz.	June 1967	Baileyolin Fastigilin C Baileyin
<i>B. pauciradiata</i>	TGW-41368-4-1-IIY	Yuma, Ariz.	April 1968	Paucin

EXPERIMENTAL

M.ps. were taken in capillaries and are corrected. TLC was carried out on precoated silica gel plates, the solvents usually being acetone-chloroform (3:7) and (for polar compounds such as paucin) ethyl acetate-methanol (4:1). Spectra were measured in the usual way. Circular dichroism measurements were taken at 25° in a 1-cm cell, with absolute methanol as solvent (conc. = 10^{-3} g/ml). Mass spectra were recorded with an AEI-MS-9 spectrometer operating at 70 eV with direct insertion.

Isolation of Paucin (I), Baileyin (VI) and Plenolin (VII).

(A). *Baileya pauciradiata* Harv. and Gray (TGW-41368-4-1-IIY) (760 g) was extracted with CHCl_3 and the solvent removed to yield 30 g of crude extract. This was dissolved in ethanol (100 ml) and after the addition of 300 ml of hot water the mixture was decanted from tarry material, filtered, and the clear aqueous filtrate extracted repeatedly with chloroform. The residue from this extract was a yellow oil (6.5 g) which showed several components on TLC. Chromatography of this oil over silica gel was performed with 500-ml portions of benzene containing increasing amounts of CHCl_3 and then CHCl_3 containing increasing amounts of acetone. Fractions of 20 ml were taken, of which those later than number 140 were evaporated to yield 61 mg of paucin, m.p. 172–173°.

(B). Extraction of 8.23 kg of *B. pleniradiata* Harv. and Gray (TGW-41368-4-1-IY; TGW-41368-1-IIIJT; TAG-42068-BLV) in the manner described in A yielded 121 g of an amber oil. Chromatography of this on 1.5 kg of silica gel was carried out with 3 l. of benzene followed by three 1-l. portions of benzene containing increasing amounts of CHCl_3 , then four 1-l. portions of CHCl_3 containing increasing proportions of acetone. Fractions of 400 ml were collected.

Fractions 59–71 yielded 3.51 g of paucin, m.p. 175–176°, $[\alpha]_D^{25} + 51.7^\circ$ (pyridine). (Found: C, 56.62, 56.23, 56.67, 56.93; H, 6.99, 7.22, 7.21, 7.38; O-acetyl, 1.12. Calc. for $\text{C}_{23}\text{H}_{32}\text{O}_{10}$: C, 56.79; H, 7.00; O-acetyl, 1.0.)

Fractions 15–38 were evaporated and the residue rechromatographed in a manner similar to that described above. From earlier fractions were isolated 23 mg of plenolin, m.p. 216–220°. (Found: C, 67.67; H, 7.80. Calc. for $\text{C}_{15}\text{H}_{20}\text{O}_4$: C, 68.16; H, 7.60.)

Fractions collected after the elution of plenolin yielded 426 mg of baileyin, m.p. 189°. (Found: C, 68.05; H, 7.77. Calc. for $\text{C}_{15}\text{H}_{20}\text{O}_4$: C, 68.16; H, 7.63%.)

Plenolin (VII) showed i.r. absorption (Nujol) at 3485, 1750, 1710 and 1580 cm^{-1} , and had λ_{max} 225 nm ($\log \epsilon$ 3.97). The mass spectrum showed the molecular ion at m/e 264. The NMR spectrum has been described above.

Baileyin (VI) had i.r. peaks at 3440, 1770, 1760 and 1660 cm^{-1} and its mass spectrum displayed the molecular ion at m/e 264. Its NMR spectrum has been discussed above.

Baileyin acetate was prepared in pyridine-acetic anhydride in the usual manner. It had m.p. 176–177°, $[\alpha]_D^{25} + 17.6$; i.r. peaks 1765, 1730, 1660 cm^{-1} ; λ_{max} (EtOH) 210 nm ($\log \epsilon$ 3.92), and showed the molecular ion at m/e 306 in the mass spectrum. Its NMR spectrum has been discussed above. (Found: C, 66.51; H, 7.29. Calc. for $\text{C}_{17}\text{H}_{22}\text{O}_5$: C, 66.65; H, 7.24%.)

Hydrogenation of Baileyin

A solution of 23.4 mg of baileyin in 5 ml of ethanol was hydrogenated in the presence of 21 mg of 10% Pd-C. 3 moles of hydrogen per mole of baileyin were absorbed. The product of the reduction could not be

crystallized. It appeared to consist of two components with nearly the same R_f (0.75) on TLC. Since the R_f of baileyin is 0.34 under the same conditions, it was concluded that hydrogenolysis of the hydroxyl group had occurred. The i.r. spectrum showed no absorption in the hydroxyl region and had a peak at 1770 cm^{-1} (lactone).

Color Reactions of Baileyin, Xanthinin and Pleniradin Acetate

(A). To 1.65 mg of baileyin was added 1 ml of conc. HCl. A deep wine-red solution resulted. The volume was brought to 250 ml with conc. HCl and the absorption spectrum measured at once. It showed λ_{\max} 542 nm (ϵ 16,000).

(B). To 1.37 mg of xanthinin was added 1 ml conc. HCl. The development of the color was not immediate, but after 30 min the solution was deep red. After dilution as in A the absorption spectra was measured: λ_{\max} 542 nm (ϵ 16,500).

(C). A solution of 1.76 mg of pleniradin acetate was treated as in A and B. The red color developed immediately; λ_{\max} 542 nm (ϵ 15,900).

Each of the above red solutions becomes yellow when made alkaline with NaOH. Acidification regenerates the color.

Paucin

(A). Molisch test: positive, bright violet ring similar to that formed in fructose control.

(B). Zimmermann tests on paucin and tetrahydrohymenin¹⁶ were strongly positive. A parallel control with fastigilin C was negative.

Paucin Triacetate

Acetylation of 213 mg of paucin with pyridine-acetic anhydride afforded 121 mg of crystalline paucin triacetate, m.p. 241–243°. The compound had i.r. peaks at 1772, 1760, 1740 and 1665 cm^{-1} , and showed the molecular ion at m/e 594 in the mass spectrometer. (Found: C, 58.53; H, 6.42; O-acetyl, 4.03, 4.06. Calc. for $\text{C}_{29}\text{H}_{38}\text{O}_{13}$: C, 58.58; H, 6.44; O-acetyl, 4.0.)

The same acetate was obtained when paucin was acetylated with isopropenyl acetate–toluenesulfonic acid.

Acid Hydrolysis of Paucin

(A). Parallel hydrolyses of paucin and salicin (control) were carried out by treatment with hot, dil. H_2SO_4 . Chromatographic examination of hydrolysates, using glucose as a control, established the presence of glucose as a product of the hydrolyses.

(B). Hydrolysis of 75 mg of paucin (75 min, 100°) with 3 ml of 5% H_2SO_4 , followed by ether extraction of the solution, yielded 20 mg of a crystalline compound, identified as aromatin (analysis, mass spectrum, NMR, i.r., mix m.p.).¹⁷

The aqueous solution after ether extraction was neutralized with BaCO_3 . Glucose phenylosazone was prepared from this solution in the usual manner, and was identified by comparison with an authentic specimen (m.p., mix m.p., TLC in four solvents).

Hydrolysis of Paucin with Potassium Carbonate

Treatment of paucin in methanol–water solution with aqu. K_2CO_3 , followed by acidification and ether extraction, yielded aromatin, identical with the authentic specimen.

Paucin Aglucon (2- α -Hydroxy-2,3-dihydroaromatin)

A suspension of 108 mg of paucin and 100 mg of hemicellulase (Nutritional Biochem. Corp.) in water were stirred at room temp. for 48 hr. Examination by TLC showed that the reaction was about 65% complete (one high- R_f material along with lower R_f unchanged paucin). CHCl_3 extraction of the solution yielded a crystalline compound, m.p. 151–153°. It had i.r. peaks at 3440, 1770, 1739, 1660 cm^{-1} , and principal peaks in the mass spectrum at m/e 264 (M^+), 246 (M-18), 231 (M-18-15) and 218. The ORD showed a positive Cotton effect for the cyclopentanone: $[\phi]_{314} +2800$; $[\phi]_{279} -290$. (Found: C, 67.88; H, 7.88. Calc. for $\text{C}_{15}\text{H}_{20}\text{O}_4$: C, 68.16, H, 7.63%.)

Periodic Acid Oxidation of Paucin

Oxidation of paucin (4.2×10^{-6} mole) with HIO_4 (8.58×10^{-6} mole) resulted in the consumption of 0.90 mole of HIO_4 after 2 hr (0.84 mole at 1 hr). When an excess of HIO_4 was used, 2 moles of oxidant were consumed, presumably as a result of the hydrolysis of the acetyl grouping on the glucose residue.

Compound BP II

Late (polar) fractions from silica gel chromatography of the crude (8.23 kg) *B. pleniradiata* extract were rechromatographed on silica gel with CHCl_3 –acetone mixtures as eluants. Fractions showing a single spot on

¹⁶ F. P. TORIBIO and T. A. GEISSMAN, *Phytochem.* 7, 1623 (1968).

¹⁷ We are grateful to Dr. J. Romo for a specimen of aromatin.

TLC (purple when sprayed with conc. H_2SO_4) were combined. The product could not be induced to crystallize. It had i.r. peaks at 3577 (OH), 1755 (γ -lactone) and 1660 ($\text{C}=\text{C}$) cm^{-1} . The yield was 45 g. Acid hydrolysis of BP II yielded glucose, identified by chromatography. All attempts to secure crystalline materials by hydrolysis, acetylation, and dihydropyranylation were unproductive.

Acknowledgements—One of us (T. G. W.) is grateful for the award of an N.D.E.A. Postgraduate Fellowship. The study was supported by a research grant, GM-14240-03, from the U.S. Public Health Service. Analyses are by Miss Heather King, UCLA. The NMR and MS instruments were obtained with financial support to the UCLA Chemistry Department by the National Science Foundation and E. I. duPont de Nemours and Co.