

Table IV gives the dihedral angles of the O-P-O planes and also the angle the O(4)-P-O(5) plane makes with the best least-squares plane of the ring.

TABLE IV
DIHEDRAL ANGLE BETWEEN PLANES IN
PROPANE-1,3-DIOL CYCLIC PHOSPHATE

Plane	Angle, degree
[O(4)-P(1)-O(5)] and [O(2)-P(1)-O(3)]	91.7
[O(4)-P(1)-O(5)] and [O(5)-P(1)-O(3)]	122.4
[O(4)-P(1)-O(5)] and [O(4)-P(1)-O(2)]	54.5
[O(3)-P(1)-O(5)] and [O(2)-P(1)-O(4)]	90.1
[O(2)-P(1)-O(5)] and [O(3)-P(1)-O(4)]	88.5
[O(4)-P(1)-O(5)] and [P(1)-O(2)-C(6)-C(7)-C(8)-O(3)]	92.3

Thus we have found that this six-membered cyclic phosphate has essentially no ring strain and has normal

tetrahedral bond angles around the phosphorus. These structural features should contribute to the stability of this molecule and give it a normally high activation energy for the formation of the five coordinated intermediate, thus accounting for the relatively slow rate of hydrolysis compared with five-membered cyclic phosphates.

Registry No.—Propane-1,3-diol cyclic phosphate, 13507-10-3.

Acknowledgment.—One of us (W. L. M.) wishes to acknowledge a NASA fellowship during the time this research was carried out. We also wish to acknowledge a grant from NIH, GM 08395-07, which has made this research possible and a grant from Montana State University for computer use in the calculations. We wish to thank Dr. K. D. Watenpaugh of the University of Washington who assisted in computer drawing of Figure 2.

Structure and Absolute Configuration of Pulchellin. Crystal and Molecular Structure of 3-Bromoanhydrodehydrodihropulchellin^{1,2}

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The structure and relative configuration of the sesquiterpene lactone pulchellin was established partially by X-ray crystallographic analysis of 3-bromoanhydrodehydrodihropulchellin (4), in which the asymmetric centers at C-2 and C-4 have been destroyed and the center at C-1 has been epimerized. Compound 4 crystallizes in an orthorhombic space group $P2_12_12_1$ with lattice parameters $a = 8.368$, $b = 14.342$, and $c = 25.161$ Å. There are eight molecules in the unit cell and two molecules in the asymmetric unit. Bromine positions were located from a three-dimensional Patterson function. The first three-dimensional Fourier electron density map was calculated. The rest of the structure was found from four additional three-dimensional Fourier maps, and the structure was refined by anisotropic full-matrix least-squares refinement to a final R of 6.6%. The complete stereochemistry and absolute configuration of pulchellin was established by correlation with aromaticin and is in agreement with the hypothesis of a biogenetic pathway involving the guaianolide gaillardin.

Pulchellin, the main sesquiterpene lactone found in coastal races of *Gaillardia pulchella* Foug., has been formulated as 1,⁶ the absolute configuration at C-2 and C-4 being based on applications of the Hudson-Klyne rule⁶ and the Horeau method.⁷ In this communication we present chemical and crystallographic evidence for its complete structure 2a.

Efforts at identification of some of the other asymmetric centers by chemical methods having proved unavailing, we decided to attack the problem by X-ray crystallography. However, attempts to prepare esters of pulchellin or dihydropulchellin containing heavy atoms consistently resulted in compounds which were

unsuitable for this purpose. Hence we decided to use a bromo derivative 4,⁸ available (see Experimental Section) from dihydroanhydrodehydrodihropulchellin (3),⁶ even though the centers at C-1 and C-3 were no longer present and the center at C-1 might have suffered epimerization as a consequence of the introduction of a carbonyl group at C-2.

Crystal Data.—3-Bromoanhydrodehydrodihropulchellin (4), $C_{15}H_{19}O_3Br$, mol wt 326.9, was orthorhombic with lattice parameters $a = 8.368 \pm 0.005$, $b = 14.342 \pm 0.006$, and $c = 25.161 \pm 0.006$ Å. The systematic absences were confined to $h00$, $0k0$, and $00l$ for h , k , and $l/2n$; the space group was therefore $P2_12_12_1$: $V = 3020$ Å³, $d_m = 1.432$ g cm⁻³, $Z = 8$, $d_c = 1.437$ g cm⁻³. The linear absorption coefficient for Cu $K\alpha$ radiation was $\mu = 40.8$ cm⁻¹. The total number of electrons in the unit cell was $F(000) = 1344$.

Determination of the Structure.—Diffraction data were collected on a crystal of dimensions $0.10 \times 0.12 \times 1.2$ mm. The crystal was mounted with the a axis parallel to the ϕ axis of the goniostat. Inten-

(1) Constituents of *Gaillardia* Species. X. Previous paper: H. Yoshioka, T. J. Mabry, N. Dennis, and W. Herz, *J. Org. Chem.*, **35**, 627 (1970).

(2) Supported in part by grants from the U. S. Public Health Service (GM-05814 and GM-12408).

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(6) W. Herz, K. Ueda, and S. Inayama, *Tetrahedron*, **19**, 483 (1963). Assignment of the secondary methyl group to C-10 rather than C-6 was based on biogenetic grounds. Since the publication of this paper, the absolute configuration of the C-7 side chain and the C-10 methyl group in a number of related compounds from *Helenium* and *Gaillardia* species has been shown to be β and α , respectively. It was plausible to assume that this would also be true for pulchellin.

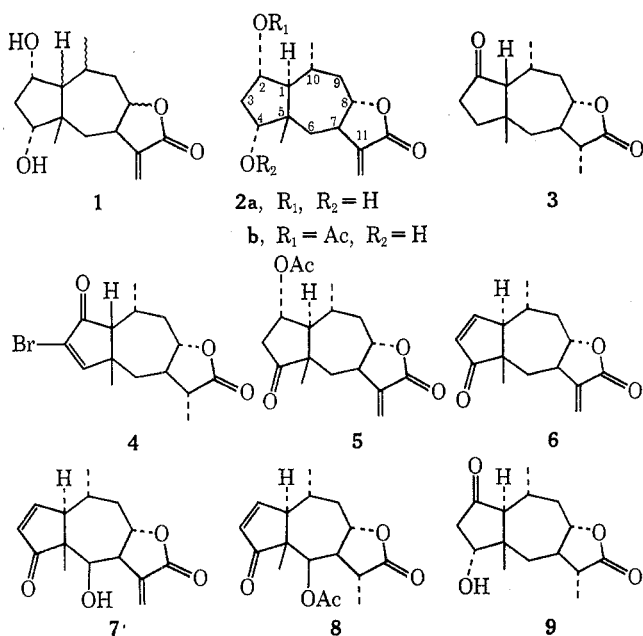
(7) W. Herz and H. B. Kagan, *J. Org. Chem.*, **32**, 216 (1967).

(8) Configurations of compounds, although unknown at the time, are depicted in the light of our final knowledge.

TABLE I
 ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS

Atom	Molecule 1			Molecule 2		
	x	y	z	x	y	z
Br	0.0718(2) ^a	0.0941(1)	0.8496(1)	0.0911(3)	0.4463(1)	0.1381(1)
C(1)	0.2206(17)	0.1022(10)	0.0089(5)	0.0178(14)	0.6102(11)	0.2762(4)
C(2)	0.2405(18)	0.1326(9)	0.9495(5)	-0.0323(16)	0.5662(8)	0.2209(5)
C(3)	0.1219(18)	0.0729(11)	0.9226(5)	0.1076(18)	0.5185(9)	0.2008(5)
C(4)	0.0512(18)	0.0101(11)	0.9535(6)	0.2398(19)	0.5256(11)	0.2305(5)
C(5)	0.1309(19)	0.0099(11)	0.0082(5)	0.2027(15)	0.5926(9)	0.2774(4)
C(6)	0.2282(15)	0.9209(11)	0.0140(5)	0.3095(17)	0.6814(10)	0.2700(5)
C(7)	0.3866(17)	0.9244(11)	0.9828(5)	0.2549(16)	0.7462(8)	0.2247(4)
C(8)	0.5245(15)	0.9663(11)	0.0159(5)	0.1257(14)	0.8129(8)	0.2419(5)
C(9)	0.5274(15)	0.0693(11)	0.0154(6)	-0.0397(14)	0.7772(8)	0.2445(4)
C(10)	0.3750(19)	0.1124(11)	0.0418(5)	-0.0524(14)	0.7041(8)	0.2888(5)
C(11)	0.4593(16)	0.8253(9)	0.9688(5)	0.3863(16)	0.8109(9)	0.2052(5)
C(12)	0.3866(23)	0.7774(13)	0.9200(5)	0.5056(21)	0.7657(13)	0.1624(6)
C(13)	0.6397(21)	0.8580(16)	0.9668(7)	0.2829(20)	0.8873(9)	0.1821(4)
C(14)	0.4092(25)	0.2174(11)	0.0554(6)	-0.2318(19)	0.6895(12)	0.3064(6)
C(15)	0.0004(18)	0.0105(13)	0.0522(6)	0.2549(16)	0.5470(10)	0.3294(4)
O(1)	0.3191(12)	0.1923(7)	0.9312(4)	-0.1569(11)	0.5773(7)	0.1995(4)
O(2)	0.7393(17)	0.8103(10)	0.9396(6)	0.3250(12)	0.9497(6)	0.1501(4)
O(3)	0.6664(11)	0.9357(8)	0.9914(4)	0.1360(10)	0.8877(5)	0.2011(3)

^a The number in parentheses is the standard deviation and refers to the least significant digit.



sities of all reflections with $2\theta \leq 130^\circ$ were measured on a GE XRD-5 diffractometer with a single-crystal orientor using a scintillation counter as detector. Nickel-filtered copper radiation was used ($\lambda = 1.5418 \text{ \AA}$). Intensities were measured using the θ - 2θ scan technique counting the background for 50 sec on each side of the peak and scanning over the reflection for 100 sec. In this way 2485 reflections were scanned; only 2376 reflections were visible above the background. Lorentz and polarization corrections were applied using an IBM 1620 data reduction program.⁹ This also provided a Wilson plot for the preliminary scale and temperature factors. No absorption corrections were applied. Form factors to calculate the structure factors were used from the literature.¹⁰

(9) All programs except the least-squares refinement program were from the Montana State University Library for Crystallographic Computing for the IBM 1620, written by C. T. Li, G. Svetich, C. H. Caughlan, R. D. Witters, and K. D. Watenpaugh.

(10) "International Tables for Crystallography," Kynoch Press, Birmingham, England, 1962, Vol. III, Table 3.31A, p 202.

A three-dimensional Patterson map was calculated. Bromine positions were found from the Harker section. The first partial three-dimensional Fourier synthesis phased on the bromine positions gave a number of peaks, but only 10 atomic positions which made some chemical sense were chosen. Four subsequent three-dimensional Fourier maps revealed the structure of both molecules in the asymmetric unit. At this point R was 28.2%. Bond distances and angles were satisfactory and it was decided to proceed with the refinement.

Three cycles of refinement using Busing, Martin, and Levy's full matrix least-squares program¹¹ and refining only the atomic positions reduced R to 20.5%. Four cycles, refining both the atom positions and the isotropic temperature factors, reduced R to 11.4%. Three additional cycles, refining atomic positions and anisotropic thermal parameters, reduced the R to 6.6%, weighting each reflection equally.

Results and Discussion of the Structure of 4.—Final atomic positions for both molecules in the asymmetric unit with their standard deviations are given in Table I. Tables of anisotropic thermal parameters, intermolecular distances below 4.0 Å, and observed and calculated structure factors, and a figure of 1 (100) projection of the structure showing the molecules in the unit cell have been deposited with the National Auxiliary Publications Service.¹² Interatomic distances and bond angles for the two molecules are shown in Figures 1 and 2. The stereoscopic diagrams down the c^* axis of both molecules are shown in Figure 3.

Both independent molecules have the same relative stereochemistry, the cyclopentanone ring being *cis* fused to the seven-membered ring and the methyl group at C-10 being *trans* to H-1. The lactone junction

(11) W. R. Busing, K. D. Martin, and H. A. Levy, Least Squares Program, U. S. Atomic Energy Commission Publication No. ORNL-TM-305, 1962.

(12) Document NAPS-00761 from ASIS National Auxiliary Publications Service, % CCM Information Sciences, Inc., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to CCMI-NAPS.

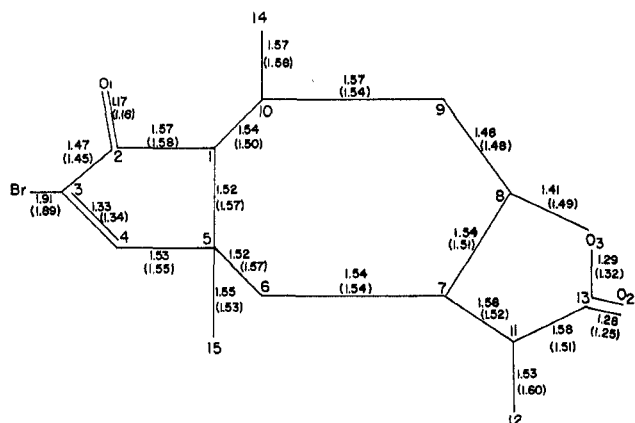


Figure 1.—Interatomic distances of 3-bromoanhydrodehydrodihdropulchellin; distances in parentheses belong to molecule 2. Standard deviations in the bond distances are 0.01–0.02 Å.

is *trans*, with the C-7 side chain *trans* to C-10 methyl and the C-11 methyl group *cis* to H-7. The conformation of the seven-membered ring is that of a somewhat deformed chair. Bond distances and angles are quite normal except for a few minor deviations and are consistent in both independent molecules. The average carbon-carbon distance is 1.54 Å. The short C-2–C-3 distance indicates conjugation. Examination of the values indicates agreement with bond distances and angles observed in bromohelenalin¹³ and bromomexicanin E.¹⁴ It should be noted that considerable anisotropy exists in the thermal motions of most of the atoms of both molecules of 4.

Relative and Absolute Configuration of Pulchellin.—

Although it seemed probable, on biogenetic grounds, that 3-bromoanhydrodehydrodihdropulchellin should be represented by 4 rather than by the mirror image, the results of the X-ray analysis of 4 required verification of this hypothesis and, as was pointed out previously, left uncertain the relative configuration of pulchellin at C-1. Simultaneously, therefore, with progress on the structure determination of 4, we continued efforts to correlate pulchellin with other pseudo-guaianolides of established structure and were eventually successful in determining the complete stereochemistry of pulchellin. After considerable experimentation, acetylation of pulchellin under controlled conditions finally furnished, in addition to the previously known diacetylpulchellin (2c),⁶ a monoacetate in 75% yield. The nmr spectrum of the monoacetate revealed that during the acetylation the C-2 hydrogen signal found in pulchellin at 4.33 ppm had suffered an appreciable paramagnetic shift to 5.08 ppm while the higher field doublet at 3.71 ppm associated with H-4¹⁵ had essentially remained unchanged. Hence the monoacetate was formulated as 2b.

Oxidation of 2b with chromic oxide–pyridine complex led to a ketoacetate 5 whose ir spectrum (band at 1749 cm⁻¹) showed the presence of a cyclopentenone.

(13) M. T. Emerson, C. N. Caughlan, and W. Herz, *Tetrahedron Lett.*, 621 (1964); Mazhar-ul-Haque and C. N. Caughlan, *J. Chem. Soc., B*, 956 (1969).

(14) Mazhar-ul-Haque and C. N. Caughlan, *ibid.*, 355 (1967).

(15) For reasons which are not immediately apparent, one of the H-3, H-4 coupling constants is generally 0 in pulchellin and its derivatives although the expected multiplicity is restored in the nmr spectra of compounds in which the cyclopentane ring is deformed by lactone ring formation.⁶

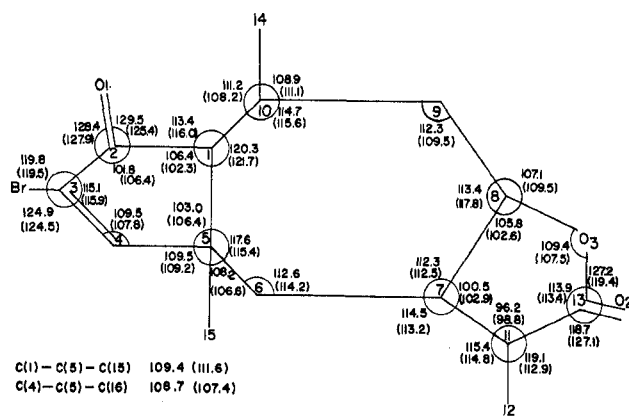


Figure 2.—Bond angles of 3-bromoanhydrodehydrodihdropulchellin; angles in parentheses belong to molecule 2. Standard deviations in the bond angles are 0.9–1.7°.

An attempt at pyrolysis of this substance resulted merely in recovery of starting material, but facile elimination of the acetoxy group occurred on exposure to pyridine. The product was an α,β -unsaturated ketone identical in all respects with aromaticin (6), a substance previously isolated from *Helenium aromaticum* (Hook) Bailey¹⁶ and a North Carolina collection of *H. amarum* Raf.¹⁷ Since the relative and absolute configuration of aromaticin has been established¹⁶ by correlation with mexicanin I (7)¹⁸ which in turn has been related to isotenulin (8),¹⁹ the absolute configuration of pulchellin at C-1, C-5, C-7, C-8, and C-10 is as represented in 2a and identical with the absolute configuration at these centers of other pseudo-guaianolides isolated from *Helenium* and *Gaillardia* species. The absolute configuration of the C-2 hydroxyl group has been established⁷ as α by use of Horeau's method which, because the two hydroxyl groups are *cis*, automatically fixes the configuration at C-4 as well.

It is not possible to say definitely whether isomerization at the C-1 position from the *trans*-bicyclo[5.3.0]decane system present in pulchellin to the more stable²⁰ *cis*-bicyclo[5.3.0]decane ring fusion present in 4 occurred during the conversion of ketol 9 to 3 or during the bromination of 3. The ORD curve of 3 displays a negative Cotton effect comparable in sign and amplitude with that of 5 α ,14 β -androstan-15-ones,²¹ which suggests that 3 is *cis* fused, but the flexibility of the seven-membered ring renders extrapolation from generalizations strictly applicable only to rigid systems somewhat questionable. Model considerations and application of the octant rule suggest that, if the

(16) J. Romo, P. Joseph-Nathan, and F. Diaz A., *Tetrahedron*, **20**, 79 (1964). We are grateful to Dr. J. Romo and Dr. A. Romo de Vivar for an authentic specimen of aromaticin.

(17) R. A. Lucas, S. Rovinski, R. J. Kiesel, L. Dorfman, and H. B. MacPhillamy, *J. Org. Chem.*, **29**, 1549 (1964).

(18) E. Dominguez and J. Romo, *Tetrahedron*, **19**, 1415 (1963).

(19) W. Herz, W. A. Rhodes, K. Rabindran, P. Jayaraman, and N. Viswanathan, *J. Amer. Chem. Soc.*, **84**, 3857 (1962); W. Herz, A. Romo de Vivar, J. Romo, and N. Viswanathan, *Tetrahedron*, **19**, 1359 (1963).

(20) W. Herz, M. V. Lakshmikantham, and R. N. Mirrington, *ibid.*, **22**, 1709 (1966); A. Romo de Vivar, L. Rodriguez-Hahn, J. Romo, M. V. Lakshmikantham, R. N. Mirrington, J. Kagan, and W. Herz, *ibid.*, **22**, 13279 (1966).

(21) C. Djerassi, G. Von Mutzenbecher, J. Fajkos, D. H. Williams, and H. Budzikiewicz, *J. Amer. Chem. Soc.*, **87**, 817 (1965); A. R. Van Horn and C. Djerassi, *ibid.*, **89**, 651 (1967).

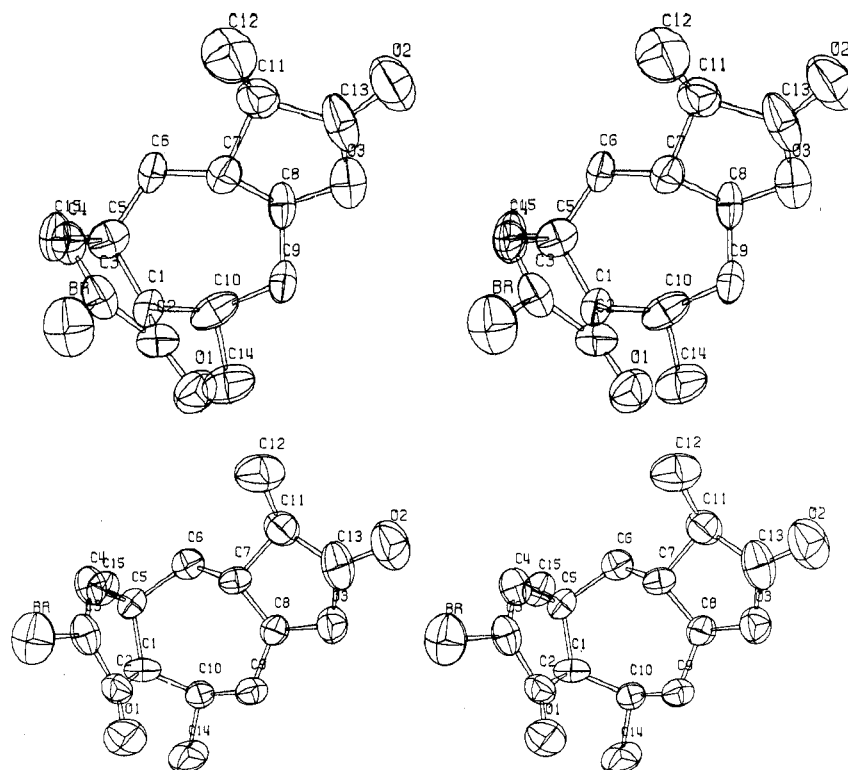
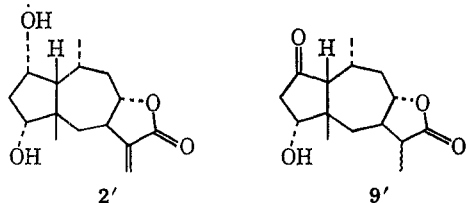


Figure 3.—Stereoscopic diagrams of the structure of 3-bromoanhydrodehydrodihydropulchellin down the c^* axis of both molecules. The diagrams were drawn using computer program ORTEP written by Carrol K. Johnson of Oak Ridge National Laboratory and adapted for computation at the University of Washington.

conformation of **3** in solution approximates that of crystalline **4**, the ring junction of **3** should be *cis*.²²

It has been demonstrated recently that the guaianolide gaillardin²⁴ from a Live Oak County, Texas, collection of *G. pulchella*²⁵ possesses the relative and absolute configuration shown in **10**. The relationship of **10** to the stereochemistry now established for pulchellin is striking. In fact the series of concerted or sequential 1,2 shifts of stereoelectronically optimally disposed *trans*-oriented groups adumbrated in Scheme I, followed by a reduction step, transforms the guaianolide gaillardin directly into the pseudoguaianolide pulchellin. It seems entirely plausible that Scheme I is paralleled by an enzyme-mediated process,

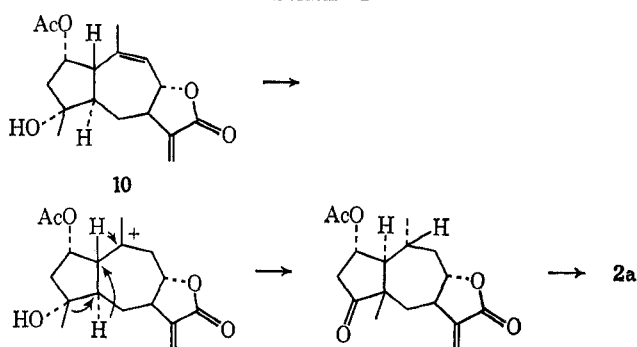
(22) It might be argued that the conversion of pulchellin into **4** via dehydrodihydropulchellin (**9**) and **3** need not be attended by epimerization at C-1, and that pulchellin and dehydropulchellin might be represented by the *cis*-fused formulas **2'** and **9'**. This is contraindicated by the strongly positive Cotton effect of dehydrodihydropulchellin which is indicative of a *trans*-A/B-ring fusion.^{21,23} Moreover, formulation of pulchellin as **2'** would require that conversion into aromatinin involve epimerization of a *cis*-fused C-1 epimer of aromatinin to the generally less stable²⁰ *trans*-bicyclo[5.3.0]-2-en-1-one system found in **6** which seems highly unlikely.



(23) J. F. Biellmann and G. Ourisson, *Bull. Soc. Chim. Fr.*, 331 (1962).
 (24) S. M. Kupchan, J. M. Cassady, J. E. Kelsey, H. K. Schnoes, D. H. Smith, and A. L. Burlingame, *J. Amer. Chem. Soc.*, **88**, 5292 (1966); T. A. Dullforce, G. A. Sim, D. N. J. White, J. E. Kelsey, and S. M. Kupchan, *Tetrahedron Lett.*, 973 (1969).

(25) This is an area from which a cytologically distinct race of *G. pulchella* has been reported (private communication from Dr. W. P. Stoutamire).

SCHEME I



a hypothesis which should be verifiable by administering suitably labeled gaillardin to plants of the coastal race of *G. pulchella*.

Experimental Section²⁶

Purification of Pulchellin.—Crude crystalline pulchellin, isolated as described earlier⁶ from the coastal race of *Gaillardia pulchella* Foug., after initial chromatography over alumina contained appreciable amounts of an impurity, as revealed by the nmr spectrum. Further purification was achieved as follows. A solution of 3.3 g of crude pulchellin in 20 ml of chloroform was chromatographed over 100 g of silic acid (Mallinckrodt, 100 mesh), 80-ml fractions being collected. Fractions 1-6 (CHCl_3) eluted nothing; fractions 7-20 (CHCl_3) eluted 1.92 g of pulchellin (nmr spectrum, tlc) recrystallization of which from ethyl acetate

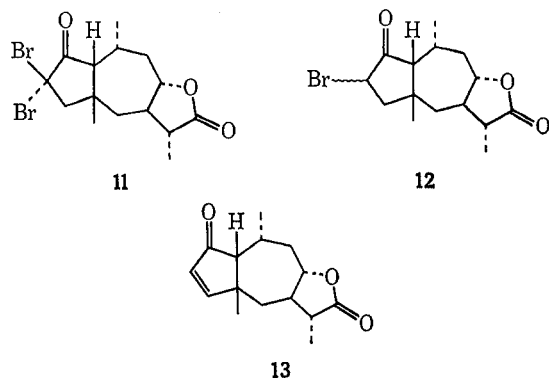
(26) Melting points are uncorrected. Rotations were run in chloroform, ultraviolet spectra in 95% ethanol, and infrared spectra in chloroform. Nmr spectra were determined in deuteriochloroform on a Varian A-60 spectrometer using tetramethylsilane as internal standard. Chemical shifts are quoted in parts per million, line separations in hertz. Signals are denoted in the usual manner: d, doublet; t, triplet; c, complex signal whose center is given; m, multiplet. Singlets are unmarked. Analyses were by Dr. F. Pascher, Bonn, Germany.

furnished pure material, mp 165–168°. Successive elution with CHCl_3 (fractions 21–27) and CHCl_3 -MeOH (10:1) gave 0.62 g of a mixture containing pulchellin and an isomeric substance (nmr spectrum). Further elution with CHCl_3 -MeOH (fractions 29–30) afforded 0.56 g of the isomer which melted at 166–167° after recrystallization from acetone. The structure of this substance is being investigated.^{26a} Later fractions contained nothing.

3-Bromoanhydrodehydrodihydropulchellin (4).—To a solution of 0.68 g of **3** in 30 ml of acetic acid containing 3 drops of acetic acid saturated with hydrogen bromide was added dropwise with stirring at 0° a solution of 0.8 g (100% excess of 2 molar equiv) of bromine in 10 ml of acetic acid. Stirring was continued for an additional hour. The mixture was poured on ice, neutralized with solid sodium bicarbonate, and extracted with ether. The ether extracts were washed, dried, and concentrated *in vacuo* to a small volume after addition of 25 ml of 2,6-lutidine. The residue was refluxed at 160–170° for 30 min, cooled, diluted with ether, and filtered to remove a precipitate of lutidine hydrobromide. The solid was washed with ether and the combined filtrate and washings were poured onto ice-hydrochloric acid. The ether layer was washed, dried, passed through a small column of acid-washed alumina, and evaporated *in vacuo*. The residue, 0.25 g, mp 138–142° (33%), was recrystallized from ether to give crystals of **4**, suitable for analysis, which had mp 144–146°; ir (CCl_4) 1785 (γ -lactone), 1735 (α -bromocyclopentanone), 1590 (conjugated double bond); λ_{max} 242 nm (ϵ 8150); $[\alpha]_{\text{D}}^{20} +34.5^\circ$ (c 1.00, acetone); nmr 7.32 (H-4), 3.84 (td, 11, 5, H-8), 1.41 (d, 7, C-10 methyl), 1.33 (C-5 methyl), 1.10 (d, 7, C-11 methyl).

Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3\text{Br}$: C, 55.03; H, 5.86; O, 14.68; Br, 24.43. Found: C, 54.90; H, 5.70; O, 14.98; Br, 25.11.

In another run the ether extract obtained after addition of 2 molar equiv of bromine to **3** was worked up without an attempt at dehydrohalogenation. This resulted in the isolation of a gummy dibromo derivative **11** [ir bands at 1780 (γ -lactone) and 1743 cm^{-1} (cyclopentanone)] which had no strong or absorption. Dehydrobromination resulted in formation of **4**; hence the bromine atoms were attached to C-3. Bromination of **3** by the method above, using 1 molar equiv of bromine, gave a gummy monobromo derivative **12** (ir 1780 and 1745 cm^{-1}) which was converted into the dibromide on further treatment with bromine. Heating the gummy monobromo derivative on the steam bath for 10 min or refluxing with 2,6-lutidine for 15 min furnished anhydrodehydrodihydropulchellin (**13**), mp 118–121°, identical in all respects with authentic material.⁶ Attempts to convert **13** into a bromo derivative by bromination-dehydrobromination in the manner described for helenalin²⁷ or ambrosin²⁸ failed.



(26a) NOTE ADDED IN PROOF.—This lactone is identical with neopulchellin: M. Yanagita, S. Inayama, and T. Kawamota, *Tetrahedron Lett.*, 131 (1970).

(27) R. G. Adams and W. Herz, *J. Amer. Chem. Soc.*, **71**, 2546 (1949).

(28) H. Abu-Shady and T. D. Soine, *J. Amer. Pharm. Assoc.*, **43**, 387 (1953); **43**, 365 (1954).

2-Acetylulchellin (2b).—A solution of 1.60 g of pulchellin in 3 ml of dry pyridine was allowed to stand with 1 ml of acetic anhydride at room temperature for 30 min, after which time starting material had disappeared [tlc, silica gel, benzene-ether (1:1)]. The product was isolated in the usual manner and was chromatographed over silica gel. Benzene- CHCl_3 (10:1) eluted 0.62 g of diacetylulchellin (**2c**) which had mp 124–125° after recrystallization from ether-petroleum ether and was identical with authentic **2c** in all respects. Benzene- CHCl_3 (2:1, 1:1) eluted 1.35 g of a solid (**2b**) which was recrystallized from ether: mp 143–144°; ir bands at 3620 and 3480 (hydroxyl), 1768 and 1678 (unsaturated γ -lactone), and 1730 and 1272 cm^{-1} (acetate); nmr signals 6.27 (d, 3.5) and 5.60 (d, 2.8) (exocyclic methylene), 5.80 (c, H-2), 4.27 (c, H-8), 3.78 (d, 5.0, H-4), 2.08 (acetate), 1.05 (d, 6.0, C-10 methyl), and 0.93 ppm (C-5 methyl).

Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_5$: C, 66.21; H, 7.84; O, 25.95. Found: C, 66.10; H, 7.85; O, 26.03.

Dehydro-2-acetylulchellin (5).—A solution of 0.465 g of **2b** in 2 ml of dry pyridine was added to 0.35 g of chromic acid in 1 ml of dry pyridine and set aside for 2 days. The mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed, dried, and evaporated and the gummy residue, 0.46 g, was chromatographed over 20 g of silica gel. Benzene eluted 0.117 g of **5** which was recrystallized from ethyl acetate: mp 156–157°; ir bands 1770, 1749, 1718, 1675, and 1255 cm^{-1} , nmr signals 6.26 (d, 3.5) and 5.60 (d, 2.8) (exocyclic methylene), 5.55 (td, 7, 1.5, H-2), 4.25 (c, H-8), 2.10 (acetate), 1.17 (d, 6.0, C-10 methyl), and 1.19 ppm (C-5 methyl). It was not analyzed but used in subsequent experiments. Benzene- CHCl_3 (10:1) eluted 0.27 g of unoxidized **2b**. Attempted pyrolysis of 40 mg of **5** at 210–230° in a nitrogen atmosphere resulted in recovery of 36 mg of starting material.

Aromaticin (6). A.—A solution of 0.32 g of **2b** in 2 ml of dry pyridine was added to 0.425 g of chromic acid in 2 ml of dry pyridine and set aside at room temperature for 6 days. The mixture was diluted with water and extracted with ethyl acetate. The organic layers were washed, dried, and evaporated. The crystalline residue, 0.28 g, was recrystallized from acetone and gave 0.12 g of aromaticin: mp 233–234°; ir bands at 1772, 1719, 1678, and 1593 cm^{-1} ; nmr signals at 7.60 (dd, 6.5, 2.0, H-2), 6.10 (dd, 6.5, 3.0, H-3), 6.13 (d, 3.2) and 5.48 (d, 3.2) (exocyclic methylene), 4.49 (c, H-8), 1.25 (d, 6.0, C-10 methyl), and 1.19 ppm (C-5 methyl), identical in all respects with an authentic sample.

B.—A solution of 32 mg of **5** in 1 ml of dry pyridine was heated on the water bath for 5 hr, cooled, diluted with water, and extracted with ethyl acetate. The organic layer was washed, dried, and evaporated. The crystalline residue of crude aromaticin, 27 mg, was recrystallized from acetone, mp 233–234°, identical in all respects with an authentic sample.

ORD Curve of 3.—The following data (c 0.007, in CH_3OH) were obtained: $[\alpha]_{\text{D}}^{20} -47^\circ$, $[\alpha]_{\text{D}}^{220} -2720^\circ$, $[\alpha]_{\text{D}}^{312} -2710^\circ$, $[\alpha]_{\text{D}}^{308} -2810^\circ$, $[\alpha]_{\text{D}}^{302} 0^\circ$, $[\alpha]_{\text{D}}^{280} +2830^\circ$, $[\alpha]_{\text{D}}^{274} +2310^\circ$ (last reading).

ORD Curve of 9.—The following data (c 0.07, in CH_3OH) were obtained: $[\alpha]_{\text{D}}^{20} +71^\circ$, $[\alpha]_{\text{D}}^{320} +2170^\circ$, $[\alpha]_{\text{D}}^{302} 0^\circ$, $[\alpha]_{\text{D}}^{280} -2080^\circ$, $[\alpha]_{\text{D}}^{270} -472^\circ$ (last reading).

Registry No.—**2a**, 6754-35-4; **2b**, 23667-91-6; **2c**, 23754-36-1; **3**, 23667-92-7; **4**, 23667-93-8; **5**, 23667-94-9; **6**, 5945-42-6; **9**, 23667-96-1.

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