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CONSTITUENTS OF *GAILLARDIA* SPECIES—III

THE STRUCTURE OF GAILLARDILIN, A NEW PSEUDOGUAIANOLIDE[1,2]

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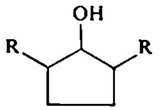
Abstract—The structure of gaillardilin, a new sesquiterpene lactone from *Gaillardia pinnatifida* Torr. and *Gaillardia arizonica* Gray, has been shown to be I.

IN EARLIER papers of this series[2,3] we reported the isolation of pseudoguaianolides from collections of *Gaillardia pulchella* Foug., *G. megapotamica* (Spreng.) Baker and *G. multiceps* Greene which illustrated the close relationship existing between this genus and *Helenium* species. We now describe the isolation and structure determination of a new pseudoguaianolide from *G. pinnatifida* Torr. and *G. arizonica* Gray.

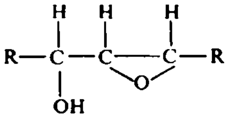
Extraction of *G. pinnatifida* Torr. gave variable yields, never exceeding 0·2%, of a new crystalline substance, $C_{17}H_{22}O_6$, m.p. 197–199°, $[\alpha]_D^{20}$ −2·03(CHCL$_3$, *c*, 2·47) which we have called gaillardilin.

The UV spectrum of gaillardilin (I; λ_{max} 210 mμ, ε, 12400) exhibited the characteristic absorption of α,β-unsaturated lactones. IR bands at 3550, 1760, 1732 and 1660 cm^{-1} coupled with the empirical formula indicated the presence of a hydroxyl group, an α,β-unsaturated lactone function and an acetate. There was no indication of the presence of a ketone since the band at 1732 cm^{-1} had an intensity corresponding to just one carbonyl.

Acetylation of gaillardilin gave an acetate thus confirming the presence of a single hydroxyl group. Hydrogenation resulted in the uptake of one mole of hydrogen. The product, dihydrogaillardilin (II), in contrast to gaillardilin furnished no formaldehyde on ozonolysis and had no UV absorption. Hence an exocyclic methylene is conjugated with the lactone function. Oxidation of II resulted in the formation of a cyclopentanone (III, extra IR band at 1750 cm^{-1}) which gave a negative Zimmermann test. Hence partial structure A was indicated.



A



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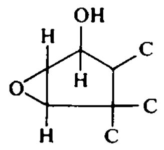

C

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[1] Supported in part by grants from the U.S. Public Health Service (GM-05814) and the National Science Foundation (GP-1962).

[2] Previous paper, W. Herz, and S. Inayama, *Tetrahedron* **20**, 347 (1964).

[3] W. Herz, K. Ueda and S. Inayama, *Tetrahedron* **19**, 483 (1963).

Five of the six oxygen atoms were thus accounted for as a lactone, acetate and hydroxyl group. The ethereal nature of the sixth was apparent from the NMR spectra (Table 1) which also confirmed the previous assignments. Gaillardilin had one methyl singlet, one methyl doublet and two doublets characteristic of the exocyclic methylene group which vanished on reduction and were replaced by an additional methyl doublet. A low-field doublet near 5·9 ppm must be ascribed to hydrogen on carbon carrying the acetate which is spin-coupled to only one adjoining proton.[4] A typical multiplet[5,6] near 4·5 ppm was the signal of hydrogen on carbon carrying the lactone ether oxygen, obviously spin-coupled to three protons. There remained a complex signal near 3·6 ppm which appeared to arise from three protons spin-coupled to each other.

The NMR spectra of acetylgaillardilin (IV) and its dihydroderivative (V) permitted disentanglement of this three-proton multiplet. One signal moved downfield, from 3·6 to 4·45 ppm, and now showed up as a doublet (J = 3). This is clearly associated with the proton on carbon carrying what was the free hydroxyl group of I which must be secondary. The remaining low-field protons associated with the inert oxygen were now clearly visible as the XY part of a three-component (X, Y and Z) system where X (triplet, J = 3) is coupled to Y and Z, and Y (doublet, J = 3) is coupled to Z only. This suggested partial structure B which must be incorporated in a 5-membered ring as in C.

In order to obtain definitive evidence for the presence of an oxirane, I was subjected to the action of BF_3. The product (VI) had IR bands at 1770 (γ-lactone) and 1750 cm^{-1} (double intensity due to the presence of an acetate and cyclopentanone group), but the OH— band had disappeared. In conjunction with the analytical values this clearly proved that BF_3 treatment had resulted in simultaneous pinacolic cleavage of an oxirane ring and dehydration. That the newly-formed double bond was not conjugated with the new cyclopentanone carbonyl was shown by the absence of long-wave UV absorption.

In the NMR spectrum of VI, the usual two doublets of the exocyclic methylene group were present as were the methyl singlet, the methyl doublet, the acetate singlet and the lactone hydrogen at 4·5 ppm. Apart from these, a signal corresponding to two protons was observed near 6 ppm. One of these must be the known hydrogen on carbon carrying the acetate group. Hence there is only one new low-field proton which must be vinylic and therefore the new double bond must be triply-substituted. The absence of bands from the region 3·5–4 ppm indicated disappearance of the oxide ring. Instead there were two new signals near 3 ppm whose appearance was reminiscent of the C_3-methylene group in mexicanin A and analogous compounds (partial structure D).[5,7]

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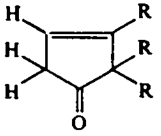
[4] There is no evidence—other than the slightly greater line separation and analogy with other pseudoguaianolides[5,6]—that this signal should be attributed to H_6 rather than to that hydrogen on C_{14} which is *trans* to the lactone carbonyl (H_b in F), to which we have tentatively (Table 1) assigned the doublet near 5·5 ppm. Double irradiation experiments (*vide infra*) offer no clue since the two H_{14} protons are not spin-coupled to each other, but to H_7, just as H_6 is.

[5] W. Herz, W. A. Rohde, K. Rabindran, P. Jayaraman and N. Viswanathan, *J. Amer. Chem. Soc.* **84**, 3857 (1962).

[6] W. Herz, A. Romo de Vivar, J. Romo and N. Viswanathan, *J. Amer. Chem. Soc.* **85**, 19 (1963).

[7] W. Herz, H. Watanabe, M. Miyazaki and Y. Kishida, *J. Amer. Chem. Soc.* **84**, 2601 (1962).

Treatment of dihydrogaillardilin with BF$_3$ confirmed these observations. The resulting unsaturated ketone (VII) had IR bands at 1775 and 1753 cm^{-1}; the latter of double intensity. In its NMR spectrum the vinyl proton appeared as a narrowly-split triplet, with the lactone hydrogen beautifully split into a symmetrical six-line pattern which indicated that the environment of the lactone ring should be represented by E.



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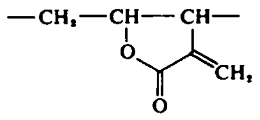
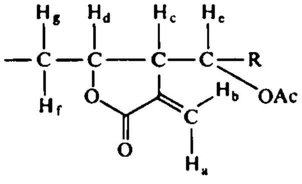


E



F

Since it seemed surprising that the dehydration should have proceeded in the direction shown (C → D) unless the stereochemistry of the C$_8$-hydroxyl and H$_8$ were not well-disposed toward *trans*-diaxial elimination, acid-catalyzed isomerization of the double bond was attempted to confirm the relative orientation of the double bond and the ketone group. Treatment of VII with methanolic hydrogen chloride resulted in formation of an equilibrium mixture from which it was possible to separate an α,β-unsaturated cyclopentenone (VIII, λ_{max} 226 mμ, ε_{max} 8900, IR bands at 1775, 1745, 1705 and 1595 cm^{-1}). This confirmed partial structure C, and led, together with consideration of E and the other requirements deduced from the NMR spectra, to expression I for gaillardilin, if the distribution of alkyl groups in the 7-membered ring follows the generalized isoprene rule.

That this is indeed the case was shown by double irradiation experiments[8] with gaillardilin which establish the presence of partial formula F and hence I. It was first shown that the protons giving rise to the three down-field doublets at 6·25, 5·93 and 5·48 were not coupled to each other. Irradiation at all of these resonance frequencies produced no result on the other two doublets. Hence the two vinyl protons (H$_a$ and H$_b$) must be allylically coupled to H$_c$ and, if formula I is correct, the latter is vicinally coupled to H$_e$.

Irradiation at 2·95 ppm (H$_c$-resonance) resulted in collapse of all three doublets to singlets which confirmed the chemical shift assigned to H$_c$ and showed that it was indeed coupled to H$_a$, H$_b$ and H$_e$. The effect produced on the H$_d$-multiplet could not be observed due to interference by the upper side band. Irradiation at 6·25 ppm produced some simplification in the complex region assigned to H$_c$.

Irradiation at 2·18 ppm resulted in collapse of the H$_d$ resonance to an apparent triplet (center somewhat broadened). Irradiation at 1·5 ppm reduced the H$_d$ signal to a broad doublet.[9] The resonances of H$_f$ and H$_g$ were thus located and the H$_d$-signal confirmed as resulting from two large couplings to H$_c$ ($J_{H_cH_d} \sim 10$) and H$_g$ ($J_{H_dH_g} \sim 9$) and one small coupling to H$_f$ ($J_{H_dH_f} \sim 3$). Irradiation at 1·27 ppm (methyl

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[8] We are greatly indebted to Professor M. T. Emerson for introducing us to the experimental aspects of this technique.

[9] Elimination of the large coupling H$_7$-H$_{8a}$ should theoretically result in a doublet of doublets. Presumably, the smaller coupling is "washed-out" because of the nearness of the irradiating frequency to the resonance frequency of H$_{8b}$.

TABLE 1. NMR SPECTRA OF GAILLARDILIN DERIVATIVES[a]

	H_2	H_3	H_4	H_6	H_8	H_{14}	C_5-Me	C_{10}-Me	C_{11}-Me	Acetate
I	3·68m[b]	3·68m[b]	3·68m[b]	5·93d(3·7)[c]	4·54m[c]	6·25d(3·4) 5·48d(3·0)	0·93	1·27d(5)		2·00 2·95c
II	3·68m[b]	3·68m[b]	3·68m[b]	5·60d(3·7)	4·65m[d]		0·98	1·22d(5)	1.18d(6)	2·06
IV	4·45d(3)	3·80t(3)	3·45d(3)	5·80d(3)[c]	4·5c	6·25d(3·4) 5·45d(3·0)	1·08	1·26d(5)		1·93, 2·15
V	4·42d(3)	3·80t(3)	3·45d(3)	5·45d(4)	4·6m		1·01	1·2d	1·17d	2·04,2·11
VI	6·05c[f]	2·92d(2) 3·02br		6·05[e,f]	4·5m	6·20d(3) 5·71d(3)	1·06	1·32d(6)		2·08
VII	5·98t(2)	2·90d(3) 3·02t(2)		5·80br[g]	4·80td(10, 5)		1·02	1·32d(7)	1·14d(7)	2·15
IX				5·64br[g]	4·69td(12, 5)		1·02	1·15d(7)	1·08d(7)	2·11

[a] Spectra were run in $CDCl_3$ solution on a Varian A-60 Spectrometer with tetramethylsilane serving as internal standard. Values given in ppm. Numbers in parentheses correspond to line separations in c/s. All signals in first six columns correspond to one proton, signals in next three to three. Singlets are unmarked, multiplets are described as follows: d doublet, t triplet, br broadened signal, c complex signal whose center is given, m multiplet.

[b] System broadened by coupling of H_3 to hydroxyl, as evidenced by sharpening after deuterium exchange.

[c] See footnote 4.

[d] Apparent td, line separations 3 and 10.

[e] H_7

[f] Signals superimposed.

[g] $W_{1/2}$ 3.

resonance) resulted in some simplification in the region near 2·6 ppm where H_{10} must therefore be located, but not farther upfield.

Structure I is the only formula which simultaneously incorporates C and F.[10] The gaillardilin transformation product VIII (which does not necessarily have the same stereochemistry at C_1 as I) is therefore a new stereoisomer of isotenulin. Its optical rotatory dispersion curve exhibits a multiple positive Cotton effect different from that of isotenulin (X) and other *trans*-fused Δ^2-4-ketopseudoguaianolides.[11,15] Catalytic hydrogenation of VIII gave a new isomer (IX) of dihydroisotenulin (XI) which could also be prepared more directly by hydrogenation of VII. The ORD curve of IX, like that of tetrahydromexicanin A,[10] exhibited a strongly negative Cotton effect. The possible implications of this will be discussed in a future paper.

Extraction of a collection of *Gaillardia arizonica* Gray furnished a 0·035% yield of gaillardilin.

EXPERIMENTAL[16]

Extraction of Gaillardia pinnatifida *Torr*. Ground above-ground material collected by Dr. H. F. L. Rock in June 1959 in Pecos County, Texas (Rock No. 1077) was extracted with $CHCl_3$ and worked up in the usual fashion. The total weight of crude gum was 33 g which was taken up in the minimum amount of $CHCl_3$–benzene (1:1) and chromatographed over 450 g alumina (Alcoa F-20). The solid fractions eluted with benzene–$CHCl_3$ and $CHCl_3$ were combined and recrystallized from acetone–pet. ether (b.p. 30–60°), wt. 2·4 g (0·2%), m.p. 196–197°. The analytical sample had m.p. 197–199°, $[\alpha]_D^{20}$ $-2·03$ (*c*, 1).

A subsequent collection of 14 lbs dry material collected by Dr. N. C. Henderson in summer 1962 near Abilene, Texas (Henderson No. 62–45) yielded 150 g crude gum and, after chromatography over 2 kg basic alumina, 5·5 g (0·1%) gaillardilin.

Large-scale collections of *G. pinnatifida* made by Mr. R. J. Barr on August 29, 1963 ten miles north of Snowflake along State Highway 77, Navajo County, and October 3, 1963 along the Silver Creek Road near Paradise, Cochise County, Arizona (Barr No. 63–498) and by Dr. B. R. Warnock near Alpine, Texas in Spring 1963, were combined. The residual crude gum, wt. 100 g, from extraction

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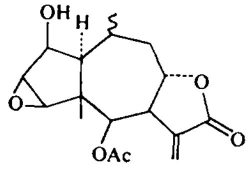
[10] The NMR data (Table 1) suggest the stereochemistry H_6-α, H_7-α, H_8-β if one assumes that the C_7-side chain is equatorial and β as in all other naturally-occurring pseudoguaianolides of established absolute configuration.[11,12] We have no real basis for deducing the stereochemistry at the other centers but if the previously demonstrated *trans*-fusion (H_1-α, C_5-methyl β) of constituents of *Helenium* species[11,13] holds for gaillardilin as well, the striking resemblance of the H_2, H_3 and H_4 signal pattern ($J_{H_1H_2} \sim 0$, $J_{H_2H_3} \sim 3$, $J_{H_3H_4} \sim 3$) to the relevant signals in the NMR spectrum of 16β,17β-epoxy-androstan-3β-ol ($J_{H_{15\alpha}H_{16}}$ 2·7, $J_{H_{15\beta}H_{16}} \sim 0$, $J_{H_{16}H_{17}}$ 3)[14] suggests expression *i* for gaillardilin.



i

[11] W. Herz, A. Romo de Vivar, J. Romo de Vivar, J. Romo and N. Viswanathan, *Tetrahedron* **19**, 1359 (1963).

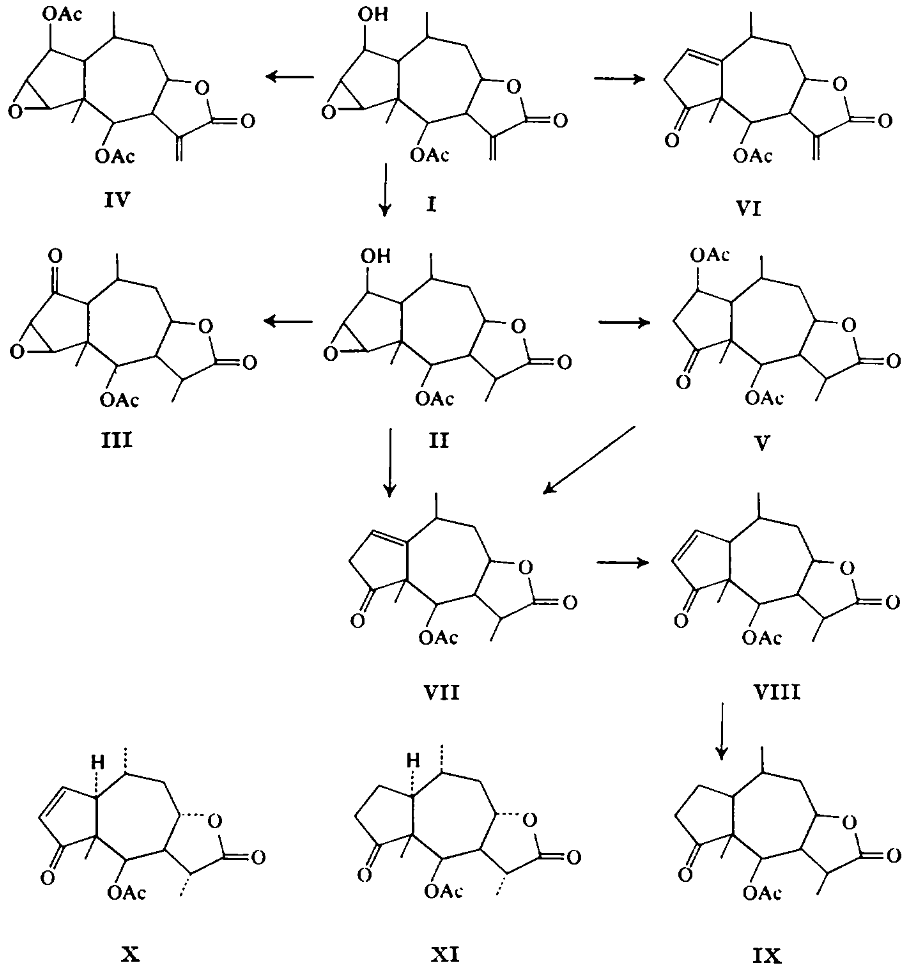
[12] D. Rogers and Mazhar-ul-Haque, *Proc. Chem. Soc.* 92 (1963).

[13] M. T. Emerson, C. N. Caughlan and W. Herz, *Tetrahedron Letters* 621 (1964).

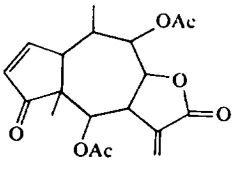
[14] K. Tori, T. Komeno and T. Nakagawa, *J. Org. Chem.* **29**, 1137 (1964).

[15] C. Djerassi, J. Osiecki and W. Herz, *J. Org. Chem.* **22**, 1361 (1957).

[16] M.ps are uncorrected. Analyses by Dr. F. Pascher, Bonn, Germany. UV spectra were run in 95% EtOH, IR spectra and rotations in $CHCl_3$ unless otherwise specified.



of a 16 lb portion was dissolved in $CHCl_3$ and chromatographed over 600 g silicic acid. Fraction 1 (1 l. $CHCl_3$), eluted oils, fractions 2–4 (1 l. each) eluted gums from which 0·35 g of a substance, $C_{19}H_{22}O_{11}$, m.p. 270° (acetone–pet. ether) was isolated, IR bands (nujol mull) at 1780 and 1655 (conjugated γ-lactone), 1760, 1750 (acetate), 1715 and 1595 cm^{-1} (cyclopentenone). The NMR spectrum suggested formula XII, signals appeared at 7·78 dd (5, 2, H_2), 6·18 dd (5, 3, H_3), 6·26 d and 5·92 d (3, H_{13}), 5·67 d (8, H_6), 4·94g (9·5, H_7 or H_8), 4·64 t (10, H_8 or H_7), 3·2 c (H_1 and H_7), 2·17 and 1·98 (two acetate methyls), 1·30 (C_5-methyl) and 1·23 d ppm (7, C_{10}-methyl).



XII

(Found: C, 62·84; H, 6·32; O, 30·74. Calc. for $C_{19}H_{22}O_{11}$: C, 62·97; H, 6·12; O, 30·91%.)

Fractions 5–8 (1 l. $CHCl_3$ each) and fractions 9 and 10 ($CHCl_3$–MeOH, 13:1) eluted gums which on crystallization furnished 6·3 g helenalin. Fraction 11 (0·75 l. $CHCl_3$–MeOH, 13:1) furnished 1·6 g mexicanin I[17], m.p. 245°, mixed with helenalin. Fractions 12–13 eluted gums, fractions 14–16 eluted gums which crystallized and furnished 4 g crude hispidulin,[18] m.p. 290° after recrystallization, identified by direct comparison and conversion to the triacetate.[18]

Since the gums from fraction 1–7 showed similar behaviour on TLC, they were combined, dissolved in the minimum of benzene–$CHCl_3$ (3:1) and rechromatographed over 200 g silicic acid. Benzene–$CHCl_3$ (four 100 ml fractions, 3:1 and one 100 ml fraction, 2:1) eluted only traces of material, benzene–$CHCl_3$ (1:1) eluted in the fourth and fifth 100 ml fraction, 1·05 g oil which crystallized on rubbing. Recrystallization furnished 0·25 g bigelovin.[19,20] Later fractions did not yield crystalline material.

The fact that no gaillardilin was isolated from this collection can perhaps be attributed to the existence of several races of *G. pinnatifida*[21] and to the difference in time of collection.

Extraction of G. arizonica *Gray.* Extraction of ground herb of *G. arizonica* (1150 g) collected by Mr. R. J. Barr on Reddington Road near the Summit of Reddington Pass, Pima County, Arizona on April 15, 1962 (Barr No. 62–253), yielded crude gum (18 g) which was chromatographed over alumina (300 g) Alcoa F-20). Fractions 3–7 (two 500 ml portions of benzene–$CHCl_3$ 1:1 and three 500 ml portions $CHCl_3$) were combined and recrystallized twice from acetone–pet. ether, yield of gaillardilin (0·41 g, 0·035%), m.p. 197–199°. Later fractions eluted with $CHCl_3$ and $CHCl_3$–MeOH could not be crystallized.

Dihydrogaillardilin II. A solution of I (0·565 g) in EtOH (100 ml) was shaken at 3 atmospheres in H_2 with 5% Pd–C (0·06 g). After 3 hr, the solution was filtered, evaporated *in vacuo* and the residue recrystallized from acetone–pet. ether, yield 0·34 g, m.p. 199–201°, IR bands at 3550 (—OH), 1775 (γ-lactone) and 1740 cm^{-1} (acetate). (Found: C, 62·66; H, 7·36; O, 30·06. Calc for $C_{17}H_{24}O_6$: C, 62·95; 7·46; O, 29·60%.)

Acetylgaillardilin (IV). A mixture of I (0·17 g), pyridine (1 ml) and acetic anhydride (2 ml) was warmed on a steam bath, allowed to stand overnight, poured on ice and the precipate filtered, dried and recrystallized from ethyl acetate–pet. ether, yield 0·11 g, m.p. 195–196°, mixed m.p. with I 155–165°, IR bands (KBr) 1758 (unsaturated γ-lactone) 1733 (double intensity, acetates) and 1650 cm^{-1} (double bond). (Found: C, 62·87; H, 6·82; O, 30·58. Calc. for $C_{19}H_{24}O_7$: C, 62·62; H, 6·64; O, 30·73%.)

Acetyldihydrogaillardilin (V). Acetylation of II (0·14 g) in the same manner and recrystallization from ethyl acetate–pet. ether furnished V (0·06 g) m.p. 160–161°, IR bands at 1775 (γ-lactone) and 1738 cm^{-1} (double intensity, acetates). (Found: C, 62·41; H, 7·30; O, 30·44. Calc. for $C_{19}H_{26}O_7$: C, 62·28; H, 7·15; O, 30·57%.)

Dehydrodihydrogaillardilin (IV). To the complex prepared from pyridine (10 ml) and CrO_3 (0·6 g) was added slowly, with stirring, II (0·3 g) in dry pyridine (5 ml). Stirring was continued overnight. The mixture was poured on ice, acidified and thoroughly extracted with ether. The washed and dried extracts were evaporated and the residue chromatographed over acid-washed alumina. Elution with benzene–ether (3:1) furnished IV, m.p. 198–200° (prior softening) after recrystallization from benzene–pet. ether, yield 0·02 g, negative $FeCl_3$ and Zimmermann test, IR bands (KBr) at 1755 (γ-lactone) and 1750 cm^{-1} (double intensity, cyclopentanone and acetate. (Found: C, 63·62; H, 6·66; O, 29·41. Calc for $C_{17}H_{22}O_6$: C, 63·34; H, 6·88; O, 29·78%.)

$\Delta^{1,2}$-*Anhydrogaillardilone* (VI). A solution of I, (0·2 g) in dry benzene (10 ml) was treated with a few drops of BF_3-etherate solution, left overnight at room temp, poured on ice and extracted with ether. The washed and dried ether extracts were concentrated and the residue chromatographed over acid-washed alumina. Elution with benzene–ether (8:1) and crystallization from ether–pet. ether gave VI, yield 0·07, m.p. 161°, IR bands (KBr) at 1770 (γ-lactone), 1750 (double intensity, cyclopentanone and acetate) and 1650 cm^{-1} (double bond). (Found: C, 67·32; H, 6·59; O, 26·41. Calc. for $C_{17}H_{20}O_5$: C, 67·09; H, 6·62; O, 26·29%.)

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[17] E. Dominguez and J. Romo, *Tetrahedron* **19**, 1415 (1963).

[18] W. Herz and Y. Sumi, *J. Org. Chem.* **29**, 3438 (1964).

[19] B. A. Parker and T. A. Geissman, *J. Org. Chem.* **27**, 4127 (1962).

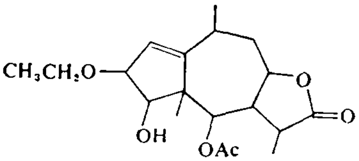
[20] W. Herz and M. V. Lakshmikantham, *Tetrahedron* **21**, (1965).

[21] Private communication from Dr. W. P. Stoutamire, Cranbrook Institute of Science.

$\Delta^{1,2}$-*Anhydrodihydrogaillardilone* (VII). BF_3 treatment of II (0·12 g) in the same manner gave, after chromatography and crystallization from ether–pet. ether, rearranged product (VII, 0·05 g) m.p. 154–156°, positive Zimmermann test, IR bands at 1775 (γ-lactone) and 1753 cm^{-1} (double intensity, cyclopentanone and acetate). (Found: C, 66·34; H, 7·17; O, 26·05. Calc. for $C_{17}H_{22}O_5$: C, 66·65; H, 7·24; O, 26·11%.)

Treatment of V (0·3 g) with BF_3-etherate gave, after the usual work-up and chromatography, VII (0·11 g).

When the rearrangement was carried out in $CHCl_3$ instead of benzene, the product isolated was XIII, m.p. 152°, IR bands at 1770 and 1750 cm^{-1}, NMR signals at 5·68 br ($W_{1/2}$ 3, H_6), 5·50 br (probable triplet, $W_{1/2}$ 5, H_2), 4·80 td (H_8), 4·50 dd (5, 2, A part of AB system, H_3), 4·10 dd (5, 2, B part of AB system, H_4), 3·679 (7, 2 protons, $-O\underline{CH_2}-CH_3$), 2·11 (acetate), 1·28 t (7, $-CH_2\underline{CH_3}$), 1·21 d (7, C_{10}- or C_{11}-methyl) 1·14 d (7, C_{11}- or C_{10}-methyl) and 0·85 ppm (C_5-methyl). (Found: C, 64·15; H, 8·01; O, 27·24. Calc. for $C_{19}H_{28}O_6$: C, 63·90; H, 8·22; O, 27·61%.)



XIII

Δ^2-*Anhydrodihydrogaillardilone* (VIII). A solution of VII (0·23 g) in MeOH (10 ml) and conc. HCl (2 ml) was heated on the steam bath for 4 hr, concentrated to small volume at red. press., diluted with water and extracted with ether. The washed and dried ether extract was evaporated and the residue chromatographed over acid-washed alumina, eluent benzene and benzene–ether (3:1, ten 10 ml fractions). The composition of the fractions was controlled by examination in the IR. Fractions 1–3 contained VII and fraction IV, a mixture of VII and VIII. Fractions 5–8 were combined and recrystallized from ether–pet. ether. This furnished VIII (0·06 g), m.p. 145–147°, λ_{max} 226 mμ (ε 8900), IR bands at 1775 (γ-lactone), 1745 (acetate), 1705 and 1590 cm^{-1} (α,β-unsaturated cyclopentenone, ORD curve (0·00168 g in 1 ml MeOH) $[\alpha]_{589}$ +9·5°, $[\alpha]_{360}$ −2·4°, $[\alpha]_{255\cdot5}$ +663°, $[\alpha]_{254}$ +568°, $[\alpha]_{253}$ +582°, $[\alpha]_{251}$ +556°, $[\alpha]_{250}$ +570°, $[\alpha]_{245}$ +548° (last reading). More VIII could be obtained from recovered VII by repeating the acid treatment. (Found: C, 66·98; H, 7·41; O, 25·73. Calc. for $C_{17}H_{22}O_5$: C, 66·65; H, 7·24; O, 26·11%.)

Dihydro-Δ^2*-anhydrodihydrogaillardilone* (IX). A solution of VIII (0·06 g) in EtOH (10 ml) was shaken in an atmosphere of H_2 with 5% Pd–C (0·02 g). After 2 hr, the solution was filtered, evaporated at red. press. and the residue recrystallized from ether–pet. ether, yield 0·042 g, m.p. 155–156°, IR bands at 1775 (γ-lactone) and 1748 cm^{-1} (double intensity, acetate and cyclopentanone), ORD curve (0·0025 g in 5 ml MeOH), $[\alpha]_{317}$ −2035°, $[\alpha]_{280}$ +1480° (last reading). (Found: C, 65·89; H, 8·00; O, 26·25. Calc. for $C_{17}H_{24}O_5$: C, 66·21; H, 7·85; O, 25·95%.)

Compound IX was prepared in better yield by direct hydrogenation of VII. A solution of 0·7 g of the latter in 30 ml acetic acid was reduced with 0·05 g PtO_2 for several hr, filtered and evaporated *in vacuo*. The residue was washed well with pet. ether and recrystallized from acetone–pet. ether, yield 0·5 g IX, m.p. 157°.

Several attempts to hydrolyze IX in order to correlate it with previously-reported 4-keto-pseudoguaianolides failed. Treatment with acid or methanolic K_2CO_3 resulted in recovery of starting material. Treatment with NaOH solution gave gums which exhibited multiple bands in the carbonyl region.

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