$[\alpha]_D$ + 40° (*c* 0.8); ultraviolet end absorption (ε 3650 at 210 mμ).

Anal. Calcd for $C_{28}H_{44}O_5$: C, 72.99; H, 9.63. Found: C, 72.95; H, 9.41.

The nmr spectrum included signals at τ 4.95 (multiplet, less than one proton), 8.97 and 9.13 (singlets, three proton total), 9.37 and 9.45 (singlets, three proton total).

Catalytic Hydrogenation of Methyl Cholenate Mixture (4 + 7a).—The mixture (25 mg) was dissolved in acetic acid (3 ml), concentrated hydrochloric acid (0.3 ml), and platinum dioxide (15 mg) added, and the mixture stirred vigorously for 2 hr under a hydrogen atmosphere. Filtration and dilution with water yielded methyl 3α-ethoxycarbonyloxycholanate (**8a**, 11 mg) as needles, mp 130–137° (lit.[14] mp 120–135°).

Hydrolysis of Methyl 3α-Ethoxycarbonyloxycholanate.—The ester (10 mg) was dissolved in 5% methanolic potassium hydroxide solution (3 ml), left at room temperature overnight, and worked up in the usual way. Crystallization of the product from aqueous methanol gave 3α-hydroxycholanic acid (**8b**) as prisms (6 mg): mp 181–182°; $[\alpha]_D$ +36° (*c* 0.5) (lit.[14] mp 182–183°; $[\alpha]_D$ + 32°).

Catalytic Hydrogenation of Methyl 3α-Acetoxychola-7,9(11)-dienate.—A solution of methyl 3α-acetoxychola-7,9(11)-dienate[15] (100 mg, mp 148–150°) in acetic acid (4 ml) was shaken with platinum dioxide (20 mg) for 1 hr under a hydrogen atmosphere. Filtration, concentration of the filtrate, and dilution with methanol yielded crystals which on recrystallization from methanol gave methyl 3α-acetoxychol-8-enate (**7b**) as plates: mp 143–145°; $[\alpha]_D$ + 55° (*c* 1.0); ultraviolet end absorption (ε 4200 at 210 mμ) (lit.[12] mp 144.5–146°; $[\alpha]_D$ +60°). Water was added to the mother liquor and, after cooling for several hours, methyl 3α-acetoxychol-8(14)-enate (**3b**) was collected as fine needles: mp 79–81°; $[\alpha]_D$ +50° (*c* 1.0); ultraviolet end absorption (ε 5900 at 210 mμ) (lit.[16] mp 81–82°; $[\alpha]_D$ +56°).

Authentic Mixture of 4 and 7a.—Methyl 3α-acetoxychol-8-enate was hydrolyzed with methanolic potassium hydroxide solution and converted into methyl 3α-ethoxycarbonyloxychol-8-enate by successive treatment with diazomethane and ethyl chloroformate in the standard manner. The methyl ester (**7a**) so obtained (10 mg) was mixed with the methyl ester (**4**, 5 mg) and the mixture dissolved in methanol. Concentration yielded the mixed crystals as needles, mp 139–140°, identical with that (**4** + **7a**) obtained by the action of zinc on **5**.

Registry No.—**3a**, 16797-63-0; **4**, 16797-64-1; **5**, 16797-65-2; **6**, 16797-66-3; **7a**, 16797-67-4; **7b**, 16797-68-5; bromine, 7726-95-6; **3b**, 16797-69-6.

Acknowledgment.—The award of Research Grant AM-03439 from the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, to R. S. is gratefully acknowledged.

(14) F. Nakada and K. Yamasaki, *Steroids*, **1**, 131 (1963).

(15) L. F. Fieser, W.-Y. Huang, and J. C. Babcock, *J. Amer. Chem. Soc.*, **75**, 116 (1953).

(16) F. Nakada, R. Osawa, and K. Yamasaki, *Bull. Chem. Soc. Jap.*, **34**, 538 (1961).

The Dehydration of Coronopilin

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Received January 29, 1968

The dehydration of coronopilin (**1**) in sulfuric acid–acetic acid was known to yield coronophilic acid (**4**), but it also yields the isomer **10** in formic or trifluoroacetic acid. $\Delta^{1,2}$-Anhydrocoronopilin (**6**), the product of thionyl chloride–pyridine dehydration of **1**, has been shown not to undergo the rearrangement. A proposed mechanism for the rearrangement is supported by nmr and CD data, and the absolute configuration of isocoronophilic acid is shown to be that expressed in **10a**.

Sesquiterpene dilactones have been isolated from some collections of *Ambrosia psilostachya*,[1-3] and we we were interested in the chemical correlation of psilostachyin B (**5**)[3] with coronopilin (**1**) through the unknown $\Delta^{1,10}$-anhydrocoronopilin (**2**). The stereochemistry of **1**, a major sesquiterpene lactone in this species, has been completely elucidated through X-ray analysis and chemical correlations,[4] but it had also been correctly postulated earlier by Geissman and Turley[5] as a result of their study of the unusual rearrangement of **1** to coronopilic acid (**4**).

When this work was initiated, the dehydration of **1** without rearrangement had not been achieved and our first goal was therefore to complete such a reaction.

Discussion

It is now known[4] that thionyl chloride–pyridine treatment of **1** yields $\Delta^{1,2}$-anhydrocoronopilin (**6**) rather than the desired $\Delta^{1,10}$ isomer. We expected that acid treatment of **6** would shift the 1,2 double bond to the more substituted 1,10 position, but we were also concerned with the possibility that this latter compound would further rearrange to **4**, as described by Geissman and Turley in their study of the acid-catalyzed dehydration of **1**.[5] These authors postulated that **2** was the first intermediate formed in the treatment of **1** with acetic acid–sulfuric acid and that it efficiently yielded the cyclopropane derivative **3**, which further reacted with acid to yield their observed product **4**.

We therefore anticipated that acid treatment of **6** would yield **4** readily and that the difficulty in the work would lie in defining the conditions required for stopping the reaction after double-bond migration to **2**. Actually, a double-bond migration into conjugation within the five-membered ring was the only reaction which was observed when **6** was submitted to the conditions of the coronopilic acid rearrangement. The conjugated ketone which was isolated after treatment was identified as epiambrosin (**7**) by direct comparison. It is therefore probable that **6** is also one intermediate in the acid-catalyzed isomerization of ambrosin (**8**) to **7**.[4]

Our failure to achieve the conversion of **6** into **2** led us to reinvestigate the acid-catalyzed reaction of corono-

(1) T. J. Mabry, H. E. Miller, H. B. Kagan and W. Renold, *Tetrahedron*, **22**, 1139 (1966).

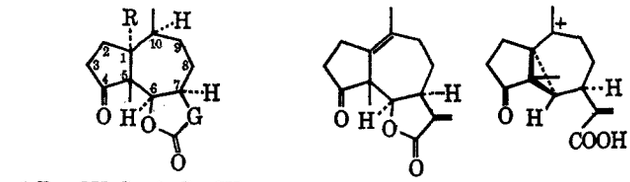
(2) H. B. Kagan, H. E. Miller, W. Renold, M. V. Lakshmikantham, L. R. Tether, W. Herz, and T. J. Mabry, *J. Org. Chem.*, **31**, 1629 (1966).

(3) T. J. Mabry, H. B. Kagan, and H. E. Miller, *Tetrahedron*, **22**, 1943 (1966).

(4) A. Romo de Vivar, L. Rodriguez, J. Romo, M. V. Lakshmikantham, R. N. Mirrington, J. Kagan, and W. Herz, *ibid.*, **22**, 3279 (1966).

(5) T. A. Geissman and R. J. Turley, *J. Org. Chem.*, **29**, 2553 (1964).

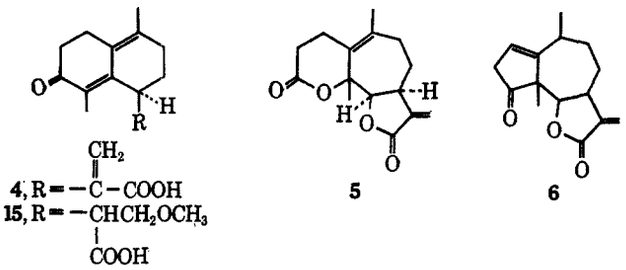
pilin. When **1** was treated with sulfuric acid in acetic acid as described by Geissman and Turley, coronopilic acid (**4**) was the only identified product. The reaction could be carried out in a sample tube at the temperature of the nmr probe, and its progress was followed continuously. The five-membered-ring vinyl protons of **6**, **7**, or **8** were not detected. Coronopilic acid itself was unstable under the conditions of the reaction, and after a maximum corresponding to the disappearance of **1**, its concentration decreased with time until the reaction mixture was completely black and the components could no longer be recognized.



1, R = OH; G = >C=CH$_2$
14, R = OH; G = >CHCH$_2$OCH$_3$
17, R = H; G = >C=CH$_2$

2

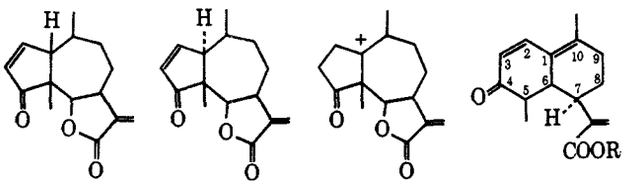
3



4, R = —C(=CH$_2$)—COOH
15, R = —CHCH$_2$OCH$_3$ (COOH)

5

6

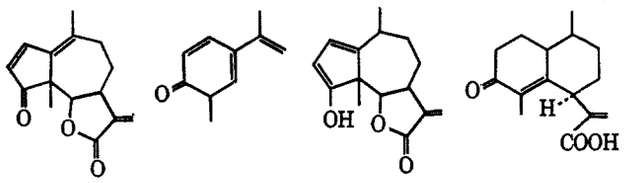


7

8

9

10, R = H
11, R = CH$_3$



12

13

16

18

We then turned to other media for the dehydration of **1**. No reaction was observed when a solution of **1** in 97% formic acid was allowed to stand for 15 hr at room temperature. When that solution was heated to 80° for 10 hr, all of the starting material disappeared. Neither **6** nor **7** was detected by nmr spectroscopy in the reaction mixture, and the acidic fraction proved to be a mixture of **4** (60%) and another product which was eventually shown to be **10** (40%).

Coronopilin was stable when heated for 18 hr at 60° in a 50% solution of trifluoroacetic acid in acetic acid. When it was heated in pure trifluoroacetic acid, a rearrangement identical with that observed in formic acid took place, and a mixture of **4** (60%) and **10** (40%) could be isolated in over 50% yield. This rearrangement was not observed when **6** was treated in these same two acids. Instead, some double-bond migration into conjugation took place.

The mixture of **4** and **10** crystallized easily, but neither component could be obtained in pure form upon recrystallization of the mixture under a variety of conditions. A small amount of the new acid **10**, mp 168–170°, pure on the basis of its nmr spectrum, was finally obtained after column chromatography of the mixture over silica gel G and recrystallization. The isomer **4** and most of **10** were lost in this process. The new acid, isocoronopilic acid (**10**), was shown by mass spectroscopy (on the methyl ester) to have the same molecular weight as **4**. Its nmr spectrum showed methylene vinyl protons at 5.73 and 6.61 ppm as broad singlets, with a shape comparable to those in **4**, departing from the sharp doublets always associated with the rigid lactone ring structure in **1** and related sesquiterpene lactones. A low field doublet (one proton) at 7.44, in conjunction with a doublet at 5.94 ppm (one proton, J = 10 cps), indicated an α,β-unsaturated ketone. The presence of a third double bond in the molecule was disclosed by a methyl peak at 1.90 ppm. Since another methyl group appeared as a doublet at 1.02 ppm (J = 6 cps), a rearrangement of the ring system must have taken place in the conversion of **1** into **10**, and the formula **10** accounts for all the analytical results on isocoronopilic acid. The most intense peak in the mass spectrum of methyl isocoronopilate (**11**) had m/e 148, which is due to the product (**13**) of a retro-Diels–Alder reaction. The experimental value for the ultraviolet absorption maximum in ethanol [λ_{max} 304 nm (ϵ 15,300) with a shoulder at 230 nm] matches perfectly the calculated value.[6] In contrast, the same chromophore in the unrearranged ring system of anhydroparthenin (**12**) has a band at λ_{max} 296 nm (ϵ 12,500).[7]

A derivative of coronopilin was prepared in order to study on another example this unusual rearrangement. The crystalline product **14** was obtained as a mixture of isomers by the base-catalyzed addition of methanol onto the exocyclic double bond of **1**. This adduct was converted into the corresponding coronopilic acid derivative **15** upon treatment with sulfuric acid in acetic acid, and, as expected, the increased bulk of the 7 substituent in this compound compared with **4** resulted in a slightly lower value (306 nm, ϵ 14,900) of the absorption maximum. The isocoronopilic acid derivative was not observed when this rearrangement was carried out in formic or trifluoroacetic acid.

Mechanism of the Acid-Catalyzed Dehydration of Coronopilin.—Several possibilities exist, which would explain the absence of **10** in Geissman and Turley's conditions for the dehydration of **1**: (a) **10** is not formed at all in these conditions; (b) **10** and **4** are both formed, but the former is unstable and yields unidentified neutral products, thus leaving **4** as the only isolated acid; (c) **10** and **4** are both formed, but **10** readily isomerizes into **4**; (d) **10** is the primary product in the reaction, but it isomerizes into **4**.

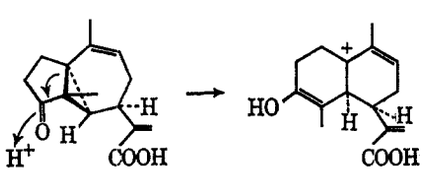
(6) The observed uv absorption maximum of **4** (310 nm)[5] is much lower than the calculated value of 337 nm. Steric interaction between the 5-methyl and the 7 substituent is probably responsible for this effect. Decoupling experiments performed on **4** at 100 Mc showed that the coupling constants between H_7 and both H_8's are smaller than 5 cps. This is a clear confirmation of the axial character of the C-7 side chain in **4**. If present in **10**, such an interaction (although necessarily of a different magnitude because of the difference in the geometry at C-5) does not affect significantly the electronic system of the dienone.

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

In order to shed some light on the process, a mixture of **4** and **10**, obtained from the reaction in formic acid, was subjected to Geissman and Turley's conditions for 1 hr. After work-up, the only acidic material was found to be **4**. When pure **10** was treated in the same manner, no acidic compound could be isolated. These experiments rule out the third and fourth hypotheses but do not allow one to decide between the first and the second. Similarly, the presence of **10** in trifluoroacetic acid and in formic acid might have resulted either from the concurrent formation of both products **4** and **10** or from partial isomerization of **4**. This latter hypothesis was not supported by the evidence, since pure **4** could be treated in the conditions of the reaction in these two media and it could be recovered without formation of **10**.

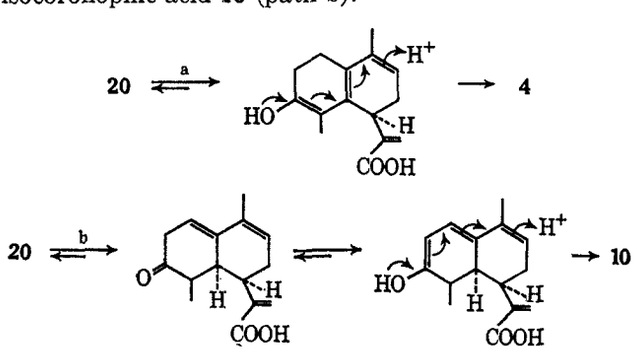
It is therefore tempting to postulate that in all cases the acid-catalyzed dehydration of **1** follows a single mechanism leading to both **4** and **10**, but that occasionally the latter compound is further degraded in the medium and escapes detection.

A mechanism accounting for the simultaneous formation of **4** and **10** incorporates the essential features of Geissman and Turley's proposal. Initial dehydration of **1** to **2** is followed by proton loss to **19**. Protonation of **19** at the ketone yields the bicyclic enol **20**, from



19 **20**

which loss of a proton may occur in two different manners, leading to coronopilic acid **4** (path a) as well as to isocoronopilic acid **10** (path b).



In support of this mechanism, we observed that the presence of the 1-hydroxyl was essential for the rearrangement to take place. Damsin (**17**), which contains all the stereochemical features of **1** but lacks the tertiary hydroxyl,[8] was treated for several days in the conditions of the coronopilic acid rearrangement. The solution became black, but **18** was not detected in the solution by nmr spectroscopy.

Our failure to observe the isomerization of **6** to **4** could have been taken as evidence against the initial formation of **2** in the acid treatment of **1**, since the 1 double bond could reasonably be expected to shift to the more substituted 10 position. However, the experimental result is easily explained if protonation of **6** takes place initially at the ketone rather than at the double bond, yielding first the enol **16** and finally the observed conjugated ketone.[9]

It must be noted that our proposed mechanism for the formation of **4** and **10** preserves the integrity of the asymmetric center at C-7 in both products, which therefore must be optically active. It was indeed observed that both coronopilic acid ($[\alpha]_D$ −441°, *c* 0.58 in $CHCl_3$) and its isomer ($[\alpha]_D$ −325°, *c* 0.50 in $CHCl_3$) had very large specific rotations. There is only one asymmetric center at C-7 in **4**, whereas there are three such centers in **10**. As the center next to the carbonyl is easily racemized in acid, one can only deduce from the presence of optical activity in **10** that the centers C-6 and C-7 had not both been epimerized.

Finally, in an attempt to locate the centers which had been protonated during the rearrangement, the dehydration of **1** was carried out in deuterated trifluoroacetic acid. Comparison of the nmr spectra of the isolated acids with those obtained in the normal medium showed incorporation of deuterium at C-3 and C-5 in **10** and at C-3 (2 atoms) in **4**. In particular, a proof that H-6 was not affected in **10** was found in the fact that it appeared as a doublet at 2.65 ppm. This clearly showed that deuterium had been incorporated at C-5 but not at C-6 or C-7. Integration of the spectra indicated that incorporation had taken place elsewhere, probably at the allylic positions, but the signals were not resolved sufficiently to allow the exact location of the label. When the same mixture of **4** and **10** prepared in normal acid was treated in deuterated trifluoroacetic acid, deuterium was incorporated at C-3 in **4** and at C-5 in **10**. In addition, some incorporation took place at saturated positions. The lack of incorporation of deuterium at C-3 in **10** in the latter experiment, coupled with the presence of label at that position in the former, demonstrated that enolization of the ketone toward C-3 had taken place before formation of **10**. The ease of enolization of **1** was shown by carrying out the rearrangement in deuterated trifluoroacetic acid to very small conversion. The nmr spectrum of the starting material showed some deuterium incorporation, in particular at the ring methylene protons which gave resonance at the lowest field. These are probably the C-3 protons.

The presence of optical activity in **4**, coupled with the results of the deuterium incorporation showing no label at C-7, allows us to conclude that formula **4** represents the absolute configuration of coronopilic acid. These results determined only the absolute configuration at the unreacted C-7 in **10**, and the configuration at the other asymmetric centers in isocoronopilic acid remained to be demonstrated.

Stereochemistry of Isocoronopilic Acid.—Since the absolute configuration at C-7 in **10** is known from that in **1**, the configuration at C-5 and C-6 relative to that at C-7 will determine the absolute stereochemistry of isocoronopilic acid.

No label was incorporated at C-6 in the deuterated acid treatment of **1** and the stereochemistry at this center must therefore be accessible from mechanistic considerations alone. The hypothesis of a backside attack by the electrons of the 1,10 double bond during the lactone ring opening in **2** fixes the stereochemistry of

(8) M. Suchý, V. Herout, and F. Šorm, *Collect. Czech. Chem. Commun.*, **28**, 2257 (1963).

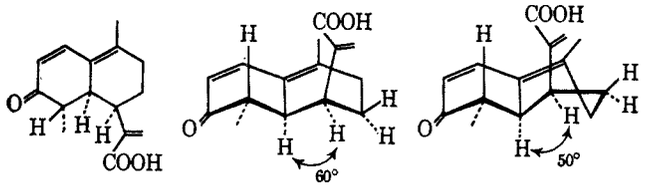
(9) Protonation at the ketone also explains why anhydroparthenin (**12**) does not undergo the rearrangement and is stable to acid.

the substituents on the cyclopropane as indicated in **3** and in **19**; C-5 is above the plane of the B ring soon to be formed, and H_6 is almost in that plane. After ketone protonation and bond breaking between C-1 and C-5, it is clear that H_6 will necessarily be *below* the B ring and axial, as expressed in **20**.

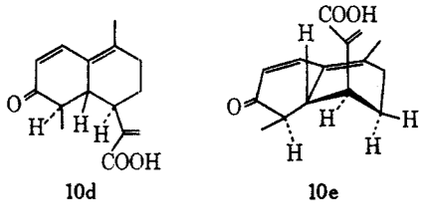
It is reasonable to postulate that the configuration at the equilibrable C-5 will be such that the methyl substituent will suffer minimum 1,3 interactions. Since the configurations at C-6 and C-7 are such that H_6 and the large C-7 substituent are both axial, the C-5 methyl will therefore be equatorial and α, as expressed in **10a** which must therefore represent the complete stereochemistry of isocoronopilic acid.[10]

The structural assignment was substantiated by the results of nmr measurements. Double resonance nmr experiments performed at 100 Mc allowed the determination of the coupling constants: $J_{H_5H_6}$ = 14 cps, $J_{H_6H_7}$ = 4.8 cps, and $J_{H_7H_8}$ = 7 cps. These coupling constants clearly indicate that H-5 and H-6 are both axial and that H_7 is equatorial, in support of the structure **10a** derived from mechanistic considerations.

Inspection of a model of **10a** shows that the A ring will necessarily be in a half-chair conformation in order to have H_5 axial, but that the B ring may have either a half-chair or a half-boat conformation. In the former case (**10b**), the dihedral angle between H_6 and H_7 is about 60°, while in the latter case (**10c**) that angle is about 50°. The observed coupling constant of 4.8 cps is reasonable in either case and does not allow one to distinguish between these conformations.



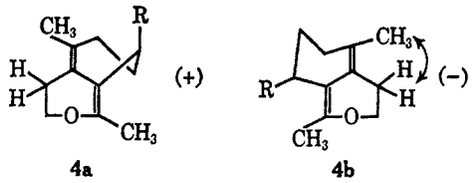
10a **10b** **10c**



10d **10e**

It must be noted that the alternative structure **10d**, where the angular hydrogen is β, possesses only one conformation (**10e**) in which the H_5 (axial), H_6 (axial), H_7 (equatorial) relationship is satisfied, but this conformation must be ruled out since the dihedral angle between H_6 and H_7 is 90° and should have resulted in no measurable coupling between these protons in the nmr spectrum.

In the absence of suitable models of known configuration, the interpretation of the observed circular dichroism is hazardous. However, its application to the simpler coronopilic acid **4** may be checked against the structure derived from the nmr data and the study of models. Of the two conformations possessing an axial C-7 side chain, **4a** appears energetically favored because the interaction between the C-10 methyl and C-2 proton indicated in **4b** is minimized



4a **4b**

Application of the CD rules for enones[11] predicts a positive value for **4a** and negative one for **4b**. The observed value was positive and gives some confidence that the rule may be applied to the more complex isomer **10**. Application of the dienone rule should give a negative dichroism for **10e** and a positive dichroism for **10b** and **c**. The experimental value was positive and therefore rules out **10e**.

In conclusion, the mechanistic proposal as well as the interpretation of the physical data point to **10a** for the absolute configuration of isocoronopilic acid.[12] The data presently available does not allow a choice between **10b** and **10c** for the actual conformation of **10a**.

Experimental Section

The nmr spectra were determined on Varian A-60 or A-60A spectrometers in chloroform and are described in parts per million downfield from an internal standard of tetramethylsilane. The ir spectra were measured in a Beckman IR-5 and the uv spectra were recorded with Beckman DB or Bausch and Lomb 505 spectrometers. The melting points were determined with a Fisher-Johns apparatus and are not corrected.

Acid-Catalyzed Isomerization of 6.—The dehydration of **1** with thionyl chloride in pyridine was carried out as described.[5] A solution of 0.100 g of **6** in 2.5 ml of acetic acid and 0.25 ml of sulfuric acid was heated for 1 hr at 80°. The dark solution was diluted with water and extracted with ethyl acetate which was then washed with sodium bicarbonate and with water. The neutral fraction was shown by nmr spectroscopy to be an almost equimolar mixture of **6** and **7**. This latter compound was isolated in low yield by preparative tlc over silica gel with chloroform–ethyl acetate (3:1). It crystallized, mp 146–148°, upon seeding with an authentic sample of epiambrosin[4] with which it was identical in all respects.

Rearrangement of 1 in Formic Acid.—A solution of **1** (1.488 g) in 20 ml 97% formic acid was heated at 80° for 10 hr. Water was added to the brown solution, which was then extracted with ethyl acetate. The organic phase was extracted with bicarbonate. The acidic fraction consisted of 0.836 g of solid which was analyzed by nmr spectroscopy to be about 60% **4** and 40% **10**.

Rearrangement of 1 in Trifluoroacetic Acid.—A solution of 0.219 g of **1** in 2 ml of trifluoroacetic acid was heated in a closed vial at 60° for 7.5 hr. After dilution with water the mixture was extracted with ethyl acetate, which was in turn extracted with bicarbonate. After acidification of the aqueous layer and usual work-up, there was obtained 0.122 g of solid, analyzed by nmr spectroscopy to be about 60% **4** and 40% **10**.

The reaction in deuterated acid was carried out under identical conditions. The acid was prepared by careful addition of the calculated amount of deuterium oxide to trifluoroacetic anhydride.

Isocoronopilic Acid (10).—A mixture of **4** and **10** (0.836 g) obtained in formic acid was placed on a 15 × 2 cm column of silica gel G (from Merck Co.) packed in chloroform. Upon elution with the same solvent a crystalline material was obtained in the fourth and fifth 25-ml fractions. After two recrystallizations from ethyl acetate there was obtained 0.046 g of **10**, mp

(10) The mechanistic argument is based on the assumption that no carbonium ion is formed at C-6 by lactone ring opening prior to cyclopropane formation. This point has already been discussed[5] and our finding that damsin (**17**) did not undergo any rearrangement despite the large relief of steric interaction to be gained gives stronger support to this assumption.

(11) G. Snatzke, *Tetrahedron*, **21**, 413, 421, 439 (1965).

(12) It is interesting to find the larger C-6 substituent axial and the smaller equilibrable C-4 substituent equatorial as one would have been tempted to predict the alternative relationship.

168–170°, pure according to nmr data. No other product could be eluted from the column.

The **nmr spectrum of 10** (100 Mc) showed the following signals: methyls, C-5 at 1.02 (d, J = 6 cps) and C-10 at 1.9 (s); ring methylenes between 1.72 and 2.3 (complex); ring methines, H_5 at 2.50, H_6 at 2.65, H_7 at 3.41 with $J_{H_5H_6}$ = 14 cps, $J_{H_6H_7}$ = 4.8 cps, and $J_{H_7H_8}$ = 7 cps; vinyl protons, exocyclic at 5.70 (s) and 6.58 (s), H_2 at 7.41, and H_3 at 5.90 ppm ($J_{H_2H_3}$ = 10 cps).

In double resonance experiments at 100 Mc, the protons at C-5 and C-6 gave partially overlapping, complex signals centered at 2.5 and 2.65, respectively, while H_7 appeared as a poorly resolved doublet at 3.41. Upon irradiation at H_7 the vinyl signals were not affected but H_6 was converted into a doublet with $J_{H_5H_6}$ = 14 cps. The area near the vinyl methyl at 1.90 was also affected, indicating the general location of the C-8 protons. The location of H_5 was ascertained by irradiating at 2.50, which converted the C-5 methyl doublet into a singlet. Conversely, irradiation at the C-5 methyl converted the complex H_5 signal into a doublet with $J_{H_5H_6}$ = 14 cps. Irradiation at H_6 sharpened H_7 into a peak with a half width of 7 cps, while irradiation at H_8 near 1.90 converted H_7 into a doublet with $J_{H_6H_7}$ = 4.8 cps. Finally, from the half width measurement of the H_7 signal (about 7 cps), one finds that $J_{H_7H_8}$ is not more than 7 cps.

Circular dichroism values in dioxane were as follows: 371 (+2.46), 353 (+4.06), 342 (+3.91), 298 (−14.90), 229 (−1.99), positive at shorter wavelengths; in ethanol, they were 344 (+5.65), 302 (−15.53), and 229 (−1.62), strongly positive at shorter wavelengths. The same solutions showed uv maxima at 298 and 230 (infl) in dioxane and at 304 and 230 nm (infl) in ethanol For comparison, in ethanol a sample of **4** containing about 20% **10** gave values of 344.5 (+4.98), 304 (−20.86), and 237 (−1.56), strongly positive at shorter wavelengths.

The methyl ester was obtained by diazomethane treatment and had mol wt 260 (mass spectroscopy). A rotation was determined on a mixture of **4** and **10** which was made 50% in each component by a preliminary treatment on a smaller column of silica gel. The observed value was $[\alpha]_D$ −383° (c 0.11, in $CHCl_3$), which corresponds to −325° for **10**. The ir spectrum of **10** in $CHCl_3$ showed absorptions at 5.9, 6.2, 6.18, and 6.31 μ.

Acid Treatment of 4 and 10.—All the acid treatment experiments on **4** and **10** were performed in nmr sample tubes kept at the appropriate temperature. After the proper reaction time the nmr spectrum was recorded, the acidic products in the reaction mixture were isolated and they were also examined by nmr spectroscopy.

Adduct 14.—A solution of 0.629 g of **1** in 15 ml of methanol was treated with a few drops of 0.1 N sodium hydroxide. After 4 hr at room temperature, the solution was diluted with water and extracted with chloroform. A quantitative yield of adduct [mol wt 296 (mass spectroscopy)] was obtained upon recrystallization of the extract from methanol. The melting point (203–235°) was raised to 235–237°, $[\alpha]_D$ 23.8 ± 2° (c 0.3, dioxane), after several recrystallizations. The nmr spectrum showed prominent signals at 1.18 (s, C-5 methyl), 1.21 (d, J = 8 cps, C-10 methyl), 3.38 (s, $-OCH_3$), 3.67 (d, J = 5 cps, $-CH_2-O-$), 4.96 ppm (d, J = 9 cps, H_6). In addition to the broad melting range, the presence of a mixture of isomers (probably at C-11) was suggested by the lack of sharpness of the 1.21 and 4.96 ppm peaks, which could be due to almost superimposed signals from both isomers.

Acid Treatment of 14. A. In Acetic Acid–Sulfuric Acid.—Two drops of sulfuric acid was added to a solution of 0.047 g of **14** in 10 ml of acetic acid. The solution was heated to 80° for 30 min. After addition of water it was worked up as usual. The acidic fraction was crystallized from ether–hexane and yielded 0.009 g of **15**: mp 176–177°; λ_{max} 212 nm (ϵ 7900), 243 (5300) and 306 (14,900). The nmr spectrum indicated two CH_3's at 1.8 ppm, characteristic for the coronopilic acidlike structure.

B. In Formic Acid.—A solution of 0.300 g of **14** in 5 ml of 97% acid was heated to 80° for 30 min. After the usual work-up, 0.064 g of acid was obtained. Its nmr spectrum and melting point were identical with those of the above products. Contrary to the results observed with **1**, the dienone isomer was not detected.

Registry No.—**1**, 2571-81-5; **10a**, 16526-71-9; **15**, 16526-72-0.

Acknowledgments.—Part of this work was carried out at the University of Texas in the laboratory of Dr. T. J. Mabry, whom we sincerely thank. We are indebted to Drs. T. J. Mabry, W. Herz, and H. E. Miller for help and useful discussions during the course of this work, Dr. R. Wolff for mass spectral studies, Dr. G. Snatzke for the circular dichroisms and their interpretation, and Mrs. L. Lacombe for the decoupling experiments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. A NATO grant to H. B. K. and support from the Robert A. Welch Foundation are also gratefully acknowledged.

Preparation and Reactions of a 3-Chlorocoumarin Photodimer

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Received February 2, 1968

The preparation of a head-to-tail 3-chlorocoumarin photodimer is described. Attempts to convert this dimer into the corresponding cyclobutadienoid system are discussed.

Both the direct and sensitized photodimerization of coumarin have been reported in the literature. Anet[1] reported that direct irradiation of coumarin in ethanol solution produces the *cis* head-to-head dimer (**1**) while Schenck[2] showed that irradiation in the presence of benzophenone gives the *trans* head-to-head dimer (**2**) along with a trace of the *trans* head-to-tail dimer (**3**). Hammond[3] reinvestigated these reactions and concluded that the direct irradiation proceeds through interaction of excited coumarin singlet whereas the sensitized irradiation involves excited-triplet coumarin. The effect of various solvents on the direct, unsensitized dimerization was later studied by Morrison.[4] He found that in nonpolar solvents the *trans* head-to-head dimer (**2**) is formed to the virtual exclusion of the *cis* head-to-head dimer (**1**). The ratio of **2** to **1** decreases in polar solvents and is reversed in methanol. Morrison suggests that **1** is formed from a singlet excimer, whereas **2** arises *via* a monomeric triplet species. These solvent effects are similar to those found independently by

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