owing to the simultaneous loss of acetyl and methyl (m* 205.2, calcd 204.8) from the ion of m/e 310 (M − $2H_2O$).

Experimental Section[14]

Samples.—The compounds studied are all known compounds whose properties agreed with those reported in the references indicated for individual compounds. Each sample was checked for purity by melting point determination, thin layer chromatography, and mass spectrometry.

Samples of the steroids employed in this study were obtained by published procedures: progesterone (I),[15] mp 129–131°; 2α-methylprogestrone (II),[16] mp 149.5–150°; 4-methylprogesterone (III),[17] mp 160–166°; 6α-methylprogesterone (IV),[18] mp 116–119°; 6β-methylprogesterone (V),[19] mp 172–174°; 7α-methylprogesterone (VI),[20] mp 191–199°; 16α-methylprogesterone (VII),[21] mp 134–137°; 16β-methylprogesterone (VIII),[22] mp 210–211; 9α-hydroxyprogesterone (XII),[23] mp 178–185°; 11α-hydroxyprogesterone (XIII),[24] mp 166–167°; 11β-hydroxyprogesterone (XIV),[25] mp 182–184°; 14α-hydroxyprogesterone (XV),[23] mp 199–201.5°; 15α-hydroxyprogesterone (XVI),[26] mp 226–232°; 16α-hydroxyprogesterone (XVII),[27] mp 222–228°; 17α-hydroxyprogesterone (XVIII),[28] mp 218–220°; 21-hydroxyprogesterone (XIX),[29] mp 140–141°; 11α-acetoxyprogesterone (XXII),[30] mp 171–175.5°; 12β,15α-dihydroxyprogesterone (XXIII),[31] mp 216–220°.

Registry No.—I, 57-83-0; II, 2636-91-1; III, 15981-49-4; IV, 903-71-9; V, 2300-06-3; VI, 2640-71-3; VII, 1239-79-8; VIII, 1424-09-5; IX, 15981-54-1; X, 80-75-1; XI, 600-57-7; XII, 16031-66-6; XIII, 600-73-7; XIV, 438-07-3; XV, 68-96-2; XVI, 64-85-7; XVII, 2268-98-6; XVIII, 599-14-4.

Acknowledgment.—We thank The Upjohn Co., Kalamazoo, Mich., for a leave of absence to M. F. Grostic while this study was undertaken. This work was supported in part by Grant No. AI 04769 from the Institute of Allergy and Infectious Diseases, National Institutes of Health. We are indebted to Mr. Joseph Wrona for assistance in determining a number of the mass spectra.

(14) Mass spectra were determined with an Atlas CH-4 mass spectrometer equipped with a T04 ion source. All samples were introduced by the direct inlet technique employing the vacuum lock. Ionizing energy was maintained at 70 eV and ionizing current at 30 μA. Peak intensities are reported as percentages of the strongest peak in the spectrum.

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The Kostanecki–Robinson Acylation and Cyclization of 3-Acyl-4-hydroxy-2-pyrones

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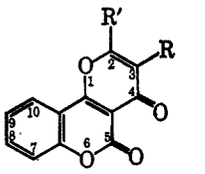
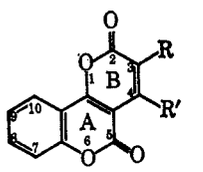
The acylation of 3-acyl-4-hydroxy-2-pyrones using the acid anhydride and salts of the corresponding acids (Kostanecki–Robinson conditions) has led to the formation of heterocyclic compounds which, depending on whether the acyl side chain has an α-CH_2 group or not, are substituted 2H,5H-pyrano[4,3-*b*]pyran-2,5-diones, or 4H,5H-pyrano[4,3-*b*]pyran-4,5-diones, respectively. The latter derivatives have been prepared by other methods, and firm spectroscopic, diagnostic methods have been established to distinguish between them.

We have investigated the acylation and cyclization of several 4-hydroxy-2-pyrones to give 4H,5H-pyrano-[4,3-*b*]benzopyran-4,5-diones I, and 2H,5H-pyrano-[4,3-*b*]benzopyran-2,5-diones II.[1]

The starting point for the well-established methods described below for preparing I or II was the observation that during the work-up of a preparation of 3-propionyl-4-hydroxycoumarin, the residues yielded a new material whose infrared spectrum was unlike the characteristic pattern of 3-acyl-4-hydroxy-2-pyrones. A new band of only moderate intensity at ~1640 cm^{-1} was observed (see Table I) in addition to the strong absorption at 1740–1750 cm^{-1} due to the lactone carbonyl which was at a slightly higher frequency than usual. The new band suggested a cyclized compound



Ia, R = R′ = CH_3
b, R = CH_3; R′ = C_2H_5
c, R = C_2H_5; R′ = CH_3
d, R = R′ = C_2H_5
e, R = $OC_6H_3Cl_2$; R′ = CH_3
f, R = H; R′ = C_6H_5
g, R = H; R′ = CH_3



IIa, R = H; R′ = CH_3
b, R = R′ = CH_3
c, R = Cl; R′ = CH_3
d, R = $CH_2C_6H_5$; R′ = CH_3
e, R = H; R′ = C_6H_5
f, R = H; R′ = OH

containing a γ-pyrone ring (I). The carbonyl stretching vibration in such a ring would be expected to give rise to an absorption near 1640 cm^{-1}. It was speculated that I could be derived from the 4-hydroxy-2-pyrone by diacylation followed by condensation. It was also realized that the condensation could proceed the other

(1) *Chemical Abstracts* describe the names used here as alternative to the preferred terminology as α-lactone derivatives of hydroxysorbic acid. We have thought it preferable to use these alternatives throughout to reveal the relationships between the different compounds.

TABLE I

CARBONYL FREQUENCIES IN PYRAN-4,5-DIONE DERIVATIVES[a]

Compd	I R	I R′	Carbonyl frequency α-Pyrone	Carbonyl frequency γ-Pyrone
	Coumarin Derivatives			
Ia	CH	CH_3	1739 s	1640 m
Ib	CH_3	C_2H_5	1748 s	1640 m
Ic	C_2H_5	CH_3	1737 s	1648 m
Id	C_2H_5	C_2H_5	1750 s	1647 m
Ie	$OC_6H_3Cl_2$[b]	CH_3	1734 s	1648 m
If	H	C_6H_5	1738 s	1636 m
Ig	H	CH_3	1751 s	1662 m
	Triacetic Lactone Derivatives			
V	H	C_6H_5	1715	1640

[a] m, medium; s, strong. [b] 2,4-Dichlorophenoxy.

TABLE II

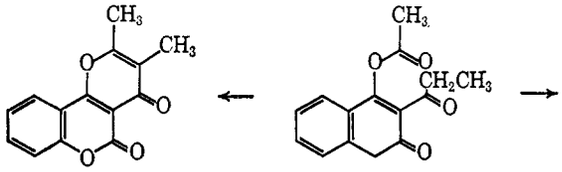
CARBONYL FREQUENCIES IN PYRAN-2,5-DIONE DERIVATIVES[a]

Compd	II R	II R′	Carbonyl frequency Ring A	Carbonyl frequency Ring B	Unassigned shoulder
	Coumarin Derivatives				
IIa	H	CH_3	1710	1733	
IIb	CH_3	CH_3	1717	1735	1750
IIc	Cl	CH_3	1715	1730	1753
IId	$CH_2C_6H_5$	CH_3	1715	1730	
IIe	H	C_6H_5	1720 s	1730 m	1742
IIf	H	OH	1685 s[b]	1732 m	

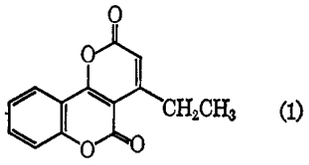
[a] m, medium, s; strong. [b] The OH group forms a six-membered internally hydrogen-bonded ring with the A-ring carbonyl group, thereby lowering its frequency by some 30 cm^{-1}.

way giving II. The nmr spectra of the two sets of materials would offer no differentiation between them as they both contain the same alkyl groups. Neighboring groups would affect the chemical shifts but not in a way that could be reliably used for identification purposes.

The problem was resolved by a careful selection of alkyl groups. By acylating 3-propionyl-4-hydroxycoumarin with an acetyl derivative the choice in reaction 1 could be presented. The product could then



Ia



II, R = H; R′ = C_2H_5 (1)

be unambiguously identified, since two methyl hydrogen resonances could only come from Ia and ethyl group signals from II. The experimental conditions chosen were those of the Kostanecki–Robinson synthesis[2] which is known to give chromones[3] or coumarins[4] with *o*-hydroxy aromatic ketones depending on conditions. A compound resulted having two single methyl group resonances clearly identifying the product as type I.[5] Firm diagnostic methods for these compounds being thus available, a study of the type II derivatives was undertaken.

A method recently described in the literature,[6] alleging to produce type I from the reaction of 4-hydroxycoumarin with ethyl acetoacetate, gave in our hands a material quite unlike type I. The infrared spectrum (see Table II) was devoid of absorption near 1640 cm^{-1}, and the lactone carbonyl frequency, now in its normal place near 1720 cm^{-1}, had a little more structure than in type I compounds. This compound was quite unlike the isomeric cyclized product from 3-acetoacetyl-4-hydroxycoumarin[7] which showed the characteristic type I spectra. Again, by a judicious choice of alkyl groups the assignment was confirmed for the suspected pyran-2,5-dione (II) derivative, by acylating 3-acetyl-4-hydroxycoumarin with a propionyl derivative under Kostanecki–Robinson conditions. The presence of two methyl group resonances in the nmr spectrum of the resulting compound suggested acylation of the 4-hydroxy group followed by condensation at the methylene group of the 4-propionoxy derivative. The confirmation of this structure also permitted reliance on the infrared spectrum to characterize type II derivatives. Substituted acylacetic esters were used to give a variety of substituted type II derivatives.

These views on the reactions of 4-hydroxy-2-pyrones contradict those of Woods,[6] but are confirmed by Praill and Whitear's reexamination[8a] of Fleischman's results[8b] in which they favor a type II structure for the product of reaction of triacetic lactone with ethyl acetoacetate. Also Mustafa, *et al.*,[7] have condensed 4-hydroxycoumarin and ethyl acetoacetate with sulfuric acid and obtained the type II structure.

The Kostanecki–Robinson reaction with *o*-hydroxy aromatic ketones affords both chromones[3,9,10] and coumarins[4] depending on conditions and substituent groups. Using the same method with 3-acyl-4-hydroxy-2-pyrones two generalizations emerge. (1) With 3-acetyl-4-hydroxy-2-pyrones, the product is a pyran-2,5-dione derivative (II). (2) With 3-acyl-4-hydroxy-2-pyrones having a methylene group next to the carbonyl group, pyran-4,5-dione derivatives (I) result.

Further substantiation for the type I structure was obtained from the preparation of If, as shown in reaction 2. The removal of one molecule of HBr from the dibromocinnamoyl derivative was effected with piperidine to produce III, the saturated analog of type I. The infrared absorption band at ~1650 cm^{-1} is appropriately placed for the carbonyl stretching frequency of a dihydropyran-4,5-dione derivative.

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(5) We have never observed a scrambling of acyl groups between the 3 and 4 positions. We believe the 3-acyl group to be strongly bound, only suffering reaction under extremely drastic conditions, for example, the preparation of triacetic lactone from dehydroacetic acid in 90% H_2SO_4 at 130°. The 4-acyloxy group is more labile and can be hydrolyzed under certain conditions.

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(8) (a) P. F. G. Praill and A. L. Whitear, *Proc. Chem. Soc.*, 112 (1961); (b) F. N. A. Fleischmann, *J. Chem. Soc.*, **91**, 250 (1907).

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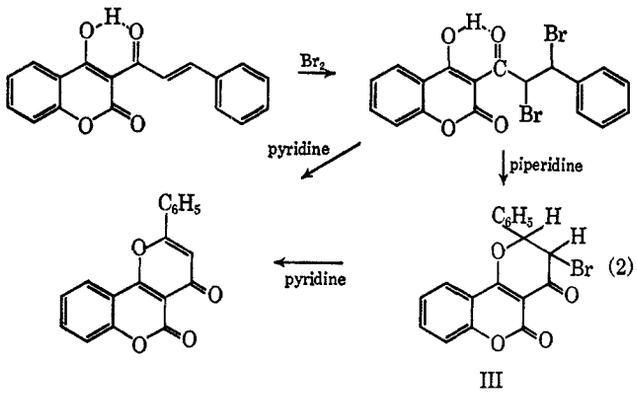
TABLE III

EXPERIMENTAL CONDITIONS FOR PREPARATION OF PYRAN-4,5-DIONE DERIVATIVES OF 4-HYDROXYCOUMARIN (I)

Compd	R	R′	3-Acyl-4-hydroxycoumarin (g)	Anhydride, (ml)	Acid salt (g)
Ia	CH_3	CH_3	COC_2H_5 (3)	$(CH_3CO)_2O$ (10)	CH_3COONa (3)
Ib	CH_3	C_2H_5	COC_2H_5 (15)	$(C_2H_5CO)_2O$ (23)	C_2H_5COOK (15)
Ic	C_2H_5	CH_3	COC_3H_7 (15)	$(CH_3CO)_2O$ (23)	CH_3COONa (15)
Id	C_2H_5	C_2H_5	COC_3H_7 (15)	$(C_2H_5CO)_2O$ (23)	C_2H_5COOK (15)
Ie	$OC_6H_3Cl_2$[a]	CH_3	$COCH_2OC_6H_3Cl_2$ (3)	$(CH_3CO)_2O$ (10)	CH_3COONa (3)

			Found, %			Calcd, %			Yield,	
			C	H	Cl	C	H	Cl	%	Mp, °C
Ia	CH_3	CH_3	69.59	3.97		69.42	4.13		60	227–28.5
Ib	CH_3	C_2H_5	70.38	4.64		70.31	4.69		52	237–28[b]
Ic	C_2H_5	CH_3	70.41	4.99		70.31	4.69		67	237–29[b]
Id	C_2H_5	C_2H_5	71.09	5.11		71.11	5.19		61	211–212.5
Ie	$OC_6H_3Cl_2$[a]	CH_3	58.71	2.41	18.31	58.61	2.57	18.25	19	320–323

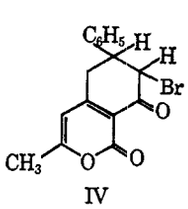
[a] 2,4-Dichloro-. [b] Mmp 196–210°.



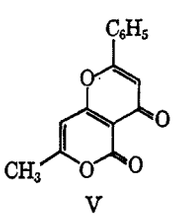
III

The second molecule of HBr was removed with pyridine. The product had an ir spectrum comparable in all respects in the 6-μ region with that of type I compounds. An exact comparison (melting point, identity of infrared spectrum, etc.) has not been possible, since no alternative method has been found to give If. Thus 3-acetyl-4-hydroxycoumarin, benzoic anhydride and sodium benzoate do not give If, in keeping with the generalization that 3-acetyl derivatives under Kostanecki–Robinson conditions generally give pyran-2,5-dione derivatives. However, in this case no α-CH_2 group is present in the Kostanecki–Robinson acylating agent so that the formation of a pyran-2,5-dione derivative is not possible. It has also not been possible to prepare If by the direct acylation of either a 4-benzoxy derivative or a 3-acyl-4-hydroxy derivative. Neither has the self-condensation of 3-acetyl-4-propionoxy-6-methyl-2-pyrone with phosphorous oxychloride proved successful; only 3-acetyl-4-hydroxy-6-methyl-2-pyrone was obtained.

In a similar manner IV, the triacetic acid analog of III, was prepared. 3-(α,β-Dibromohydrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone gave IV when treated with



IV



V

piperidine or V when refluxed with pyridine. Both IV and V had infrared bands in the pyrone region corresponding to those in the coumarin series.

Experimental Section[11]

A. 4-Hydroxycoumarin Compounds. 1.—Reactions of 3-Acyl-4-hydroxycoumarins with Anhydrides and Salts of the Corresponding Acids (Kostanecki–Robinson Conditions). i.—Pyran-4,5-dione Derivatives Ia–e.—The experimental conditions and analytical data[12] are listed in Table III. The method consisted in heating the reaction mixture for 2 hr at 130°, then pouring into cold water, filtering, and recrystallizing the solid.

ii.—Pyran-2,5-dione Derivatives IIa, IIb.—The experimental conditions and analytical data are listed in Table IV. The ingredients were refluxed at 135° for 2 hr, then cooled and poured into water. The brown solid was filtered and crystallized from dimethylformamide. Compound IIb prepared in this manner had identical infrared spectrum and no melting point[13] depression with that described in Table V. However, IIa was more difficult to purify; the infrared spectrum of the resulting compound was quite similar to that described in Table V. A comparison of the mass spectral fragmentation patterns showed the sample to consist of IIa along with higher molecular weight species (330, 396, and not identified). None of the isomeric compound Ig was found.

2. Preparation of Ib by $POCl_3$ Method.[14]—4-Hydroxycoumarin (100 g), 250 ml of propionic acid, and 250 ml of $POCl_3$ were refluxed for 2 hr. A light yellow solution was poured off and ultimately yielded 68 g (52%) 4-hydroxy-3-propionylcoumarin. The viscous residue was diluted with methanol and on cooling gave 23 g (15%) Ib, mp 237–238°. The infrared spectrum was identical with that obtained as shown in Table I.

3. Preparation of Ig.—3-Acetoacetyl-4-hydroxycoumarin was obtained by the acylation of 3-acetyl-4-hydroxycoumarin and then cyclized to Ig with sulfuric acid as described by Mustafa, *et al.*:[7] mp 246–248°, lit.[7] mp 245°; mmp 210–215° with compound IIa.

4. Reaction of 4-Hydroxycoumarin with β-Keto Esters.[6]—Experimental details are given in Table V.

5. Preparation of III.—3-(α,β-Dibromohydrocinnamoyl)-4-hydroxycoumarin (2 g, 0.0044 mol) and 0.44 ml (0.0044 mol) of piperidine were mixed with 5 ml of $CHCl_3$. Excess water was added to the green solution and it was then extracted with 5 ml of $CHCl_3$. Evaporation of the solvent gave a white solid, mp 240–255°. *Anal.* Calcd for $C_{18}H_{11}BrO_4$: C, 58.23; H, 2.97; Br, 21.54. Found: C, 58.57; H, 2.95; Br, 21.38. Infrared bands in 1600-cm^{-1} region were at 1745, 1603, and 1592 cm^{-1}.

6. Preparation of 3-(α,β-Dibromohydrocinnamoyl)-4-hydroxycoumarin.—Bromine (2.1 ml, 0.041 mol) was added dropwise to a mixture of 12 g of 3-cinnamoyl-4-hydroxycoumarin[15] (0.041

(11) In the description of nmr spectra the first figure is the chemical shift in cycles per second, the letter the multiplicity, and the final figure the area under the peak.

(12) By L. E. Swim and associates, The Dow Chemical Co., Midland, Mich.

(13) Uncorrected.

(14) J. Klosa, *Arch. Pharm.*, **288**, 356 (1955).

(15) 3-Cinnamoyl-4-hydroxycoumarin was prepared analogous to 3-cinnamoyl-4-hydroxy-6-methyl-2-pyrone: R. H. Wiley, C. J. Jarboe, and H. G. Ellert, *J. Amer. Chem. Soc.*, **77**, 5102 (1955). The melting point of 213–214° agrees with the value of 212° reported by T. Ukita, M. Matsumoto, and T. Tamura, *J. Pharm. Soc., Jap.*, **72**, 800 (1952).

TABLE IV

EXPERIMENTAL CONDITIONS FOR THE PREPARATION OF PYRAN-2,5-DIONE DERIVATIVES OF 4-HYDROXYCOUMARIN (II)

	R	R′	3-Acyl (g)	Anhydride (ml)	Acid salt (g)	Yield, %
IIa	H	CH_3	CH_3CO (2)	$(CH_3CO)_2O$ (3.3)	CH_3COONa (2)	18[a]
IIb	CH_3	CH_3	CH_3CO (4)	$(C_2H_5CO)_2O$ (6.6)	C_2H_5COOK (4)	22

[a] Yield based on the product described in the Experimental Section.

TABLE V

REACTIONS OF 4-HYDROXY-2-PYRONES AND β-KETO ESTERS ($R'COCHRCOOC_2H_5$) IN TRIFLUOROACETIC ACID

	4-Hydroxy-coumarin, g	β-Keto ester R	β-Keto ester R′	β-Keto ester ml	TFA, ml	Reflux time,[a] hr	Yield, %	Mp, °C	Lit. mp, °C
IIa	16.2	H	CH_3	12.8	20	15	17[c]	246–248	243[d]
IIb	16.2	CH_3	CH_3	14.2	20	15	18	216–217.5	
IIc	16.2	Cl	CH_3	13.8	20	15	19	265–265.7	
IId	16.2	$CH_2C_6H_5$	CH_3	21.1	20	15	11	181.5–184	
IIe	16.2	H	C_6H_5	17.4	20	15	10	216–218	204–205[d]
IIf[b]	15	H	OH	20 g		1	32	264.5–266	248[e] 250[f]

	R	R′	Found, % C	Found, % H	Found, % Cl	Calcd, % C	Calcd, % H	Calcd, % Cl
IIa	H	CH_3	68.18	3.25		68.42	3.51	
IIb	CH_3	CH_3	69.33	3.82		69.42	4.13	
IIc	Cl	CH_3	59.92	2.62	13.17	59.42	2.67	13.52
IId	$CH_2C_6H_5$	CH_3	75.51	4.34		75.47	4.40	
IIe	H	C_6H_5	74.20	3.25		74.49	3.45	
IIf	H	OH	62.61	2.82		62.62	2.61	

[a] After refluxing, the liquid was cooled, diluted with methanol, and the solid was filtered. [b] Malonic acid and lactone in 150 ml of $C_2H_2Cl_4$ at 125° for 1 hr with 15 ml of $POCl_3$. Solvent was removed and residue was extracted with $CHCl_3$. Extracts diluted with MeOH yielding solid, recrystallized from $C_2H_2Cl_4$. [c] Concentration of the filtrate and dilution of the residue with chloroform yielded 5.35 g (33%) of 4-hydroxycoumarin. Further repeated concentrations and crystallization from ethanol resulted in an additional 6.8 g (42%) of 4-hydroxycoumarin. [d] See ref 7. [e] E. Ziegler, H. Junek, and H. Biemann, *Montatsh.*, **92**, 927 (1961). [f] E. Ziegler, H. Junek, and G. Wildtgrube, *ibid.*, **87**, 836 (1956).

mol) and 50 ml of chloroform cooled in ice water. After the addition was complete, the mixture was kept cold for 10 min and then heated to the boiling point; the chloroform was evaporated. The residue was boiled with ethanol, filtered hot, and the precipitate crystallized from acetic acid: yield 13.4 g, 76%. At about 180° the product rearranges to the cyclic dehydrobrominated compound. Ziegler, *et al.*,[16] report a melting point of 295°. *Anal.* Calcd for $C_{18}H_{12}Br_2O_4$: C, 47.81; H, 2.66; Br, 35.37. Found: C, 48.01; H, 2.43; Br, 34.62. The nmr spectra ($CDCl_3$) showed hydrocinnamoyl, 335 d (1.1) ($J \sim 12.2$ cps) and 417 d (0.9) ($J \sim 12.2$ cps); aromatic, 435–492 m (9.2).

7. Effect of Heat on 3-(α,β-Dibromohydrocinnamoyl)-4-hydroxycoumarin.—3-(α,β-Dibromohydrocinnamoyl)-4-hydroxycoumarin (2 g) was heated at 200° in a test tube for 2 min, then cooled and boiled with benzene. Hot filtration gave a solid If, 1.0 g (78%), mp 262–264°. *Anal.* Calcd for $C_{18}H_{10}O_4$: C, 74.48; H, 3.45. Found: C, 74.30; H, 3.36.

8. Reaction of III with Pyridine.—A mixture of 7 g of III (R = Br) and 10 ml of pyridine was refluxed for 1 hr. Evaporation of solvent and work-up as in section 7 gave If. The infrared spectra of section 7 and 8 products are identical.

B. Triacetic Lactone Compounds. 1. Reaction of 3-(α,β-Dibromohydrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone with Pyridine.—3-(α,β-Dibromohydrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone (14 g, 0.037 mol) and 40 ml of pyridine were mixed and, after standing for 0.5 hr, were refluxed for 0.5 hr. The pyridine was then evaporated, methanol was added, and the solid was filtered to give 6.4 g (68%) of V, mp ≈270° with decomposition. *Anal.* Calcd for $C_{15}H_{10}O_4$: C, 70.87; H, 3.94. Found: C, 70.65; H, 3.76.

2. Reaction of 3-(α,β-Dibromohydrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone with Piperidine.—3-(α,β-Dibromohydrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone (20 g, 0.05 mol) and 5 ml (0.05 mol) of piperidine were added to 50 ml of $CHCl_3$ and the mixture was allowed to stand for 0.5 hr. The mixture was diluted with water and the solid IV was filtered, washed with acetone, and crystallized from acetic acid: 11.3 g (68%); mp 265–270° dec, darkening at 185°. *Anal.* Calcd for $C_{15}H_{11}BrO_4$: C, 53.75; H, 3.29; Br, 23.86. Found: C, 54.04; H, 3.35; Br, 23.79. Infrared bands in 1600-cm^{-1} region were at 1739, 1650, and 1628 cm^{-1}.

3. Reaction of IV with Pyridine.—Compound IV (2 g) and 5 ml of pyridine were refluxed for 1 hr. The pyridine was evaporated and the residue was washed with methanol. The product obtained had mp ~280° dec. The infrared of this compound was identical with that of V prepared from 3-(α,β-dibromohydrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone.

4. Preparation of 3-(α,β-Dibromohydrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone.—The method was similar to that used for the coumarin analog: mp 156–158°. *Anal.* Calcd for $C_{15}H_{12}Br_2O_4$: C, 43.29; H, 2.89; Br, 38.43. Found: C, 43.34; H, 2.97; Br, 38.32. The nmr spectra showed ($CDCl_3$) CH_3, 137 s (3); hydrocinnamoyl, 334 d (1) and 409 d (1); CH, 363 s (1); ring CH, 435–470 b (5); OH, 945 s (1).

An A-60 spectrometer was used to record the nmr spectra and the infrared spectra were obtained from a Perkin-Elmer 221G prism-grating spectrometer using Nujol–Fluorolube mulls.

Registry No.—Ia, 16052-69-0; Ib, 16052-70-3; Ic, 16052-71-4; Id, 16052-72-5; Ie, 16052-73-6; If, 16052-74-7; Ig, 16052-75-8; IIa, 2289-06-7; IIb, 2289-07-8; IIc, 16052-78-1; IId, 16052-79-2; IIe, 16052-80-5; IIf, 16052-81-6; III, 16052-82-7; IV, 16052-85-0; V, 16052-8-38; 3-(α,β-dibromohydrocinnamoyl)-4-hydroxycoumarin, 16052-84-9; 3-(α,β-dibromohydrocinnamoyl)-4-hydroxy-6-methyl-2-pyrone, 16109-81-2.

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(16) E. Ziegler, H. Junek, and G. Wildtgrube, *Monatsh.*, **87**, 439 (1956).