(16 l.). Only a small amount of the biologically active material remained in the aqueous phase. The ethyl acetate extract, which was very active in the bioassay, was evaporated to dryness *in vacuo*.

D. Silicic Acid Chromatography.—A mixture of 133 g. of silicic acid[26] and 67 g. of celite was tamped dry into a column 3 × 90 cm. which was washed with successive portions of ethyl ether (75 ml.), ethyl ether–acetone (75 ml.), ethyl ether (50 ml.) and chloroform (100 ml.). The residue from the ethyl acetate extract at *p*H 2 was adsorbed on 15 g. of silicic acid–celite (2:1), and the mixture transferred to the column. The column was developed with chloroform (1 l.), increasing concentrations of from 5 to 28% ethyl acetate in chloroform (2.2 l.), 30% ethyl acetate in chloroform (10.4 l.) and ethyl acetate (1 l.). Seventy-eight 200-ml. fractions were collected.

Evaporation of fractions 17–24 yielded 0.87 g. of a brown oil which was highly active in the bioassay for *d-5* but only slightly active for *d-1*. The active material in this fraction is referred to as bean factor II.

Evaporation of fractions 25–53 yielded 1.14 g. of a brown oil which was highly active in the bioassay for both mutants, *d-1* and *d-5*. The active material in this fraction is referred to as bean factor I. Fractions 54–73 also contained small quantities of bean factor I.

E. Charcoal Chromatography.—Sixty-seven g. of charcoal and 133 g. of celite were slurried in water, poured into a column 4.5 cm. in diameter, packed under a small pressure head of nitrogen to a height of 26 cm. and washed with water. The bean factor II fraction (0.87 g.) from silicic acid chromatography was added in 15 ml. of acetone–water (1:1) to the column which was then developed with 50% acetone in water (1 l.), increasing concentrations of from 60 to 90% acetone in water (0.8 l.) and acetone (1.4 l.). Thirty 100-ml. fractions were collected. Evaporation of fractions 16–23 yielded 0.07 g. of a pale yellow oil containing bean factor II.

F. Countercurrent Distribution.—The fraction from charcoal chromatography containing bean factor II (0.07 g.) was distributed between 10 ml. of the upper phase and 10 ml. of the lower phase of a two phase system resulting from the equilibration of equal volumes of *n*-butyl alcohol and 0.02 *M* ammonium hydroxide–ammonium chloride buffer (*p*H 8). These solutions were introduced into tube O of a countercurrent distribution machine,[27] and ninety-nine transfers were effected in this solvent system. The contents of tubes 16–40, which showed activity in the *d-5* bioassay, were acidified to *p*H 2 with hydrochloric acid (concd.), and the phases were separated. The lower phase was re-extracted with several portions of *n*-butyl alcohol. Evaporation of the combined *n*-butyl alcohol extracts yielded 33 mg. of an almost colorless oil.

G. Isolation of Crystalline Bean Factor II.—The bean factor II fraction (33 mg.) from countercurrent distribution was dissolved in acetone–water (95:5), and the solution was passed over a small charcoal column. The residue (15 mg.) obtained on evaporating the column effluent was extracted with warm ethyl acetate, and the solution filtered. The volume of the filtrate was reduced to 1 ml. in a stream of nitrogen and 1 ml. of petroleum ether was added.[28] A flocculent precipitate separated on standing. It was removed and petroleum ether was again added to incipient turbidity. On standing and cooling a crystalline precipitate separated. Two milligrams of bean factor II was recovered as platelets which melted with decomposition from 250–255°.

Methylation.—N-Nitrosomethylurea (25 mg.) dissolved in ethyl ether was treated with 1 ml. of 50% potassium hydroxide, and the diazomethane generated was distilled into ethyl ether according to a procedure described.[29] Approximately 0.5 mg. of bean factor II was triturated with the diazomethane solution. The solvent and excess diazomethane were removed by evaporation. The solid residues mixed with a small quantity of Florisil[30] were slurried in petroleum ether[28] and added to a Florisil column (1 × 5 cm.). The column was developed with 25% ethyl ether (10 ml.), 75% ethyl ether in petroleum ether (10 ml.), ethyl ether (60 ml.), and 5% ethanol in ethyl ether (60 ml.). The ethyl ether eluate and the first 20 ml. of the 5% ethanol in ethyl ether eluate were combined and evaporated to dryness. The oily residue was dissolved in 10 microliters of chloroform and transferred to a microcell for the determination of infrared absorption spectrum. The methylation of gibberellin A_1 was carried out in a similar manner.

Acknowledgments.—The authors wish to thank Mrs. Joseph Rogers for technical assistance and also Frank H. Stodola, Northern Regional Research Laboratory, U.S.D.A., Peoria, Ill. for a supply of gibberellin A_1 and gibberellic acid, James Merritt of Merck and Co., Inc., Rahway, New Jersey for supplies of gibberellic acid and methyl gibberellate, and Y. Sumiki, Department of Agricultural Chemistry, University of Tokyo, Tokyo, Japan for a supply of gibberellin A_2.

(26) Merck reagent grade obtained from Merck and Co., Rahway, New Jersey.

(27) Model 2-B, H. O. Post Scientific Instrument Co., Maspeth, N. Y.

(28) Skelly Solve B, boiling range 60–80°.

(29) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 165.

(30) A synthetic adsorbent obtained from Floridin Co., Tallahassee, Florida.

LOS ANGELES, CALIFORNIA

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY AND THE INSTITUTO DE QUIMICA AGRICOLA, MINISTERIO DA AGRICULTURA, RIO DE JANEIRO]

Naturally Occurring Oxygen Heterocyclics. IV.[1] The Methylation of Pyronones[2]

BY DAVID HERBST, WALTER B. MORS, OTTO RICHARD GOTTLIEB AND CARL DJERASSI

RECEIVED NOVEMBER 10, 1958

The contradictory reports in the literature on the diazomethane methylation of pyronones are reviewed and it is shown that such treatment of 6-methyl-2,4-pyrononе (triacetic lactone) and 6-phenyl-2,4-pyrononе leads in each case to a chromatographically separable mixture of the 2-methoxy-γ-pyrone and the 4-methoxy-α-pyrone. These results have a bearing on the structures of several naturally occurring pyrones and attention is again directed to the utility of infrared measurements in settling this point.

Recently, we have reported the isolation from different species of rosewood (*Aniba* species) of anibine (I),[3] 4-methoxyparacotoin (II)[3,4] and 5,6-dehydrokavain (III).[4] The skeletal structures were established rigorously by the course of the alkaline degradation, but the alternate isomeric

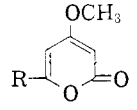
(1) Paper III, P. Crabbé, P. R. Leeming and C. Djerassi, THIS JOURNAL, **80**, 5258 (1958). The present paper should also be considered Part IV in the series "Chemistry of Rosewood." For part III see ref. 4.

(2) The work at Wayne State University was supported by grant number H-2574 from the National Heart Institute of the National Institutes of Health, U. S. Public Health Service, while the investigations in Rio de Janeiro received financial aid from the Conselho Nacional de Pesquisas, Brazil.

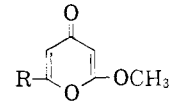
(3) W. B. Mors, O. R. Gottlieb and C. Djerassi, THIS JOURNAL, **79**, 4507 (1957).

(4) O. R. Gottlieb and W. B. Mors, *J. Org. Chem.*, **24**, 17 (1959).

arrangement—the 6-substituted-2-methoxy-γ-pyrone formulation (IV)—was excluded largely on the basis of the infrared spectrum which exhibited a band at 5.77 μ attributed[3] to the lactone ring of I–III. In addition, in the case of 5,6-dehydrokavain (III) it was possible to make a direct comparison[4] with a synthetic product of undisputed structure. A few months ago, there appeared a synthesis[5] of anibine (I) which confirmed our earlier structural assignment, but which suffered from the weakness that the last step involved methylation with diazomethane of 6-(3′-pyridyl)-2,4-pyronone (Vd) and thus could lead either to an α- or γ-pyrone. It is with this latter aspect that the present paper is concerned.



I, R = 3-pyridyl
II, 3,4-(CH_2O_2)C_6H_3—
III, R = C_6H_5CH=CH—



IV

4-Methoxy-α-pyrones (VIb,c) and 2-methoxy-γ-pyrones (VIIb,c) are the respective methyl enol ethers of the two tautomeric forms VIa and VIIa of the parent 2,4-pyronone (Va,b). In spite of extensive work carried out in this area, the course of the diazomethane methylation of such 2,4-pyronones (V) is still the subject of considerable controversy.

The earlier literature on the methylation of 6-methyl-2,4-pyronone (triacetic lactone) (Va)[6] has been reviewed by Arndt and Eistert[7] who favored the 6-methyl-4-methoxy-α-pyrone (VIb) structure for the diazomethane methylation product of triacetic lactone (Va), which in turn was identical with the product derived from the interaction of the silver salt of Va with methyl iodide.

In a subsequent article, Arndt and Avan[8] emphasized that treatment of triacetic lactone (Va) yields only one product (m.p. 86–87°) which was now assigned the alternate 6-methyl-2-methoxy-γ-pyrone (VIIb) expression because of the formation of a hydrochloride. Shortly thereafter, a group of Polish workers[9,10] re-examined this diazomethane methylation in detail and concluded that 6-methyl-4-methoxy-α-pyrone (VIb) (72% yield, m.p. 88–89°, λ_{max}^{EtOH} 280 mμ) as well as 6-methyl-2-methoxy-γ-pyrone (VIIb) (20% yield, m.p. 92–94°, λ_{max}^{EtOH} 240 mμ) are produced in this reaction. The separation of the two isomers VIb and VIIb was accomplished by taking advantage of the fact that γ-pyrones form pyroxonium salts,[11] the hydrochloride of the 2-methoxy-γ-pyrone (VII) being insoluble in ether.[12] In fact Borsche and Gerhardt[13] assigned the 2-methoxy-γ-pyrone structure VIId to yangonin by citing—in addition to other evidence—the observation that the substance formed addition compounds with chloroplatinic and other mineral acids. Borsche's synthesis[14] of yangonin involved as the last step the methylation of the 2,4-pyronone Vc and isolation of *only one* methylation product, identical with yangonin. However Janiszewska-Drabarek[10] showed that both isomeric methoxypyrones VIb and VIIb formed complex salts with chloroplatinic acid, thus weakening Borsche's structural evidence based on salt formation. Indeed, in 1954, Borsche's 2-methoxy-γ-pyrone structure VIId for yangonin was shown to be incorrect[15] since repetition of the methylation of Vc led to both possible methyl ethers VId and VIId, of which the former proved to be identical with yangonin.

In the light of these results which finally seemed to settle the methylation of 2,4-pyronones, it is surprising that Wiley and Jarboe[16] reopened the question by stating that they were unable to repeat the work of the Polish group,[10] that only one isomer (m.p. 89°) was formed in the methylation of triacetic lactone and that this isomer was admixed with unreacted triacetic lactone. The methylation product, even though forming a hydrochloride, was assigned the 4-methoxy-α-pyrone structure VIb on the basis of infrared evidence. No explanation was offered for this discrepancy with the earlier work[9,10] and no reference was made to the important ultraviolet spectral data of the Polish investigators.[9]

Since this confusing situation had a very direct bearing on the structures of the methoxylated pyrones isolated by us,[3,4] it was decided to resolve this question once and for all. Consequently, the methylation of 6-methyl-2,4-pyronone (triacetic lactone) (Va) in ether solution with diazomethane was repeated and the total reaction mixture was subjected to chromatographic separation rather than using the equivocal method of salt formation. Without any difficulty, there was obtained a sharp separation which led to 64% of 6-methyl-4-methoxy-α-pyrone (VIb) (m.p. 86.5–87.5°) and 19% of 6-methyl-2-methoxy-γ-pyrone (VIIb) (m.p. 94–94.5°). The physical constants and ultraviolet spectra were in excellent agreement with the values reported by the Polish investigators[9,10] and there remains no question of the correctness of their results.

Encouraged by this facile chromatographic separation of the two isomers, we directed our attention toward the methylation of 6-phenyl-2,4-pyronone (Vb). This substance has been synthesized by several routes[6b,17] and its methylation has been examined[10] under various conditions, including treatment with diazomethane. In each

(5) E. Ziegler and E. Nölken, *Monatsh.*, **89**, 391 (1958). No direct comparison between natural and synthetic anibine is reported in this paper but this has since been carried out in Prof. Ziegler's laboratory with a sample sent by us, thus establishing conclusively the identity of the two specimens, see E. Ziegler, E. Nölken and H. Bayzer, *ibid.*, **89**, 716 (1958).

(6) For pertinent references on triacetic lactone see (a) J. Collie, *J. Chem. Soc.*, **59**, 609 (1891); (b) F. Arndt, B. Eistert, H. Scholz and E. Aron, *Ber.*, **69**, 2373 (1936); (c) J. A. Berson, THIS JOURNAL, **74**, 5172 (1952).

(7) F. Arndt and B. Eistert, *Ber.*, **68**, 1572 (1935).

(8) F. Arndt and S. Avan, *ibid.*, **84**, 343 (1951).

(9) I. Chmielewska and J. Cieślak, *Przemysł Chem.*, **8**, 196 (1952).

(10) S. Janiszewska-Drabarek, *Roczniki Chem.*, **27**, 456 (1953).

(11) *Cf.* J. N. Collie and T. Tickle, *J. Chem. Soc.*, 710 (1899).

(12) J. Cieślak, *Roczniki Chem.*, **26**, 483 (1952).

(13) W. Borsche and M. Gerhardt, *Ber.*, **47**, 2902 (1914).

(14) W. Borsche and C. K. Bodenstein, *ibid.*, **62**, 2515 (1929).

(15) (a) I. Chmielewska and J. Cieślak, *Roczniki Chem.*, **28**, 38 (1954); (b) I. Chmielewska, J. Cieślak, K. Gorczynska, B. Kontnik and K. Pitakowska, *Tetrahedron*, **4**, 36 (1958).

(16) R. H. Wiley and C. H. Jarboe, THIS JOURNAL, **78**, 624 (1956).

(17) K. Balenkovic and D. Sunko, *Monatsh.*, **79**, 1 (1948); E. Ziegler and H. Junek, *ibid.*, **89**, 323 (1958).

case, only one isomer was encountered and this was considered[10] to be 6-phenyl-4-methoxy-α-pyrone (VIc). Upon repeating this reaction but employing the chromatographic technique mentioned above, there was isolated as the major product 6-phenyl-4-methoxy-α-pyrone (VIc),[18] but in addition there was isolated a small amount of 6-phenyl-2-methoxy-γ-pyrone (VIIc).

As far as differentiating the α-(VI) and γ-(VII)-pyrone isomers is concerned, ultraviolet spectral evidence of the type employed by the Polish workers[9] is satisfactory, provided no additional chromophore is present. In the 6-methyl series (Va), the 4-methoxy-α-pyrone(VIb) exhibited λ_{max}^{EtOH} 280 mμ (log ε 3.80), while the 2-methoxy-γ-pyrone showed λ_{max}^{EtOH} 240 mμ (log ε 4.13). However with additional chromophoric substituents at C-6, as was the case with the naturally occurring α-pyrones I, II[3] and III[4], ultraviolet data cannot be used very effectively in the absence of the other isomer. When both isomers are available, then the one with the longer wave length maximum represents the α-pyrone derivative and this is exemplified with 6-phenyl-4-methoxy-α-pyrone (VIc) (λ_{max}^{EtOH} 314 mμ, log ε 4.13) as compared to 6-phenyl-2-methoxy-γ-pyrone (VIIc) (λ_{max}^{EtOH} 276 mμ, log ε 4.29).

Wiley and Jarboe[16] pointed out that α-pyrones show an infrared carbonyl band near 5.8 μ, while the first carbonyl band in 2-hydroxymethyl-5-hydroxy-6-(α-hydroxypropionyl)-γ-pyrone does not appear until close to 6.0 μ.[15b,19] It was on this basis that these authors attributed (correctly) the 6-methyl-4-methoxy-α-pyrone (VIb) structure to the single product isolated by them in the methylation of triacetic lactone (Va). In view of the confusion in the earlier literature and the recent importance of methoxylated 2,4-pyrononones among natural products, we have summarized the relevant infrared carbonyl absorption data in Table I. Since these include two pairs of isomeric methoxylated α- and γ-pyrones (VIb,c and VIIb,c), there exists no question that the infrared spectral evidence can be used as a secure criterion for differentiating between the possible tautomeric forms of 2,4-pyrononones and between their respective methylation products—the γ-pyrone derivatives (VII) exhibiting their first carbonyl band near 6.0 μ, while α-pyrones absorb near 5.80 μ (somewhat variable depending upon the solvent; see Table I),[20] typical of unsaturated six-membered lactones.

Attention has been called[16] to the fact that the infrared spectrum (potassium bromide pellet) of triacetic lactone (Va) contains a strong band at 5.8 μ, indicating that the substance exists largely as the α-pyrone tautomer VIa. It is interesting to note that in our hands the corresponding 6-phenyl analog Vb appears to exist largely as the γ-pyrone tautomer VIIa in the solid state. However in ethanol solution, the predominant tautomer is the 4-hydroxy-α-pyrone (VIa), since its ultraviolet absorption maximum at 317 mμ closely resembles that (314 mμ) of the methyl ether VIc.

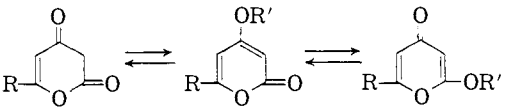
TABLE I

INFRARED ABSORPTION DATA OF METHOXYLATED PYRONES

4-Methoxy-α-pyrones	First CO band, μ	2-Methoxy-γ-pyrones[c]	First CO band, μ
6-Methyl-4-methoxy-α-pyrone (VIb)	5.85[a]	6-Methyl-2-methoxy-γ-pyrone (VIIb)	5.98[a]
6-Phenyl-4-methoxy-α-pyrone (VIc)	5.86[a]	6-Phenyl-2-methoxy-γ-pyrone (VIIc)	5.97[a]
4-Methoxyparacotoin (II)	5.75[b,3]		
Anibine (I)	5.77[a,3]		
5,6-Dehydrokavain (III)	5.84[a]		
Yangonin (VId)	5.85[a]		

[a] Chloroform solution. [b] Nujol mull. [c] Three non-methoxylated γ-pyrones were also measured at the same time: maltol ($\lambda_{max}^{CHCl_3}$ 6.04 μ), kojic acid (λ_{max}^{Nujol} 5.99 μ) and pyromeconic acid ($\lambda_{max}^{CHCl_3}$ 6.04 μ).

In conclusion it can be stated (a) that methylation of 2,4-pyrononones with diazomethane usually yields mixtures of the two possible isomers, the actual proportions depending on the nature of other substituents; (b) that spectral evidence can be used to good advantage in differentiating between the two possible enol ethers; and (c) that all methylated 2,4-pyrononones which have so far been encountered in nature are 4-methoxy-α-pyrones.



Va, R = CH_3
b, R = C_6H_5
c, R = *p*-$CH_3OC_6H_4CH{=}CH-$
d, R = 3′-pyridyl

VIa, R = CH_3 or C_6H_5; R′ = H
b, R = R′ = CH_3
c, R = C_6H_5; R′ = CH_3
d, R = *p*-$CH_3OC_6H_4CH{=}CH-$; R′ = CH_3

VIIa, R = CH_3 or C_6H_5; R′ = H
b, R = R′ = CH_3
c, R = C_6H_5; R′ = CH_3
d, R = *p*-$CH_3OC_6H_4CH{=}CH-$; R′ = CH_3

Experimental[21]

Methylation of 6-Methyl-2,4-pyrononone (Triacetic Lactone) (Va).—Triacetic lactone (Va)[6] (1.26 g., m.p. 188–189°, recrystallized from acetonitrile) was treated at room temperature with an ethereal solution of diazomethane prepared[22] from 21.5 g. of *p*-tolylsulfonylmethylnitrosamide. All solid dissolved within 15 minutes and after 6 hr. at room temperature, the mixture was left at 10° for an additional 16 hr. and was then evaporated to dryness *in vacuo*. The resulting sticky solid (1.58 g., m.p. 55–65°) dissolved in 7 cc. of benzene was placed on a column of 50 g. of Alcoa grade F-20 alumina (deactivated by shaking in hexane suspension with 1.5 cc. of 10% aqueous acetic acid). Elution with 1:1 hexane–benzene, pure benzene and 1:1 benzene–ether furnished 0.90 g. (64%) of 6-methyl-4-methoxy-α-

(18) Here, as well as with 6-methyl-2-methoxy-γ-pyrone (VIIb)—the preparation of which was questioned (ref. 16)—direct infrared comparison with specimens kindly provided by Dr. S. Janiszewska-Drabarek (University of Warsaw) confirmed the identity with her samples (ref. 10).

(19) L. L. Woods, THIS JOURNAL, **77**, 3161 (1955).

(20) It should be emphasized that this refers only to the first absorption band in the carbonyl region. All 4-methoxylated-α-pyrones listed in Table I also show an intense band near 6.05 μ, which has been assigned (ref. 3) to the enol ether grouping.

(21) Melting points were determined on the Kofler block. We are indebted to Dr. H. Kovacs and Miss B. Bach for the infrared measurements and to Mr. K. Hutchinson for the ultraviolet absorption spectra. Several of the spectral measurements were obtained through the courtesy of Dr. J. M. Vandenbelt and associates of Parke, Davis and Co.

(22) T. J. DeBoer and H. J. Backer, *Org. Syntheses*, **36**, 16 (1956).

pyrone (VIb), m.p. 84–86°; two recrystallizations from cyclohexane yielded 0.62 g. of pure material, m.p. 86.5–87.5°, λ_{max}^{EtOH} 280 mμ (log ε 3.80), λ_{min}^{EtOH} 238 mμ (log ε 2.96); $\lambda_{max}^{CHCl_3}$ 5.85(s), 6.05(m) and 7.94(s) μ.

Further elution of the column with 1:1 ether–ethanol led to 0.27 g. (19%) of slightly yellowish crystals (m.p. 91–93°) of **6-methyl-2-methoxy-γ-pyrone** (VIIb); this material was obtained in a colorless state (0.17 g.) after two recrystallizations from cyclohexane and exhibited m.p. 94–94.5°, λ_{max}^{EtOH} 240 mμ (log ε 4.13); $\lambda_{max}^{CHCl_3}$ 5.98(s), 6.17(m) and 7.92(s) μ. These physical and spectral constants are in excellent agreement with those recorded in the literature.[9,10,18]

When the methylation was conducted at 0–5° exactly as described by Wiley and Jarboe[16] and the mixture processed as above by chromatography, there was isolated 52% of 6-methyl-4-methoxy-α-pyrone (VIb) (m.p. 80–84°, raised to m.p. 87–88° after one recrystallization), and 8% of 6-methyl-2-methoxy-γ-pyrone (VIIb) (m.p. 89–93°, raised to 91–93° after one recrystallization). Identity of these products with the ones isolated in the room temperature methylation experiment was established by mixture melting point determination and by coincidence of the relevant infrared and ultraviolet absorption spectra.

Methylation of 6-Phenyl-2,4-pyronone (Vb).—A mixture of 8.0 g. of ethyl benzoylacetate, 50 mg. of pulverized potassium bicarbonate and 50 cc. of nitrobenzene was refluxed for 2 hr., most of the nitrobenzene was distilled at 100° under reduced pressure, ether was added and the solution was extracted ten times with 30-cc. portions of 10% potassium bicarbonate solution. Acidification of the alkaline extracts followed by extraction with chloroform and evaporation left 2.68 g. of **3-benzoyl-4-hydroxy-6-phenyl-α-pyrone**,[6b] m.p. 161–168°, which was used in the next step. The analytical sample was secured from carbon tetrachloride and melted at 169–171°, λ_{Max}^{EtOH} 348 mμ (log ε 3.92), $\lambda_{max}^{CHCl_3}$ 5.72(m) and 6.10(s) μ.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 73.96; H, 4.14; O, 21.90. Found: C, 73.76; H, 4.07; O, 21.60.

6-Phenyl-2,4-pyronone (Vb)[6b,17] (1.0 g.) was heated at 120° for 10 min. with 2.85 cc. of concd. sulfuric acid and 0.15 cc. of water. The solid, obtained upon pouring into ice-water, was collected and washed with cold water and then carbon tetrachloride in order to remove benzoic acid. After drying, the cream-colored solid (0.67 g., m.p. 232–241° dec.) was recrystallized from methyl ethyl ketone whereupon it exhibited m.p. 235–236° (dec.; variable depending upon rate of heating), λ_{max}^{EtOH} 317 mμ (log ε 4.11), λ_{max}^{Nujol} 6.10(s) and 7.90(s) μ.

Anal. Calcd. for $C_{11}H_8O_3$: C, 70.21; H, 4.29. Found: C, 70.50; H, 4.40.

The methylation of 0.57 g. of 6-phenyl-2,4-pyronone was performed exactly as described above for triacetic lactone except that the reaction mixture was left at room temperature for 16 hr. Chromatography of the total reaction product (m.p. 112–121°) on 20 g. of Alcoa grade F-20 alumina (deactivated with 0.6 cc. of 10% aqueous acetic acid) and elution with benzene gave 0.33 g. of **6-phenyl-4-methoxy-α-pyrone** (VIc), m.p. 123–132°, raised to m.p. 129.5–131.5°[18] upon further recrystallization from cyclohexane; λ_{max}^{EtOH} 314 mμ (log ε 4.13); $\lambda_{max}^{CHCl_3}$ 5.86(s), 6.10(s) and 6.40(s) μ).

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 71.28; H, 4.98; O, 23.74; OCH_3, 15.35. Found: C, 71.12; H, 5.08; O, 23.56; OCH_3, 15.13.

In a second experiment, where methylation of 0.42 g. of Vb gave 0.36 g. of 6-phenyl-4-methoxy-α-pyrone (VIc) (m.p. 125–130°), further development of the chromatogram column with ether and with chloroform yielded 60 mg. of crude **6-phenyl-2-methoxy-γ-pyrone** (VIIc), m.p. 84–112°. After evaporative distillation at 150° and 0.02 mm. followed by three recrystallizations from isopropyl ether, there was obtained 33 mg. of the colorless, analytical sample, m.p. 112.5–114.5°, λ_{max}^{EtOH} 276 mμ (log ε 4.29), $\lambda_{max}^{CHCl_3}$ 5.97(s), 6.10(s) and 6.20(s) μ.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98; O, 23.74; OCH_3, 15.35. Found: C, 71.51; H, 5.00; O, 23.45; OCH_3, 14.90.

DETROIT, MICHIGAN
RIO DE JANEIRO, BRAZIL

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

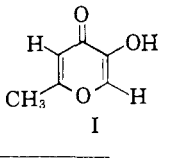
Structure of the Compound Obtained by Reaction of Acrylonitrile with α-Deoxykojic Acid

BY CHARLES D. HURD AND SWIATOSLAW TROFIMENKO[1]

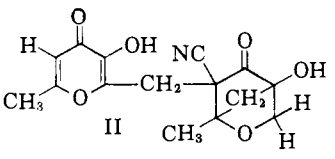
RECEIVED OCTOBER 29, 1958

The major product, "D-I," from the reaction of α-deoxykojic acid with acrylonitrile has been investigated. The structure best fitting the evidence is 2-(3-hydroxy-4-oxo-6-methyl-γ-pyran-2-yl)-methyl-3-oxo-4-hydroxy-1-methyl-6-oxabicyclo-[2.2.1]heptane-2-carbonitrile. Reasons are offered for eliminating other less suitable structures.

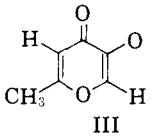
It was shown earlier[2] that some 3-hydroxy-1,4-pyrones condense abnormally with acrylonitrile and other acrylic derivatives to yield products consisting of two molecules of the hydroxypyrone and one of the acrylic moiety. This paper deals with the structure of compound D-I, $C_{15}H_{15}NO_6$, the major product from the reaction of α-deoxykojic acid (I) and acrylonitrile. Of the more plausible structures, II agrees best with the evidence at hand and is tentatively proposed as representing D-I. For brevity in presentation of structures to follow, the two radicals from the enol and keto forms of I will be referred to as III and IV, respectively.



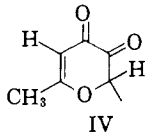
I



II



III



IV

D-I was a high-melting white solid, quite insoluble in ether, chloroform, ligroin, ethyl acetate and water, very sparingly soluble in alcohol, and moderately soluble in pyridine and dimethylformamide as well as dilute aqueous solution of alkali, ammonia or 10% sodium carbonate. The anion of D-I was yellow in solution, but the solid sodium salt was white; D-I was insoluble in saturated sodium bicarbonate at room temperature, but it dissolved when the suspension was heated on a steam-bath.

(1) Allied Chemical and Dye Corporation Fellow, 1957–1958.

(2) C. D. Hurd, R. J. Sims and S. Trofimenko, THIS JOURNAL, **81**, 1684 (1959).