Anal. Calcd. for $C_{10}H_{16}NOCl$ (blue); N, 6.94; Cl, 17.58. Found: N, 6.78; Cl, 17.87.

Anal. Calcd. for $C_{10}H_{16}NOCl$ (white): Cl, 17.58. Found: Cl, 17.20.

Hydrogenation of Spiro(4,5)deca-6-ene.—The olefin (7 g., 0.052 mole, n^{25}_D 1.4856, b.p. 184° (735 mm.), d^{20}_4 0.8995; M_D 43.53 (calcd.), 43.62 (found)), 50 ml. of heptane and 0.5 g. of Baker PtO_2 catalyst was shaken for 7 hours at 66° and 2 atm. of hydrogen. It absorbed 97.4% of the theoretical amount of hydrogen. The platinum was removed by filtration and the filtrate was distilled to yield 5.1 g. (73%) of hydrocarbon, b.p. 87° (40 mm.), n^{25}_D 1.4686. Its infrared absorption spectum is identical with that of spiro(4,5)decane, n^{25}_D 1.4687, b.p. 97° (50 mm.).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Anomalous Reactions of Kojic Acid and Related Compounds with Acrylonitrile and Acrylic Ester

BY CHARLES D. HURD, REX J. SIMS[1] AND SWIATOSLAW TROFIMENKO[2]

RECEIVED SEPTEMBER 10, 1958

Some 3-hydroxy-1,4-pyrones satisfying certain structural requirements were found to undergo anomalous reactions with acrylonitrile and methyl acrylate. The scope and conditions of the former reaction have been investigated in some detail.

The well-known reactions of phenols with acrylonitrile[3] or acrylic esters in the presence of base normally involve addition at the phenolic oxygen; but some phenols, notably phloroglucinol, resorcinol[4] or 2-naphthol[5] that are capable of keto–enol tautomerism undergo cyanoethylation ortho to the phenolic hydroxyl. Such a cyanoethylation is presumably through the anion of the keto form, since ketones containing α-hydrogens are cyanoethylated at their α-positions.

Kojic acid (Ia) is phenolic, and under alkaline conditions is known to react through either of the resonance forms of its anion.[6] Cyanoethylation might have been expected, therefore, and indeed a claim was made[7,8] for such a reaction by Woods but this claim was proved invalid.[9]

We have discovered, however, that kojic acid does react readily with acrylonitrile, but the reaction is far from a simple cyanoethylation. The product, labeled "compound A," melted with decomposition at 261–262°. It analyzed for $C_{15}H_{14}O_9$ and presented an intriguing structural problem.

Compound A gave a positive ferric chloride enolic test and could be titrated as a weak monobasic acid. It could be acetylated and benzoylated. It was inert toward the usual carbonyl reagents and yielded tars with a number of other reagents (thionyl chloride, bromine, sodium bromoacetate, methyl iodide and silver oxide, succinic anhydride and sodium succinate, phosphorus pentachloride, thionyl chloride). Its infrared spectrum (Fig. 1) showed a strong hydroxyl band at 2.94, carbonyl bands at 5.63 and 5.78, along with pyrone bands at 6.02, 6.18 and 6.36 μ.

The difficulty in approaching the structure of A lay in the absence of nitrogen and presence of many oxygens in the molecule. With nitrogen absent it would obviously be troublesome to determine which part of the molecule had arisen from the original acrylonitrile. The band at 5.63 μ suggested a γ-lactone and support for this contention was found on isolating a material by slight modification of the conditions of reaction, which contained labile nitrogen and had carbonyl bands at 5.76 and 5.93 μ. When this material was allowed to stand with concentrated acid at room temperature, crystals of A separated. The quantity of material was too small for anything but spectral study, but it is safe to assume that it is a direct precursor of A, probably an imido lactone that changed to the lactone itself on hydrolysis.

As the lactonization seemed to involve reaction between the nitrile group and a hydroxymethyl group, it appeared promising to circumvent the lactonization by the use of an appropriate derivative of kojic acid incapable of such reaction, and from which the results could be extrapolated to kojic acid.

α-Chloro-α-deoxykojic acid (Ib) was selected first since it was accessible. On reaction with acrylonitrile it yielded a well defined material, called compound C. Its infrared spectrum showed bands at 3.03, 4.38, 5.77, 6.12 with shoulder at 6.07 and 6.24 μ. Of particular significance was the presence of the nitrile band at 4.38 and the absence of the lactone band at 5.63 μ. The compound was difficult to purify in view of its sparing solubility in most solvents. After recrystallization from boiling acetic acid it analyzed for $C_{15}H_{13}Cl_2NO_6$, although carbon was 0.7% high and nitrogen 0.5% low, indicating some solvolysis during purification.

This result did support the initial hypothesis that loss of nitrogen in the formation of A was caused by lactonization and that the hydroxymethyl group is not necessary for the abnormal reaction with acrylonitrile. To test the generality of this anomalous reaction several α-keto enols were prepared and in particular a number of 3-hydroxy-1,4-pyrones, since this was apparently the nucleus responsible for the unusual course of reaction.

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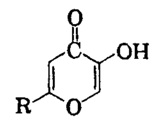
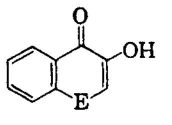
The first compound in this series was α-deoxykojic acid (Ic). As expected, it reacted with acrylonitrile and yielded a new compound, called D-I, the infrared spectrum of which was very similar to that of C. Its empirical formula was $C_{16}H_{16}NO_6$. Like A, it was high melting and was generally insoluble, except in alkali.

The next compound tested was pyromeconic acid (Id). It reacted satisfactorily with acrylonitrile and gave a compound, $C_{13}H_{11}NO_6$, called F. This material was analogous to D-I but it was more soluble and lower melting.

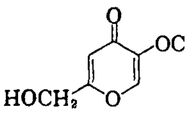
The remainder of the compounds tested all failed to react with acrylonitrile under comparable conditions. The starting materials were recovered as such almost quantitatively. This included methyl kojate (II), 6-propyl-α-deoxykojic acid (III), 6-bromo-α-deoxykojic acid, 3-hydroxychromone (IVa), 3-hydroxythiachromone (IVb), 2-hydroxy-1,4-naphthoquinone and tropolone (V).



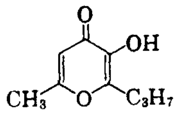
Ia, R = CH_2OH
b, R = CH_2Cl
c, R = CH_3
d, R = H



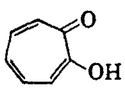
IVa, E = D
b, E = S



II



III



V

Since compounds of structure I gave a positive reaction it may be assumed that the essential parts of its structure are the free hydroxyl and the adjacent hydrogen atom.

Compound D-I was selected for more detailed study since its precursor (Ic) was readily available and was devoid of the interfering alcoholic hydroxyl group.

Although the stoichiometry of the reaction indicated that only α-deoxykojic acid and acrylonitrile were the reactants, it was necessary to show that the reaction was independent of the nature of the base or the solvent employed. In the preliminary study it was established that formation of A proceeds readily in the presence of one-half equivalent of base but not with one full equivalent, also that one-half equivalent of Triton B gives the same results as the corresponding amount of sodium methoxide. The formation of D-I was investigated under the following conditions: 1. A procedure that will be referred to as the "standard procedure" with methanol as the solvent and one-half equivalent of sodium methoxide as base. D-I was formed rapidly and in good yield. This procedure also was used in preparing A. 2. With aqueous ethanol as solvent and one-half equivalent of potassium hydroxide, D-I was the only detectable product and in fair yield. 3. Using methanol as solvent and 0.1 equivalent of sodium methoxide D-I was still the only product isolated; however, reaction was much slower than in procedure 1. 4. No solvent was used at all, except for excess of acrylonitrile, and with only a trace of sodium methoxide. These conditions resemble most closely those of normal cyanoethylation of phenols. Again only D-I was isolated, but a prolonged reaction time was required.

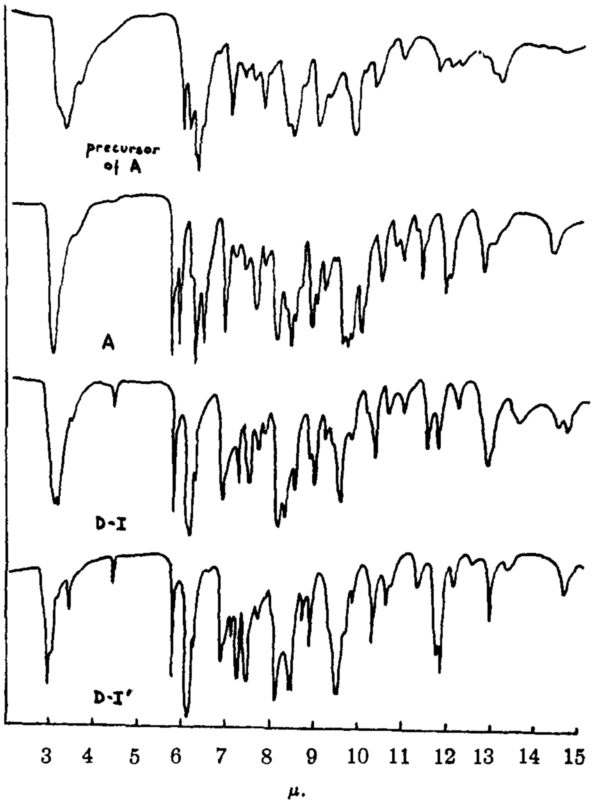


Fig. 1.—Infrared spectra of selected compounds.

Although the yields in procedures 2, 3 and 4 were inferior to those in procedure 1, no attempts were made to achieve optimum yields under these conditions. Instead the purpose was to see if the solvent or base affected the nature of the product; it can be considered established that they do not.

Actually, D-I is not the only product formed in this reaction; when procedure 1 was run on a larger scale one-tenth as much of a more soluble, isomeric compound, D-I', was isolated. Its infrared spectrum was similar to that of D-I. Also it was enolic like D-I and the other abnormal reaction products.

Treatment of α-deoxykojic acid with methyl acrylate under conditions similar to the reaction with acrylonitrile produced two compounds, E-I and E-I', in ratio of about 10:1. E-I was a crystalline solid more soluble and lower melting than D-I. It gave a positive ferric chloride test and contained the following characteristic bands in the infrared: sharp OH bands at 2.87 and 3.06, weak CH bands at 3.26, 3.38 and 3.43, carbonyl band at 5.77 and a strong band at 6.13 along with a medium band at 6.24 μ. The analysis was in good agreement for $C_{16}H_{16}O_6$. Presence of methanol on hydrolysis was established experimentally.

E-I' had a similar spectrum to that of E-I but its analysis did not fit any simple formula.

The work on the structure of these several products will be reported in papers to follow.

Experimental

Materials.—Reported procedures with only minor modifications were used for the synthesis of methyl kojate.[10] 6-propenylkojic acid,[11,12] 6-bromo-α-deoxykojic acid.[13] α-deoxykojic acid,[14] 6-propyl-α-deoxykojic acid,[14] 3-hydroxychromone,[15,16] 3-hydroxythiachromone,[17] 2-hydroxy-1,4-naphthoquinone,[18] tropolone[19,20] and pyromeconic acid.[21,22]

Infrared spectra were taken on a Baird double-beam recording spectrophotometer (sodium chloride prism) using potassium bromide pellets.

Compound A.—A mixture of 8.0 g. of kojic acid (0.056 mole), 1.5 g. of sodium methoxide (0.028 mole) (or 0.028 mole of Triton B) and 12 cc. of redistilled acrylonitrile, added in that order, was refluxed in 80 cc. of methanol for one hour. The clear yellow solution darkened gradually to a reddish solution which was acidified with concentrated hydrochloric acid (color lightened) and evaporated on a steam-bath in an air stream. To the residue 30 cc. of 20% hydrochloric acid was added. The mixture was cooled, stirred, filtered and the solid was washed with cold 2-propanol until the washings were colorless. The yield of crude material, dec. 255–257°, was 5.7 g.

On recrystallization from methanol (100 cc. of boiling methanol saturated with A deposited on cooling 310 mg. of A) a product, m.p. 261–262° dec., was obtained. An alternate route to purify A was through its sodium or ammonium salts, from which A could be readily recovered on acidification.

Anal. Calcd. for $C_{15}H_{14}O_9$: C, 53.30; H, 4.15. Found: C, 52.97; H, 4.34.

If equivalent amounts of kojic acid and sodium methoxide are taken in the above reaction the only effect is prompt precipitation of sodium kojate. Compound A then is not formed. The concentration of the sodium methoxide should be examined carefully since titration of some commercial samples that we tested indicated material that might have been the dimethanolate, $CH_3ONa \cdot 2CH_3OH$.

The Precursor of A (the Imido Lactone).—Ten grams of kojic acid, 20 cc. of redistilled acrylonitrile and 4 pellets of potassium hydroxide were refluxed in 125 cc. of methanol for 12 hr. A small amount of precipitate (about 30 mg.) had separated at that time, which was filtered off. Acidification of the filtrate and evaporation of the solvent resulted in a black tar. The precipitate contained nitrogen by sodium fusion. Its infrared spectrum was significantly different from that of A. A portion of the precipitate was dissolved with concentrated hydrochloric acid; after 15 hr. the solution was evaporated by blowing air over the surface. Water was then added giving rise to crystals after standing overnight. The infrared spectrum of this material was identical with that of authentic A.

Compounds D-I and D-I′.—1. α-Deoxykojic acid (25.2 g., 0.2 mole) was dissolved in 150 cc. of hot methanol. To the solution was added sodium methoxide (5.4 g., 0.1 mole) in 100 cc. of methanol and the resulting solution was refluxed for an hour with 35 cc. of redistilled acrylonitrile. The yellow solution was acidified with concentrated hydrochloric acid, 50 cc. of water was added, and the decolorized solution was evaporated in an air stream at 20–25° overnight. The first crop of white precipitate weighed 20.8 g., m.p. about 262–264° dec.; the second crop 3.5 g., making a total yield of 24.3 g. (80%). The two crops of D-I had identical infrared spectra.

On further standing, 2.13 g. (7%) of another substance (D-I′) separated in two crops, m.p. 207–217°. The crystalline form was quite different from that of D-I, as was its spectrum; D-I′ was recrystallized from methanol, giving white crystals melting at 221–222°.

Since D-I was sparingly soluble in most solvents it was purified by repeatedly dissolving it in alkali, treating with Norit, filtering and acidifying. Pure D-I was a white solid with an ill-defined melting point, darkening somewhat around 250° and decomposing rapidly around 262°. Instances of lower decomposition temperature with apparently pure material were also encountered.

Anal. Calcd. for $C_{15}H_{15}NO_6$ (D-I): C, 59.02; H, 4.92; N, 4.59. Found: C, 59.02; H, 4.77; N, 4.88.

Anal. Calcd. for $C_{15}H_{15}NO_6$ (D-I′): C, 59.02; H, 4.92; N, 4.59. Found: C, 58.78; H, 4.94; N 4.91.

2. α-Deoxykojic acid (26 g., 0.20 mole) was treated with potassium hydroxide (5.7 g., 0.10 mole) in 125 cc. of water. To the refluxing solution 35 cc. of acrylonitrile was added and the heating was continued. Since phase separation occurred, 10 cc. of ethanol was added to effect miscibility. After an hour of refluxing the solution was acidified with hydrochloric acid and cooled. The precipitate which came down on standing was washed with water, methanol and acetone. Part of it dissolved, being presumably unreacted α-deoxykojic acid. After drying, the product had an infrared spectrum identical with that of D-I, m.p. 258–260° dec., yield 16.3 g. or 48%.

3. α-Deoxykojic acid (2.5 g., 0.02 mole) was heated on a steam-bath under reflux with acrylonitrile (10.6 g., 0.2 mole) and a few mg. of sodium methoxide for 10 hours. The precipitated white solid was separated and washed thoroughly with methanol. The yield of D-I. identified spectrally, was 1.9 g. or 63%, m.p. 255–257° dec.

4. Two grams of α-deoxykojic acid was refluxed in 40 cc. of methanol with 0.08 g. of sodium methoxide and 5 cc. of acrylonitrile for 18 hr. Some solid separated. The mixture was acidified, cooled and filtered; yield 1.22 g. The mother liquor was evaporated, anhydrous sodium sulfate was added and the residue was extracted with boiling ethyl acetate. Evaporation of the solvent yielded a sirup from which a white solid (0.16 g.) separated on trituration with methanol. This also was D-I, raising the yield to 56%. Next, crude D-I′ was obtained from the mother liquor in two crops, a total of 0.23 g. or 9%, m.p. 207–217°. The materials were identified by comparison of the infrared spectra.

Compound C, from α-Chloro-α-deoxykojic Acid.—Following procedure 1, a 62% yield of this compound was obtained, m.p. 235–237° dec. After recrystallization from methanol, then from acetic acid, material of m.p. 243–244° dec. was obtained.

Anal. Calcd. for $C_{15}H_{13}Cl_2NO_6$: C, 46.89; H, 3.41; N. 3.65. Found: C. 47.60; H, 3.39; N, 3.17.

Compound F, from Pyromeconic Acid.—Procedure 1 was followed. A viscous resin was obtained after the solvent was removed from the acidified solution. The resin was treated with saturated sodium bicarbonate solution until alkaline (carbon dioxide evolved) and then acidified with acetic acid. The precipitate, after washing with water and methanol, darkened around 200° and decomposed around 208°; yield 56%. The melting point, after recrystallization from ethanol was 209° dec.

Anal. Calcd. for $C_{13}H_{11}NO_6$: C, 56.32; H, 4.01; N, 5.07. Found: C, 56.46; H, 3.88; N, 4.80.

Non-reactions. 6-Bromo-α-deoxykojic Acid.—A material was obtained (procedure 1) which, on recrystallization with concomitant losses, gave 50% of the starting marterial as indentified by identity of infrared spectra and mixed m.p. determination (m.p. 181–183°, mixed m.p. 181–183°).

6-Propyl-α-deoxykojic Acid.—Following procedure 3, the only solid obtained was the starting material in 85% yield as identified by comparison of infrared spectra.

2-Hydroxy-1,4-naphthoquinone.—Procedure 1 was followed, but complete solution of the materials could not be achieved even though some water was added. On processing, 90% of the starting materials was recovered, identified by comparison of infrared spectra, m.p. 192–193° (lit. 191–192°).

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3-Hydroxychromone.—Following procedure 1, 65% of the starting material was recovered, m.p. 178–179.5° (lit. 181°) and identified by comparison of infrared spectra. The yield was based only on recrystallized material.

3-Hydroxythiachromone.—Following procedure 1 only the starting material was recovered, m.p. 167–169° (lit. 172°), in about 90% yield and identified by comparison of infrared spectra.

Tropolone.—Procedure 3 was followed and a material was obtained that was thought to be a tropylium chloride as it gave a red-colored mineral acid test with Davidson AII indicator,[23] positive ferric chloride test, immediate precipitate with silver nitrate solution, and had an infrared spectrum typical of ionic compounds of pyronium type; *i.e.*, the spectrum was singularly devoid of well-defined bands, except for a sharp doublet at 6.26 and 6.29 μ, and very strong and broad hydroxyl absorption from 3.00 μ on. The simplicity of the spectrum of tropylium salts has been commented on earlier.[24,25] The yield of recovered tropolone, as hydrochloride, was 85%.

Compounds E-I and E-I′ from α-Deoxykojic Acid and Methyl Acrylate.—Two products were obtained following procedure 1, but substituting 40 cc. of methyl acrylate for acrylonitrile. The first crop of 21.5 g. was E-I; m.p. after several recrystallizations from methanol was 219–220°.

Concentration of the mother liquor yielded 6.2 g. of E-I′. Recrystallization from methanol gave crystals that on slow heating melted at 110–115°, then resolidified and melted at 210–212°. Placed on a block at 205° the material decomposed, but at 170° it melted, resolidified and remelted around 200°. It seemed to be impure material and analysis also was unsatisfactory for any reasonable formula.

Anal. Calcd. for $C_{16}H_{18}O_8$ (E-I): C, 56.81; H, 5.36. Found: C, 56.68; H, 5.12. Calcd. for $C_{16}H_{18}O_8$ (E-I′): C, 56.81; H, 5.36. Calcd. for $C_{16}H_{20}O_9$: C, 53.9; H, 5.62; for $C_{15}H_{16}O_8$: C, 55.55; H, 4.97. Found: C, 55.35; H, 5.73.

Acknowledgment.—Analysis of A was by Miss M. Nielson. All other analyses were by Miss H. Beck.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CIBA PHARMACEUTICAL PRODUCTS INC., AND THE INSTRUMENT DIVISION, VARIAN ASSOCIATES]

The Stereochemistry of Steroidal Sapogenins. III. N.m.r. Spectra

BY WILLIAM E. ROSEN, J. BENJAMIN ZIEGLER, ANTHONY C. SHABICA AND JAMES N. SHOOLERY

RECEIVED JULY 14, 1958

Nuclear magnetic resonance spectra of steroidal sapogenins have been used to study the side chain stereochemistry. The spectra are consistent with structures previously proposed, in part on the basis of mechanistic considerations and in part on the basis of optical rotatory and chemical data.

The side chain stereochemistry of steroidal sapogenins has attracted considerable attention since Scheer, Kostic and Mosettig[1] proved that sapogenins of the so-called "normal" and "iso" series differed in absolute configuration at C-25. Only two of the four possible isomers in each series are known, and various attempts have been made to assign appropriate structures. Two sets of assignments were based on mechanistic considerations of the acid-catalyzed ring closures of the pseudosapogenins: (1) *trans*-addition of the proton and the C-26 oxygen across the C-20, C-22 double bond,[2] and (2) two-stage addition of the proton and C-26 oxygen across the C-20, C-22 double bond, with the proton addition resulting in a stabilized carbonium ion and the subsequent cyclization to form ring F always resulting in an equatorially oriented C-27.[3] Several other suggestions have been made, but only the set based on optical rotations[4] has also received serious consideration recently.

The elegant work of Callow and Massy-Beresford[5] eliminated from consideration the set which required equatorial C-27 groups in all structures, but rigorously established only that the thermodynamically stable spiroketals of the "normal" (25L) and the "iso" (25D) series did not differ at C-20 or at C-22. The greater stability of the "iso" series sapogenins permitted the assignment of structure I to sarsasapogenin ("normal" series sapogenin) and structure II to smilagenin ("iso" series sapogenin), assuming for ring F the chair form shown. The spiroketal isomer within the "normal" series which is thermodynamically less stable, but is kinetically favored under acid cyclizing conditions, has structure III according to both the "*trans*-addition" and "optical rotation" hypotheses. The two hypotheses differ, however, on the assignment of structure to the corresponding less stable spiroketal isomer in the "iso" series. Structure IV is expected according to the principle of *trans*-addition, and structure V was proposed on the basis of optical rotations.

We have examined the nuclear magnetic resonance spectra[6] of sarsasapogenin, neosarsasapogenin,[2a,7] smilagenin, neosmilagenin, diosgenin and

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[6] Spectra were taken on deuterated chloroform solutions with a Varian Associates V-4300-C High Resolution Nuclear Magnetic Resonance Spectrometer operating at 60 mc. for hydrogen nuclei in a magnetic field of 14,096 gauss. Spectra were calibrated by the audio side band method with an accuracy of approximately ±1 c.p.s.

[7] (a) Various names have been used for these metastable spiroketal structures. We have retained the "neo" prefix in the absence of general agreement on nomenclature. (b) NOTE ADDED IN PROOF: The use of "cyclopseudosapogenins"[2b] for the unstable isomers has steadily gained favor, and promises to become generally accepted. We therefore withdraw our "neosapogenin" terminology in favor of "cyclopseudosapogenin."