acetic acid in a stream of nitrogen. The residue crystallized from cyclohexane as needles of IX, m. p. 120–121°.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.04; H, 6.07.

Mixtures of these needles with those melting at 105–106° melted between 106 and 121°. The 105–106° melting needles thus appear to be mixed crystals containing IX.

1,2,3,6-Tetrahydro-*cis*-3-methyl-*trans,cis*-phthalic Anhydride, X.—The mother liquor from the needles melting at 105–106° was concentrated and crystallized from hexane. In this way 0.53 g. of fine needles was secured which melted at 125–126°. This product appeared homogeneous. Titration of 0.4753 g. required 5.67 ml. (calcd. 5.73 ml.) of 1 *N* sodium hydroxide. The titration solution was acidified with 0.5 ml. of concd. hydrochloric acid and the mixture extracted with ether. The ether layer was evaporated and the residue crystallized from benzene. In this way 0.38 g. (72%) of crude acid, m. p. 115–120°, was obtained. Recrystallization from benzene gave a colorless product, m. p. 127–128°.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.66; H, 6.57. Found: C, 58.82; H, 6.57.

Cyclizing this acid with acetic anhydride gave needles melting at 133°, believed to be pure X. Mixtures with 125–126° melting needles all melted between 126 and 133°.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.11; H, 6.09.

The product melting at 125–126° thus indicated to be mixed crystals containing X and, presumably, IX was also prepared in 1% yield by the reaction of pure *cis*-piperylene (4.5 g.), fumaric acid (5.8 g.) and 25 g. of acetic anhydride at 100–124° during twenty-four hours. The volatile product m. p. about 108° was separated from the polymeric materials by sublimation at 0.15 mm. The only product isolated was that melting at 125–126° though small amounts of unidentified substances were present.

Isomerization of IX and X.—These anhydrides when heated to 280° with traces of dibutylaniline rearranged as did I to form a mixture of I and IV. Hydrolysis of this mixture yielded the acids, melting at 156–158° and 161–162°, respectively. Anhydrides IX and X also isomerized merely by heating. Thus during ten minutes at 150° the melting point of IX dropped 16° and that of X dropped 12°. Similar treatment of I resulted in no change in the melting point. In view of the tendency of IX and X to isomerize it is somewhat surprising that they could withstand distillation. Therefore, a repetition of the reaction (this time conducted for six hours at 78–94°) of *trans*-piperylene, fumaric acid and acetic anhydride was run. Low pressure evaporation of the acetic anhydride provided the theoretical yield of crude anhydride, m. p. 105–106°. This was fractionally crystallized from mixtures of benzene and cyclohexane. The higher melting anhydride is much more soluble in these solvents than the other isomer and benzene is a much better solvent for both of them than is cyclohexane. The highest melting point for a sample rich in IX was 115° (or at 117–119° mixed with IX) and this was from pure benzene. Similarly the highest melting point for a fraction rich in X was 126° (or at 128–130° mixed with X) and this was from pure cyclohexane. Only a trace of material melting below 100° was secured after 4 stages of the fractionation. Mixtures of IX with X melted at about 104–108° over a wide range of intermediate concentrations.

Summary

1. The well-known maleic anhydride adduct of *trans*-piperylene, m. p. 63°, was found to have the *cis,cis,cis* configuration.

2. The two *trans* anhydride isomers, m. p. 121° and 133°, were both synthesized by the reaction of the *trans* diene with the *trans* dienophile fumaric acid. The higher melting anhydride corresponds to *cis*-piperylene from which it was also prepared.

3. These three anhydrides rearrange in the presence of an organic base to the fourth possible racemic anhydride, m. p. 41°, which was also synthesized by the reaction of *cis*-piperylene with maleic anhydride.

4. The configuration of the Diels–Alder adducts reported on were found to be those predicted on the basis of Alder Rules I and II.

5. *cis*- and *trans*-3-methyl and *cis*- and *trans*-4-methylhexahydro-*cis,cis*-phthalic anhydrides were synthesized.

Brecksville, Ohio Received May 16, 1949

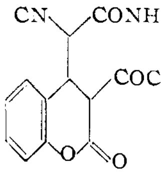
[Contribution from the School of Chemistry of the University of Minnesota]

Condensations of 3-Acetocoumarin with Amides, and with Amides and Ketones[1]

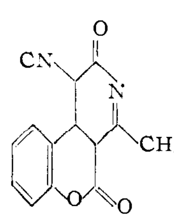
By C. F. Koelsch and S. A. Sundet

Contrary to expectation and to published report,[2] 3-acetocoumarin does not react with cyanoacetamide to yield a normal Michael product (I) or the cyclized anhydro-derivative (II) of such a substance. Instead, two molecules of 3-acetocoumarin unite with a molecule of ammonia furnished by the amide to form III.

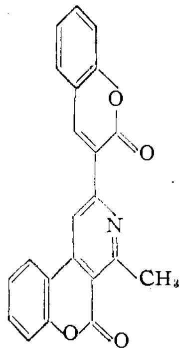
No plausible reason can be advanced for the preferential reaction of the acceptor (3-acetocoumarin) with the ketonic addendum (3-acetocoumarin), rather than with cyanoacetamide acting as an addendum.[3] But such preference appears to be characteristic. When 3-acetocoumarin is treated with cyanoacetamide and a different ketonic addendum, the latter substance



I



II



III

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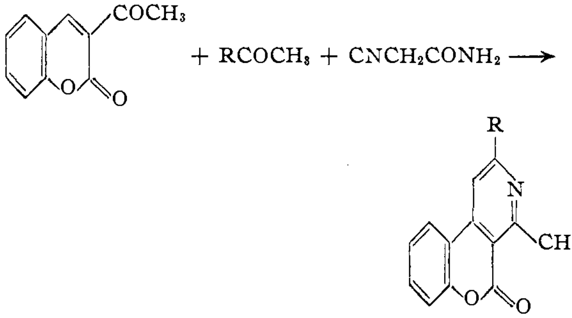
[1] From the Ph.D. Thesis of Sherman A. Sundet, June 1948.

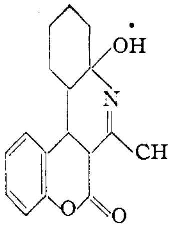
[2] Sastry and Seshadri, *Proc. Indian Acad. Sci.*, **16A**, 29 (1942).

[3] Speculations regarding this and other phases of the mechanism of the reaction are found in Dr. Sundet's Thesis.

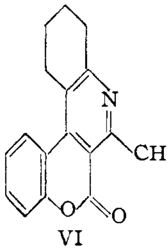
takes part in the reaction, the cyanoacetamide simply furnishes ammonia, and there is formed a 2,4-disubstituted 5-keto[1]benzopyrano[3,4-c]pyridine (IV). Examples of the reaction have been studied involving acetone (R is CH_3, yield of IV 32%), methyl ethyl ketone (R is C_2H_5, yield of IV 42%), and acetophenone (R is C_6H_5, yield of IV 21%). No pure product has been isolated when the ketone used is diethyl ketone, benzalacetone, or propiophenone. But cyclohexanone furnishes a 46–48% yield of V, and this substance is converted into VI when it is heated with hydrochloric acid.



IV



V



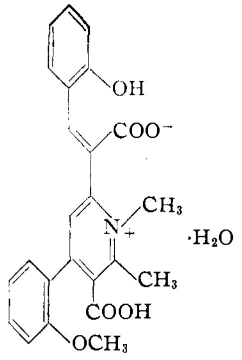
VI

3-Propionylcoumarin reacts with cyanoacetamide, but the product, whose structure is still not determined, is not analogous to III. However, 3-aceto-8-methoxycoumarin reacts with cyanoacetamide forming a dimethoxy derivative of III, and it also reacts with acetone and cyanoacetamide forming a monomethoxy derivative of IV.

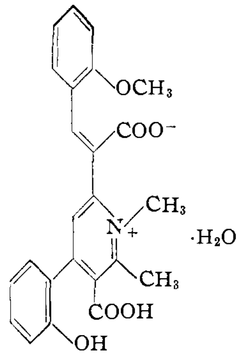
Successful reaction of 3-acetocoumarin has not been achieved when alcoholic ammonia or ammonium acetate is used in place of cyanoacetamide. Early experiments indicated that acetamide could not be used in place of cyanoacetamide, but later it was found that acetamide containing a little ammonium acetate, formamide containing ammonium formate, crude stearamide, urea, or malonamide are as suitable as cyanoacetamide for furnishing ammonia for the condensation.

Proof of structure of the compound represented by III was difficult. It is a remarkably stable substance, and can be recovered unchanged after treatment with boiling 10% sodium hydroxide for two hours, or with boiling 70% sulfuric acid for five hours, or with 40% hydrobromic acid at 250° for six hours. It is not affected by carbonyl reagents, by boiling acetic anhydride, or even by four hours treatment with phosphorus pentachloride at 200°. Nitration gives a product too insoluble to be purified. Limited solubility makes molecular weight determinations untrustworthy, and a great tendency to retain solvents renders analytical figures not entirely reliable. The best figures indicate the (correct) formula $C_{22}H_{13}NO_4$.

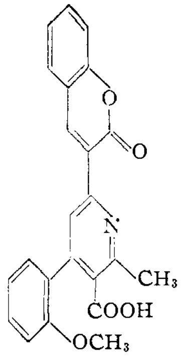
Methylation with alkali and methyl sulfate indicates that two coumarin nuclei are present in the substance. The product is an unstable acidic material, $C_{24}H_{23}NO_7$, which appears to be a mixture, probably VII and VIII. When the methylation product is heated (150–160°), there is obtained an acid $C_{23}H_{17}NO_5$ (IX, from VII by loss of methanol and water), and a neutral substance $C_{22}H_{17}NO_3$ (X, from VIII by loss of methanol, water and carbon dioxide).



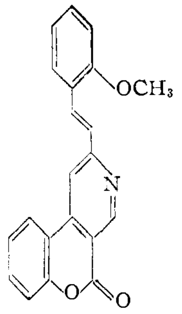
VII



VIII



IX

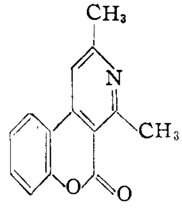


X

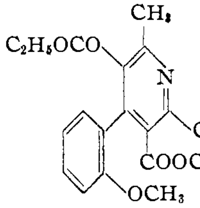
Oxidation with permanganate yields pyridine-2,3,4,6-tetracarboxylic acid, proving the presence of a pyridine nucleus.

Fusion with sodium hydroxide (175–225°) gives salicylic acid and a base $C_{14}H_{11}NO_2$, which can be oxidized to pyridine-2,3,4,6-tetracarboxylic acid. Structure XI has been established for this base by synthesis from known XII. These data establish III as the only likely structure for the original condensation product.

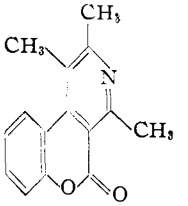
Synthesis of XI also affords a proof of structure for the substance obtained from 3-acetocoumarin, cyanoacetamide, and acetone, for this substance



XI



XII



XIII

(IV, R = CH_3) is identical with XI. Proof of structure IV, R = C_6H_5, for the compound obtained using acetophenone rests on analogy; proof for IV, R = C_2H_5 rather than the isomeric structure XIII for the compound obtained using methyl ethyl ketone rests on analogy and on the observation that diethyl ketone does not condense with 3-acetocoumarin and cyanoacetamide. Proof of VI for the compound obtained using cyclohexanone is found in the observation that this compound yields pyridinepentacarboxylic acid when it is oxidized with permanganate.

Experimental

2-(3-Coumarinyl)-5-keto-4-methyl[1]benzopyrano[3,4-c]pyridine, III.—Studies of the conditions for the reaction, beginning with those of Sastry and Seshadri[2] (yield 32%), showed that piperidine was unnecessary and that a solvent was best omitted.

A mixture of 135.5 g. of 3-acetocoumarin and 33 g. of cyanoacetamide was heated and stirred at 165°. After ten minutes, vigorous boiling began; the reaction was complete after a total of fifteen minutes. The mixture was cooled to 100° and diluted with 300 ml. of alcohol. The product was removed and washed with alcohol and acetone, giving 57–66 g. (45–52%) of pale yellow needles, m. p. 293–294° (block). The use of malonamide in place of cyanoacetamide gave a yield of 49%; formamide gave 11%; formamide containing 20% of ammonium formate gave 47%; urea gave 47%; ammonium acetate in alcohol gave a good yield of a substance m. p. 248–250°, dec., which was not III and was not investigated.

Compound III crystallized well from pyridine or chloroform, but because it was impossible to remove these solvents completely, it was necessary to prepare a sample for analysis by crystallization from a large volume of benzene. The pure substance melted and sublimed at 295° (block).

Anal. Calcd. for $C_{22}H_{13}NO_4$: C, 74.4; H, 3.7; N, 3.9. Found: C, 74.2; H, 3.7; N, 4.2.

The compound is difficultly soluble in the common organic solvents. It is insoluble in dilute hydrochloric acid, but dissolves readily in acetic acid only when a few drops of sulfuric acid is added. It dissolves slowly in boiling aqueous sodium hydroxide, and precipitation from this solution by acids is accelerated by heat, a behavior characteristic of coumarins.

7-Methoxy-5-keto-2-(8-methoxy-3-coumarinyl)-4-methyl[1]benzopyrano[3,4-c]pyridine was obtained in a yield of 64% by heating a mixture of 8.4 g. of cyanoacetamide and 21.8 g. of 3-aceto-8-methoxycoumarin[4] at 205°. After it had been sublimed twice, the yellow crystalline product melted at 336–337° (block).

Anal. Calcd. for $C_{24}H_{17}NO_6$: C, 69.4; H, 4.1. Found: C, 70.0; H, 4.4.

Condensations with Acetone.—A mixture of 5.0 g. of 3-acetocoumarin, 2.5 g. of cyanoacetamide and 25 ml. of acetone was heated in a sealed tube at 175–180° for four hours. The acetone was then removed and the residue was digested with 100 ml. of 10% hydrochloric acid at 100°. The resulting solution was filtered, cooled and made basic with sodium carbonate. The precipitated **5-keto-2,4-dimethyl[1]benzopyrano[3,4-c]pyridine** (IV, R = CH_3) was crystallized from dilute acetone, giving pale yellow needles, m. p. 199–199.5° alone or mixed with the same substance prepared by alkali fusion of III (see below). A mixture of acetone, acetocoumarin and cyanoacetamide was unchanged after it had been boiled in an open vessel for sixteen hours.

When a mixture of 5 g. of 3-aceto-8-methoxycoumarin, 2.5 g. of cyanoacetamide and 25 ml. of acetone was heated at 175–180° for six hours, there was obtained 1.9 g. (32%) of **5-keto-7-methoxy-2,4-dimethyl[1]benzopyrano[3,4-c]pyridine**, nearly colorless plates from benzene–ligroin, m. p. 193.5°.

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.5; H, 5.1. Found: C, 70.3; H, 5.1.

Condensation with Methyl Ethyl Ketone.—A mixture of 5 g. of 3-acetocoumarin, 2.5 g. of cyanoacetamide and 33 g. of methyl ethyl ketone heated at 175–180° for four hours gave 2.7 g. (42%) of **2-ethyl-5-keto-4-methyl[1]benzopyrano[3,4-c]pyridine** (IV, R = C_2H_5), colorless crystals from alcohol, m. p. 160–161°.

Anal. Calcd. for $C_{15}H_{13}NO_2$: C, 75.3; H, 5.4. Found: C, 75.0; H, 5.5.

Condensation with Acetophenone.—A mixture of 5 g. of 3-acetocoumarin, 2.5 g. of cyanoacetamide and 50 ml. of acetophenone heated at 175–180° for four hours gave 1.6 g. (21%) of **5-keto-4-methyl-2-phenyl[1]benzopyrano[3,4-c]pyridine** (IV, R = C_6H_5), pale yellow prisms from acetone, m. p. 206–206.5°.

Anal. Calcd. for $C_{19}H_{13}NO_2$: C, 79.4; H, 4.5. Found: C, 79.2; H, 4.5.

Condensation with Cyclohexanone.—A mixture of 10 g. of 3-acetocoumarin, 7.5 g. of cyanoacetamide and 50 ml. of cyclohexanone was boiled for four and one-quarter hours under an air condenser, water being allowed to escape. The mixture was then cooled, and the solid product was removed and washed with alcohol; yield 7.3 g. (48%). Repeated crystallization from chloroform and then from benzene gave white matted fibers of **1,2,3,4,4a,6a,12b,12c-octahydro-4a-hydroxy-7-keto-6-methyl[1]benzopyrano[3,4-c]-quinoline** (V), m. p. 242.5–243° (block).

Anal. Calcd. for $C_{17}H_{19}NO_3$: C, 71.6; H, 6.7. Found: C, 71.9; H, 6.9.

A mixture of 21.2 g. of V with 250 ml. of 1:1 hydrochloric acid was boiled for twelve hours, then cooled, decanted from gummy material and basified with sodium carbonate. The resulting **1,2,3,4-tetrahydro-7-keto-6-methyl[1]benzopyrano[3,4-c]quinoline** (VI) (15.5 g., 79%) was crystallized from alcohol, giving white needles, m. p. 212.5°.

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 77.0; H, 5.7. Found: C, 76.9; H, 5.6.

A solution obtained by boiling 13.3 g. of VI with 40 g. of sodium hydroxide in 120 ml. of water was diluted with 500 ml. of water and stirred while 142 g. of potassium permanganate was added in small portions. Stirring was continued while the mixture was heated for forty-eight hours on a steam-bath. The mixture was then filtered, and the filtrate was brought to *p*H 4, filtered again and evaporated until salts began to separate. It was then mixed with 60 g. of copper acetate in 400 ml. of water and

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[4] Horning and Horning, THIS JOURNAL, **69**, 968 (1947).

kept at 100° for two hours. The precipitated copper oxalate[5] (21.2 g.) was removed from the hot mixture and identified by conversion into oxalic acid and methyl oxalate. The mother liquor was cooled, and the mixture of copper salts that separated (3.1 g.) was treated with hydrogen sulfide. The resulting free acids were esterified with diazomethane, and methyl oxalate and **methyl pyridinepentacarboxylate** (10 mg.), m. p. 128–129°, were separated by crystallization from methanol. The latter ester was synthesized for comparison from authentic pyridinepentacarboxylic acid.[5]

Anal. Calcd. for $C_{15}H_{15}NO_{10}$: C, 48.8; H, 4.1. Found: C, 48.9; H, 4.3.

Methylation of III.—A solution prepared by boiling 39.4 g. of III with 73 g. of sodium hydroxide in 144 ml. of water was cooled to room temperature and stirred while 58 g. of methyl sulfate was added. The temperature rose to 65–70°. After it had been stirred for four hours, the mixture was acidified with hydrochloric acid. The precipitate was removed and mixed with 32 g. of potassium carbonate in 150 ml. of water.. The suspension was heated to 88° to coagulate insoluble material, and the latter (mainly unchanged III) was removed. The filtrate was acidified with acetic acid and heated to 100°. The precipitate was redissolved in carbonate and reprecipitated with acetic acid, giving 11 g. (48%) of crude methylation product. This was purified by cautious precipitation from acetone with water. The resulting **mixture (VII and VIII)** formed clusters of fine light yellow needles, m. p. 152–157° dec.

Anal. Calcd. for $C_{24}H_{23}NO_7$: C, 65.9; H, 5.3; mol. wt., 438. Found: C, 65.5, 66.1, 66.5, 66.6; H, 5.3, 5.0, 5.2, 5.3; neut. equiv., 216, 236.

The methylation product was heated at 175°, and the resulting two substances, formed in equal amounts, were separated by treatment with dilute aqueous sodium carbonate. **4-*o*-Anisyl-6-(3-coumarinyl)-2-methylnicotinic acid (IX)** formed colorless plates from dilute acetone, m. p. 274–276°.

Anal. Calcd. for $C_{23}H_{17}NO_5$: C, 71.3; H, 4.4. Found: C, 71.2, 71.6, 71.2; H, 4.7, 4.5, 4.6.

5-Keto-2-(*o*-methoxystyryl)-4-methyl[1]benzopyrano[3,4-c]pyridine (X) formed pale yellow crystals from dilute alcohol, m. p. 188–189°. It was insoluble in aqueous alkali, but the amorphous material obtained by adding water to its solution in acetone slowly dissolved when it was treated with sodium hydroxide.

Anal. Calcd. for $C_{22}H_{17}NO_3$: C, 76.9; H, 5.0; N, 4.1. Found: C, 76.9, 76.9, 76.9; H, 5.2, 4.7, 4.9; N, 4.3.

Oxidation of III.—A solution prepared by heating 3.4 g. of III with 30 g. of 50% sodium hydroxide at 100° for several hours was mixed with 30 ml. of water and stirred at 100° while potassium permanganate in 3% solution was added in portions. An approximate end-point (37.5 g. of permanganate) was reached in nine hours. The product was isolated through its copper salt and converted to **methyl pyridine-2,3,4,6-tetracarboxylate** (0.6 g.) with diazomethane; colorless prisms, m. p. 135–136°.

Anal. Calcd. for $C_{13}H_{13}NO_8$: C, 50.1; H, 4.2; N, 4.5. Found: C, 50.2; H, 4.2; N, 4.6.

The same ester was obtained by the action of diazomethane on authentic pyridine-2,3,4,6-tetracarboxylic acid, synthesized in 60–70% yield by the method of Mumm and Hunecke.[6]

Alkali Fusion of III.—A melt of 200 g. of sodium hydroxide and 20 ml. of water was stirred and heated in a metal-bath at 220–225° while 46.4 g. of III was added in portions during eighty minutes. More sodium hydroxide was then added (30 g.), and heating and stirring were continued for an additional hour. The melt was then allowed to cool until it started to solidify, whereupon 250 ml. of water was added cautiously. The resulting solution was acidified with hydrochloric acid, cooled and brought to *p*H 8–9 with soda. Benzene (500 ml.) was added; the mixture was shaken, filtered and separated.

The carbonate solution furnished salicylic acid and a small amount of a more difficultly soluble acid, yellow crystals from acetone, m. p. 287° dec. (block). (Found: C, 62.8, 62.4; H, 4.1, 3.9; N, 5.6, 5.6.) When this acid was melted, it gave carbon dioxide and another acid; purified by sublimation and crystallization from ethyl acetate, the latter formed faintly yellow crystals, m. p. 217.5–218.5° (Found: C, 69.5, 69.0, 69.1; H, 5.5, 5.4, 5.6; N, 7.1; neut. equiv., 220).

The benzene solution furnished 12.7 g. (43%) of **5-keto-2,4-dimethyl[1]benzopyrano[3,4-c]pyridine** (XI), needles from acetone, m. p. 199.5°.

Anal. Calcd. for $C_{14}H_{11}NO_2$: C, 74.7; H, 4.9; N, 6.2. Found: C, 74.9; H, 4.7; N, 6.3.

The **picrate** of XI, bright yellow needles from alcohol, sublimed and decomposed at 175–200°.

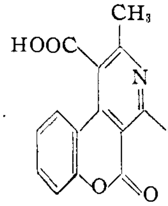
Anal. Calcd. for $C_{20}H_{14}N_4O_9$: C, 52.8; H, 3.1. Found: C, 53.1; H, 3.3.

When 2.4 g. of XI was dissolved in 50 ml. of 4% sodium hydroxide by heating, and oxidized with 13 g. of potassium permanganate, there was obtained pyridine-2,3,4,6-tetracarboxylic acid. The acid was isolated through its copper salt, and for identification was converted into its methyl ester (0.2 g.) with diazomethane.

Synthesis of XI.—4-*o*-Anisyl-3,5-dicarbethoxy-2,6-lutidine (XII) was obtained in a yield of 77% by boiling 15.4 g. of the dihydro derivative[7] with 100 ml. of water containing 25 ml. of nitric acid, d. 1.42, for ten minutes.

A solution of 11.8 g. of XII in 150 ml. of 40% hydrobromic acid was boiled for seven hours, then cooled, filtered from tar, and evaporated. The residue was heated in a sealed tube with 50 ml. of 40% hydrobromic acid for four hours at 175° and two hours at 200°. The mixture was then diluted, cooled, and filtered. The filtrate was made alkaline with potassium carbonate, and the resulting precipitate was crystallized from acetone, giving 1.4 g. (19%) of XI.

The material filtered directly from the diluted hydrobromic acid was largely **5-keto-2,4-dimethyl[1]benzopyrano[3,4-c]pyridine-1-carboxylic acid (XIV)**. This substance was purified by solution in potassium carbonate and reprecipitation with acetic acid. It separated from water in the form of a dihydrate (Found: H_2O, 12.2), large yellow prisms that lost water at 80–85°. The anhydrous substance decomposed slowly above 200°; m. p. 279°.



XIV

Anal. Calcd. for $C_{15}H_{11}NO_4$: C, 66.9; H, 4.1. Found: C, 66.9; H, 4.3.

A considerable amount of XIV remained in the various mother liquors of the preceding preparations. These were combined, made strongly acid with hydrochloric acid, and evaporated to dryness. The resulting salt cake was powdered and extracted with absolute alcohol. The solution was saturated with hydrogen chloride and boiled for seven hours. Concentration, treatment with aqueous soda and extraction with benzene gave 1.5 g. of the **ethyl ester** of **XIV**, colorless crystals from acetone, m. p. 134–134.5°.

Anal. Calcd. for $C_{17}H_{15}NO_4$: C, 68.7; H, 5.0. Found: C, 68.6; H, 5.1.

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[5] Pyridinepentacarboxylic acid is easily oxidized to oxalic acid by permanganate; Hantzsch, *Ann.*, **215**, 62 (1882).

[6] Mumm and Hunecke, *Ber.*, **51**, 150 (1918).

[7] Hinkel and Madel, *J. Chem. Soc.*, 750 (1929).

Summary

3-Acetocoumarin reacts with certain ketones in the presence of amides, forming derivatives of 5-keto-4-methyl[1]benzopyrano[3,4-c]pyridine. The condensation involves a Michael reaction, in which 3-acetocoumarin functions as an acceptor and a ketone as an addendum. It is remarkable that cyanoacetamide, like other amides, acts only as a source of nitrogen and not as an addendum.

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[CONTRIBUTION FROM THE OREGON FOREST PRODUCTS LABORATORY, AND THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Composition of the Wax in Douglas-Fir Bark

BY E. F. KURTH

Douglas-fir [*Pseudotsuga taxifolia* (Poir.) Britt.] bark was reported previously to contain from 3.6 to 6.0% of a light-colored wax, which was extracted with hexane.[1] At that time an examination of the literature revealed that little information was available concerning the chemical composition of this wax. Warth[2] reported the presence of a wax in the corky layers of the Douglas-fir bark with m. p. 63°. Although no experimental data were presented, he mentioned that free melissic acid, an unsaturated alcohol and an ester of melissic acid were possible constituents of this wax. Evidence is now presented that the chief constituents of this wax are lignoceric acid, lignoceryl alcohol, ferulic acid (4-hydroxy-3-methoxycinnamic acid), and their corresponding esters. Oleic acid and phytosterol are minor constituents. The acid constituents of the wax are present in the free and combined state. Treatment of a hexane solution of the wax with 5% potassium carbonate solution extracted both the fatty acid and the aromatic acid. The largest part of both acids was obtained only after saponification. The composition of the bark wax is different from that obtained from the lignin residue produced in the hydrolysis of Douglas-fir sawmill residues.[3]

The properties of the hexane soluble waxes produced in this Laboratory from different lots of bark were

Melting point, °C.	60 to 63
Acid number	30 to 70
Saponification number	130 to 164
Unsaponifiable, %	18 to 30
Hanus iodine number	18 to 22

The color was yellow to light brown. They were non-tacky and brittle when cold. When broken they presented a granular non-crystalline fracture. The specific gravity of the solid waxes was greater than one and hence they commonly separated as a granular powder on cooling a hot water suspension.

On saponification of the waxes with alcoholic potassium hydroxide solution followed by extraction of the unsaponifiable matter with ethyl ether or hexane there was obtained a mixture of lignoceryl alcohol and phytosterol crystals. Acidification of the alkaline soap solution and extraction with hexane gave white crystals of lignoceric acid on evaporation of the solvent. Suspended in the aqueous solution following the removal of the fatty acid fraction, was a light brown resin. This was completely soluble in ethyl ether and partially soluble in benzene. It was crystallized from both these solvents. The identity of ferulic acid was established by methoxyl group determination, preparation of the acetyl derivative, methylation, and oxidation of the fully methylated acid to veratric acid. The presence of this aromatic acid does not appear to have been established previously in a natural wax. It has long been of interest in lignin chemistry. The basic nucleus of the lignin molecule, $(CH_3O)(OH)C_6H_3CH{=}CH{-}C$, from conifers is patterned after ferulic acid. Lignin conceivably could be derived from ferulic acid in nature.

Other extractives in addition to the above wax have been isolated from Douglas-fir bark in this Laboratory. These were a reddish-brown wax insoluble in hexane, but soluble in benzene, dihydroquercetin, tannin and sugars. The dihydroquercetin has been obtained in yields of 5 to 8% in relatively pure form by extracting wax-free bark with diethyl ether. Similarly, it has been obtained in yields as high as 19% from the cork in the bark. The hexane insoluble wax appeared to possess a more complicated composition than the hexane soluble wax. It had a melting point of 60 to 63°, and there has been tentatively isolated from this material on saponification a fatty acid mixture in about 25% yield, a dark-colored phlobaphene in 24% yield, a dark colored ether soluble acid fraction in 26% yield, unsaponifiable matter in 5% yield and glycerol.

Experimental

Extraction of the Wax from the Bark.—In the course of the experimental work, several lots of bark were extracted with hexane in a stainless steel extractor which had a capacity of about 50 pounds of bark ground to pass a screen containing $^3/_8$ inch perforations. Stainless steel was used for the reason that iron and copper caused discoloration of

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[1] Kurth, Kiefer and Hubbard, *The Timberman*, **49**, no. 8, 130–131 (1948).

[2] Warth, "The Chemistry and Technology of Waxes," Reinhold Publishing Corp., New York 18, N. Y., 1947, p. 148.

[3] Kurth, *The Chemurgic Digest*, **6**, 366 (1947).