2. The structures of the hexatriene polymers are elucidated.

3. Work is being continued on the chemistry of these compounds and also on the synthesis of similar compounds containing substituent groups.

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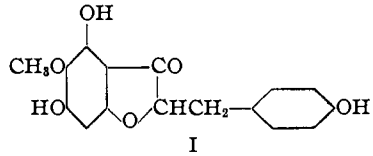
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Derivatives of Coumaran. IV. The Structure of Tectorigenin

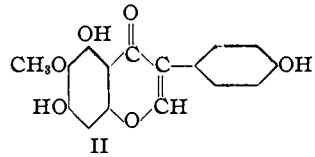
BY R. L. SHRINER, EDWARD J. MATSON AND R. E. DAMSCHRODER

The glucoside, tectoridin, was isolated by Shibata[1] from the rhizomes of *Iris tectorum* Maxim. Recently Mannich, Schumann and Lin[2] have shown that the glucoside, shekanin, in the rhizomes of the blackberry lily, *Belamcanda chinensis* (L.) Leman, is identical with tectoridin. Hydrolysis of tectoridin produced glucose and tectorigenin. Since the products of alkaline decomposition of tectorigenin were *p*-hydroxyphenylacetic acid, formic acid and iretol (V), Shibata first proposed the coumaran-3-one structure shown in formula I. Later, on the basis of the absorption spectrum, Asahina, Shibata and Ogawa[3] suggested the isoflavone structure of formula II. It is obvious that the isomeric formulas III and IV also represent possible structures which would yield the same degradation products.

The coumaranone structures I and III have two atoms of hydrogen more than the isoflavone structures but the combustion analyses were not sufficiently accurate to distinguish between them. None of these structures has been synthesized previously. This paper reports the synthesis of the two isomeric coumaranone structures, I and III, and of their completely methylated derivatives.



I



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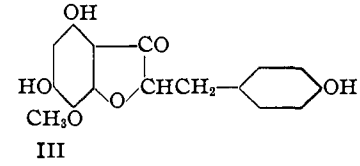

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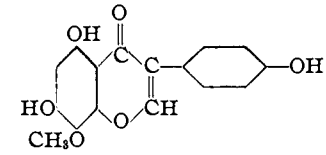


IV

The general method[4] of synthesis used involved the preparation of the coumaranones properly substituted in the benzene nucleus, condensation of the active methylene group in the heterocyclic ring with an aldehyde followed by reduction. The necessary coumaranones are most conveniently made by treating phenols with chloroacetonitrile followed by hydrolysis and ring closure.

Application of this method to iretol (V) yielded two isomeric coumaranones which were separated by fractional crystallization. The structure of the two isomeric coumaranones produced by hydrolysis and ring closure of α-chloro-2,4,6-trihydroxy-3-methoxyacetophenonimine hydrochloride (VI) was established by methylation and synthesis of each of the methylated compounds. The less soluble isomer was 4,6-dihydroxy-5-methoxycoumaran-3-one (VII); the more soluble was 4,6-dihydroxy-7-methoxycoumaran-3-one (X).

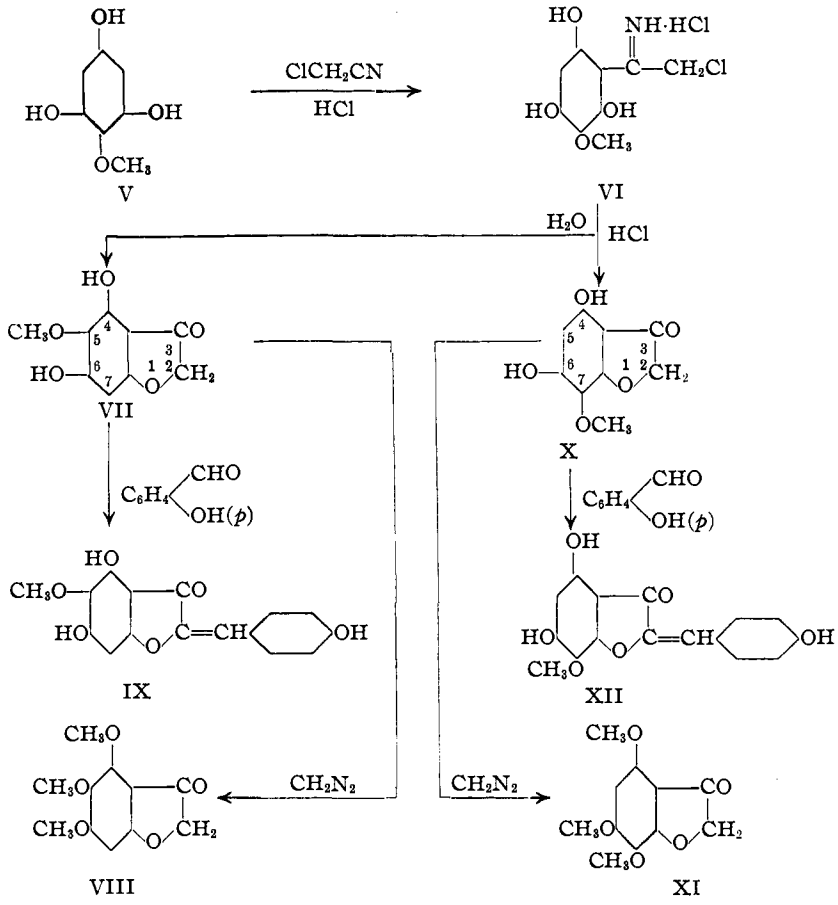
The methylated isomer, 4,5,6-trimethoxycoumaran-3-one (VIII), was prepared from antiarol (XIII), which underwent a Hoesch reaction with chloroacetonitrile to yield the α-chloroacetophenone (XIV). Ring closure gave the desired coumaranone (VIII). In a similar fashion the isomeric methylated compound, 4,6,7-trimethoxy-

(1) Shibata, *J. Pharm. Soc. Japan*, **47**, 380 (1927).

(2) Mannich, Schumann and Lin, *Arch. Pharm.*, **275**, 317 (1937).

(3) Asahina, Shibata and Ogawa, *J. Pharm. Soc. Japan*, **48**, 1087 (1928).

(4) Shriner and Damschroder, THIS JOURNAL, **60**, 894 (1938); Shriner and Anderson, *ibid.*, **60**, 1415 (1938).



coumaran-3-one (XI), was synthesized from 2,5-dimethoxyresorcinol (XVII).

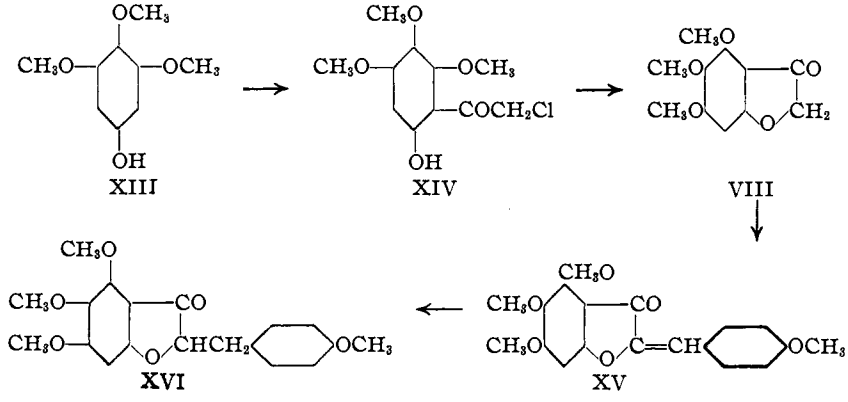
A Hoesch reaction gave the α-chloroacetophenone (XVIII), which was cyclized to the coumaranone (XIX). Methylation with diazomethane gave the completely methylated ether (XI).

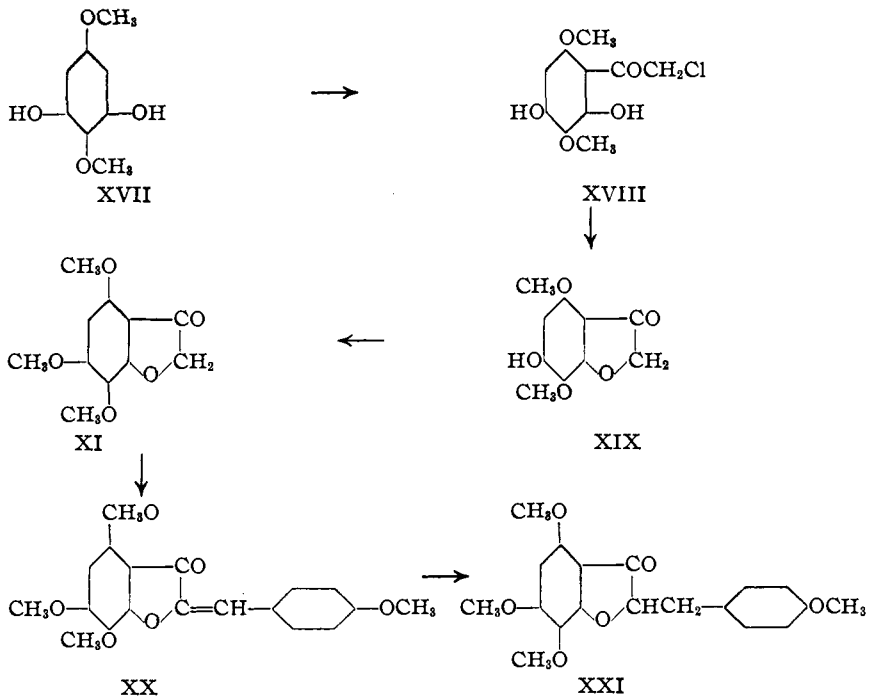
In order to obtain the 2-(*p*-hydroxybenzyl)-coumaranones (I and III) each of the isomeric coumaranones (VII and X) was condensed with *p*-hydroxybenzaldehyde and the benzal derivatives were reduced catalytically. The products of reduction proved to be very unstable and could not be isolated in the pure state but their properties were totally different from those of the natural product, tectorigenin.

The synthesis of the methylated derivatives was accomplished by condensing the trimethoxycoumaranones (VIII and XI) with anisaldehyde and reducing the anisal derivatives. The two isomeric methylated coumaranones (XVI and XXI) were isolated.

For purposes of comparison, tectoridin was isolated from the rhizomes of *Iris tectorum* and hydrolyzed to tectorigenin. Methylation of the latter yielded dimethyltectorigenin, which could not be methylated to trimethyltectorigenin although eleven different methylation procedures were used. Mannich, Schumann and Lin[2] also found that only a dimethyl derivative of tectorigenin could be obtained.

Although it was not possible to make a direct comparison with trimethyltectorigenin, the properties of the two synthetic trimethoxycoumaranones are quite different from those of the known methylated derivatives of tectorigenin. Compound XVI melts at 93–94°, and compound XXI at 116°. The melting points of tectorigenin and





its derivatives are: demethylated tectorigenin,[2] 270°; tectorigenin,[1] 230°; monomethyltectorigenin,[2] 191–192°; dimethyltectorigenin,[2] 188°.

The remarkable resistance to complete methylation exhibited by tectorigenin is probably due to the fact that the hydroxyl group ortho to the carbonyl group is strongly chelated as well as sterically hindered. This constitutes some evidence that the heterocyclic ring is six-membered rather than five-membered. It will be noted that the 4-hydroxyl group in the coumaranone (VII) was readily methylated.

The instability of the unmethylated coumaranones (I and III) obtained by reduction of IX and XII, and the differences in ease of methylation exhibited by all these coumaranones in comparison with tectorigenin show that the natural product is not a coumaranone derivative and favors the isoflavone structure II.

Experimental

α - Chloro - 2,4,6 - trihydroxy - 3 - methoxyacetophenonimine Hydrochloride (VI).—Dry hydrogen chloride gas was passed into a solution of 3 g. of iretol[5] and 1.5 g. of chloroacetonitrile[6] dissolved in about 300 cc. of dry ether. After forty-five minutes the solution became warm and after one hour yellow crystals began to be formed on the walls of the flask. The stream of hydrogen chloride was maintained eight hours longer, at which time the volume of ether had decreased to 100 cc. The flask was stoppered and allowed to stand overnight. The yellow crystals were then collected on a filter and washed quickly with dry ether. The yield of the crude product was 4.5 g. (87.5%).

The sample analyzed was purified by dissolving it in absolute alcohol into which dry hydrogen chloride had been passed for fifteen minutes. This solution was diluted with five volumes of dry ether. After the solution had stood for several hours, golden-yellow crystals precipitated. These were collected and dried in a vacuum desiccator over calcium chloride. The pure compound decomposed at 164–165°.

Anal. Calcd. for $C_9H_{11}Cl_2NO_4$: N, 5.22. Found: N, 5.37.

Hydrolysis of the Ketimine Hydrochloride.—A solution of 4 g. of the ketimine hydrochloride (VI) in 50 cc. of water was refluxed for one hour. The light-yellow solution gradually became red. The solvent was then removed slowly by surrounding the flask containing the hydrolysis mixture with calcium chloride in a vacuum desiccator. The pressure was reduced carefully until the water began to boil. After twenty-four hours the calcium chloride was replaced. When one-half the solvent had been removed in this manner, the rose-colored precipitate was removed by filtration. This less soluble fraction was recrystallized twice from water using norit and 0.9 g. of colorless needles of 4,6-dihydroxy-5-methoxycoumaran-3-one (VII) melting at 208.5 to 209.5° obtained.

Anal. Calcd. for $C_9H_8O_5$: C, 55.09; H, 4.11. Found: C, 55.29; H, 4.30.

The dark red filtrate from the above was concentrated to a volume of 8 cc. and the red precipitate filtered. Two recrystallizations from water using norit gave 1.5 g. of colorless crystals of 4,6-dihydroxy-7-methoxycoumaran-3-one (X) which melted at 177–178°.

Anal. Calcd. for $C_9H_8O_5$: C, 55.09; H, 4.11. Found: C, 55.05; H, 4.32.

Methylation of 4,6-Dihydroxy-5-methoxycoumaran-3-one.—A dioxane solution of diazomethane was prepared according to the method of Arndt.[7] Thirty-five milligrams of the coumaranone was dissolved in 25 cc. of dioxane and to this was added 1 cc. of the diazomethane solution containing about 90 mg. of the reagent, four times the theoretical amount necessary. The solution was allowed to stand overnight, and then the same amount of diazomethane was added again. After the solution had stood for ten hours longer it was evaporated to dry-

(5) Damschroder and Shriner, THIS JOURNAL, **59**, 931 (1937).
(6) Steinkopf, *Ber.*, **41**, 2541 (1908).
(7) Arndt, *Org. Syn.*, **15**, 4 (1935).

ness. The yield of colorless needles of 4,5,6-trimethoxycoumaran-3-one (VIII) was quantitative. The material was purified by repeated crystallization from absolute alcohol. It melted at 142.5–143.5°.

Anal. Calcd. for $C_{11}H_{12}O_5$: C, 58.93; H, 5.36. Found: C, 59.03; H, 5.48.

Methylation of 4,6-Dihydroxy-7-methoxycoumaran-3-one (X).—Sixty milligrams of this coumaranone was dissolved in 4 cc. of dioxane and 1.7 cc. of the above diazomethane solution was added. This contained about 150 mg. of diazomethane, four times the theoretical amount required. The procedure followed was the same as above and quantitative methylation resulted. The colorless needles of 4,6,7-trimethoxycoumaran-3-one (XI) melted at 153.5–154.5°.

Anal. Calcd. for $C_{11}H_{12}O_5$: C, 58.93; H, 5.36. Found: C, 59.28, 59.24; H, 5.25, 5.21.

Antiarol (3,4,5-Trimethoxyphenol) (XIII).—Antiarol was prepared from pyrogallol trimethyl ether according to the procedure of Chapman, Perkin and Robinson[8] except that the reduction of the intermediate 2,6-dimethoxyquinone was accomplished with sulfur dioxide instead of hydrogen sulfide, as recommended by Hattori.[9] The product used melted at 148°.

α - Chloro - 2 - hydroxy - 4,5,6 - trimethoxyacetophenone (XIV).—In 25 cc. of dry ether were suspended 5 g. of antiarol, 1.5 g. of chloroacetonitrile, and 2 g. of powdered anhydrous zinc chloride. Dry hydrogen chloride was passed into the mixture. Almost at once a paste began to form and heating occurred. The stream of hydrogen chloride was continued six hours, during which time half the ether evaporated. The flask was stoppered and allowed to stand overnight, then 25 cc. of cold water was added slowly. The resulting solution was shaken thoroughly with 25 cc. of ether, and the water layer was separated and refluxed one-half hour. The flask was cooled in ice and the voluminous precipitate which had formed was removed by filtration. The yield was 3 g. (42%). The sample analyzed was purified by repeated recrystallization, each time with the aid of norit. The crystals were dissolved in hot absolute alcohol, norit was added and the solution was warmed for a few minutes. The solution was filtered and then warmed again to boiling, and warm water was added until the solution was permanently cloudy. The flask was allowed to stand until it had reached room temperature. The pure product consisted of small colorless needles which, in the mass, had a faint greenish tinge. The m. p. was 107–107.5°.

Anal. Calcd. for $C_{11}H_{13}ClO_5$: C, 50.67; H, 4.99; Cl, 13.60. Found: C, 50.82; H, 4.93; Cl, 13.31.

4,5,6-Trimethoxycoumaran-3-one (VIII).—In a 25-cc. Erlenmeyer flask were mixed 0.71 g. of the above chloro ketone, 0.83 g. of powdered sodium acetate, and 7 cc. of alcohol. The mixture was refluxed two hours, becoming rose-colored, and was then poured into 110 cc. of a cold saturated sodium chloride solution. The voluminous rose-colored precipitate, collected on a filter, contained some sodium chloride. It was extracted with boiling absolute alcohol which was then treated twice with norit. The final filtrate was cooled in a dry ice–ether mixture, and the colorless needles formed were separated by filtration. A recrystallization gave no change in the m. p. of 142.5–143.5°. Decomposition occurred at the melting point. The yield of pure product was 0.55 g. (91%).

Anal. Calcd. for $C_{11}H_{12}O_5$: C, 58.93; H, 5.36. Found: C, 58.79; H, 5.37.

A mixed melting point with the methylation product of 4,6-dihydroxy-5-methoxycoumaran-3-one (VII) showed no depression.

2,5-Dimethoxyresorcinol (XVII).—This compound was prepared from pyrogallol tribenzyl ether by the method of Baker, Nodzu and Robinson[10] as modified by Shah, Mehta and Wheeler.[11]

α - Chloro - 2,4 - dihydroxy - 3,6 - dimethoxyacetophenone (XVIII).—About 3.5 g. of 2,5-dimethoxyresorcinol was dissolved in 40 cc. of dry ether, along with 1.55 g. of chloroacetonitrile. Dry hydrogen chloride was passed into the solution for six hours, crystals appearing on the walls of the flask a short time after the reaction was started. The reaction mixture was allowed to stand overnight, and then the ether was decanted. The brownish mass was washed with dry ether and then was treated with 40 cc. of water. The mixture was warmed on a steam-bath for one hour and then cooled, when the oil which had separated solidified. A small amount of pink crystals, weighing 0.16 g., remained suspended in the water. This was collected on a filter and recrystallized by dissolving in absolute alcohol, treating the solution with norit, and reprecipitating by adding 3 volumes of water to the filtrate. The total yield of product, after one recrystallization, was 1.3 g. (about 25%). The colorless needles of the pure compound had a m. p. of 150.5–151.5°.

Anal. Calcd. for $C_{10}H_{11}ClO_5$: C, 48.70; H, 4.50. Found: C, 48.53; H, 4.66.

4,7-Dimethoxy-6-hydroxycoumaran-3-one (XIX).—In 12 cc. of alcohol were put 1.1 g. of the above chloro ketone and 1.2 g. of powdered sodium acetate. The solution was refluxed two and one-half hours, during which time it gradually became red, and then was poured into 190 cc. of cold saturated sodium chloride solution. After standing overnight in a refrigerator, the precipitate was removed by filtration. It consisted of a mixture of cubic sodium chloride crystals and the colorless monoclinic prisms of the product. This mixture was extracted with 40 cc. of boiling absolute alcohol. This extract was treated with norit, concentrated to 5 cc., and cooled. This solid was collected on a filter and was recrystallized to constant melting point from absolute alcohol. The pure compound melted at 180–181° with decomposition. The yield of purified material was 0.4 g. (43%).

Anal. Calcd. for $C_{10}H_{10}O_5$: C, 57.15; H, 4.80. Found: C, 57.31; H, 4.94.

4,6,7-Trimethoxycoumaran-3-one (XI).—In 25 cc. of dioxane was dissolved 0.32 g. of the above hydroxycoumaranone. Seven cubic centimeters of the diazomethane solution previously mentioned was added; this contained about 0.45 g. of diazomethane, four times the theoretically required amount. The solution was allowed to

(8) Chapman, Perkin and Robinson, *J. Chem. Soc.*, 3028 (1927).
(9) Hattori, *Acta Phytochim.* (*Japan*), **5**, 226 (1931).
(10) Baker, Nodzu and Robinson, *J. Chem. Soc.*, 77 (1929).
(11) Shah, Mehta and Wheeler, *ibid.*, 1557 (1938).

stand overnight, and then the same amount of diazomethane solution was added again. Seven hours later the solution was evaporated to dryness *in vacuo* to give 0.27 g. (80%) of colorless needles, which were recrystallized from absolute alcohol to give a product melting at 153.5–154.5°.

A mixed melting point with the methylation product of 4,6-dihydroxy-7-methoxycoumaran-3-one (X) showed no depression.

4,6 - Dihydroxy - 2 - (*p* - hydroxybenzal) - 5 - methoxycoumaran-3-one (IX).—The method of von Auwers and Pohl[12] was employed. A solution of 0.5 g. of 4,6-dihydroxy-5-methoxycoumaran-3-one and 0.4 g. of *p*-hydroxybenzaldehyde in 10 cc. of absolute alcohol was warmed to 65–70°. Five drops of concentrated hydrochloric acid was then added, the solution immediately becoming red. The temperature was kept at 65–70° for two hours, and the solution was then poured into 200 cc. of water. After the mixture had stood for two days the brown precipitate which had formed was removed by filtration and was dissolved in a few cubic centimeters of alcohol. This red solution was treated with norit and then filtered. The orange filtrate was diluted with 5–10 volumes of water. After the flask had been cooled and scratched with a glass rod, yellow needles formed which weighed 0.55 g. (72%). The sample analyzed was recrystallized again as described. The golden-yellow needles were dried in a vacuum desiccator at 2 mm. over calcium chloride for twenty-four hours, and then for three hours in an Abderhalden drier over phosphorus pentoxide at 2 mm. and 110°. The product so prepared decomposed at 291° on a Maquenne block.

Anal. Calcd. for $C_{16}H_{12}O_6$: C, 63.98; H, 4.03. Found: C, 64.18; H, 3.99.

A small amount of this material in alcoholic solution was treated with hydrogen at 3 atm. pressure and with an equal weight of platinum oxide catalyst present. Reduction occurred rapidly; the solution on evaporation to dryness under reduced pressure in a nitrogen atmosphere gave a white residue melting at 114–117° which decomposed rapidly and could not be purified.

2 - (*p* - Anisal) - 4,5,6 - trimethoxycoumaran - 3 - one (XV).—In 5.5 cc. of warm absolute alcohol was dissolved 0.6 g. of 4,5,6-trimethoxycoumaranone, 0.42 g. of anisaldehyde, and 2 drops of concentrated hydrochloric acid. The mixture was heated at 60–70° for two hours, the solution gradually becoming red. It was poured into 60 cc. of water and the mixture was allowed to cool. The reddish-brown solid formed was separated by filtration and after one recrystallization from alcohol weighed 0.7 g. (77%). Repeated recrystallization from alcohol, with the aid of norit, gave golden-yellow crystals melting at 148–149°. The solid quickly assumed an orange color on exposure to air.

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.65; H, 5.30. Found: C, 66.63; H, 5.18.

2 - (*p* - Anisyl) - 4,5,6 - trimethoxycoumaran - 3 - one (XVI).—One-tenth gram of the above anisalcoumaranone and 0.1 g. of platinum oxide catalyst were suspended in 30 cc. of absolute alcohol, and the mixture was shaken with hydrogen at 3 atm. pressure. Absorption was complete and the solution was colorless in five minutes. The alcohol was distilled *in vacuo* to 1 cc., low-boiling petroleum ether was added, and the solution was cooled in an acetone–dry-ice bath. Seventy milligrams (70%) of colorless needles was collected on a filter and was recrystallized with absolute alcohol and low-boiling petroleum ether to give 6 mg. of a product melting at 93–94°. Some decomposition seemed to occur at each crystallization, since the alcoholic solution became slightly yellow when heated.

Anal. Calcd. for $C_{19}H_{20}O_6$: C, 66.25; H, 5.85. Found: C, 65.73; H, 5.95.

4,6 - Dihydroxy - 2 - (*p* - hydroxybenzal) - 7 - methoxycoumaran-3-one (XII).—To a solution of 1 g. of 4,6-dihydroxy-7-methoxy-coumaranone and 0.8 g. of *p*-hydroxybenzaldehyde in 10 cc. of absolute alcohol at 65–70°, 10 drops of concentrated hydrochloric acid was added. The deep red solution was kept at 65–70° for two hours and was then poured into 200 cc. of water. The brick-red precipitate weighed 1.4 g. (92%).

The sample analyzed was purified by dissolving in 75% alcohol, treating the solution with norit, filtering, and diluting the filtrate with 4 volumes of water. The mixture was allowed to stand in the refrigerator for two days. The red crystals formed were removed by filtration and again dissolved in alcohol. Addition of 10 volumes of water caused rapid precipitation of the product as an orange powder. This was dried in an Abderhalden drier over phosphorus pentoxide at 2 mm. and 110° for eighteen hours. The product so prepared decomposed at 282° on a Maquenne block.

Anal. Calcd. for $C_{16}H_{12}O_6$: C, 63.98; H, 4.03. Found: C, 64.16; H, 4.25.

A small amount of this material in alcoholic solution was treated with hydrogen at 3 atm. pressure in the presence of an equal weight of platinum oxide catalyst. Reduction took place rapidly; the solution on evaporation to dryness under reduced pressure in a nitrogen atmosphere gave a light-yellow solid which melted with decomposition at about 155–170°. The material decomposed when manipulated and could not be purified.

2 - (*p* - Anisal) - 4,6,7 - trimethoxycoumaran - 3 - one (XX).—In 3.5 cc. of absolute alcohol were suspended 0.26 g. of 4,6,7-trimethoxycoumaranone, 0.18 g. of anisaldehyde, and 2 drops of concentrated hydrochloric acid. This mixture was held at 65–70° for one and one-half hours. The red solution was then poured into 35 cc. of water, and the mixture was allowed to stand for one hour. The red solid was collected on a filter; it weighed 0.3 g. (76%). The solid was dissolved with difficulty in 125 cc. of boiling absolute alcohol; the solution was filtered and concentrated *in vacuo* to 5 cc. On cooling a greenish-yellow precipitate was formed which was separated by filtration. Water added to the filtrate caused the formation of another precipitate which after several recrystallizations decomposed over a wide range at about 180°; it was discarded. The first precipitate was recrystallized by dissolving in a large volume of boiling absolute alcohol and reprecipitating by adding water. The yellow prisms, melting at 195–196°, tended to take on a greenish tinge on exposure to air.

(12) Von Auwers and Pohl, *Ann.*, **405**, 243 (1914).

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.65; H, 5.30. Found: C, 66.61; H, 5.27.

2 - (*p* - Anisyl) - 4,6,7 - trimethoxycoumaran - 3 - one (XXI).—A suspension of 85 mg. of the above anisalcoumaranone and 85 mg. of platinum oxide catalyst in 30 cc. of absolute alcohol was treated with hydrogen at 3 atm. pressure. Reduction was practically complete in two minutes. After ten minutes the platinum catalyst was removed by filtration and the filtrate was concentrated *in vacuo* to 1 cc. Low-boiling petroleum ether was added, causing precipitation of colorless needles. After two hours 70 mg. (82%) of product was collected on a filter. The material was recrystallized by dissolving in hot absolute alcohol and precipitating with low-boiling petroleum ether. Since this was a rather complete precipitation, there were also precipitated the products of the serious decomposition caused by heating the alcoholic solution. Consequently, the last two recrystallizations were carried out by cooling the alcohol solution in a dry ice–acetone bath and collecting the crystals which formed. This materially improved the product, but the loss of product in each crystallization was great and only two such manipulations could be employed. The final product, weighing 2 mg., melted at 116°.

Anal. Calcd. for $C_{19}H_{20}O_6$: C, 66.25; H, 5.85. Found: C, 65.87; H, 6.06.

Isolation of Tectoridin.—Difficulty was experienced in attempting to follow the procedure given by Shibata.[1] The following modification proved satisfactory. A 2950-g. quantity of the fresh rhizomes of *Iris tectorum* Maxim was trimmed of sprouts and adventitious roots, leaving 1985 g. of the stripped rhizomes. These were cut in 1/4-in. (6-mm.) slices and were dried at 80° for thirty hours under a 25-in. vacuum. They then weighed 675 g. This material was ground to a fine powder by passing the dried rhizomes three times through a colloid mill.

The powder was extracted twice for one and one-half hours with 1400-cc. portions of ethyl alcohol. The volume of the alcoholic solution was reduced *in vacuo* to 700 cc. The tannin impurities were then precipitated by adding a 5% alcoholic solution of lead acetate in portions until no further precipitation was observed. The lead tannate precipitate was removed by filtration and the excess lead in the filtrate was precipitated with hydrogen sulfide. The filtrate from the lead sulfide was evaporated to dryness under reduced pressure.

The residue was treated twice with 500-cc. portions of boiling ethyl acetate, for one hour. The extract was discarded. The mass remaining was stirred into 500 cc. of water. The white solid left suspended in the water was collected on a filter and was washed with absolute alcohol and then ether. The tectoridin thus obtained weighed 5.4 g. and melted at 258°.

A further 55 mg. of tectoridin was recovered from the lead tannate precipitate by suspending it in alcohol, removing the lead with hydrogen sulfide, and adding benzene to the concentrated alcoholic filtrate.

By the above procedure a total of 9.4 g. of tectoridin was isolated from 4550 g. of fresh rhizomes.

Tectorigenin.—One gram of crude tectoridin was heated with 75 cc. of 20% sulfuric acid, with stirring, in an oil-bath maintained at 90°. After the mixture was cooled, 0.83 g. of tectorigenin, m. p. 230°, was separated by filtration.

Dimethyltectorigenin.—Tectorigenin was methylated by the reaction with methyl sulfate and alkali according to the method of Mannich, Schumann and Lin.[2] This ether was also made by methylation with diazomethane. It melted at 188°.

Attempts to convert dimethyltectorigenin into trimethyltectorigenin were made by treatment with an excess of methyl sulfate and alkali, treatment with an excess of diazomethane in methanol and dioxane solutions, methyl iodide and silver oxide, methyl iodide and sodium in liquid ammonia, methyl iodide and phenyllithium, methyl iodide and triphenylmethylsodium. Acetylation of dimethyltectorigenin by acetic anhydride and pyridine yielded the acetyl derivative which melted at 213–214°. Attempts to convert this acetyl derivative to the methyl derivative according to Nierenstein's method[13] were not successful.

Summary

The structure of the two isomeric coumaranones produced by ring closure of α-chloro-2,4,6-trihydroxy-5-methoxyacetophenone was established by methylation and synthesis of each of the methylated compounds. One of these methylated isomers, 4,5,6-trimethoxycoumaran-3-one, was obtained by the following sequence: pyrogallol trimethyl ether ⟶ 2,6-dimethoxyquinone ⟶ 2,6-dimethoxyhydroquinone ⟶ 3,4,5-trimethoxyphenol (antiarol) ⟶ α-chloro-2-hydroxy-4,5,6-trimethoxyacetophenone ⟶ 4,5,6 - trimethoxycoumaran-3-one. The isomeric product, shown to be 4,6,7-trimethoxycoumaran-3-one, was synthesized as follows: pyrogallol tribenzyl ether ⟶ 2,6-dibenzyloxyquinone ⟶ 2,6-dibenzyloxyhydroquinone ⟶ 2,6-dibenzyloxy-1,4-dimethoxybenzene ⟶ 2,5-dimethoxyresorcinol ⟶ α-chloro-2,4-dihydroxy - 3,6 - dimethoxyacetophenone ⟶ 6 - hydroxy - 4,7 - dimethoxycoumaran - 3 - one ⟶ 4,6,7-trimethoxycoumaran-3-one.

Condensation of each of these trimethoxycoumaranones with anisaldehyde yielded the 2-anisal derivatives, which were reduced and the two isomers 2-(*p*-anisyl)-4,5,6-trimethoxycoumaran-3-one and 2-(*p*-anisyl)-4,6,7-trimethoxy-coumaran-3-one were isolated.

Tectoridin was isolated from the rhizomes of *Iris tectorum* Maxim and hydrolyzed to tectorigenin. Methylation of tectorigenin yielded only a dimethyl derivative. No trimethyltectorigenin could be obtained, even under drastic conditions. Comparison of the properties of the known methyl derivatives of tectorigenin with those of the above synthetic coumaranones showed that tectorigenin does not possess the coumaranone structure.

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