tube bubbled through the lime water so fast that it was not so completely absorbed by the lime water. Thus, the effect of the sulfate is the same during a short fermentation period as it is during the maximum fermentation period.

These results lead to the conclusion that the optimum calcium sulfate concentration for fermentation is the same as, or perhaps very slightly less than, the optimum for growth. Most water supplies furnish more calcium than, this optimum. This may not be unfortunate, however, because much larger concentrations of the salt seem to be desirable in baking,[8] and improvers containing considerable amounts of the sulfate, such as the Arcady,[9] are frequently added to the doughs. This increased tolerance is probably due to some buffer action.

Summary

It was found that the best concentration of calcium sulfate for the most efficient growth and fermentation of the yeast *S. cerevisiae* is at about 0.0001 *M*. Higher concentrations of the salt inhibit growth and fermentation, and lower concentrations are inadequate for best growth and fermentation. Growth was studied by examination of a synthetic culture medium over various periods of time up to 98 hours. Fermentation was studied during both short and maximum periods of time. A study of the calcium sulfate content of water supplies shows that the concentration is usually greater than the optimum indicated above for the yeast and may occasionally be fifty times as great.

EUGENE, OREGON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRISTOL]

ATTEMPTS TO SYNTHESIZE MYRICETIN

BY H. F. DEAN AND M. NIERENSTEIN

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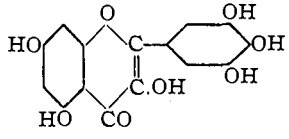
In the present communication we describe a series of experiments to synthesize myricetin (I) and although we have failed in these attempts our results establish the interesting fact that the method of Kostanecki for the synthesis of the flavanols so far generally applicable breaks down in the case of myricetin.

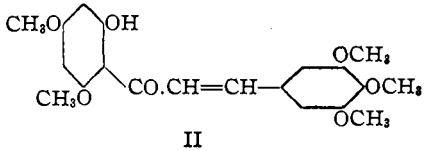
Following Kostanecki's procedure we have prepared 2-hydroxy-4,6,-3′,4′,5′-pentamethoxy-chalcone (II), from which we have obtained 4,6,-3′,4′,5′-pentamethoxy-flavanone (III). However, all our attempts to prepare the corresponding *iso*nitroso-flavanone, which would have ultimately yielded myricetin (I), have only led to negative results.

[8] Kohman and others, *J. Ind. Eng. Chem.*, **8**, 781 (1916).

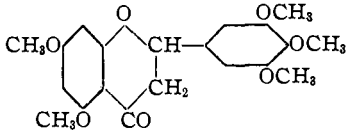
[9] *Connecticut Agr. Exp. Sta. Rept., Bull.*, **200** (1917).



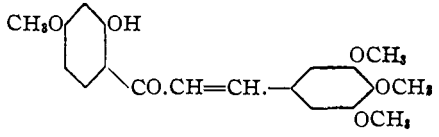
I



II



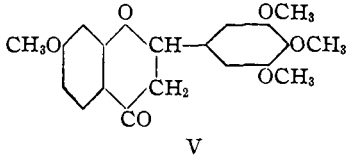
III



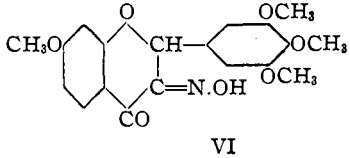
IV

We were at first inclined towards the assumption that the abnormal behavior of the flavanone (III) in not yielding an *iso*nitroso derivative was due to steric influence[1] of the pyrogallol nucleus.

That this is not the case is, however, evident from the fact that 4,3′-4′,5′-tetramethoxy-flavanone (V), which we have prepared from 2-hydroxy-4,3′,4′,5′-tetramethoxy-chalcone (IV) gives an *iso*nitroso derivative (VI).



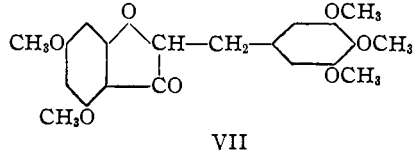
V



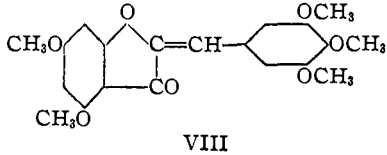
VI

There remained, therefore, the possibility that the product obtained by us from Substance II is not a flavanone (III), but some other product. We have therefore considered the following reasonable possibilities.

(1) That 1,3,3′,4′,5′-pentamethoxy-benzyl-coumaranone (VII) had been produced. Substance VII was therefore prepared by reducing 1,3,3′,4′,5′-pentamethoxy-benzylidene-coumaranone (VIII) and it was found to differ in every respect from the product obtained by us from substance II.



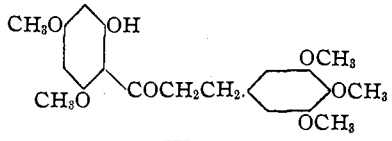
VII



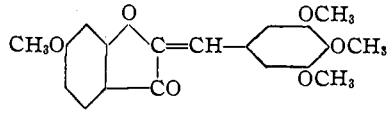
VIII

(2) That Substance III is either the *cis* or the *trans* form of II. It was, however, found that *only* Substance II can be reduced with hydrogen in the presence of palladium when 2-hydroxy-4,6,3′,4′,5′-pentamethoxy-dihydro-chalcone (IX) is produced.

[1] That the phloroglucinol nucleus does not exert such steric influence is evident from the synthesis of quercetin. See Kostanecki, Lampe and Tambor, *Ber.*, **37**, 1402 (1904).



IX

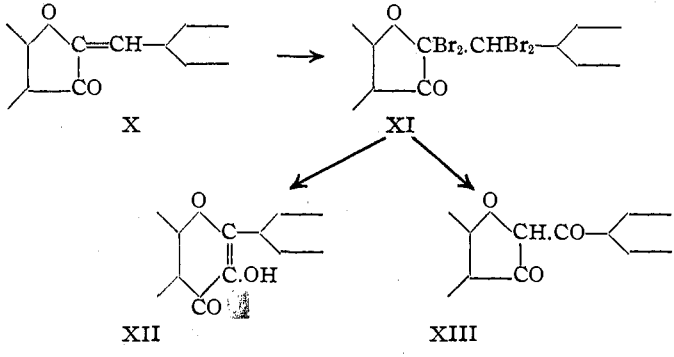


XIV

(3) That Substance III is a dimolecular condensation product of II. That this is not the case is evident from the monomolecular weight of Substance III and from the ease with which II is produced from it.

These observations leave very little doubt that Substance II is really a flavanone which for some unaccountable reason does not yield an *iso*-nitroso derivative.

In view of these results we have also attempted to synthesize myricetin by the less generally applicable method of Auwers.[2] The general scheme of this method is represented by Formulas X, XI, XII and XIII.



X XI XII XIII

Our results with the coumaranones VIII and XIV have shown that they only lead to the formation of products which are derived from Formula XIII, which is in agreement with later work published by Auwers.[3] The fact that only Substance VIII yields a product derived from Formula XIII obviously excludes the possibility of a synthesis of myricetin by Auwers' method.

From these results it is evident that neither the Kostanecki nor the Auwers method is capable of producing myricetin. However, further attempts to synthesize myricetin and other flavonols on different lines from those indicated by Allan and Robinson[4] are now in progress in this Laboratory.

[2] Auwers and Müller, *Ber.*, **41**, 4233 (1908).

[3] Auwers and collaborators, *Ann.*, **405**, 243 (1914); *Ber.*, **48**, 85 (1915); *Ann.*, **421**, 1 (1920).

[4] Allan and Robinson, *J. Chem. Soc.*, **125**, 2193 (1924). Reference must also be made to a communication by Kalff and Robinson that they have synthesized myricetin by this method. See *Chemistry and Industry*, **43**, 1195 (1924).

Experimental Part

2-Hydroxy-4,6,3′,4′,5′-pentamethoxy-chalkone. (II).—This chalkone was prepared by condensing phloro-acetophenone dimethyl ether with gallaldehyde trimethyl ether, which involved the preparation of the following intermediary products.

(1) Phloroglucinol was methylated according to Ryan and Walsh[5] and according to Freudenberg.[6] The yields thus obtained were 23 and 75%, respectively. A yield of 53% was obtained when methylating phloroglucinol tricarbomethoxy ether.

(2) Phloro-acetophenone trimethyl ether was prepared according to the method of Nencki and Stober.[7] It was found to melt at 99–100°, as given by Nencki and Stober, and Tutin and Caton[8] and not at 102–103° as found by Rennie, Cooke and Finlayson.[9]

(3) Phloro-acetophenone dimethyl ether was prepared according to the procedure of H. Schmidt.[10] It melted correctly at 86–87°.

(4) Gallaldehyde trimethyl ether was prepared according to the method of Rosenmund and Zetsche,[11] Sonn and Müller[12] and an adaptation of Rosenmund's method, the yields being 26.8, 24.4 and 75.5%, respectively.[13]

For the preparation of the chalcone (II) we have used an adaptation of the following methods described for the preparation of other chalcones: the method of (1) Kostanecki,[1] (2) of N. Juckel[14] and (3) of Crabtree and Robinson,[15] the yields being 50, 30 and 60%, respectively.

The procedure adopted from the last named method (Crabtree and Robinson) was as follows. To a solution of 1 g. each of gallaldehyde trimethyl ether and phloro-acetophenone dimethyl ether 1.5 cc. of 50% aqueous potassium hydroxide was added and the mixture kept at a temperature of 60–70° for three to four hours. On acidification with dil. hydrochloric acid a yellow solid was precipitated, which crystallized from absolute alcohol in yellow needles; m. p., 180°. The chalcone was very soluble in benzene, toluene, chloroform and ethyl acetate. Its solution in concd. sulfuric acid was deep red; in caustic alkali, deep yellow.

Anal. Subs., 0.1180: CO_2, 0.2782; H_2O, 0.0632. Calcd. for $C_{20}H_{22}O_7$: C, 64.1; H, 5.9. Found: C, 64.3; H, 6.0.

The *acetyl* derivative crystallized from alcohol in very pale yellow needles; m. p., 146–147°.

Anal. Subs., 0.1324: CO_2, 0.3080; H_2O, 0.0746. Calcd. for $C_{22}H_{24}O_8$: C, 63.4; H, 5.8. Found: C, 63.4; H, 6.3.

2-Hydroxy-4,6,3′,4′,5′-pentamethoxy-dihydrochalcone (IX).—Pure electrolytic hydrogen was passed through a warm solution of 0.2 g. of chalcone in 150 cc. of alcohol

[5] Ryan and Walsh, *Proc. Roy. Dublin Soc.*, **15**, 114 (1916).

[6] Freudenberg, *Ber.*, **53**, 1425 (1920).

[7] Nencki and Stober, *Ber.*, **30**, 1768 (1897).

[8] Tutin and Caton, *J. Chem. Soc.*, **97**, 2067 (1910).

[9] Rennie, Cooke and Finlayson, *ibid.*, **117**, 345 (1920).

[10] H. Schmidt, *Dissertation*, Berne, **1910**, p. 28.

[11] Rosenmund and Zetsche, *Ber.*, **51**, 585 (1918).

[12] Sonn and Müller, *Ber.*, **52**, 1933 (1919).

[13] A detailed description of our experiences concerning the preparation of gallaldehyde trimethyl ether will be published elsewhere.

[14] Juckel, *Dissertation*, Berne, **1911**, p. 23.

[15] Crabtree and Robinson, *J. Chem. Soc.*, **121**, 1038 (1922).

in which 0.5 g. of 50% palladium asbestos was suspended. The reduction process was continued until the solution was colorless, when the palladinized asbestos was filtered off and the filtrate evaporated to a small bulk. The concentrated solution was again filtered and water added to the filtrate until a slight cloudiness was produced. On standing, faintly yellow needles separated, which were purified by crystallization from absolute alcohol. White needles were obtained. They melted at 123° and dissolved in concd. sulfuric acid, giving a pale yellow solution.

Anal. Subs., 0.1594: CO_2, 0.3712; H_2O, 0.0842. Calcd. for $C_{20}H_{24}O_7$: C, 63.8; H, 6.4. Found: C, 63.3; H, 5.9.

1,3,3',4',5'-Pentamethoxy-flavanone (III).—Attempts to convert the chalcone into the flavanone by the general methods of Kostanecki, using hydrochloric acid or sulfuric acid gave poor yields of the flavanone, and finally the following procedure was adopted. A solution of 5 g. of chalcone in 700 cc. of alcohol was boiled for 50 hours with 30 g. of phosphorus pentoxide dissolved in 60 cc. of water. At the end of this period, the solution which had darkened only slightly (boiling with sulfuric or hydrochloric acid as used by Kostanecki produces very dark solutions) was evaporated under diminished pressure to approximately one-third of its volume. After standing overnight about 1 g. of yellow needles separated; these were filtered off and washed with a small quantity of alcohol. They consisted of unchanged chalcone (m. p. and mixed m. p., 177–179°). The filtrate was again evaporated under diminished pressure to half its volume and the resulting deep red solution poured into a large volume of water, a yellow solid being precipitated; yield, 25%. After several crystallizations from absolute alcohol, white needles melting at 177–178° were obtained. This melting point was depressed to 159–163° on admixture with the chalcone. The same melting point was obtained for the flavanone prepared by boiling the chalcone with sulfuric or hydrochloric acid.

For the preparation of further quantities of the flavanone, the chalcone that separated during the fractionation process and a weight of this substance equal to that of the pure flavanone obtained were dissolved in the alcoholic mother liquors from the purification of the flavanone. The volume was then made up to 700 cc. and the solution treated as described above. By proceeding in this manner 8 g. of the pure flavanone was obtained from 10 g. of the chalcone.

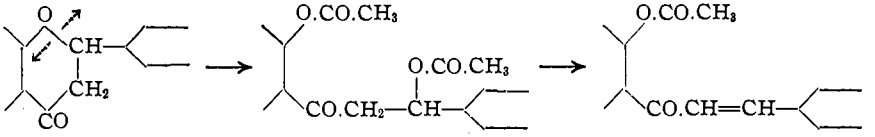
The flavanone was soluble in all the usual organic solvents with the exception of ligroin. Its solubility in alcohol was considerably greater than that of the chalcone. It dissolved in concd. sulfuric acid, giving a pale yellow solution.

Anal. Subs., 0.1786: CO_2, 0.4186; H_2O, 0.0994. Subs., 0.4392 g. dissolved in 22.11 g. of benzene: $\Delta t = 0.150°$. Calcd. for $C_{20}H_{22}O_7$: C, 64.1; H, 5.9; mol. wt., 374. Found: C, 63.9; H, 6.2; mol. wt., 361.

(*a*) **Conversion of the Flavanone (III) into the Chalcone (II).**—A solution of 0.1 g. of flavanone in 5 cc. of alcohol was allowed to stand overnight with 3 cc. of 10% potassium hydroxide solution. The yellow solid obtained on dilution with water and acidification with dil. hydrochloric acid crystallized from alcohol in yellow needles; m. p., 180°. The melting point was not depressed on admixture with authentic chalcone.

(*b*) **Conversion of the Flavanone (III) into Mono-acetyl-chalcone.**—One g. of flavanone was boiled for two hours with excess of acetic anhydride. When the mixture was cooled and poured into water, a yellow solid was precipitated, which crystallized from alcohol in yellow needles (m. p., 146–147°; mixed m. p. with authentic mono-acetyl-chalcone, 146–147°). This acetyl derivative gave chalcone on hydrolysis with dil. sulfuric acid (m. p. and mixed m. p., 180°).

The production of acetyl-chalcone from the flavanone on boiling with acetic anhydride is quite unique and has so far not been recorded. We are inclined to represent this process provisionally as follows.



2-Hydroxy-4,3′,4′,5′-tetramethoxy-chalcone (IV).—This chalcone was prepared by condensing resacetophenone monomethyl ether with gallaldehyde trimethyl ether. The intermediary products were prepared as follows. (1) Resacetophenone was prepared according to the method of Nencki;[16] yield, 87%. (2) Resacetophenone monomethyl ether was prepared according to the method of Tahara;[17] yield, 47%.

To a solution of 4.9 g. of gallaldehyde trimethyl ether and 4.2 g. of resacetophenone monomethyl ether in 50 cc. of alcohol, 12 cc. of 50% potassium hydroxide solution was added in small portions, the mixture being well shaken. After remaining for three to four days, the dark red solution was poured into water and acidified with dil. hydrochloric acid. Yellow needles melting at 132–133° were obtained after several crystallizations from alcohol; yield, 40%. The chalcone dissolved in alkali to form a yellow solution; concd. sulfuric acid gave a deep red solution.

Anal. Subs., 0.1378: CO_2, 0.3353; H_2O, 0.0709. Calcd. for $C_{19}H_{20}O_6$: C, 66.3; H, 5.9. Found: C, 66.4; H, 5.9.

The *acetyl derivative* crystallized in thick, yellow needles from alcohol; m. p., 125–127°.

Anal. Subs., 0.1578: CO_2, 0.3777; H_2O, 0.0796. Calcd. for $C_{21}H_{22}O_7$: C, 65.3; H, 5.7. Found: C, 65.3; H, 5.6.

4,3′,4′,5′-Tetramethoxy-flavanone (V).—A solution of 3 g. of chalcone in 400 cc. of alcohol was boiled for 50 hours with a solution of 20 g. of phosphorus pentoxide in 40 cc. of water. On concentrating the light yellow solution to half its volume under diminished pressure, faintly yellow needles separated, which after recrystallization from alcohol were pure white; m. p., 148–149°; yield, 60%. With concd. sulfuric acid the flavanone gave a yellow solution.

Anal. Subs., 0.1390: CO_2, 0.3385; H_2O, 0.0742. Calcd. for $C_{19}H_{20}O_6$: C, 66.3; H, 5.9. Found: C, 66.4; H, 6.0.

(*a*) *Action of Alkali on the Flavanone (V).*—The procedure was the same as that employed in the case of the previous flavanone. The solid precipitated on the addition of water was filtered off and dil. hydrochloric acid added to the filtrate. By crystallization from alcohol, yellow needles were obtained; m. p., 132–133°. This melting point was not depressed on admixture with authentic chalcone.

(*b*) *Action of Acetic Anhydride on the Flavanone (V).*—A solution of 0.5 g. of flavanone in an excess of acetic anhydride was boiled for two hours under a reflux condenser. After cooling, the light yellow solution was poured into a large volume of water and the pale yellow solid which separated was crystallized from alcohol. White needles melting at 148–149° were obtained; this melting point was not depressed when the substance was mixed with authentic flavanone. The filtrate was poured into water and the solid precipitated was crystallized from a small quantity of alcohol. It also melted at 148–149°. Flavanone V differs therefore fundamentally from Flavanone III, which yields mono-acetyl-chalcone under the same conditions.

Isonitroso-4,3′,4′,5′-tetramethoxy-flavanone (VI).—A solution of 0.5 g. of flavanone in 50 cc. of alcohol was warmed to 60–70° with 1.0 cc. of amyl nitrite and 16 cc. of concd. hydrochloric acid. After 24 hours, yellow needles separated, which were recrystallized

[16] Nencki, *J. prakt. Chem.*, **23**, ii, 147 (1881).

[17] Tahara, *Ber.*, **24**, 2457, 2847 (1891).

from alcohol and water. The pale yellow needles obtained melted at 193° and were readily soluble in cold caustic alkali, forming an intense yellow solution. Concd. sulfuric acid also formed a yellow solution.

Anal. Subs., 0.1320: 4.1 cc. of N (19°, 768 mm., over 33% KOH). Calcd. for $C_{19}H_{19}O_7N$: N, 3.8. Found: 3.7.

1,3,3′,4′,5′-Pentamethoxy-benzylidene-coumaranone (VIII).—The intermediary products required for the preparation of this substance were made as follows. (1) ω-Bromophloro-acetophenone trimethyl ether was prepared according to the method of Dumont and Tambor;[18] m. p., 126°; yield, 43%. (2) 1,3-Dimethoxy-coumaranone was prepared by the method of Dumont and Tambor;[19] m. p., 132°; yield, 27%.

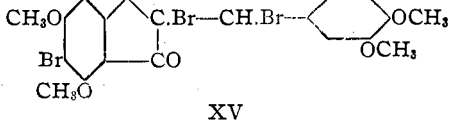
To a solution of 0.6 g. of gallaldehyde trimethyl ether and 0.6 g. of 1,3-dimethoxy-coumaranone, 2 cc. of 10% sodium hydroxide was added. The solution immediately became deep red and a yellow crystalline 1,3,3′,4′,5′-pentamethoxy-benzylidine-coumaranone commenced to separate. After 24 hours, the solid was crystallized from acetic acid and water, yellow needles melting at 214–216° being obtained; yield, 50%. The substance was soluble in the usual organic solvents with the exception of ligroin. It dissolved in concd. sulfuric acid forming a deep red solution.

Anal. Subs., 0.1452: CO_2, 0.3430; H_2O, 0.0755. Calcd. for $C_{20}H_{20}O_7$: C, 64.5; H, 5.4. Found: C, 64.4; H, 5.8.

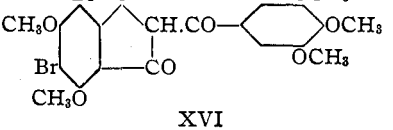
1,3,3′,4′,5′-Pentamethoxy-benzyl-coumaranone (VII).—Pure hydrogen, prepared by electrolyzing a saturated solution of barium hydroxide, was passed through a suspension of the benzylidene coumaranone (VIII) in 200 cc. of warm alcohol, containing 0.5 g. of 50% palladinized asbestos. The reduction process was continued until the solution became colorless, when the catalyst was filtered off and the alcoholic solution evaporated to a small bulk. After the solution had again been filtered, it was diluted with twice its volume of water when, on standing, white silky needles separated; m. p., 138–139°. With concd. sulfuric acid a faintly yellow solution was obtained, caustic alkali gave only a yellow coloration after boiling.

Anal. Subs., 0.1476: CO_2, 0.3464; H_2O, 0.0801. Calcd. for $C_{20}H_{22}O_7$: C, 64.1; H, 5.9. Found: C, 64.0; H, 6.1.

2,4-Dibromo-1,3,3′,4′,5′-pentamethoxy-benzoyl-coumaranone (XVI).—On bromination, 1,3,3′,4′,5′-pentamethoxy-benzylidene-coumaranone (VIII) yields 2,4-dibromo-1,3,3′,4′,5′-pentamethoxy-benzylidene-coumaranone dibromide (XV), which on treatment with alkali according to Auwers' method yields 2,4-dibromo-1,3,3′,4′,5′-pentamethoxy-benzoyl-coumaranone (XVI).



XV



XVI

The bromination of the phloroglucinol nucleus in Substance XV precedes the addition of bromine to the —C=CH— group, as will be seen from the following observations.

To a solution of 0.6 g. of coumaranone in 15 cc. of dry chloroform, 0.43 g. (1 molecular equivalent) of bromine dissolved in 15 cc. of the same solvent was gradually added; a deep red solution was formed and hydrogen bromide was evolved. The solid remaining after the chloroform had evaporated was dried in a vacuum over potassium hydroxide and paraffin wax (obtained, 0.76 g.; required for monobromo derivative, 0.73

[18] Dumont and Tambor, *Ber.*, **43**, 1969 (1910).

[19] Dumont and Tambor, *Ber.*, **43**, 1971 (1910).

g.). A portion of the dark red solid was crystallized from acetic acid and water, when yellow needles, which contained bromine and melted at 217–219°, were obtained. Mixed with the unbrominated derivative (m. p., 214–216°), the melting point was depressed to 186–194°. With concd. sulfuric acid, the characteristic coumaranone coloration was obtained. This substance was not analyzed. The remainder (0.4 g.) was dissolved in 10 cc. of chloroform and treated with a solution of 0.3 g. (2 equivalents) of bromine in the same solvent. Hydrogen bromide was evolved and a deep red solid precipitated. On standing, this gradually disappeared leaving a pale yellow solution, which deposited a light yellow solid on evaporating the chloroform in a current of air. After the residue had been dried in a vacuum over paraffin wax and potassium hydroxide, 0.65 g. of solid was obtained (required for the tetrabromo derivative, 0.62 g.). This substance was very soluble in benzene, acetone, carbon tetrachloride; nearly insoluble in alcohol; insoluble in petroleum ether. It was crystallized from a mixture of alcohol and benzene, thick white needles, which melted at 204–205° with evolution of gas, being obtained. With concd. sulfuric acid a yellow solution was formed.

Anal. Subs., 0.1350: AgBr, 0.1462. Calcd. for $C_{20}H_{18}O_7Br_4$: Br, 46.4. Found: 46.1.

Substance XVI was prepared as follows. To a suspension of 1 g. of finely powdered tetrabromo derivative in 200 cc. of boiling alcohol, 29.0 cc. (2 molecular equivalents), of 0.1 *N* aqueous potassium hydroxide was gradually added. The solid slowly disappeared with the formation of a deep yellow solution, which was concentrated until yellow, glistening needles commenced to separate; these were purified by recrystallization from a mixture of alcohol and a small quantity of benzene. The yellow needles obtained melted at 260–261°; they dissolved in concd. sulfuric acid with the formation of an intensely crimson solution.

Anal. Subs., 0.1950: AgBr, 0.1329. Calcd. for $C_{20}H_{18}O_8Br_2$: Br, 29.3. Found: 29.0.

3,3′,4′,5′-Tetramethoxy-benzylidene-coumaranone (XIV).—The 3-methoxy-coumaranone required for the preparation of this substance was made according to the method of Blom and Tambor;[20] yield, 87%. It crystallized from alcohol in yellow needles that melted at 123°, as observed by Blom and Tambor. In this connection it is interesting to note that Clibbens and Nierenstein,[21] who have prepared this substance by a different method have obtained it in colorless needles that melted at 125°.

To a solution of 2.2 g. of 3-methoxy-coumaranone and 2.8 g. of gallaldehyde trimethyl ether in 70 cc. of absolute alcohol, 5.0 cc. of 10% sodium hydroxide solution was added. The solution became deep red and a crystalline solid separated which was recrystallized from alcohol, giving yellow needles; m. p., 187–188°; yield 4.0 g. This coumaranone was soluble in chloroform, benzene, acetic acid and boiling alcohol, and insoluble in ligroin. It dissolved in concd. sulfuric acid with the formation of a deep red solution.

Anal. Subs., 0.1783: CO_2, 0.4324; H_2O, 0.0914. Calcd. for $C_{19}H_{18}O_6$: C, 66.6; H, 5.3. Found: C, 66.2; H, 5.7.

Monobromo-3,3′,4′,5′-tetramethoxy-benzoyl-coumaranone (Compare Formula XIII).—As in the previous case, substitution precedes addition of bromine on the bromination of Substance XIV.

The intermediary products which have led to the formation of monobromo-3,3′,-4′,5′-tetramethoxy-benzoyl-coumaranone, in which the position of the bromine atom is not certain, have been obtained as follows.

[20] Blom and Tambor, *Ber.*, **38,** 3590 (1905).

[21] Clibbens and Nierenstein, *J. Chem. Soc.*, **107,** 1494 (1915).

(*a*) **Monobromo-3,3′,4′,5′-tetramethoxy-benzylidene-coumaranone.**—To a solution of 1.0 g. of coumaranone in 20 cc. of chloroform, 0.47 g. of bromine (1 molecular equivalent) dissolved in the same solvent was gradually added. A dark red solid separated which subsequently redissolved with the evolution of hydrogen bromide. After standing overnight, the solution was poured into an open dish and the yellow solid dried in a vacuum over potassium hydroxide and paraffin wax; yield, 1.32 g. (required for a monobromo derivative, 1.23 g.). On crystallization from acetone and water, yellow needles melting at 163–164° were obtained. This substance dissolved in concd. sulfuric acid forming a deep red solution, characteristic of the benzylidene-coumaranones. By the action of alkali it was recovered unchanged.

Anal. Subs., 0.4125: AgBr, 0.1819 g. Calcd. for $C_{19}H_{17}O_6Br$: Br, 19.0. Found: 18.8.

(*b*) **Monobromo-3,3′,4′,5′-tetramethoxy-benzylidene-coumaranone Dibromide.**—To a solution of 1 g. of benzylidene-coumaranone in 30 cc. of chloroform, 0.94 g. of bromine (2 equivalents) dissolved in the same solvent was gradually added. A dark red solid was at first formed, which disappeared with the evolution of hydrogen bromide. After 12 hours, the solution, which had become pale yellow, was allowed to evaporate in the open air. The light yellow solid remaining was dried in a vacuum over potassium hydroxide and paraffin wax (obtained, 1.71 g.; required for a tribromo derivative, 1.90 g.). This substance was soluble in chloroform, acetic acid, carbon tetrachloride and benzene, sparingly soluble in alcohol, insoluble in ligroin. White needles which melted at 180° with evolution of gas were obtained by crystallization from a mixture of alcohol and benzene. With concd. sulfuric acid a pale yellow solution was obtained.

Anal. Subs., 0.3116: CO_2, 0.4516; H_2O, 0.1226. Subs., 0.1523: AgBr, 0.1465. Calcd. for $C_{19}H_{17}O_6Br_3$: C, 39.2; H, 2.9; Br, 41.3. Found: C, 39.5; H, 4.4; Br, 40.9.

Monobromo-3,3′,4′,5′-tetramethoxy-benzoyl-coumaranone was prepared as follows. To a suspension of 1 g. of tribromo derivative in 50 cc. of boiling alcohol, 35 cc. (2 molecular equivalents) of 0.1 *N* potassium hydroxide solution was gradually added. The white solid disappeared with the production of a deep yellow solution. On cooling, yellow needles separated, which were crystallized from alcohol; m. p., 162°. A mixed melting point of this substance and the corresponding monobromo-benzylidene-coumaranone gave a depression of 10–14°. This substance dissolved in concd. sulfuric acid with the formation of a deep red solution.

Anal. Subs., 0.4206: AgBr, 0.1794. Calcd. for $C_{19}H_{17}O_7Br$: Br, 18.3. Found: 18.2.

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Summary

Attempts to synthesize myricetin by the generally applicable method of Kostanecki and by the less general method of Auwers are described, all of which have only yielded negative results.

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