XXI.—*Addition of Auxochromes in the Flavone Group.*

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IN a former communication (Watson, T., 1914, **105**, 338), experiments were described which had as their object the introduction of an additional hydroxyl group into the quercetin molecule. By the methods employed, however, this could not be effected, because it was found impossible to convert aminoquercetin pentamethyl ether, by means of the diazo-compound, into the corresponding hydroxy-derivative. On the other hand, aminoquercetin was successfully prepared, and it was shown that the amino-group exerted but little effect on the tinctorial property of the dye.

With the same objects in view, namely, to deepen the colour of the dye and to prepare new polyhydroxyflavones which might prove of future service in the study of the natural members of this group,

identical methods have been applied to both luteolin and morin. Here, however, additional difficulties arise, for although quercetin can be obtained in quantity with comparative facility, the colouring matters in question, especially the former, are far from easy to isolate in quantity and in a pure condition. The work has consequently been hampered by a paucity of raw material.

Luteolin.—It was considered possible that the difficulty experienced in converting the aminoquercetin derivative into the corresponding hydroxy-compound was owing to the hydroxy-group already present in the pyrone ring:

Such an assumption would involve, in the case of aminoquercetin pentamethyl ether, a demethylation of the pyrone methoxy-group, and the formation of a diazo-oxide linking between this and the diazonium hydroxide, during the attempted decomposition of the latter. With morin, for instance, which contains the pyrone hydroxyl group and a hydroxyl group in the same position (6') as this amino-group, an anhydro-sulphate (T., 1896, **59**, 1442) is readily produced, and this formation of an anhydro-compound apparently arises only when two hydroxyl groups are present in these positions.

In luteolin, the pyrone hydroxyl group is absent, and it is interesting to observe, whatever explanation of the anomaly may be forthcoming in the future, that there is no difficulty in preparing hydroxytetraethyl-luteolin from the corresponding diazo-derivative.

For the purpose of this investigation, the luteolin available was converted into the tetraethyl compound, because this is more economically prepared than the tetramethyl ether, and no material difference in the behaviour of these compounds was anticipated. Most probably this has been a mistake, because, although quercetin and morin pentamethyl ethers both readily yield a mononitro-compound, with luteolin tetraethyl ether under the most varied conditions of nitration a tetranitro-derivative could only be obtained. When opportunity occurs, the behaviour of luteolin tetramethyl ether under the same conditions will be studied.

The introduction of one nitro-group into luteolin tetraethyl ether was subsequently effected by means of the monobromo-derivative. With bromine in acetic acid solution, *bromoluteolin tetraethyl ether perbromide*, $C_{23}H_{25}O_6Br.HBr_3$, is produced, and this, on boil-

ing with water, yields a mixture of *bromoluteolin tetraethyl ether* and *tetrabromoluteolin tetraethyl ether*. When, however, one molecule of halogen is used, *bromoluteolin tetraethyl ether hydrobromide*, $C_{28}H_{26}O_6Br.HBr$, separates, which, on treatment with water, gives pure monobromoluteolin tetraethyl ether. From this, by nitration, *bromo-6'-nitroluteolin tetraethyl ether* could be prepared, which, on reduction, was converted into the corresponding amino-derivative. By diazotising, and subsequently boiling with water, *bromo-6'-hydroxyluteolin tetraethyl ether* was readily obtained.

The conversion of the latter compound into hydroxyluteolin would, it was anticipated, be a simple operation; but this, unfortunately, did not prove to be the case, and this compound has not been prepared in a pure condition. Thus, by the action of boiling hydriodic acid (D 1.7) for one hour only, two ethyl groups were apparently eliminated, and a compound, probably *bromo-6'-hydroxyluteolin diethyl ether*, was obtained. As incomplete de-ethylation had apparently been caused by the insolubility of the substance in hydriodic acid, a mixture of hydriodic acid and acetic anhydride was now employed, and there was thus produced a small amount of a substance, which was either an impure *6'-hydroxyluteolin* or *6'-hydroxyluteolin monoethyl ether*. Although the analytical figures are somewhat too high, it is probable that the first supposition is correct, but, owing to the meagre amount available, no elaborate process of purification was possible. The matter is, however, reserved for further study, when it seems likely that, by the employment in the first place of luteolin tetramethyl ether, this desired compound will be more readily obtained.

The compound forms yellow needles, closely resembling luteolin itself, soluble in alkalis with a yellow colour, and no deepening of shade had occurred as the result of the introduction of the new hydroxyl group. When bromonitroluteolin tetraethyl ether is oxidised with permanganate, a *nitro-3:4-diethoxybenzoic acid* is produced, from which it is evident that the nitro-group is present in the catechol nucleus. Such an acid has not been previously prepared, but little doubt can exist that the nitro-group in bromonitroluteolin diethyl ether occurs in the 6'-position.

The course of bromination studied in the case of luteolin tetraethyl ether makes it probable from analogy that the compound previously described (*loc. cit.*) as dibromoquercetin pentamethyl ether hydrobromide is, in reality, *bromoquercetin pentamethyl ether perbromide*.

In certain cases, the colour of the compounds here described is interesting, being in marked contrast to the very similar deriv-

atives of quercetin. Thus, bromo-6'-nitro- and tetranitro-luteolin tetraethyl ethers are practically colourless, whereas 6'-nitro-quercetin pentamethyl ether is bright yellow. Again, bromo-6'-aminoluteolin tetraethyl ether and its hydrochloride are bright yellow, the latter becoming scarlet in a vacuum, whereas the stannichloride, $(C_{23}H_{26}O_6NBr)_4 \cdot H_4SnCl_6$, is deep crimson. On the other hand, 6'-aminoquercetin pentamethyl ether and its hydrochloride are almost white. There is possibly some similarity between the scarlet and crimson derivatives of fully ethylated flavones (see also Watson, *loc. cit.*, pp. 339, 346, 347) and the coloured hydrochlorides of styryl methyl ketone and other unsaturated aromatic ketones described by Francesconi and Cusmano (*Gazzetta*, 1908, **38**, ii, 70). In this connexion, attention may also be drawn to the deep red phenyl piperidylstyryl ketone previously described (T., 1904, **85**, 1323).

Morin.—Morin pentamethyl ether gives, on nitration, *nitromorin pentamethyl ether*, which, on reduction, is converted into the corresponding amino-derivative. As in the case of the analogous quercetin compound, attempts to displace the amino-group by hydroxyl have hitherto failed. *Dibromomorin pentamethyl ether* has been prepared, but from this, by nitration, no appreciable quantity of a nitro-compound could be produced.

Aminomorin hydriodide, from nitromorin pentamethyl ether and hydriodic acid (D 1.7), is soluble in alkalis with a yellowish-brown tint, the additional auxochrome in this case, also, not having caused any noteworthy deepening of colour. Spectroscopic studies which are being carried out by one of us appear to offer an explanation of the difficulty already mentioned (Watson, T., 1914, **105**, 766), namely, that whereas an increase of auxochromes deepens the colour very considerably in certain groups of dyes, as is shown in the difference between alizarin and alizarin-blue, W.R., and fluorescein and gallein, in other cases, such as the flavone group, a similar multiplication of auxochromes has very little effect on the colour.

A multiplication of auxochromes appears to widen the principal absorption band and shift it a little towards the red end of the spectrum, but whereas a slight broadening or shift of a band in the red, yellow, or green part of the spectrum has a great effect on the colour of the substance, the broadening or shifting to an equal extent of a band in the violet, extending from the ultra-violet into the violet end of the spectrum, has very little effect on the visible colour.

E X P E R I M E N T A L.

Derivatives of Luteolin.

The luteolin tetraethyl ether employed in this investigation was prepared by the method previously described (P., 1912, **28**, 328).

Tetranitroluteolin tetraethyl ether, $C_{15}H_2O_2(OEt)_4(NO_2)_4$, was most readily obtained in a pure condition by slowly adding powdered luteolin tetraethyl ether (1 part) to fuming nitric acid (10 parts) at the ordinary temperature. The clear solution was at once poured into water, the precipitate collected, dried, and crystallised from a mixture of acetic acid and alcohol. The yield of the substance, which consisted of colourless, slender prisms, melting at 196° , was equal to that of the luteolin tetraethyl ether originally employed. This substance could also be obtained by nitrating with equal parts of sulphuric acid and nitric acid (D 1.42 or 1.5) at the ordinary temperature, but the yield was not good. Mixtures of nitric acid and acetic acid at the ordinary temperature and at 60° were experimented with in the hope of preparing a mononitro-compound, but without success. The tetranitro-derivative is sparingly soluble in alcohol, but more readily so in acetic acid.

Found, N = 9.4, 9.4.

$C_{23}H_{22}O_{14}N_4$ requires N = 9.7 per cent.

Bromoluteolin tetraethyl ether perbromide,

—Two grams of bromine (4 mols.) dissolved in 20 c.c. of acetic acid were added to a solution of luteolin tetraethyl ether (1 gram) in 20 c.c. of acetic acid. The bright, orange-yellow precipitate thus formed became crystalline (slender prisms) on boiling the mixture for a few minutes. After remaining overnight, the perbromide was collected, washed with acetic acid, and dried over soda-lime. It softens at 157° , and melts and decomposes at 161° .

Found, C = 38.5; H = 4.36; Br = 45.0.

$C_{23}H_{26}O_6Br_4$ requires C = 38.4; H = 3.6; Br = 44.5 per cent.

Bromoluteolin tetraethyl ether hydrobromide,

was obtained when luteolin tetraethyl ether in acetic acid solution was treated with 1 molecule of halogen. On boiling the mixture, the precipitate became crystalline, and consisted of hair-like needles of a paler yellow colour than those of the perbromide. The same substance could be obtained by the addition of hydrobromic acid to a glacial acetic acid solution of bromoluteolin tetraethyl ether. For analysis, it was dried over soda-lime.

Found, C=49·2, 48·4; H=5·1, 5·3; Br=25·2, 25·8.

$C_{25}H_{30}O_8Br_2$ requires C=48·5; H=4·9; Br=25·8 per cent.

Bromoluteolin tetraethyl ether, $C_{15}H_5O_2Br(OEt)_4$, was obtained in quantitative yield by boiling the hydrobromide with water. Nine grams were obtained from 10 grams of luteolin tetraethyl ether by this method. It is also the main product of the action of boiling water, alcohol and water, or dilute sulphurous acid on the perbromide described above, and may also be prepared by brominating luteolin tetraethyl ether in acetic acid solution and in the presence of sodium acetate. In these circumstances, however, by-products are formed, and the purification of the material is troublesome. It crystallises from a mixture of alcohol and acetic acid in colourless, hexagonal plates, melting at 183°.

Found, C=57·8; H=5·5; Br=16·9.

$C_{23}H_{25}O_6Br$ requires C=57·8; H=5·3; Br=16·8 per cent.

Tetrabromoluteolin tetraethyl ether, $C_{15}H_2O_2Br_4(OEt)_4 \cdot H_2O$, is one of the products of the bromination of luteolin tetraethyl ether with two molecules of halogen in acetic acid solution in the presence of sodium acetate. The slight precipitate of oxonium salt was removed, water added to the filtrate, and the product collected and crystallised from a mixture of alcohol and acetic acid. The first deposit consisted chiefly of the monobromo-compound, whereas the tetrabromo-derivative subsequently separated. A better method of separation consisted in adding hydrobromic acid to an acetic acid solution of the mixture, in which case the monobromo-compound was precipitated as hydrobromide, whereas tetrabromoluteolin tetraethyl ether, which does not yield a hydrobromide, remained in solution, and was subsequently deposited in colourless, lenticular crystals, melting at 111–114°.

Found, C=37·9; H=3·4; Br=43·1.

$C_{23}H_{24}O_7Br_4$ requires C=37·7; H=3·3; Br=43·7 per cent.

Bromo-6'-nitroluteolin tetraethyl ether, $NO_2 \cdot C_{15}H_4O_2Br(OEt)_4$.—Finely powdered bromoluteolin tetraethyl ether (1 part) was gradually added to nitric acid (D 1·4: 5 parts), which had been previously boiled with carbamide nitrate. Towards the end of the addition, the oxonium nitrate of the unchanged tetraethyl ether separated in bright, yellow needles. The mixture was now heated to 60° for half an hour, and, on cooling, the nitro-compound was deposited as an oil, which quickly changed to large, rhombic crystals. Water was then added, and the precipitate collected and crystallised from a mixture of acetic acid and alcohol. It consisted of pale, cream-coloured rhombs, melting at 170–171°. Thirteen grams of bromoluteolin tetraethyl ether gave 11·4 grams of the nitro-compound.

Found, C=53.0; H=4.6; Br=15.0.

$C_{23}H_{24}O_8NBr$ requires C=52.9; H=4.6; Br=15.3 per cent.

Bromo-6'-aminoluteolin tetraethyl ether.—A mixture of 0.5 gram of the nitro-compound, 12 c.c. of alcohol, 2.5 c.c. of concentrated hydrochloric acid, and 1.25 grams of stannous chloride was gently boiled for a few minutes, causing the development of a deep crimson colour. After a few hours, the product was poured into water acidified with hydrochloric acid, and the crimson precipitate (which consists of the tin double chloride of the base) was collected, well washed, and finally boiled with water, causing it to become yellow, owing to the production of the free base. This was collected, dried, and, by crystallisation from alcohol, was obtained in short, yellow prisms, melting at 165—169°, readily soluble in alcohol or acetic acid. In a second preparation, 11 grams of the nitro-compound gave 7.3 grams of the crystalline base.

Found, C=56.3; H=5.6; Br=15.8.

$C_{23}H_{26}O_6NBr$ requires C=56.1; H=5.3; Br=16.3 per cent.

The *hydrochloride*, $C_{15}H_4O_2Br(OEt)_4 \cdot NH_2, HCl, H_2O$, separates when a few drops of hydrochloric acid are added to a solution of the base in alcohol or acetic acid. It forms bright yellow needles which, when dried over soda-lime, become scarlet, and melt and decompose at 187°.

Found, C=50.8, 50.7; H=5.7; Br+Cl=21.2, 21.6.

$C_{23}H_{29}O_7NBrCl$ requires C=50.5; H=5.3; Br+Cl=21.1 per cent.

The *stannichloride*, $(C_{23}H_{26}O_6NBr)_4, H_4SnCl_6$, the intermediate product of the preparation of the base, can also be obtained by adding stannous chloride and hydrochloric acid to the alcoholic solution of the latter. Two c.c. of hydrochloric acid and 0.4 gram of stannous chloride were added to a solution of 0.4 gram of the base in 16 c.c. of boiling alcohol. Hot water was cautiously added, and the mixture allowed to cool, when the salt was deposited in stout, crimson prisms, which were collected, washed with alcoholic hydrochloric acid, and dried in a desiccator. It is remarkable that when bromonitroluteolin tetraethyl ether is mixed with a solution of stannous chloride in hydrochloric acid, no crimson colour develops, but the orange-coloured substance so obtained becomes red on treatment with alcohol or water.

Found, Sn=4.8.

$(C_{23}H_{26}O_6NBr)_4, H_4SnCl_6$ requires Sn=5.1 per cent.

The reduction of bromonitroluteolin tetraethyl ether by alcoholic sodium sulphide proceeds in a different manner, the main product of the reaction being a substance melting at 187°, and crystallising from alcohol in cream-coloured needles. This has not yet been further investigated.

Bromo-6'-hydroxyluteolin tetraethyl ether, $C_{15}H_4O_2Br(OEt)_4 \cdot OH$.—Half a gram of the base was treated with 0.7 c.c. of hydrochloric acid (6 mols.) and 8 c.c. of water, the mixture being boiled in order to convert the base completely into hydrochloride, cooled, and then treated with 0.07 gram of sodium nitrite (1 mol.). The amino-hydrochloride almost completely dissolved, and, on agitation, needle-shaped crystals of *bromoluteolin tetraethyl ether diazonium chloride* were deposited. After keeping for a short time, the mixture was added to 250 c.c. of water, and the resulting solution of the diazonium chloride boiled vigorously for fifteen minutes. The clay-coloured precipitate of the bromohydroxy-compound was collected, and could be crystallised from much boiling acetic acid, but as partial acetylation occurred during this process, it was better first to prepare the acetyl compound by means of boiling acetic anhydride and pyridine, and purify this by crystallisation from acetic acid with the aid of animal charcoal. A small quantity of a red-coloured impurity was thus removed, and the acetyl compound was obtained in white needles, melting at 270—272°. Unfortunately, the employment of the charcoal considerably decreased the yield. By avoiding its use, 4 grams of acetyl derivative possessing a faint pink colour, but melting correctly, could be obtained from 5 grams of the bromoamino-compound.

Found, C=55.9, 55.5; H=5.2, 5.3; Br=14.9.

$C_{25}H_{27}O_3Br$ requires C=56.1; H=5.1; Br=14.9 per cent.

By hydrolysing the acetyl derivative, bromohydroxyluteolin tetraethyl ether was obtained in yellow needles, melting at 255°, almost insoluble in alcohol or benzene, but soluble in cold sulphuric acid with a cherry-red coloration.

Bromo-6'-hydroxyluteolin diethyl ether, $C_{15}H_4O_2Br(OH)_3(OEt)_2$.—When bromohydroxyluteolin tetraethyl ether or its acetyl derivative is digested with boiling hydriodic acid (D 1.7), no solution apparently occurs. One gram of the acetyl derivative was boiled with 50 c.c. of hydriodic acid for one hour, and the product poured into dilute sodium hydrogen sulphite solution. A yellow, semi-crystalline solid was thus obtained, which was not completely soluble in aqueous potassium hydroxide. On acetylation in the usual manner with acetic anhydride and pyridine, this yielded a buff-coloured acetyl derivative, which crystallised in uniform needle-shaped crystals, melting at 213°. The product is apparently *bromo-6'-hydroxyluteolin diethyl ether triacetate*.

Found, C=53.0; H=4.8; Br=15.3.

$C_{25}H_{23}O_{10}Br$ requires C=53.3; H=4.1; Br=14.2 per cent.

It appeared probable that the incomplete de-ethylation of the tetraethyl ether arose from its insolubility in boiling hydriodic

acid, and 1 gram of the substance was now treated with a mixture of 50 c.c. of the acid and 25 c.c. of acetic anhydride for two hours. On pouring into water containing a little sodium hydrogen sulphite, a yellow, gelatinous precipitate (0.36 gram), soluble in alkali, was obtained. This, on acetylation, gave an acetyl derivative, crystallising from acetic anhydride in white needles, which began to sinter at 225° , and melted at $250\text{--}256^{\circ}$. A second digestion with acetic anhydride and hydriodic acid was without further result. Distinct preparations of the acetyl compound were analysed.

Found, C=59.4, 59.7, 59.9; H=4.4, 4.4, 4.4.

$\text{C}_{15}\text{H}_5\text{O}_2(\text{OAc})_5$ requires C=58.6; H=3.9 per cent.

As stated in the introduction, these figures were disappointing, and although it suggested itself that this arose from incomplete de-ethylation, on consideration it seemed more likely that the compound was, in reality, hydroxyacetyl-luteolin contaminated with a small amount of some impurity. In the latter case, it was conceivable that, under the drastic treatment employed, an elimination of a hydroxyl group from a portion of the substance had occurred, the second substance in question being thus either luteolin itself or an isomeric tetrahydroxyflavone. Whichever of these suggestions is correct must remain for future decision, for, owing to the exhaustion of the material, attempts to solve the matter by fractional crystallisation processes were out of the question. On hydrolysis in the usual way, the acetyl derivative yielded the free hydroxy-compound as a gelatinous precipitate, which was subsequently obtained in needle-shaped crystals. It dissolved in alkali solutions with a yellowish-brown colour, and was very similar to luteolin itself.

Nitro-3:4-diethoxybenzoic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_2(\text{OEt})_2\cdot\text{CO}_2\text{H}$.—The oxidation of bromo-6'-nitroluteolin tetraethyl ether with permanganate under the conditions found suitable for the oxidation of nitroquercetin pentamethyl ether gave no satisfactory result, but, on the other hand, the use of this reagent in alkaline solution proved successful. Two grams of the substance, obtained in the gelatinous condition by solution in sulphuric acid and precipitation with water, being subsequently well washed, were rubbed into a paste with an aqueous solution containing 5 grams of potassium permanganate and 5 grams of sodium hydroxide. In about a day, the permanganate having disappeared, the manganese oxide was filtered off, and the pale yellow filtrate acidified and extracted with ether. From the ether a yellow, crystalline residue was obtained, which, after two recrystallisations from benzene, separated in colourless needles, melting at $145\text{--}148^{\circ}$. The yield was 0.2 gram.

Found, C=51·7; H=5·4.

$C_{11}H_{13}O_6N$ requires C=51·8; H=5·1 per cent.

It was evidently nitro-3:4-diethoxybenzoic acid.

Derivatives of Morin.

Morin pentamethyl ether.—The preparation of this substance was effected by two methods:

(1) The modification of Valiaschko's process, which proved so successful for the preparation of quercetin pentamethyl ether, and is described in the former communication (Watson, *loc. cit.*). The first stage of the process gave mainly morin dimethyl ether, and the second stage had to be repeated before the pentamethyl ether could be obtained in the pure condition. The yield was 25 per cent.

(2) Herzig and Hofmann's method, with slight modification (*Ber.*, 1909, **42**, 155). Five grams of morin (either the yellow or the colourless variety) were dissolved in a 10 per cent. solution of sodium hydroxide (4 mols.) and shaken in an atmosphere of coal-gas with methyl sulphate (4 mols.). This operation was repeated four times, and, after the last two additions, the flask was heated for half an hour on the water-bath. The product was collected, washed, dried, dissolved in 50 c.c. of alcohol, and poured into 500 c.c. of ether. After removal of insoluble matter, the ethereal solution was shaken three times with 5 per cent. potassium hydroxide solution, and then with water. This caused the separation of the pentamethyl ether in white crystals, which were removed with some difficulty from the mixture of ether and water. The yield was 2·3 grams, and no recrystallisation was necessary.

Nitromorin pentamethyl ether, $C_{15}H_4O_2(OMe)_5 \cdot NO_2$.—The nitration of morin pentamethyl ether proved to be a troublesome operation. As oxidation readily occurs if the nitration mixture is allowed to remain, the process must be carried out rapidly, and quantities greater than 0·2 gram should not be employed at one time. The finely powdered substance was added to 2 c.c. of cold nitric acid (D 1·4), previously boiled with carbamide nitrate, and as soon as all had dissolved, the dark, greenish-blue-coloured solution was poured into water. The precipitate, at first grey, soon became ochreous, and was collected, drained on tile, and crystallised from alcohol, from which it was deposited in reddish-brown needles, melting at 223—225°. The yield was approximately 50 per cent.

Found, N=3·7.

$C_{20}H_{19}O_9N$ requires N=3·4 per cent.

It is moderately soluble in alcohol, but more readily so in acetone.

Aminomorin pentamethyl ether, $C_{15}H_4O_2(OMe)_5 \cdot NH_2$.—A mixture of 1 gram of nitromorin pentamethyl ether, 30 c.c. of alcohol, 2 grams of powdered tin, and 6 c.c. of hydrochloric acid was heated slowly until the greater portion of the alcohol had been driven off. On cooling, yellow needles of the stannichloride separated, which were collected, and treated in warm aqueous solution with excess of sodium carbonate, whereby a precipitate, consisting chiefly of lenticular crystals, was deposited. The dried product was extracted with about 250 c.c. of alcohol, and, on concentrating the solution, 0.5 gram of aminomorin pentamethyl ether was deposited in almost colourless, hexagonal plates, melting at 204—205°.

Found, C=61.9; H=5.8.

$C_{20}H_{21}O_7N$ requires C=62.0; H=5.4 per cent.

It is very readily soluble even in cold dilute hydrochloric acid, and this solution, on addition of platinic chloride, gradually deposits the *platinichloride*, $(C_{20}H_{21}O_7N)_2 \cdot H_2PtCl_6$, in stout, yellow prisms.

As stated in the introduction, attempts to prepare the corresponding hydroxymorin pentamethyl ether from the amino-compound by the diazotisation method were unsuccessful, and, indeed, no definite product could thus be isolated.

Dibromomorin pentamethyl ether, $C_{15}H_3O_2Br_2(OMe)_5$.—When brominated in acetic acid solution, the behaviour of morin pentamethyl ether is not the same as that of the luteolin compound above described, for with one molecular proportion of bromine no precipitation of oxonium salt occurs. The following method was eventually adopted.

A solution of 2.25 grams of morin pentamethyl ether in 5 c.c. of boiling acetic acid was treated with 2.9 grams of bromine (3 mols.) in 20 per cent. acetic acid solution, causing the separation of a crystalline precipitate, and, after keeping overnight, this was collected, washed with acetic acid, and dried over soda-lime. This product (3.75 grams), at first brick-red, gradually assumed a pale colour, and may be the *dibromopentamethyl ether perbromide*, which thus slowly loses bromine, with the formation of *dibromomorin pentamethyl ether hydrobromide*. Analysis gave C=36.7; H=3.5; Br=50.0 per cent., and these figures agree approximately with those required by the formula $(C_{20}H_{18}O_7Br_2 \cdot HBr)_3 \cdot Br$.

It was now digested with boiling sodium hydrogen sulphite solution, and the colourless precipitate was collected, dried, and treated with about 25 c.c. of boiling acetic acid. The almost clear liquid, while still hot, deposited rhombic crystals, melting at 254—264°, in amount equal to the morin pentamethyl ether originally taken. This compound, which consists of *dibromomorin penta-*

methyl ether, after several recrystallisations, melted at 263—270°. It is only sparingly soluble in acetic acid or alcohol, more readily so in chloroform, but is not easy to obtain from these solvents in a well-crystallised condition.

Found, C=45·5; H=3·8; Br=29·8.

C₂₀H₁₈O₇Br₂ requires C=45·3; H=3·4; Br=30·2 per cent.

A substance melting at 200—205°, probably bromomorin pentamethyl ether, can be isolated by the employment of one molecular proportion of bromine in the presence of acetic acid, and subsequent addition of a little concentrated hydrobromic acid. The bright yellow oxonium hydrobromide thus precipitated is collected, digested with boiling water, and recrystallised from acetic acid and alcohol. The yield, however, was poor, and on this account the substance was not further investigated.

Attempts to nitrate dibromomorin pentamethyl ether under varied conditions gave unsuccessful results.

Aminomorin, C₁₅H₄O₂(OH)₅·NH₂.—This substance was obtained by digesting nitromorin pentamethyl ether with boiling hydriodic acid (D 1·7) for one hour. The mixture, on cooling slowly, deposited *aminomorin hydriodide*, C₁₅H₄O₂(OH)₅·NH₂·HI·H₂O, as either spherulites or square platelets, according to the concentration of the solution. For analysis, it was separated from the acid by decantation, drained on tile, and dried in a vacuum desiccator. The product contained a small amount of free iodine, but as this could not be removed by sulphurous acid without partial hydrolysis occurring, it has been allowed for in interpreting the analytical results.

Found, C=37·1; H=3·6; I=31·1, or, deducting free iodine, C=39·0; H=3·7; I=27·4.

C₁₅H₁₁O₇N·HI·H₂O requires C=38·9; H=3·0; I=27·4 per cent.

It possesses a yellowish-brown colour, is not readily soluble in water or dilute acids, but dissolves in aqueous potassium hydroxide to form a brownish-yellow solution. With acetic anhydride and sodium acetate, a colourless acetyl derivative is produced; this is readily soluble in acetic acid, but, like the acetylation product of morin itself, has not been obtained in a crystalline condition.

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