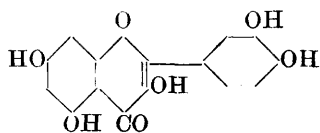


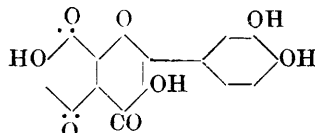
XCV. —isoQuercetone.

By MAXIMILIAN NIERENSTEIN.

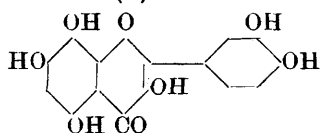
By the oxidation of quercetin (I) with chromic acid, Nierenstein and Wheldale (*Ber.*, 1911, **44**, 3487) obtained quercetone (II), which yields hydroxyquercetin (III) on simultaneous acetylation and reduction and subsequent saponification. The latter is isomeric with gossypetin, quercetagetin, and myricetin, but not identical with either of them (A. G. Perkin, T., 1913, **103**, 661). A similar oxidation product was obtained by Perkin by the action of *p*-benzoquinone on gossypetin; he assigned to it the name gossypetone, and the probable constitution of an ortho-quinone. The present communication appears to confirm Perkin's interpretation of his reaction, since hydroxyquercetin, on oxidation with *p*-benzoquinone, also gives an ortho-quinone, for which the name *isoquercetone* (IV) is proposed.



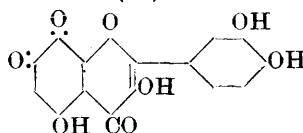
(I.)



(II.)



(III.)



(IV.)

EXPERIMENTAL.

The preparation of *isoquercetone* was the same as that given by A. G. Perkin (*loc. cit.*) for gossypetone, the average yield being 87 per cent. of the theoretical:

0.1156 gave 0.2411 CO₂ and 0.0286 H₂O. C=56.88; H=2.77.

C₁₅H₈O₈ requires C=56.95; H=2.53 per cent.

isoQuercetone resembles gossypetone in its general properties and colour reactions, but apparently differs from it in its dyeing qualities. The following shades are produced on mordanted cotton:

Chromium.	Aluminium.	Tin.	Iron.
Chocolate-brown.	Greenish-brown.	Brick-red.	Greenish-brown.

In order to convert *isoquercetone* into hydroxyquercetin, 0.5 gram of the former in 50 c.c. of acetic anhydride was heated for

five hours with 10 grams of zinc dust, and the filtered solution, when cold, diluted with water. The white precipitate thus obtained gave on hydrolysis 0.47 gram of crude hydroxyquercetin, which crystallised from alcohol and water (2:3) in microscopic yellow needles, melting at 351—354°. (Found, C=56.59; H=3.26. $C_{15}H_{10}O_8$ requires C=56.63; H=3.17 per cent.)

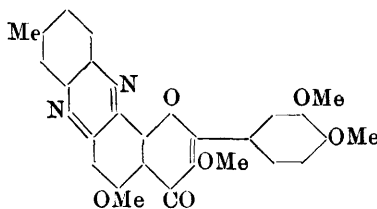
Methylation.—All attempts to methylate isoquercetone with methyl sulphate or methyl iodide having failed, diazomethane was used as a methylating agent, but here also difficulties had to be overcome, since it was found that the isoquercetone tetramethyl ether was formed only if the exact theoretical amount of diazomethane (4 mols.) was used. When an excess (5—5½ mols.) of diazomethane was employed, the products were 7:8-methylenedioxy-3:5:3':4'-tetramethoxyflavone and traces of a nitrogenous substance, which has, so far, not been fully investigated.* The ethereal solutions of diazomethane were therefore always quantitatively tested by the benzoic acid method of Marshall and Acree (*Ber.*, 1910, **43**, 2323) before using them for methylation.

isoQuercetone tetramethyl ether, $C_{15}H_4O_4(OMe)_4$, crystallises from absolute alcohol in glistening yellow needles, which melt at 242—244°. It is also moderately soluble in acetic acid or acetone, from which solutions it is obtained in felted, yellow needles:

0.1533 gave 0.3461 CO_2 and 0.0602 H_2O . C=61.57; H=4.39.

$C_{19}H_{16}O_8$ requires C=61.29; H=4.32 per cent.

isoQuercetone tetramethyl ether condenses with tolylene-3:4-diamine, forming the azine:



For this purpose, 0.5 gram of the tetramethyl ether was dissolved in 8 c.c. of glacial acetic acid, and heated on the water-bath with 0.5 gram of the tolylenediamine in 5 c.c. of glacial acetic acid. After about forty-five minutes crystals commenced to separate, and soon afterwards the mixture became apparently solid. The product, after being collected and washed with acetic

* I am at present engaged in an investigation of the behaviour of diazomethane towards α -diketones, and am under the impression that the formation of similar products is a fairly general one, as already observed by Francis and Wilson (*T.*, 1913, **103**, 2240) in the case of 5:5-dibromo-1:1:2:2-tetramethylcyclopentane-3:4-dione.

acid, was redissolved in glacial acetic acid, from which it separated in deep red prismatic needles, melting and decomposing at about 328—331°:

0.1962 gave 11.0 c.c. N_2 at 30° and 716 mm. $N=6.17$.

$C_{26}H_{22}O_6N_2$ requires $N=6.11$ per cent.

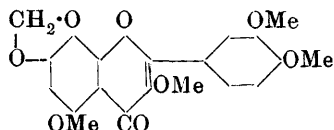
When fused with alkali or boiled with alcoholic potassium hydroxide, *isoquercetone* tetramethyl ether yields veratric acid (small needles from water, m. p. 179—180°). (Found, $C=59.12$; $H=5.72$. $C_9H_{10}O_4$ requires $C=59.32$; $H=5.49$ per cent.) Here, as in the case of quercetone (Nierenstein and Wheldale, *loc. cit.*) and chrysone (Nierenstein, *Ber.*, 1912, **45**, 499), no definite fission product derived from the second nucleus was formed, although the methyl ether had been used for hydrolysis.

Tetra-acetylisoquercetone, $C_{15}H_4O_4(O\cdot CO\cdot CH_3)_4$, is formed in the usual way by boiling *isoquercetone* with acetic anhydride. It crystallises from *s*-tetrachloroethane in long yellow needles, which melt and decompose at about 238—242°. It is sparingly soluble in boiling alcohol, from which it separates in prismatic needles, which have the somewhat sharper melting point 240—242°; this preparation was therefore used for analysis:

0.1132 gave 0.2387 CO_2 and 0.0342 H_2O . $C=57.51$; $H=3.38$.

$C_{23}H_{16}O_{12}$ requires $C=57.02$; $H=3.35$ per cent.

7:8-Methylenedioxy-3:5:3':4'-tetramethoxyflavone,



This compound can be prepared either by methylating *isoquercetone* with an excess of diazomethane, or, preferably, by treating *isoquercetone* tetramethyl ether suspended in ether with one and a-half molecular proportions of diazomethane. On evaporation of the ether, a mixture consisting of the methylenedioxy-derivative and a nitrogenous substance is left; the two substances can be separated by repeated recrystallisation from benzene, in which the methylenedioxy-derivative is less readily soluble. The pure 7:8-methylenedioxy-3:5:3':4'-tetramethoxyflavone crystallises from benzene and alcohol in pale yellow prismatic needles, which melt at 192—193°:

0.1946 gave 0.4457 CO_2 and 0.0832 H_2O . $C=62.46$; $H=4.78$.

$C_{20}H_{18}O_8$ requires $C=62.22$; $H=4.68$ per cent.

In order to eliminate the methylene group, 5 grams of the pro-

duct dissolved in 25 c.c. of absolute alcohol were heated in a sealed tube for five hours at 200° with 75 c.c. of absolute alcohol saturated with hydrogen chloride. The tube contained a considerable amount of carbon, which had been formed, as in the case of piperonal, when heated with hydrogen chloride under the same conditions (Fittig and Remsen, *Annalen*, 1872, **168**, 96). The solution was filtered, and the residue extracted with alcohol. The alcoholic solutions were then evaporated to dryness under diminished pressure, and the residue was extracted with cold alkali. The solution gave, when acidified with sulphuric acid, a bulky precipitate, which, however, did not crystallise, although it was soluble in alcohol, acetic acid, ethyl acetate, or acetone. The precipitate appeared to consist mainly of 7:8-dihydroxy-3:5:3':4'-tetramethoxyflavone, since, on treatment with an excess of diazomethane, it gave 3:5:7:8:3':4'-hexamethoxyflavone, which was also identified by comparing it with the same hexamethoxyflavone obtained by methylating with diazomethane 3-hydroxy-5:7:8:3':4'-pentamethoxyflavone, previously described by Nierenstein and Wheldale (*loc. cit.*).

The substance crystallises from alcohol or benzene in colourless needles, melting at $142\text{--}144^{\circ}$. A mixture of the two preparations melted at $142\text{--}143^{\circ}$. (Found, C=62.36; H=5.86. $\text{C}_{21}\text{H}_{22}\text{O}_8$ requires C=62.68; H=5.47 per cent.)

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