LXXVII.—*Rhamnazin*.

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IN a previous communication (Perkin and Geldard, Trans., 1895, 67, 496), it was shown that Persian berries, the fruit of various species of *Rhamnus*, contain, in addition to the glucosides of quercetin and rham

netin (quercetin monomethyl ether), that of a third substance, $C_{17}H_{14}O_7$, which was named rhamnazin. This, which was distinguished from the above colouring matters by its solubility in boiling toluene, when treated with hydriodic acid, yielded quercetin and two molecules of methylic iodide, being therefore a quercetin dimethyl ether; the production from it of triacetyl and tribenzoyl derivatives also corroborated this fact. An interesting point in connection with this substance was, that it showed but slight indications of dyeing power, iron mordants being coloured a faint brown, whilst the portion mordanted with alum acquired only a pale-yellow tinge. Owing to the difficulty of preparing any quantity of this substance, it was not possible at that time to make an examination into the positions occupied by the two methoxyl groups, and the present investigation has been undertaken with this object.

About 10 grams of rhamnazin were therefore prepared according to the method previously described. It melted at $214-215^\circ$, and on analysis gave $C = 61.69$; $H = 4.30$ per cent., $C_{17}H_{14}O_7$ requiring $C = 61.82$; $H = 4.24$ per cent.

In examining Herzig's formula for quercetin,

it was at first necessary to determine if a methoxyl group in rhamnazin occupied an *ortho*-position relatively to the carbonyl group. If this were the case, most probably, on methylation, a quercetin pentamethyl ether would be formed, an extremely interesting compound if obtainable, for quercetin itself only yields a tetramethyl ether by such treatment, the hydroxyl under discussion refusing to react by the ordinary methods. For this purpose, rhamnazin dissolved in a solution of potassium hydroxide (3 mols.) in methylic alcohol was boiled with excess of methylic iodide for 12 hours. On cooling, the semi-solid mass of crystals formed was collected, washed, first with a little alcohol, then with a dilute potassium hydroxide solution, and purified by crystallisation from alcohol.

0.1187 gave 0.2768 CO_2 and 0.0540 H_2O . $C = 63.59$; $H = 5.05$.

$C_{15}H_6O_3(OCH_3)_4$ requires $C = 63.68$; $H = 5.02$ per cent.

This product consisted of glistening, pale-yellow needles melting at $156-157^\circ$, and was evidently identical with the quercetin tetramethyl ether obtained by Herzig (*Monatsh.*, 1884, 5, 83) from the direct methylation of quercetin. This was further corroborated by its

acetylation, a colourless acetyl compound being thus formed melting at 167—168°, and having the properties assigned to monacetyl quercetin tetramethyl ether.

It thus appeared that rhamnazin does not contain a methoxyl group in the ortho-position relatively to the carbonyl group, but it was still possible that such a group, being unstable, might be decomposed by the alkali during the above methylation. For instance, the alizarin α -monomethyl ether described by one of us and J. J. Hummel (Trans., 1893, 63, 1160) as existing in the *Oldenlandia umbellata* root, by simple digestion with baryta water, is converted into alizarin. Rhamnazin was therefore treated in a similar manner, and also with boiling alkaline solutions of varied strength, but in no case could any derivative of quercetin other than unchanged rhamnazin be detected.

Decomposition with Fused Alkali.—Rhamnazin was heated with 10 parts of caustic potash and a little water at 180—200° for half an hour, and the pale brown melt thus produced dissolved in a little water, neutralised with acid, and extracted with ether. A crystalline product was thus obtained which was dissolved in a little water, treated with lead acetate solution, and the precipitated lead compound collected and washed. To the filtrate, sulphuric acid was added, the clear liquid decanted from lead sulphate, neutralised with sodium hydrogen carbonate, and extracted with ether. On evaporation, a residue was obtained which, after crystallisation from water, formed colourless needles melting at 210°, and gave all the reactions of *phloroglucinol*, and on decomposing the lead precipitate with acid, *protocatechuic acid* was obtained in colourless needles melting at 195—196°.

Action of Alcoholic Potash.—Rhamnazin, on boiling with alcoholic potash, was decomposed but slowly, the action requiring three days for completion. The brown solution thus formed was evaporated to dryness, the residue dissolved in water, and after extraction with ether to remove an oily product present in very small quantity, A, was neutralised with carbonic anhydride, and again extracted with ether (B). The aqueous liquid on acidification deposited a crystalline precipitate, which was removed by means of ether, dissolved in boiling water, and filtered from some insoluble matter; the crystals which separated on cooling were collected and purified by recrystallisation from benzene.

This product consisted of colourless needles melting at 205—206°, which in aqueous solution yielded a precipitate with lead acetate, but no coloration with ferric chloride. It was evidently *vanillic acid*, and no further confirmation of this could be necessary, seeing that, from the previous results, it could not be other than a derivative of protocatechuic acid.

The extract A, on evaporation, yielded the oily matter above referred to; this had the unmistakable odour of *vanillin*, suggesting that in

the above decomposition the formation of the aldehyde precedes that of the acid. An analogous result was obtained by one of us (see preceding paper), in the examination of the products of the decomposition of apigenin dimethyl ether formed in a like manner, not only anisic acid, but also the aldehyde being produced. From extract B, a somewhat viscid product was obtained, an aqueous solution of which gave the phloroglucinol reaction. Attempts to isolate this substance by the usual methods were unsuccessful, and its existence in the free state was thus doubtful.

Could phloroglucinol be obtained from rhamnazin by some gentle decomposition, proof would exist that this portion of the molecule contained no methoxyl group.

By the exposure of alkaline solutions of quercetin and fisetin to air, Herzig obtained respectively phloroglucinol and resorcinol, and the decomposition products obtained from rhamnazin in a similar way were therefore examined; the result, however, was that only vanillic acid and a viscid product having properties analogous to the one obtained by the action of alcoholic potash were isolated, and from the latter, as before, no crystallised phloroglucinol could be extracted. The quantity of material available for these experiments was certainly small, but, on the other hand, even comparative traces of this substance are in most cases readily isolated.

From the above results, it is evident that one methoxyl group in rhamnazin is present in the catechol nucleus. Beyond the fact that the second does not occur in the phloroglucinol nucleus in the ortho-position relatively to the carbonyl, no further knowledge as to its position could be gained. The constitution of rhamnazin must therefore be represented in one of the two following ways :

by the former of which, according to generally accepted views, it would be a rhamnetin monomethyl ether.

Rhamnazin possesses very feeble dyeing properties, which, owing to its method of purification, cannot be considered as due to adherent traces of rhamnetin or quercetin; and these must be considered in discussing its constitution.

The tinctorial properties of quercetin are due to the arrangement of two distinct pairs of hydroxyl groups in its molecule, and could either pair be singly removed, the substance thus produced would still possess the characteristics of a dyestuff. This is readily seen by a comparison

of its formula with that of chrysin, and an isomeric dihydroxyflavone lately prepared by Friedländer and Neudorfer (*Ber.*, 1897, 30, 1077),

the former of which is a comparatively feeble dye, whereas the latter is apparently normal in this respect. The tinctorial effect of the ortho-hydroxyls in the dihydroxyflavone is neutralised in rhamnazin by the substitution of methoxyl for one of them, and its dyeing property can thus only be due to the presence in it of the meta-hydroxyls which it contains analogous to chrysin. The formula, therefore, which represents rhamnazin as rhamnetin monomethyl ether must be considered as the most probable. Experiment has since shown that chrysin monomethyl ether (tectochrysin), in which the methoxyl occupies a para-position relatively to the CO- group, is devoid of dyeing power, a fact pointing strongly to the correctness of this view.

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