

XLVII.—*Rhamnazin and Rhamnetin.*

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ALTHOUGH rhamnetin has been shown to be a monomethyl ether of quercetin (Herzig, *Monatsh.*, 1888, 9, 548), the locality of the methoxyl group has hitherto not been definitely ascertained, and either the (3) or the 7-position might equally well be assigned to it. Similarly, in rhamnazin (Trans., 1897, 71, 818), a quercetin dimethyl ether although the position of one methoxyl group is known, that of the

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second, as in the case of rhamnetin, is uncertain. Thus if rhamnetin or rhamnazin be decomposed by digestion with boiling alcoholic potash or by the aspiration of air through its alkaline solution.

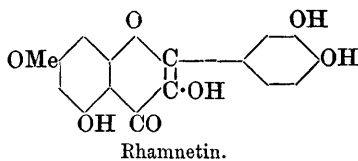
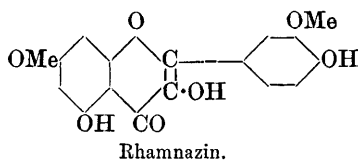
0.1136 gave 0.2715 CO_2 and 0.0475 H_2O . $\text{C}=65.17$; $\text{H}=4.64$.

0.1157 „ 15.6 c.c. nitrogen at 14° and 746 mm. $\text{N}=15.57$.

0.1788 „ 0.1234 AgI . $\text{OCH}_3=4.40$.

$\text{C}_{18}\text{H}_{13}\text{O}_2\text{N}_4 \cdot \text{OCH}_3$ requires $\text{C}=65.51$; $\text{H}=4.59$; $\text{N}=16.09$; $\text{OCH}_3=4.31$ per cent.

This compound is therefore *disazobenzene phloroglucinol monomethyl ether*, and the phenol obtained both from rhamnazin and from rhamnetin is phloroglucinol monomethyl ether. The relationship of these colouring matters may, therefore, be indicated by the formulæ,



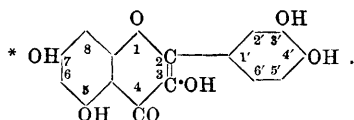
and the suggestion (*loc. cit.*) that rhamnazin was rhamnetin monomethyl ether is thus shown to be correct.

The shades given by these colouring matters upon mordanted wool are as follows:

	Chromium.	Aluminium.	Tin.	Iron.
Rhamnetin	Red-brown.	Brown-orange.	Bright orange.	Olive-black.
Rhamnazin	Golden-yellow.	Orange-yellow.	Lemon-yellow.	Olive-brown.

These results show that the dyeing properties of rhamnetin are identical with those of quercetin, and are interesting in that they prove that in quercetin the hydroxyl (7) * has no effect on its dyeing properties. On the other hand, the replacement of the hydroxyl (3') by methoxyl with production of rhamnazin (compare also *isorhamnetin*, quercetin monomethyl ether [$\text{OMe}=3'$] *Trans.*, 1898, **73**, 267) has a most marked effect on the dyeing properties; this was to be expected, as the compound does not then possess *o*-hydroxyl groups. A third quercetin monomethyl ether has been shown to exist in minute quantity in the *Tamaris Africana* (*Trans.*, 1898, **73**, 380), and an attempt is now being made to obtain sufficient substance for the location of its methoxy-group in the above manner.

Quercetin Tetramethyl and Tetraethyl Ethers.—These compounds, as Herzig has shown (*Monatsh.*, 1888, **9**, 552), when decomposed with alcoholic potash, give respectively protocathechuic acid dimethyl and diethyl ether, and also phenolic compounds which are derivatives of phloroglucinol; to determine the constitution of the latter, their azo-



benzene compounds were examined, with the result that the one derived from quercetin tetramethyl ether was found to be *disazobenzene phloroglucinol monomethyl ether*, m. p. 250—252°

The phenol from the tetraethyl ether gave a disazobenzene compound crystallising in orange-red needles melting at 212—214° :

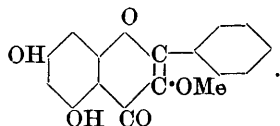
0.0828 gave 0.2015 CO₂ and 0.0365 H₂O. C = 66.36 ; H = 4.89.

0.0771 „ 10.5 c.c. nitrogen at 18° and 751 mm. N = 15.53.

(C₆H₅N₂)₂C₆H(OH)₂·OC₂H₅ requires C = 66.24 ; H = 4.94 ; N = 15.47 per cent.

It was evidently *disazobenzene phloroglucinol monoethyl ether*.

Kampherol Monomethyl Ether.—A trace of this substance, recently described by Testoni (*Gazzetta*, 1900, 30, ii, 327) as a constituent of Galanga root (*Alpinia officinarum*), was available for examination. When decomposed by the aspiration of air through its alkaline solution, it yielded benzoic acid, (m. p. 121°), and a phenolic compound which gave the phloroglucinol reaction. In the presence of sodium carbonate, this gave an azobenzene compound, identified as trisazobenzene phloroglucinol, and consequently there was no methoxy-group in this portion of the molecule. Adopting the constitution for kampherol suggested by Kostanecki, it is evident that the above methyl ether must be represented as follows :



This method of analysis has already been employed with the decomposition products of the ethers of luteolin (*Trans.*, 1900, 77, 1314), myricetin (*Trans.*, 1902, 81, 203), and genistein (*Trans.*, 1900, 77, 1310), with the result that in all cases the ethers of phloroglucinol were isolated. There is no reason to doubt that the corresponding derivatives of chrysin and apigenin would by similar methods give a like result, and it appeared unnecessary to undertake their preparation for this purpose.

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