"Examining this equation in the light of Equation 35 itself, it will be found that each of the terms on the right hand side is the average value of some property of the molecules or of the modes of vibration that enter into the reaction; we obtain

$$\frac{\mathrm{d}\, ln\, k_1}{\mathrm{d}T} = \frac{\bar{\bar{E}}_\mathrm{A} - \bar{E}_\mathrm{A} + \bar{\bar{E}}_R - \bar{E}_R}{kT^2} \tag{38}$$

where $\bar{\bar{E}}_\mathrm{A}$ is the average energy of the molecules which actually enter into the reaction, $\bar{E}_\mathrm{A}$ is the average energy of all of the molecules of this kind in the system, $\bar{\bar{E}}_R$ is the average radiant energy of the modes of vibration upon participation in the reaction, and $\bar{E}_R$ is the average radiant energy of such modes of vibration whether or not they are in a reactive condition."

Equation 44 on p. 2524 should read

$$\frac{\mathrm{d}\, ln\, k_\nu}{\mathrm{d}T} = \frac{\bar{\bar{E}}_\mathrm{A} - \bar{E}_\mathrm{A}}{kT^2}. \tag{44}$$

Since Equations 38 and 44 for the temperature coefficient, respectively, of thermal reaction rate and photochemical reaction rate were the most important deductions obtained in the article, it seemed necessary to call attention to these corrections. RICHARD C. TOLMAN.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE PREPARATION OF RHAMNOSE.

BY C. F. WALTON, JR.

Received January 13, 1920.

Owing to the lack of a satisfactory method for preparing rhamnose in the laboratory, this methyl pentose sugar has properly been classed as one of the rarer sugars. Rhamnose is formed by the enzymotic or the dilute acid hydrolysis of many of the rhamnosides, among which quercitrin and xanthorhamnin are the best known and most easily obtainable. Xanthorhamnin has been studied by Liebermann and Hörmann,[2] Perkin and Geldard,[3] Tanret,[4] and Votoček and Fric,[5] among other investigators.

Quercitrin, however, has been most often used as a source for rhamnose, as it occurs in the bark of *Quercus coccinea*, var. *tinctoria*, Gray, known commonly as Quercitron, Yellow-barked, or Black Oak, large quantities of which are used in various forms in the tanning and dyeing industries.

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[1] THIS JOURNAL, **42**, 2506 (1920).

[2] Liebermann and Hörmann, *Ber.*, **11**, 952 (1878); *Ann. Chem.*, **196**, 299 (1879).

[3] Perkin and Geldard, *Chem. News*, **71**, 240 (1895).

[4] Tanret, *Bull. soc. chim.*, **21**, 1073 (1899).

[5] Votoček and Fric, *Z. Zuckerind. Böhmen*, **25**, 1 (1900).

The work reported in this paper was done in continuation of the project on the preparation of the sugars initiated by C. S. Hudson, formerly in charge of this laboratory. Hudson and Harding did much very valuable preliminary work on preparing rhamnose from black oak bark. More recently, however, it has been found by an examination of many materials containing quercitrin that as a raw material the bark is less desirable than a certain product which is prepared commercially from it. This observation has led to the use of a very rich source of the glucoside and the development of a method by which rhamnose is one of the easiest and least expensive of all the sugars to make. The method recommended will presently be described in detail.

Preparation and Composition of Quercitrin.—The preparation of quercitrin in a pure condition and the study of its composition were the objects of many of the earlier investigators, among whom may be mentioned Liebermann and Hamburger,[1] and Herzig.[2] More recently, Brauns,[3] Moore,[4] and Perkin[5] have agreed that the formula of air-dried quercitrin is $C_{21}H_{20}O_{11}.2H_2O$, although Katz[6] has advanced evidence to show that the water is present in the form of a solid solution in the quercitrin rather than as true water of crystallization. The hydrolysis, therefore, seems to be best represented by the equation,

$$\begin{array}{ccccccc} C_{21}H_{20}O_{11} & + & H_2O & \longrightarrow & C_{15}H_{10}O_7 & + & C_6H_{12}O_5 \\ \text{Quercitrin} & & & & \text{Quercetin} & & \text{Rhamnose} \\ \text{(anhydrous)} & & & & & & \text{(anhydrous)} \end{array}$$

From water solution, however, rhamnose hydrate, $C_6H_2O_{15}.H_2O$, is always formed.

The powdered bark itself, "Quercitron Powder," "Quercitron Extract," and "Flavin" are the most common commercial products containing quercitrin. It has long been realized, however, that such preparations vary greatly in quercitrin content, and on account of the difficulties experienced in preparing a good grade of quercitrin economically, the details of its manufacture on a commercial scale have been guarded with great secrecy.

A resinous quercitrin, said to be the settlings obtained in the manufacture of quercitron extract, was used by Kruis[7] and Rayman[8] as a good source for quercitrin from which rhamnose was prepared directly without the necessity of first isolating the glucoside. More recently Clark[9] has

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[1] Liebermann and Hamburger, *Ber.*, **12**, 1178 (1879).

[2] Herzig, *Monatsh.*, **14**, 55 (1893).

[3] Brauns, *Arch. Pharm.*, **242**, 561 (1904).

[4] Moore, *J. Chem. Soc.*, **26**, 182 (1910).

[5] Perkin, *ibid.*, **30**, 151, 201 (1914).

[6] Katz, *Z. physiol. Chem.*, **95**, 1–15 (1915); *Kolloidchem. Beihefte.*, **9**, 1–182 (1917).

[7] Kruis, *K. Sitzb. böhm. Gesell. Wiss. Prag.*, **1878**, p. 158.

[8] Rayman, *Bull. soc. chim.*, **47**, 668 (1887).

[9] Clark, *J. Biol. Chem.*, **38**, 255 (1919).

described a method for making rhamnose directly from a commercial quercitron extract with a yield of about 3%.

As a step in the procedure formerly in use in this laboratory for preparing rhamnose from quercitrin, the glucoside was isolated from the bark by a method somewhat similar to that described by Rochleder.[1] The finely powdered bark was extracted with 5 parts of boiling water. After filtration at the boiling temperature the extract was set aside for several days until crystallization of the very insoluble glucoside was judged complete. The quercitrin settled out readily and the supernatant liquor could be siphoned off almost entirely. The quercitrin was then filtered on a Büchner funnel and washed thoroughly with cold water. The yield of glucoside, however, was only about 2%, which seemed too small, on account of the labor involved in working with large quantities of bark, to justify the continued practise of this method on a laboratory scale.

Best Source for Quercitrin.—In view of the difficulties experienced in the small scale methods tested out for preparing quercitrin directly from the bark it seemed best to make an examination of the various commercial preparations to discover, if possible, a more satisfactory source.

Of the materials obtained from the manufacturers, a product called "Lemon Flavin,"[2] proved by far the richest in quercitrin.[3] Repeated extractions of this flavin with 50 parts of boiling water gave in each case, on cooling the filtrate, a crystalline substance which was identified as quercitrin by its m. p., 183–185°.[4] As quercetin melts at a temperature above 300°,[5] it is easy to distinguish between the glucoside and its insoluble decomposition product. The solubility of quercitrin in boiling water is approximately 1–400,[6] hence the need of repeated extraction to get it all into solution.

Procedure.—It is easy to prepare pure quercitrin from flavin by alcoholic or water extraction and subsequent recrystallization, but it was found unnecessary to do this in the preparation of pure crystalline rhamnose. The simplest method proved to be the following. To 600 g. of flavin are added 6 liters of tap water and 20 cc. of sulfuric acid, sp. gr. 1.84, corresponding to approximately 0.5% of acid by weight of the mixture. Solution of the slightly soluble flavin proceeds at the boiling temperature with the hydrolysis, which is complete in 30 minutes, as can readily be determined by measuring the optical rotation of samples of the solu-

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[1] Rochleder, *J. prakt. Chem.*, **77**, 34 (1859).

[2] This material was supplied by J. S. Young and Co., Hanover, Pa., at a price of $0.90 per pound.

[3] In Thorpe's "Dictionary of Applied Chemistry," **4**, 446 (1913), it is stated that Perkin in a private communication suggested the use of flavin as a source for quercitrin.

[4] Brauns, *loc. cit.;* Moore, *loc. cit.*

[5] Kostanecki, *Ber.*, **37**, 1405 (1904).

[6] Bolley, *Ann. Chem.*, **37**, 101 (1841); Rigaud, *ibid.*, **90**, 283 (1854).

tion taken at intervals during the reaction. Owing to the formation of quercetin, which exhibits markedly the phenomenon of swelling when formed in contact with water,[1] the mixture becomes thick and changes to a slightly darker yellow color. It is cooled to room temperature to permit all the quercetin to precipitate out (quercetin is practially insoluble in water at room temperature) and then filtered through paper on large Büchner funnels. The washing of this residue, which is extremely bulky, can best be accomplished by returning it to the kettle and boiling again with 2 to 3 liters of water. The combined filtrates are now made neutral to litmus with barium carbonate at the boiling temperature, filtered, the barium sulfate washed free from sugar with hot water, and the solution decolorized by the use of a few grams of active decolorizing carbon. The colorless filtrate is now boiled down under diminished pressure to a density of about 40% total solids. At this concentration the sugar is still in solution since its solubility is 47[2] to 57[3] parts of sugar in 100 cc. of water at 18°. Three volumes of warm absolute ethyl alcohol are now added to precipitate a small amount of inorganic impurity derived from the flavin and still present in the solution. After filtration the solution is again concentrated under diminished pressure to the consistency of a thin syrup (70–80% solids). The syrup is perfectly clear and colorless before removal from the flask, but crystallization begins almost at once and before it is cool the mass is nearly solid. A few cc. of glacial acetic acid are added to prevent lump formation and to enable careful washing of the crystals on filtration. The sugar is washed first with a little cold absolute ethyl alcohol, then with a 1 : 1 mixture of absolute alcohol and ether, and finally with a little absolute ether. It is dried in a desiccator over sulfuric acid or in a vacuum oven at 30°. On concentrating the mother liquor an additional crop of crystals is usually obtained. The total yield corresponds to 20–25% of the weight of flavin taken. Since the theoretical yield of rhamnose hydrate from pure air dried quercitrin is 37%, it is obvious from the yield of sugar obtained that flavin of the right quality is an exceptionally good source for quercitrin and rhamnose.

Recrystallization of the sugar may be easily accomplished by dissolving in 3 parts of 80% ethyl alcohol on the steam-bath, filtering through decolorizing carbon, diluting the clear filtrate with about an equal volume of water and concentrating to a thin syrup. Large or small crystals may be obtained at will, depending on the density of the syrup, as rhamnose crystallizes very easily from water solution.

A sample of sugar prepared by the above method and once recrystallized ($C_6H_{12}O_5.H_2O$) gave a clear, 10% water solution, and showed the constant specific rotation $[\alpha]_D^{20} = +8.5°$.

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[1] Katz, *loc. cit.*

[2] Hlasiwetz and Pfaundler, *Ann. Chem.*, **127**, 362 (1863).

[3] Liebermann and Hörmann, *loc. cit.*

Summary.

A convenient laboratory method is described for preparing rhamnose from "flavin," a commercial product rich in quercitrin. The flavin is hydrolyzed by boiling for 30 minutes with 10 parts of water and 0.5% sulfuric acid. The residue is washed free from sugar and the combined filtrates are neutralized with barium carbonate, decolorized, and concentrated under diminished pressure to a density of about 40% solids. The inorganic impurities are now precipitated by the addition of ethyl alcohol, and crystallization is readily accomplished by concentrating the filtrate to a density of 70–80% solids. The yield of rhamnose is 20–25% of the weight of flavin taken.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

A CATALYTIC DECOMPOSITION OF CERTAIN PHENOL SILVER SALTS. III. THE ACTION OF MERCURY ON TRIBROMOPHENOL BROMIDE.[1]

BY W. H. HUNTER AND G. H. WOOLLETT.

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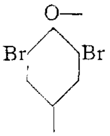
The purpose of the present paper is to show that the same result is attained by removing 2 atoms of bromine from tribromophenol bromide (tetrabromo-cyclo-hexadienone), as by removing a silver atom and a bromine atom from either of the silver salts of tribromophenol, *viz.*, the formation of residues[2]



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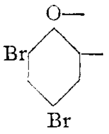

which then polymerize to a compound of high molecular weight, $(C_6H_2Br_2O)_n$, for which the name poly-dibromo-phenylene oxide has been suggested.[3]

A secondary purpose is to show that the so-called "hexabromo-diphenoquinone" of Benedikt[4] is not obtained by the action of tribromophenol bromide on the red silver salt of tribromophenol, as claimed by Kastle and Loevenhart.[5]

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[1] The work described in this paper formed part of a thesis presented to the Faculty of the Graduate School of the University of Minnesota by Guy Haines Woollett in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Cf. Hunter and Joyce, THIS JOURNAL, 39, 2640 (1917).

[3] Hunter, *et al.*, *ibid.*, 38, 1761 (1916).

[4] Benedikt, *Ann.*, 199, 128 (1879).

[5] Kastle and Loevenhart, *Am. Chem. J.*, 27, 21–52 (1902).