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# CLASSIFICATION OF CARBOHYDRASES

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ABSTRACT

A system for the classification of the carbohydrases has been proposed by Weidenhagen, and, although it has considerable value, it also has a number of obvious deficiencies. It is demonstrated in the present paper that many of these difficulties may be obviated by considering the individual enzymes of Weidenhagen, e. g., $\alpha$-glucosidase, as classes of enzymes of similar action but varying according to the source. The results of more recent studies of the specificity of the carbohydrases are considered, and the action of enzymes on pentoses, hexoses, and heptoses of similar ring conformations is interpreted. These results and the conception of the complex nature of Weidenhagen's individual enzymes are utilized in the establishment of a provisional system for the classification of the carbohydrases.

CONTENTS



## I. INTRODUCTION

Certain enzymes, found in many products of biological origin, catalyze the hydrolysis and synthesis of glycosides, oligosaccharides, and polysaccharides. As a group, they are usually termed "carbohydrases" or "glycosidases." In the present discussion, the entire group will be designated "carbohydrases," those hydrolyzing glycosides and oligosaccharides as "glycosidases," and those hydrolyzing polysaccharides as "polysaccharidases." A system for the classification of these enzymes, presented by Weidenhagen, has proved of considerable value and has stimulated much research, but it has received a great deal of criticism. The purpose of the present paper is to show that by making a few changes in the Weidenhagen postulates, a system of considerably more general validity may be developed. In addition, the results of more recent researches will be considered and incorporated into a system for the classification of the carbohydrases. Although the modified system does not entirely possess the appealing simplicity of the original Weidenhagen classification, it agrees much better with the experimental results. In any case, it is believed that the function of a system of classification is

principally to illustrate the connection between the structures of the substrates and the action of the enzymes and not, as stated by Hofmann,[1] merely to reduce the number of enzymes to a few individuals. Additional experimental work is required before the new system can be substantiated, and it is hoped that workers in the field will test the more questionable points as the opportunities arise.

In its original form, the Weidenhagen system[2] demanded that there be only one enzyme for each glycosidic type. One enzyme should hydrolyze all β-*D*-glucosides (β-glucosidase), one all α-*D*-glucosides (α-glucosidase), one all α-*D*-galactosides (α-galactosidase), etc. The disaccharides were considered as glycosides, and the same enzyme was made responsible for the hydrolysis of related polysaccharides, disaccharides, and glycosides. The system required that β-glucosidase hydrolyze alkyl and aryl β-*D*-glucosides, cellobiose, gentiobiose, and cellulose. Similarly, α-glucosidase should catalyze the hydrolysis of alkyl and aryl α-*D*-glucosides as well as maltose, and invertase (β-fructofuranosidase) should hydrolyze both sucrose and inulin. Obvious disagreement with the experimental facts later led to the somewhat modified theory, in which the enzymes hydrolyzing polysaccharides (polysaccharidases) were separated, at least provisionally, from the enzymes hydrolyzing the glycosides and oligosaccharides (glycosidases).[3]

## II. CLASSIFICATION OF CARBOHYDRASES

The principal differences between the system proposed in the present paper and that of Weidenhagen are (1) the individual enzymes of his system are now considered as classes of enzymes acting on the same substrates but with different specificities and other properties and (2) the more recent knowledge of the action of carbohydrases on pentoses, hexoses, and heptoses of similar structures and configurations is introduced into the system of classification. The modified classification is summarized in table 1, which gives the main enzyme classes now known and the substrates on which they act.

TABLE 1.—*Detailed classification of carbohydrases*

| Enzyme class | Other or older names for members of class | Substrates [a] |
|---|---|---|
| GLYCOSIDASES HYDROLYZING SIMPLE GLYCOSIDES AND OLIGOSACCHARIDES [b] | | |
| β-Glucosidases | Emulsin, cellobiases, gentiobiases. | β-*D*-Glucosides, β-*D*-xylosides, cellobiose, gentiobiose, β-*D*-and *L-glycero-D-gluco*-aldoheptosides (?), β-*D*-glucuronides (?). |
| α-Glucosidases | Maltases, trehalases | α-*D*-Glucosides, α-*D*-xylosides (?) maltose, sucrose, α-*D*- and *L-glycero-D-gluco*-aldoheptosides (?). |
| β-Galactosidases | Lactases | β-*D*-Galactosides, α-*L*-arabinosides, β-*D*-fucosides (?), lactose, β-*D*- and *L-glycero-D-galacto*-aldoheptosides, α-*D*-galacturonides (?). |
| α-Galactosidases | Melibiases | β-*D*-Galactosides, β-*L*-arabinosides, α-*D*-fucosides (?), melibiose, α-*D*- and *L-glycero-D-galacto*-aldoheptosides. |
| β-Fructofuranosidases or invertases. | Sucrase | Fructofuranosides; sucrose; inulin (?). |
| α-*D*-Mannosidases | | α-*D*-Mannosides, α-*D*-lyxosides, β-*D*- and *L-glycero-D-manno*-aldoheptosides (?). |
| β-Thioglucosidases | Myrosin | β-Thioglucosides, thioxylosides (?), etc. |
| Nucleosidases | | *N*-Glycosides, nucleosides. |

Footnotes are at end of table.

[1] E. Hofmann, Biochem. Z. **285**, 429 (1936).
[2] R. Weidenhagen, Ergeb. Enzymforsch. **1**, 168 (1932).
[3] R. Weidenhagen, in Handbuch der Enzymologie by Nord-Weidenhagen, p. 519 (Akademische Ver lagsgesellschaft, Leipzig, 1940).

TABLE 1.—*Detailed classification of carbohydrases*—Continued

| Enzyme class | Other or older names for members of class | Substrates [a] |
|---|---|---|
| | POLYSACCHARIDASES [b] | |
| Amylases | Diastases | Starch, glycogen. |
| α-Amylases | Dextrogenic or liquifying amylases. | Branched chain starch and glycogen. |
| *Bacillus macerans* amylase | Dextrogenic or liquifying amylases. | Glycogen and branched chain starch. |
| Disaggregating amylases | Amylophosphatase | Whole starches are broken, possibly at phosphate linkages, into large molecules. |
| β-Amylases | Saccharifying amylase | Straight chain starches (poly-α-*D*-glucosides). |
| Phosphoamylases | Phosphorylases | Straight chain starches and glycogen by process involving phosphorylation. |
| Inulases (possibly identical with invertases). | | Inulin, irisin and poly-fructofuranosides. |
| Cellulases | | Cellulose and poly-β-glucopyranosides, certain glucosans. |
| Hexosanases and pentosanases. | Cytases | Hexosans, pentosans and hemicelluloses. |
| Chitinases | | Chitin and lower molecular weight homologs. |
| Pectinases | | Pectins. |
| Protopectinase | | Hydrolyzes native pectins *in situ* to soluble pectins. |
| Pectolase | | Polygalacturonides. |
| (Pectase) | | An esterase hydrolyzing esters of galacturonic acid. |

[a] The nomenclature adopted for the heptoses follows that suggested by the Committee on Carbohydrate Nomenclature of the American Chemical Society. The "*D-glycero*" refers to the configuration of the terminal asymmetric carbon and the "*D-gluco-*" or "*D-galacto*" to the configuration of carbons 2, 3, 4, and 5. The alpha-beta nomenclature of Isbell is followed except for the arabinosides, which are named by Hudson's system.

As far as known, the glycosides followed by question marks have never been tested, at least under sufficiently drastic conditions to indicate "nonhydrolyzability." The others have been tested for at least one member of the enzyme class, usually the corresponding enzyme in almond emulsin.

[b] There is probably overlapping between the two main classes of carbohydrases, but, in general, the action of the one group of enzymes on the substrates of the second class is small and may usually be neglected.

## III. POSTULATES AND EVIDENCE FOR THE SYSTEM OF CLASSIFICATION

### 1. GLYCOSIDASES

The classification presented depends on the validity of the following assumptions, some adequately and some inadequately established.

1. Changes in the aglycon group affect the rate of enzymic hydrolysis of the glycoside, but profound changes are required before the rate becomes inappreciable (aglycon specificity).

2. Glycosides having different configurations for the glycosidic carbon, require different enzymes (alpha-beta specificity).

3. Enzymes from different sources which catalyze the same reaction vary in the specificity which they exhibit, i. e., they are affected to different extents by changes in the aglycon and sugar groups.

4. Substitution of the ring hydroxyls of hydrolyzable glycosides by other groups makes the glycosides unhydrolyzable by the same enzyme.

5. Changing the configuration of one or more ring carbons or of the ring type, e. g., from pyranose to furanose, makes a hydrolyzable glycoside unhydrolyzable by the same enzyme. This brings together the previous "ring", "*D, L*", and "sugar" specificity (ring-type specificity).

6. Changes made outside of the sugar ring affect the rate of enzymic hyrolysis, but usually do not result in requiring a new enyzme for the hydrolysis.

7. In natural products, only those enzymes are to be expected which are capable of hydrolyzing glycosides of the same basic ring type as that of a naturally occuring glycoside.

8. *Thio-* and *N*-glycosides, with the glycosidic linkage taking place through a sulfur or nitrogen atom rather than an oxygen atom, require enzymes different from those hydrolyzing the ordinary glycosides.

Some of these assumptions are corollaries of others. Thus, 2 is a special case of 5 and 1 of 6, but their importance makes it desirable to list them separately. The status of the above assumptions and some of the evidence upon which they are based will now be discussed.

*Postulate 1.*—It is usually accepted from the earlier work of Fischer [4] and Willstätter, Kuhn, and Sobotka [5] that the nature of the aglycon has only a quantitative effect on the rate of enzymic hydrolysis of a glycoside. Probably the best argument for this assumption is the great number of $\beta$-glucosides which have been prepared by Fischer, Helferich, Veibel and others, all of which have been found hydrolyzable by almond emulsin. An important exception occurs when the aglycon is a sugar, since there are numerous claims that fungal enzymes hydrolyze maltose but not methyl $\alpha$-glucoside.[6] However, none of these experiments can be said to be in contradiction to the assumption made, since the preparations were relatively inactive, and in most instances a difference of 100 times in the relative rates of hydrolysis would hardly have been detectable. Since the various $\alpha$-*D*-glucosides under standard conditions show a variation in the rate of hydrolysis, according to the nature of the aglycon group, of more than 40,000,[7] conditions must be chosen for the testing of the action against maltose and methyl, or preferably phenyl $\alpha$-*D*-glucoside, such that comparable differences of specificity may be observed.

The experiments of Hestrin [8] are in more direct contradiction to this postulate. It was found that heat destroyed the ability of *A. oryzae* emulsin (Takamaltase) to hydrolyze sucrose and methyl $\alpha$-*D*-glucoside under conditions such that the maltose hydrolyzing ability was not greatly affected. Since both sucrose and methyl $\alpha$-glucoside are believed to have $\alpha$-glucosidic linkages, this work must stand in contradiction to the postulation made, although two possible explanations may be given. The observed hydrolysis of methyl $\alpha$-glucoside by the unheated enzyme was very small (2 percent after 24 hours), and this may have been so close to the experimental error that a slight destruction of the enzyme would make the hydrolysis less than the experimental error. Secondly, as suggested by Hestrin, the emulsin may contain several enzymes of the $\alpha$-glucosidase type of variable heat resistance. The latter explanation is particularly necessary to explain the loss of sucrose inversion power.

*Postulate* 2.—There is practically universal agreement that hydrolyzable glycosides, which differ in the configuration of the glycosidic carbon, e. g., methyl $\alpha$- and $\beta$-glucosides, require different enzymes. This was established by the work of Fischer.[9] Almond

[4] E. Fischer, Z. physiol. Chem. **26**, 60 (1898); **107**, 176 (1919).
[5] R. Willstätter, R. Kuhn, and H. Sobotka, Z. physiol. Chem. **129**, 33 (1923).
[6] H. Pringsheim, H. Borchardt, and F. Loew, Z. physiol. Chem. **202**, 23 (1931); K. Myrbäch, Z. physiol. Chem. **205**, 248 (1932).
[7] B. Helferich, Ergebn. Enzymforsch. **7**, 83 (1938).
[8] S. Hestrin, Enzymologia **8**, 193 (1940).
[9] E. Fischer, Ber. deut. Chem. Ges. **27**, 2985 (1894).

emulsin can hydrolyze both $\alpha$- and $\beta$-galactosides, but it has been demonstrated that two enzymes are required. [10]

*Postulate* 3.—Fischer's work led him to believe that yeast and animal $\alpha$-glucosidases were different.[11] With the notable exception of Weidenhagen, most workers in the field have accepted the conclusion that enzymes catalyzing the same reactions but from different sources are different, and considerable experimental evidence is available to prove the point.[12]

Helferich has expressed the opinion that there may be only two enzymes of each type[13], but such a limitation of the number requires a great deal of additional work before it can be accepted.

*Postulate 4.*—The investigation of the effect of substitution in the pyranose ring on the enzymic hydrolysis of the glycoside has been devoted almost exclusively to the glucoside series and to the hydrolysis by the $\beta$-glucosidase of almond emulsin. Helferich's results lead to the conclusion that the substitution of one or more hydroxyls of carbons, 2, 3, and 4 of a $\beta$-*D*-glucoside by methoxyl and tosyl groups makes the glucoside unhydrolyzable.[14]

*Postulate 5.—Influence of Ring Type.*—Although almond emulsin hydrolyzes $\beta$-glucopyranosides, the furanosides are not affected.[15] Similarly, invertase (fructofuranosidase) hydrolyzes fructofuranosides, but not the known fructopyranosides.[16]

*D,L Specificity.*—The available evidence indicates for all of the substances studied that a change in the configuration of *all* the asymmetric carbons in the molecule of a hydrolyzable glycoside (a change from the *D* to the *L* series) produces an unhydrolyzable glycoside. The best example is given by a pair of *D* and *L*-arabinosides.[17] Although both of the phenyl $\beta$- and $\alpha$-*L*-arabinosides are hydrolyzed by the enzymes of almond emulsin (probably by the $\alpha$- and $\beta$-galactosidase) the mirror images, the *D*-arabinosides are virtually unaffected. This is in agreement with the earlier results of Fischer on the *D*- and the *L*-glucosides [18] and with those of Helferich, Günther and Pigman [19] for the $\beta$-*D*-xylosides and the $\beta$-*L*-xylosides.

*Sugar Specificity.*—Changes of configuration of carbons 2, 3, and 4 of the hexosides produce the various hexose sugar types.[20] The enzymes in almond emulsin do not hydrolyze appreciably the methyl *D*-gulosides [21] and phenyl $\alpha$-*D*-taloside.[22] Thus, changes in the configuration of a single carbon changes the glycoside from a hydrolyzable to an unhydrolyzable type, e. g., the mannosides and the talosides differ in the configuration of only a single carbon, carbon 4.

[10] B. Helferich, S. Winkler, R. Gootz, O. Peters, and E. Günther, Z. physiol. Chem. **208**, 91 (1932); W. W. Pigman, Z. physiol. Chem. **261**, 82 (1939).
[11] E. Fischer, Z. physiol. Chem. **26**, 60 (1898).
[12] K. Hill, Ber. Verhandl. sächs. Akad. Wiss. Leipzig. Math. phys. Klasse **86**, 115 (1934); B. Helferich and F. Vorsatz, Z. physiol. Chem. **237**, 254 (1935); E. Hofmann, Biochem. Z. **285**, 429 (1936); T. Miwa, C. Cheng, M. Fujisaki, and A. Toishi, Acta Phytochim. (Japan) **10**, 155 (1937); R. Weidenhagen and A. Renner, Z. Ver. deut. Zucker-Ind. **86**, 22 (1936); W. W. Pigman, J. Research NBS **30**, 159 (1943) RP1526.
[13] B. Helferich, W. Richter, and S. Grünler, Ber. Verhandl. sächs. Akad. Wiss. Leipzig. Math. phys. Klasse **89**, 385 (1937).
[14] B. Helferich and S. Grünler, J. pract. Chem. **148**, 107 (1937); B. Helferich and O. Lang, Z. physiol. Chem. **216**, 123 (1933); J. prakt. Chem. **132**, 321 (1932); W. W. Pigman and N. K. Richtmyer, J. Am. Chem. Soc. **64**, 374 (1942).
[15] E. Fischer, Ber. deut. chem. Ges. **47**, 1980 (1914).
[16] R. Weidenhagen, Z. Ver. deut. Zucker-Ind. **82**, 921 (1932).
[17] B. Helferich, H. Appel, and R. Gootz, Z. physiol. Chem. **215**, 277 (1933); B. Helferich, S. Winkler, R. Gootz, O. Peters, and E. Günther, Z. physiol. Chem. **208**, 91 (1932).
[18] E. Fischer, Ber. **27**, 2985 (1894).
[19] B. Helferich, E. Günther, and W. W. Pigman, Ber. deut. chem. Ges. **72**, 1953 (1939).
[20] H. S. Isbell and W. W. Pigman, J. Research NBS **18**, 141 (1937) RP969; H. S. Isbell and H. Frush, J. Research NBS **24**, 125 (1940) RP1274.
[21] B. Helferich, W. W. Pigman, and H. S. Isbell, Z. physiol. Chem. **261**, 55 (1939).
[22] W. W. Pigman, J. Research NBS **26**, 197 (1941) RP 1369.

In general, it seems probable that each of the hexose types requires a special enzyme. The principal evidence opposed to this generalization is that in spite of considerable work to settle the question, Helferich [23] has never been able to separate the β-glucosidase and the β-galactosidase activities of almond emulsin. However, in alfalfa emulsin (lucerne emulsin), a β-galactosidase is present, although the β-glucosidase activity is small.[24] A possible explanation of Helferich's results is, that a single enzyme molecule may catalyze different reactions but that active areas or groups in different portions of the molecule may be responsible, so that while the enzyme is the same the activities may be ascribed to different portions of the molecule.

*Postulate 6.*—Changes remote from the ring usually produce only secondary effects on the rate of hydrolysis. The effect of the structure of the aglycon has been discussed (postulate 1). Substitution at the primary alcoholic group is another possibility, which has received attention by Helferich, but the data are available only for the glycosidases of almond emulsin. Substitution of various groups or atoms for the hydroxyl of carbon 6 of β-*D*-glucosides affects the rate of hydrolysis in measure dependent on the size of the substituent group[25] and similar effects are found for the *D-glycero-D-galacto*-aldoheptosides[26] (*D*-α-mannoheptosides), which are derivatives of the hydrolyzable *D*-galactosides in which a hydrogen of the primary alcoholic group has been replaced by a $CH_2OH$ group.

When the primary alcoholic group is replaced by a hydrogen, a hexoside is converted to a pentoside, for example, glucose is changed to xylose, and the general conformation of the rings is usually similar in the two compounds. Although such changes may produce considerable effects on the conformation of the pyranose ring, the evidence indicates that enzymes hydrolyzing the hexoside also hydrolyze the corresponding pentoside. In all probability, β-glucosidase splits the β-glucosides and β-*D*-xylosides,[27] β-galactosidase the β-galactosides and the α-*L*-arabinosides,[28] and α-mannosidase the α-mannosides and the α-lyxosides.[29]

*Postulate 7.*—If the preceding postulates are correct, it would seem almost self-evident that naturally occurring enzymes would be only of the type to hydrolyze naturally occurring hexose *types*. Since *D*-gluosides and *D*-talosides are not known to occur in plant or animal materials, it appears improbable that special enzymes would be present in plant materials to hydrolyze these glycosides, and the previous evidence cited would eliminate the possibility of the hydrolysis of these substances by the known enzymes (β-glucosidase, β-galactosidase, α-mannosidase, α-galactosidase, and the other enzymes of the almond emulsin).

*Postulate 8.*—The thioglucosides are not hydrolyzed by the β-glucosidase of almond emulsin[30], but myrosin, an enzyme contained in black-mustard emulsin, hydrolyzes thioglucosides. Although there is not a great deal of information available on the *N*-glycoside hydrolyzing enzymes, almond emulsin does not hydrolyze nucleosides

[23] B. Helferich, Ergebn. Enzymforsch. **7**, 83 (1938).
[24] K. Hill, Ber. Verhandl. sächs. Akad. Wiss. Leipzig. Math. phys. Klasse **86**, 115 (1934).
[25] B. Helferich, S. Grünler, and A. Gnüchtel, Z. physiol. Chem. **248**, 85 (1937); W. W. Pigman and N. K. Richtmyer, J. Am. Chem. Soc. **64**, 374 (1942).
[26] W. W. Pigman, J. Research NBS **26**, 197 (1941) RP1369.
[27] B. Helferich and U. Lampert, Ber. deut. chem. Ges. **67**, 1667 (1934).
[28] B. Helferich, S. Winkler, R. Gootz, O. Peters, and E. Gunther, Z. physiol. Chem. **208**, 91 (1932); B. Helferich and U. Lampert, Ber. deut. Chem. Gesell. **68**, 1266 (1935).
[29] W. W. Pigman, J. Am. Chem. Soc. **62**, 1371 (1940).
[30] W. W. Pigman, J. Research NBS **26**, 197 (1941). RP1369.

(purine or pyrimidine *N*-glycosides), but enzymes are known[31] that will hydrolyze nucleosides. Since the nucleosides are usually *N*-ribosides or *N*-desoxyribosides, the nucleosidases might be expected not to hydrolyze *N*-glucosides. Until more information is available, these enzymes must be classified as separate groups of glycosidases.

The above assumptions are those on which the classification of the glycosidases depend. Most of these have fair experimental foundation, the main deficiencies being in the limited number of sources of enzymes which have been studied. The enzymes of almond emulsin have received considerable attention, and yeast invertase has been studied, but detailed evidence of the action of other enzymes is needed.

The preceding discussion brings up several other problems which cannot be answered at the present time but which ultimately may have to be considered. The polysaccharides, as emphasized by Weidenhagen in his original classification, are glycosides, and according to the first assumption, should be hydrolyzed by the same enzyme as that acting on the corresponding simple glycosides. Cellulase and β-glucosidase were considered by Weidenhagen to be the same, but the evidence which has accumulated indicates that the two are different. However, the question is still unanswered as to whether the cellulases may exert some slight activity for the hydrolysis of β-glucosides, and it may be that the two types of enzymes differ solely in their aglycon specificity.[32] In either case, from a practical standpoint, it seems desirable to classify carbohydrases hydrolyzing glycosides and oligosaccharides separately from the polysaccharidases although there may be a relationship between the classes of the type suggested by Weidenhagen. The possibility of special biosidases splitting the glycoside of a disaccharide into aglycon and disaccharide, has not been considered, since the literature on this subject is in a state of considerable confusion. Helferich and Weber[33] found no evidence for considering that the enzymes of almond emulsin hydrolyze the vanillin β-cellobioside and β-maltoside into vanillin and disaccharide in spite of earlier claims[34] to the contrary for the corresponding methyl derivatives. It seems probable, however, that certain emulsins may contain true biosidases and that when more work has been done, new classes of biosidases which hydrolyze the glycosides of disaccharides into *aglycon* and *disaccharide* may be necessary. An example of this type is the report that *Rubia tinctorum* emulsin (madder) hydrolyzes ruberytheric acid into 1,2-dihydroxyanthraquinone and 6-glucose β-D-xyloside (primeverose).[35]

Undoubtedly, other enzymes will have to be added to the list, since sugars of hexose types other than those upon which the classification is based are known to be naturally occurring. *L*-Rhamnose (*L*-mannosidases), *D*-ribose (*L*-talosidases, *D*-allosidases, *D*-ribosidases), and *L*-galactose (*L*-galactosidases) are some of the naturally occurring sugars for which it seems probable that corresponding enzymes exist. If the sugars of glycosides are formed in the plant by an irreversible process from another hexose type or by irreversible changes in the ring structure or configuration, then the corresponding enzymes may not be found. A possible illustration may be the re-

[31] H. Bredereck, Ergebn. Enzymforsch. **7**, 105 (1938).
[32] W. W. Pigman and N. K. Richtmyer, J. Am. Chem. Soc. **64**, 369 (1942).
[33] B. Helferich and E. Weber, Ber. deut. Chem. Ges. **69**, 1411 (1936).
[34] E. Fischer and E. F. Armstrong, Ber. deut. Chem. Ges. **34**, 2896 (1901); **35**, 3154 (1902).
[35] D. Richter, J. Chem. Soc. (1936) 1701; see also, M. Bridel and C. Charaux, Pharm. Acta Helv. **1**, 107 (1926).

ported absence of enzymes in *Digitalis* and *Strophanthus* emulsins capable of hydrolyzing the digitoxose and cymarose glycosides from the same sources.[36]

Another possibility which is not considered is, that all of the enzymes may exhibit a slight but general nonspecific catalysis for the hydrolysis of glycosides and polysaccharides. In many instances where compounds are considered unhydrolyzable, small extents of hydrolysis close to the experimental error have been observed and in any case, "unhydrolyzable" means [37] an enzyme efficiency (Wertigkeit) of less than $10^{-5}$.

### 2. POLYSACCHARIDASES

The classification of the polysaccharidases given in the second part of table 1 is not greatly different from that commonly accepted for this group of enzymes. That for the amylases follows Ohlsson and Gore,[38] and includes the results of more recent work, such as the possibility of a disaggregating amylophosphatase,[39] the production of Schardinger dextrins by *Bacillus macerans* emulsin,[40] and the discovery of amylolytic phosphorylases hydrolyzing certain starches and glycogen to glucose 1-phosphate.[41] The suggestions of Kertesz [42] are followed for the pectinases, and sufficient is not known to classify the other enzymes of this group in other than the conventional manner. It is believed, however, that enzymes such as cellulases and the various amylases also represent classes of enzymes rather than invariable individuals.

## IV. NOMENCLATURE OF INDIVIDUAL ENZYMES

As mentioned previously[43], it seems advisable to restrict the term "emulsin" to mixtures of enzymes such as are obtained by extracting plants, animal organs, and microorganisms. The source is designated by an appropriate adjective, e. g., almond emulsin, yeast emulsin, etc. The main classes of glycosidic hydrolyzing enzymes are designated according to the alpha or beta hexose type involved, as $\alpha$ or $\beta$-hexosidases. In some instances it may be preferable to use other ring types, but hexose types should be used when possible. Since the enzymes generally act on the *D*-pyranosides, these designations are omitted from the name unless the furanose or "*L*" forms of the hexosides are involved.

The suggestion was originally made by Duclaux[44] that individual enzymes be named by adding the suffix "ase" to the name of the substrate. This has been done in the naming of the classes of glycosidases, but application to individual enzymes seems undesirable, since the action of none of the glycosidases known is limited to a single substrate and until all possible aglycon structures have been studied, it would not be known which is the most easily hydrolyzed.

[36] A. Stoll and J. Renz, Enzymologia **7**, 362 (1939).
[37] B. Helferich, H. Appel, and R. Gootz, Z. physiol. Chem. **215**, 277 (1933); W. W. Pigman and N. K. Richtmyer, J. Am. Chem. Soc. **64**, 374 (1942).
[38] H. C. Gore, Ind. Eng. Chem. **28**, 86 (1936); E. Ohlsson, Z. physiol. Chem. **189**, 17 (1930).
[39] E. Waldschmidt-Leitz and K. Mayer, Z. physiol. Chem. **236**, 168 (1935).
[40] E. B. Tilden, M. Adams, and C. S. Hudson, J. Am. Chem. Soc. **64**, 1432 (1942).
[41] C. S. Hanes, Proc. Royal Soc. (London), [B] **128**, 421 (1940); [B] **129**, 174 (1940); A. A. Green, G. T. Cori, and C. F. Cori, J. Biol. Chem. **142**, 447 (1942).
[42] Z. I. Kertesz, Ergeb. Enzymforsch. **7**, 83 (1938).
[43] W. W. Pigman, J. Research NBS **30**, 159 (1943) RP1526.
[44] E. Duclaux, Microbiologie, p. 141 (1883); quoted by J. B. S. Haldane, Enzymes, p. 192 (Longmans, Green & Co., London, 1930).

The classification of Tauber and Kleiner[45] of α-glucosidases as "*True α-glucosidases*" and "*pseudo-α-glucosidases*" may be objected to on the same basis as the Duclaux system. The classification of Tauber and Kleiner is explained in the following quotation: "In fact, however, there appear to exist two groups of maltases: one which splits α-methylglucoside and other α-glucosides as well as maltose rapidly, which we propose to name *true α-glucosidases;* the second group of maltases which hydrolyze maltose rapidly, but which act very slowly on some α-glucosides, and do not act on others at all. We suggest that the latter be called *pseudo-α-glucosidases.*" There seems to be no valid reason for not considering maltose as a true glucoside, except that carbohydrate chemists, for convenience, have usually placed it in a separate classification as a disaccharide. Also, in the β-glucoside series "true glucosides" (heterosides) are known which are hydrolyzed both more slowly and more rapidly than the disaccharide cellobiose, and additional investigation in the α-glucoside series would undoubtedly find the same situation there.

It is suggested that, until more information on the specificity of individual enzymes is available, the individual glycosidases be named according to their source and general type of action. For the polysaccharidases, for which still less information is available, the name can be based on the general type of action and the source. Some of the common enzymes would then be: sweet almond β-glucosidase, yeast fructofuranosidase (or yeast invertase), yeast α-glucosidase (yeast maltase), yeast α-galactosidase (yeast melibiase), wheat β-amylase, pancreatic α-amylase, *A. niger* cellulase, etc.

WASHINGTON, December 26, 1942.

[45] H. Tauber and I. S. Kleiner, J. Biol. Chem. **105**, 681 (1934).