بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

رَبِّ اشْرَحْ لِیْ صَدْرِیْ O وَیَسِّرْلِیْ اَمْرِیْ O
وَ ا حْلُلْ عُقْدَةً مِّنْ لِّسَانِیْ O یَفْقَهُوْا قَوْلِیْ O

اے میرے رب! میرا سینہ کھول دے اور میرے لیے میرا کام آسان کر دے اور
میری زبان کی گرہ کھول دے تا کہ لوگ میری بات سمجھ سکیں

رَبِّ زِدْنِی عِلْمًا

MY LORD! INCREASE ME IN KNOWLEDGE.

FST-311. FOOD BIOCHEMISTRY 3(3-0)

L # 32-36. PROTEINS IN FOOD APPLICATIONS
FOOD APPLICATIONS OF PROTEINS AND REDUCING SUGRAS: MAILLARD REACTION

B. Sc. (Hons). Food Science and Technology
Semester-V (R+SS)
Fall -2020

Dr. Shahid Mahmood Rana
Associate Professor

INSTITUTE OF FOOD SCIENCE AND NUTRITION (IFSN)

UNIVERSITY OF SARGODHA, SARGODHA-PAKISTAN

BROWNING IN THERMALLY PROCESSED FOODS: THE MAILLARD REACTION

Louis-Camille Maillard (1878 - 1936)

Photographed in his laboratory *ca* 1915

1912 – 1916:
He published 8 papers on his observations of colour changes on mixing amino acids and sugars.

No one else took much interest in the reaction until 1950s

John Hodge: 1914 -1996

- Chemist at USDA in Illinois (1941 – 1980)
- His proposed mechanism for the chemistry of non-enzymic browning is largely unchanged after 60 years.

Citations since 1970

Paper	Citations
Hodge, J. E. Chemistry of browning reactions in model systems. *J. Agric. Food Chem.* 1953, **1**: 928-943.	**890**
Maillard, L. C. Action des acides amines sur les sucres: formation des melanoidines par voie methodique. *Compt. Rend.* 1912, **154**: 66-68.	**634**

Maillard-**Hodge** Reaction?

FOOD MODIFICATIONS: THERMAL TREATMENT

RESULTS IN

- PROTEIN DENATURATION
- PHYSICAL CHANGES
  - STARCH GELATINIZATION
  - STRUCTURAL ALTERATIONS OF CELL WALL DEPOLYMERIZATION OF DIETARY FIBRE
- LIPID OXIDATION
- DEGRADATION OF SOME BIOACTIVE COMPONENTS

FOOD MODIFICATIONS: THERMAL TREATMENT

- REACTION BETWEEN DIFFERENT COMPONENTS GENERATE NEW COMPOUNDS
- PROTEINS-SUGAR: MAILLARD REACTION (FORMATION OF ADVANCED GLYCOSILATION END PRODUCTS (AGES)
- LIPID-PROTEIN: ADVANCED LIPOXIDATION END PRODUCTS (ALES)

THE CHEMICAL PROCESSES IN THE FOOD CHEMISTRY AND FOOD TECHNOLOGY

- **CARBONYL-AMINE INTERACTIONS (MAILLARD REACTION)**
- THERMAL TRANSFORMATIONS OF α-AMINOACIDS, PROTEINS, VITAMINS, CARBOHYDRATES (CARAMELIZATION)
- THERMAL-OXIDATIVE DESTRUCTION AND AUTOXIDATION OF FOOD LIPIDS
- POLYPHENOL COLORING OF THE FOODSTUFFS
- CHANGES OF THE FOOD COMPONENTS BY FOOD IRRADIATION AND OTHER TREATMENTS

FOOD MODIFICATIONS: THERMAL TREATMENT

THE SAME CHEMISTRY

- THE REACTION IS IN BOTH CASES (SUGARS OR OXIDISED LIPIDS) BETWEEN A **CARBONYL MOIETY** AND AN **AMINO** GROUP

THE SAME PRODUCTS

- THE FINAL PRODUCT OF BOTH REACTION PATHWAYS (AGES AND ALES) ARE POLYMERIC BROWN MACROMOLECULES
- Advanced Glycoxidation and Lipoxidation end Products (AGEs and ALEs)

FOOD MODIFICATIONS: THERMAL TREATMENT

AGEs

- Advanced Glycation End Products are proteins or lipids that become glycated as a result of exposure to sugars
- Foods highest in AGEs include **meat** (especially **red meat**), certain **cheeses**, fried eggs, **butter**, cream **cheese**, margarine, mayonnaise, oils, and nuts. Fried foods and highly processed products also contain high levels.
- Advanced glycation end products (**AGEs**) are proteins or lipids that become glycated as a result of exposure to sugars. They are a bio-marker implicated in aging and the development, or worsening, of many degenerative diseases, such as diabetes, atherosclerosis, chronic kidney disease, and Alzheimer's disease.

FOOD MODIFICATIONS: THERMAL TREATMENT

ALEs

- Advanced Lipoxidation End Products

THE MAILLARD REACTION IN FOODS

- PRODUCES AROMAS IN HEATED FOODS
- RESPONSIBLE FOR COLOUR FORMATION (NON-ENZYMATIC BROWNING)
- MAILLARD PRODUCTS HAVE ANTIOXIDANT PROPERTIES
- CAN CAUSE LOSS OF NUTRIENTS
- SOME PRODUCTS MAY BE TOXIC

IMPORTANT TYPES OF BROWNING

- ENZYMATIC (POLYPHENOLOXIDASE). FRESH CUT VEGETABLES, NON-TOXIC, NO FLAVOR
- CARAMELIZATION. SUGARS AT VERY HIGH TEMPERATURES
- LIPID BROWNING. POLYMERIZATION OF FRYING OILS
- VITAMIN C BROWNING. SIMILAR TO MAILLARD
- THE **MAILLARD** REACTION

MAILLARD REACTION / BROWNING

"THE SEQUENCE OF EVENTS THAT BEGINS WITH REACTION OF THE AMINO GROUP OF AMINO ACIDS WITH A GLYCOSIDIC HYDROXYL GROUP (CARBONYL CARBON) OF (REDUCING) SUGARS AT VERY HIGH TEMPERATURE (140-165°C); THE SEQUENCE TERMINATES WITH THE FORMATION OF BROWN NITROGENOUS POLYMERS OR MELANOIDINS."

(John deMan)

REDUCING SUGAR

- A REDUCING SUGAR IS ANY SUGAR THAT IS CAPABLE OF ACTING AS A REDUCING AGENT BECAUSE IT HAS A FREE ALDEHYDE GROUP OR A FREE KETONE GROUP
- ALL MONOSACCHARIDES ARE REDUCING SUGARS, ALONG WITH SOME DISACCHARIDES, OLIGOSACCHARIDES, AND POLYSACCHARIDES
- THE MONOSACCHARIDES CAN BE DIVIDED INTO TWO GROUPS: THE ALDOSES, WHICH HAVE AN ALDEHYDE GROUP, AND THE KETOSES, WHICH HAVE A KETONE GROUP
- KETOSES MUST FIRST TAUTOMERIZE TO ALDOSES BEFORE THEY CAN ACT AS REDUCING SUGARS
- THE COMMON DIETARY MONOSACCHARIDES GALACTOSE, GLUCOSE AND FRUCTOSE ARE ALL REDUCING SUGARS

REDUCING SUGAR

- DISACCHARIDES ARE FORMED FROM TWO MONOSACCHARIDES AND CAN BE CLASSIFIED AS EITHER REDUCING OR NON-REDUCING
- NON-REDUCING DISACCHARIDES LIKE SUCROSE AND TREHALOSE HAVE GLYCOSIDIC BONDS BETWEEN THEIR ANOMERIC CARBONS AND THUS CANNOT CONVERT TO AN OPEN-CHAIN FORM WITH AN ALDEHYDE GROUP; THEY ARE STUCK IN THE CYCLIC FORM
- REDUCING DISACCHARIDES LIKE LACTOSE AND MALTOSE HAVE ONLY ONE OF THEIR TWO ANOMERIC CARBONS INVOLVED IN THE GLYCOSIDIC BOND, MEANING THAT THEY CAN CONVERT TO AN OPEN-CHAIN FORM WITH AN ALDEHYDE GROUP

MAILLARD REACTION / BROWNING

OCCURS BETWEEN REDUCING SUGARS AND AMINES AT HIGH TEMPERATURES

- PRODUCES FLAVOR
- PRODUCES COLOR
- PRODUCES ANTIOXIDANT PRODUCTS
- PRODUCES TOXIC PRODUCTS
- DESTROYS NUTRIENTS (LYSINE)

CONTROL STEPS

- RAPIDLY ACCELERATED BY TEMPERATURE
- SIGNIFICANT ACCELERATION AT INTERMEDIATE WATER ACTIVITIES
- SUGAR TYPE
  - PENTOSE > HEXOSE > DISACCHARIDE >> POLYSACCHARIDE
- PROTEIN CONCENTRATION (FREE AMINES)
- INHIBITED BY ACID
  - AMINES ARE PROTONATED AND USED UP, pH DROPS
- SULFUR DIOXIDE

MAILLARD REACTION

TYPE OF THE CARBOHYDRATE

- PENTOSES > HEXOSES
- RIBOSE – THE MOST REACTIVE SUGAR (PENTOSES)
- GALACTOSE – THE MOST REACTIVE SUGAR (HEXOSES)
- RIBOSE : XYLOSE: GALACTOSE = 100 : 6 : 1
- LACTOSE – THE MOST REACTIVE DISACCHARIDES

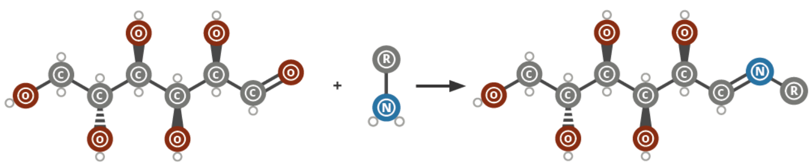
TYPE OF THE AMINO COMPOUND

- LYSINE – THE MOST REACTIVE AMINO ACID

A GUIDE TO THE MAILLARD REACTION

The Maillard reaction occurs during cooking, and it is responsible for the non-enzymatic browning of foods when cooked. It actually consists of a number of reactions, and can occur at room temperature, but is optimal between 140-165˚C. The Maillard reaction occurs in three stages, detailed here.

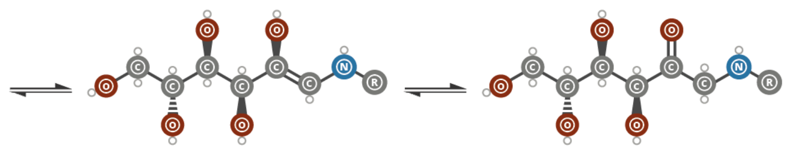
1 The carbonyl group on a sugar reacts with a protein or amino acid's amino group, producing an N-substituted glycosylamine.



SUGAR (GLUCOSE) + AMINO GROUP → GLYCOSYLAMINE (+ WATER)

2 The glycosylamine compound generated in the first step isomerises, by undergoing Amadori rearrangement, to give a ketosamine.

GLYCOSYLAMINE



1,2-ENAMINOL

AMADORI COMPOUND

3 The ketosamine can react in a number of ways to produce a range of different products, which themselves can react further.

ALKALINE CONDITIONS

FISSION PRODUCTS

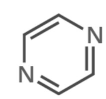
REDUCTONES

ACIDIC CONDITIONS

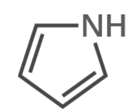
HYDROXYMETHYLFURFURAL

Classes of Maillard Reaction Products

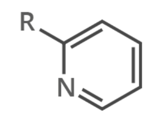
The Maillard reaction produces hundreds of products; a small subset of these contribute to flavour and aroma, some groups of which are described below. Melanoidins are also formed, brown, polymeric substances which contribute to the colouration of many cooked foods.



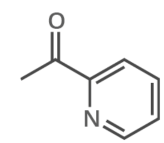
PYRAZINES
cooked
roasted
toasted



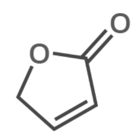
PYRROLES
cereal-like
nutty



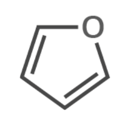
ALKYLPYRIDINES
bitter
burnt
astringent



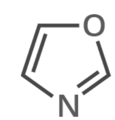
ACYLPYRIDINES
cracker-like
cereal



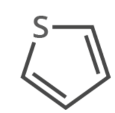
FURANONES
sweet
caramel
burnt



FURANS
meaty
burnt
caramel-like

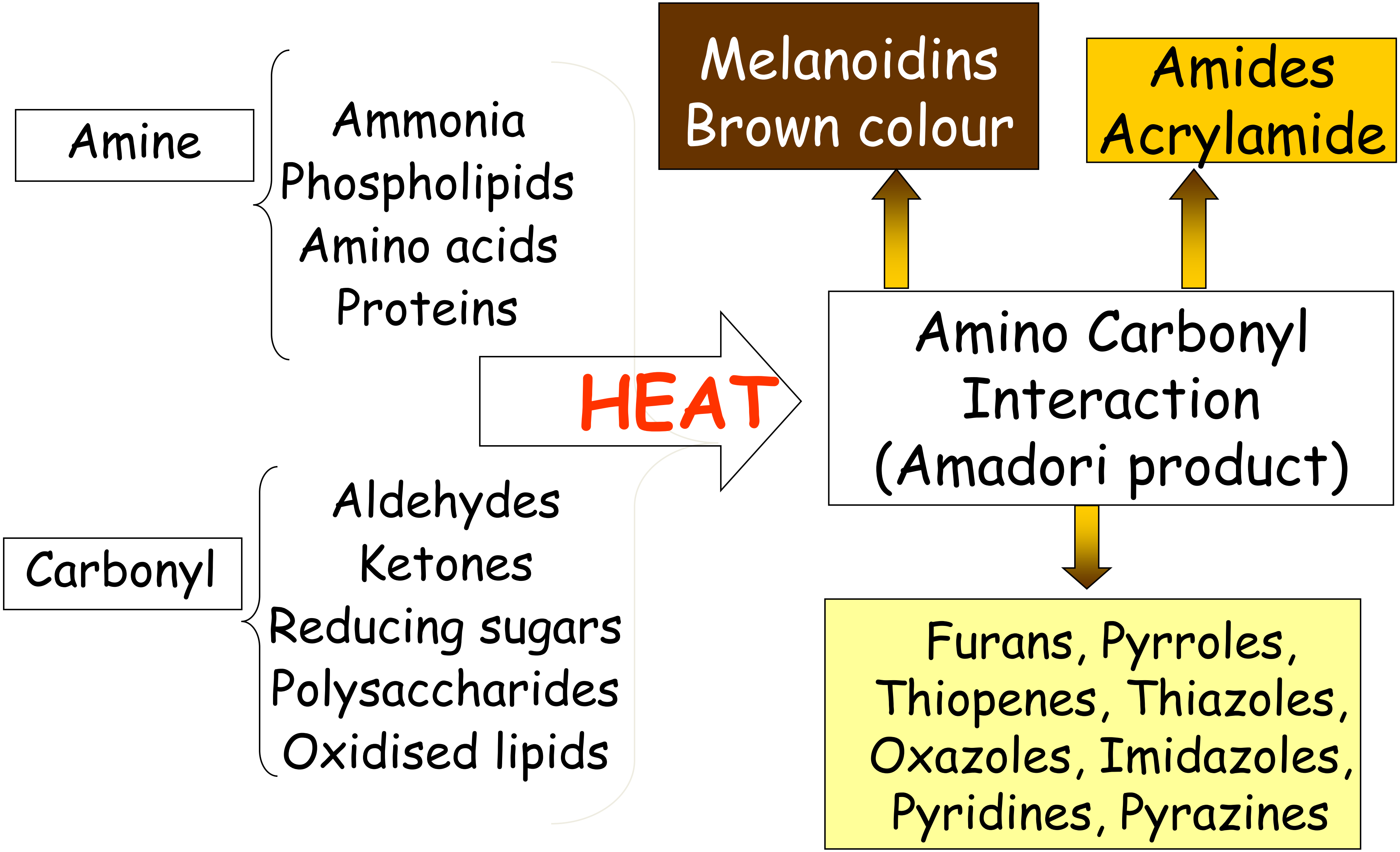


OXAZOLES
green
nutty
sweet



THIOPHENES
meaty
roasted

GENERAL SCHEME OF MR BROWNING



MANY REACTIONS THOUSANDS OF PRODUCTS

PRODUCTS FORMED DEPENDS ON

- CHEMICAL NATURE OF THE REACTANTS
- TIME AND TEMPERATURE OF HEATING
- TECHNOLOGICAL CONDITIONS
- WATER ACTIVITY
- pH

MR - POSSIBLE TOXICANTS

- ACRYLAMIDE
- FURAN
- HETEROCYCLIC AMINES
- 3-MPCD (MONO CHLORO PROPAN DIOL)
- 3-METHYL IMIDAZOLONE

DEVELOPMENT OF MITIGATION STRATEGIES TO REDUCE THEIR CONCENTRATION

CHANGES IN FOOD PROTEINS…

- MAILLARD REACTION IS A REACTION THAT OCCURS BETWEEN PROTEINS (AMINO GROUPS) AND REDUCING SUGARS
- VOLATILES AND DARK PIGMENTS ARE FORMED AS A RESULT OF MAILLARD REACTION, THAT CAUSE THE BROWNING OF THE COLOR AND SOMETIMES CHANGES IN TEXTURE OF THE FOOD PRODUCT
- IT IS CHARACTERIZED BY BROWNING OF PRODUCTS ACCOMPANIED BY A LOSS OF NUTRITIVE VALUE

CHANGES IN FOOD PROTEINS…

MECHANISM OF MAILLARD REACTION

- THE REACTION PROCESS INVOLVES REACTION TO FORM AN UNSTABLE SCHIFF'S BASE (DOUBLE BOND BETWEEN THE CARBON ATOM OF THE GLUCOSE AND THE NITROGEN ATOM OF THE LYSINE)
- THEN TRANSFORMATION THROUGH THE AMADORI REARRANGEMENT (HYDROGEN ATOM FROM THE HYDROXYL GROUP ADJACENT TO THE CARBON-NITROGEN DOUBLE BOND MOVES TO BOND TO THE NITROGEN, LEAVING A KETONE)
- THE REACTIONS CONTINUE FURTHER THROUGH THE STRECKER DEGRADATION AND POLYMERIZATION REACTIONS TO FORM VOLATILES AND DARK PIGMENTS
- THIS CAUSES A BROWNING OF THE COLOR AND SOMETIMES CHANGES IN TEXTURE OF THE FOOD PRODUCT

RATE OF MAILLARD REACTION

- THE RATE OF THIS REACTION INCREASE WITH INCREASE IN HEATING TIME, TEMPERATURE, AND FREE ALDEHYDE AND AMINE GROUPS
- RATE OF MAILLARD REACTION HAS BEEN FOUND TO VARY WITH WATER ACTIVITY (a_W), WITH A MAXIMUM RATE TYPICALLY OCCURRING AT a_W BETWEEN 0.6 AND 0.8, AND LOWER REACTION RATES AT BOTH HIGHER AND LOWER a_W
- MAILLARD REACTION ALSO DEPENDS ON PH, AND RARELY OCCURS AT LOW pH
- THE REACTION IS ALSO CATALYZED WITH METAL IONS SUCH AS Cu AND Fe

CHANGES IN FOOD PROTEINS…

EFFECTS OF MAILLARD REACTION

- PRODUCTS SUCH AS DEHYDRATED FRUITS AND VEGETABLES, POTATO POWDER, DRIED EGG AND LIQUID & DRIED MILK PRODUCTS ARE KNOWN TO BE SUSCEPTIBLE TO THE MAILLARD REACTION WHICH CAN LIMIT THEIR SHELF LIVES
- MAILLARD REACTION IS NORMALLY ASSOCIATED WITH A LOSS IN NUTRITIONAL VALUE.
- THE ESSENTIAL AMINO ACID LYSINE READILY REACTS WITH REDUCING SUGARS AND IS QUICKLY LOST DURING THE REACTION

CHANGES IN FOOD PROTEINS…

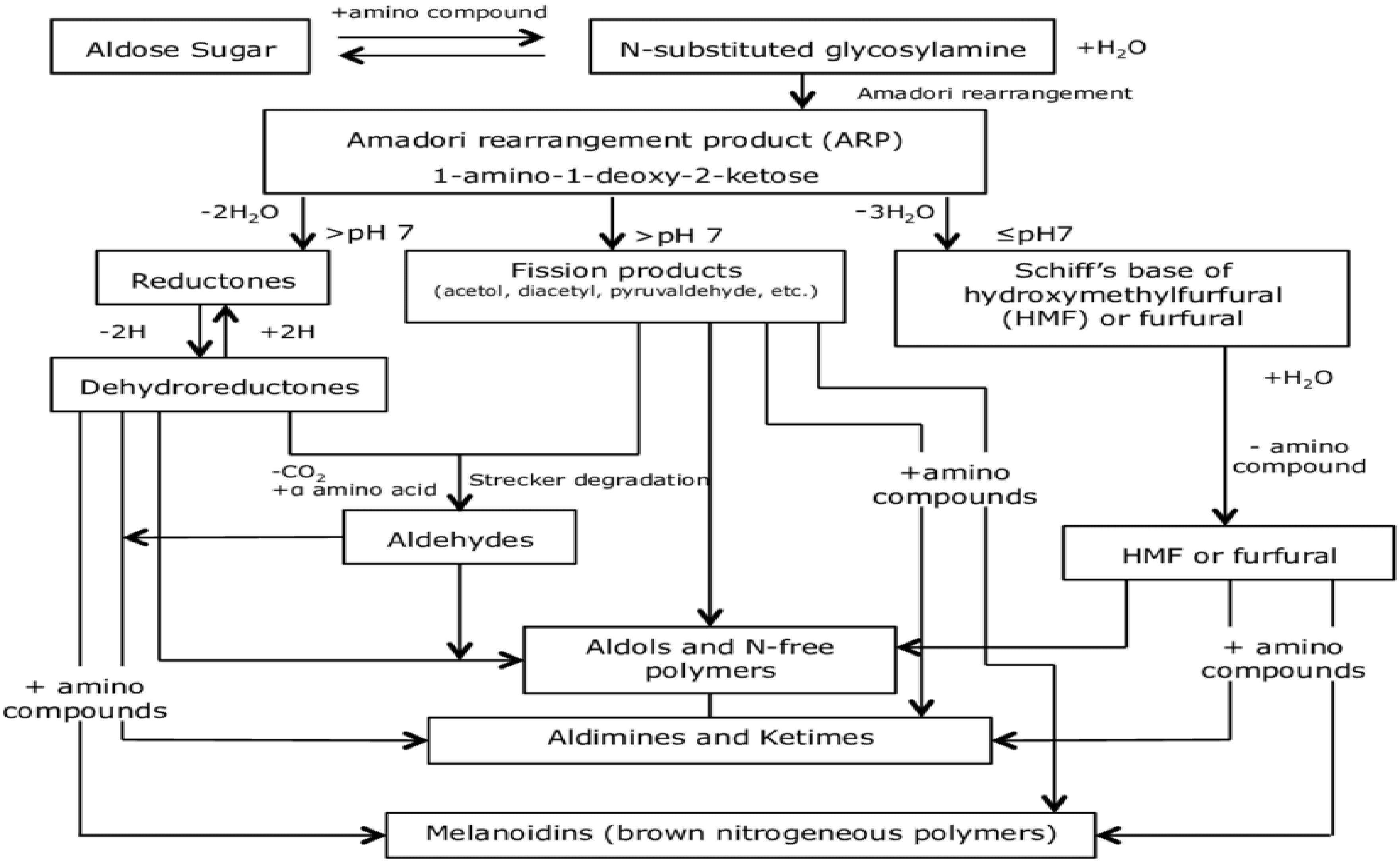
MAILLARD REACTION IN MILK

- IN ALL TYPES OF HEAT TREATMENT (LTLT/HTST PASTEURIZATION AND UHT)-THE MAILLARD REACTION CAN OCCUR IN MILK
- IN THE CASE OF MILK, LACTOSE REACTS WITH THE FREE AMINO ACID SIDE CHAINS OF MILK PROTEINS (MAINLY E-AMINO GROUP OF LYSINE) TO PROCEED MAILLARD REACTION AND FORMS VARIOUS MAILLARD REACTION PRODUCTS
- THE MAILLARD REACTION RESULTS IN THE FORMATION OF MELANOIDINS (BROWNING COMPOUNDS) IN MILK
- THE FORMATION OF FLAVOR AND BROWNING COMPOUNDS IS CAUSED AS THE CONSEQUENCES OF THE MAILLARD REACTION BETWEEN LACTOSE AND MILK PROTEINS
- THE MAILLARD REACTION SHOWS VARIOUS EFFECTS ON MILK PROTEINS SUCH AS BIOAVAILABILITY, SOLUBILITY, EMULSIFYING PROPERTY AND HEATING STABILITY

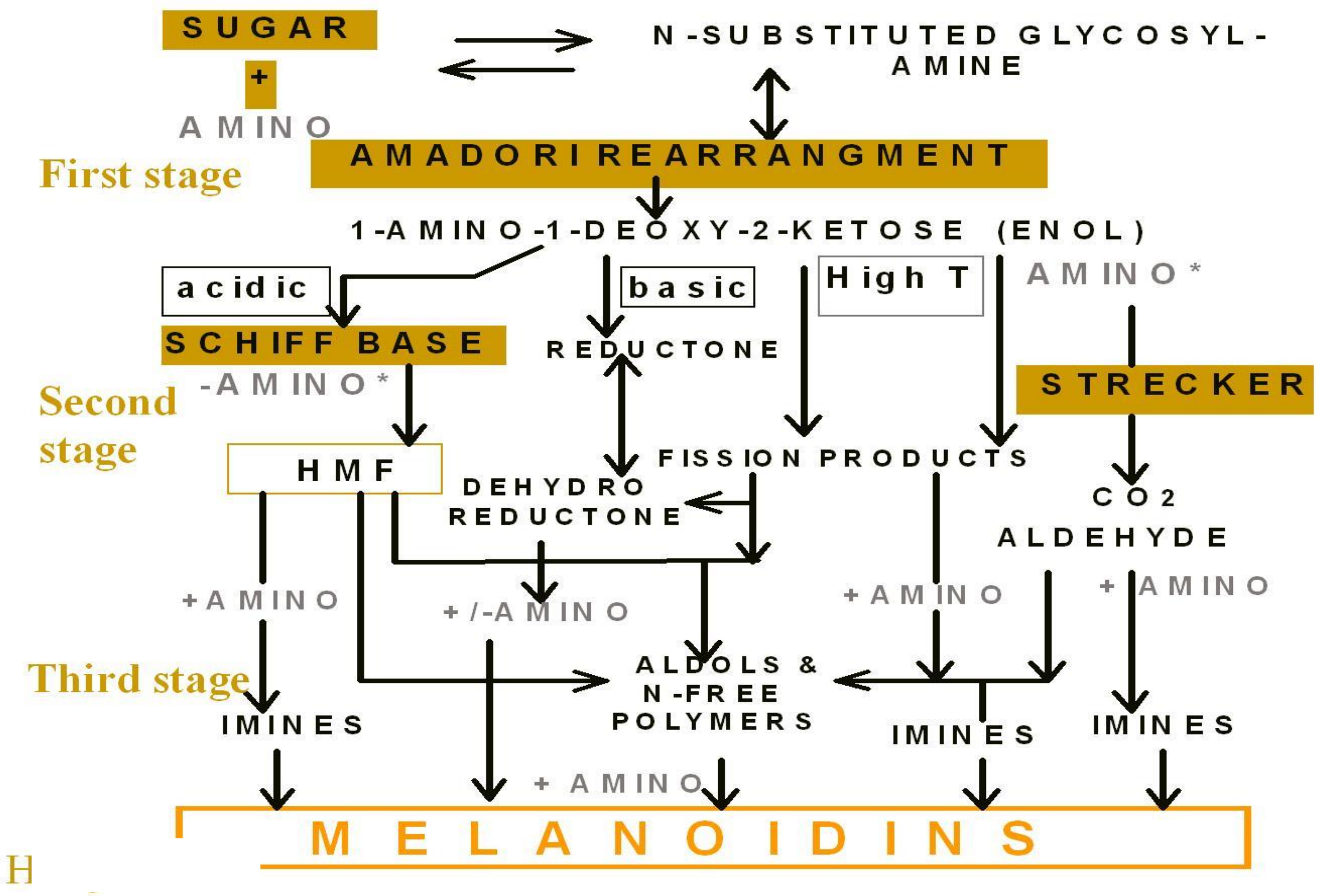
JOHN EDWARD HODGE

- Born (1914-1996) was an African-American chemist, born in Kansas City, Kansas.
- Hodge, J. E. (1953). "Dehydrated Foods, Chemistry of Browning Reactions in Model Systems". Journal of Agricultural and Food Chemistry. 1 (15): 928–943. doi:10.1021/jf60015a004

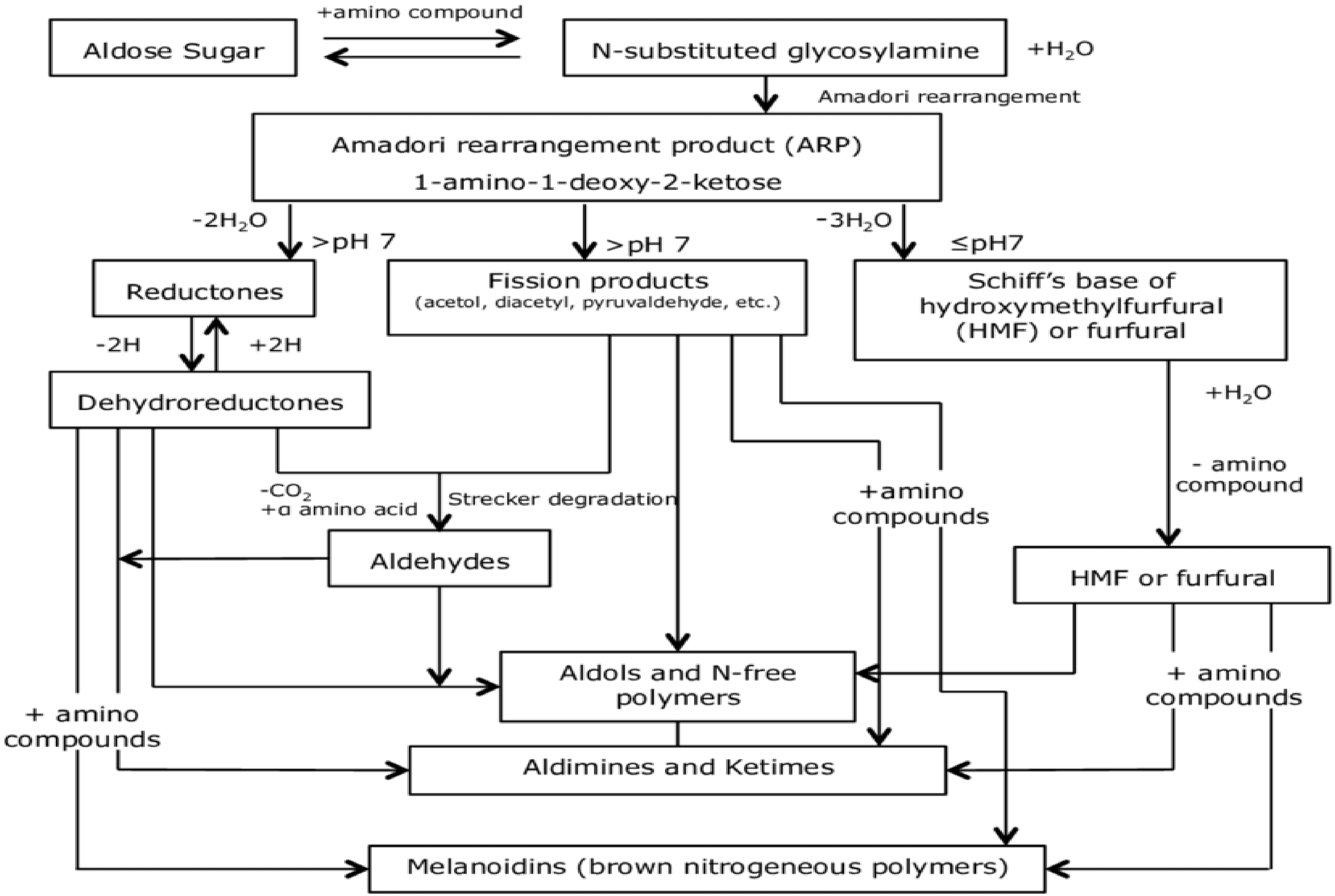
HODGE SCHEME



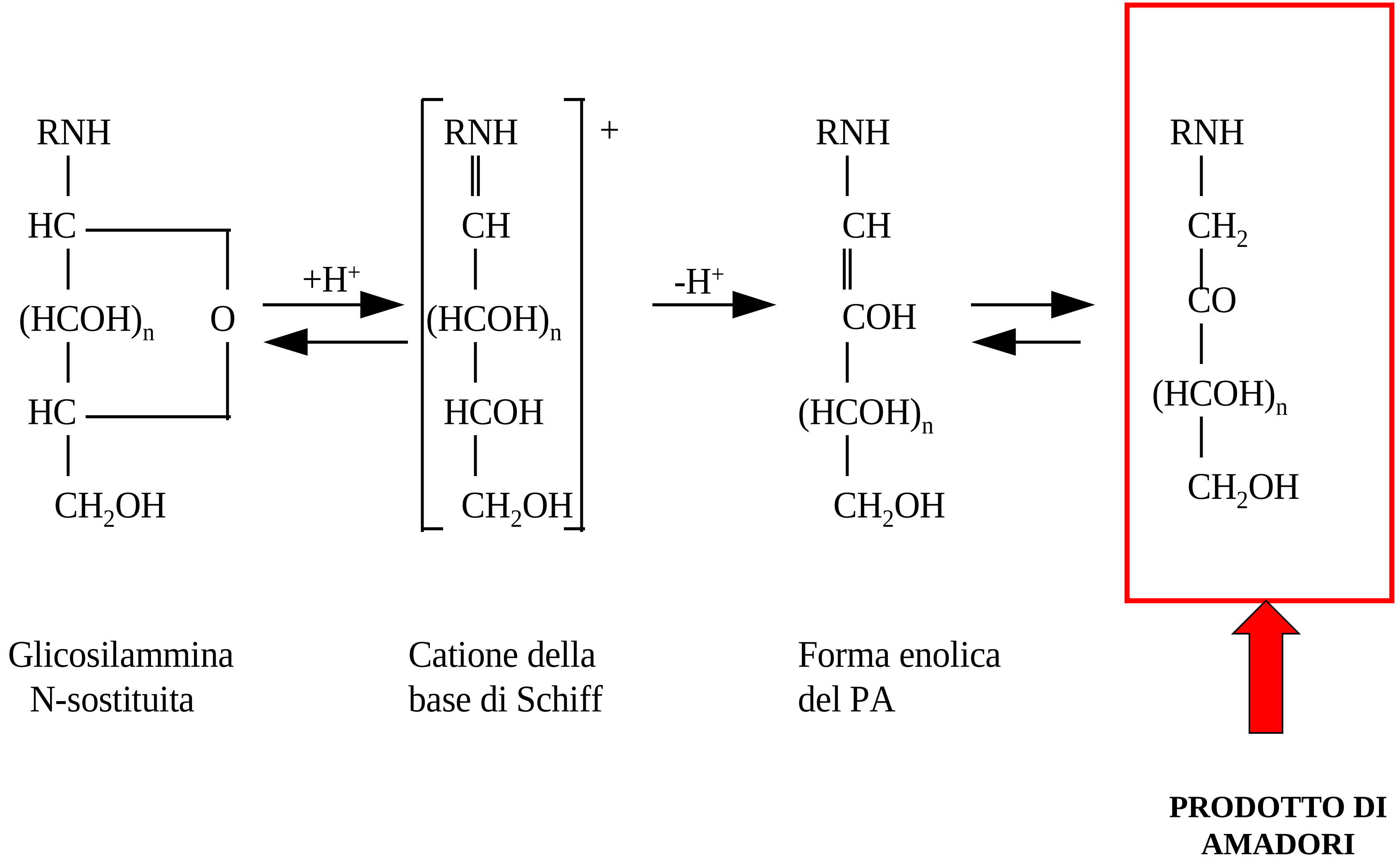
HODGE SCHEME

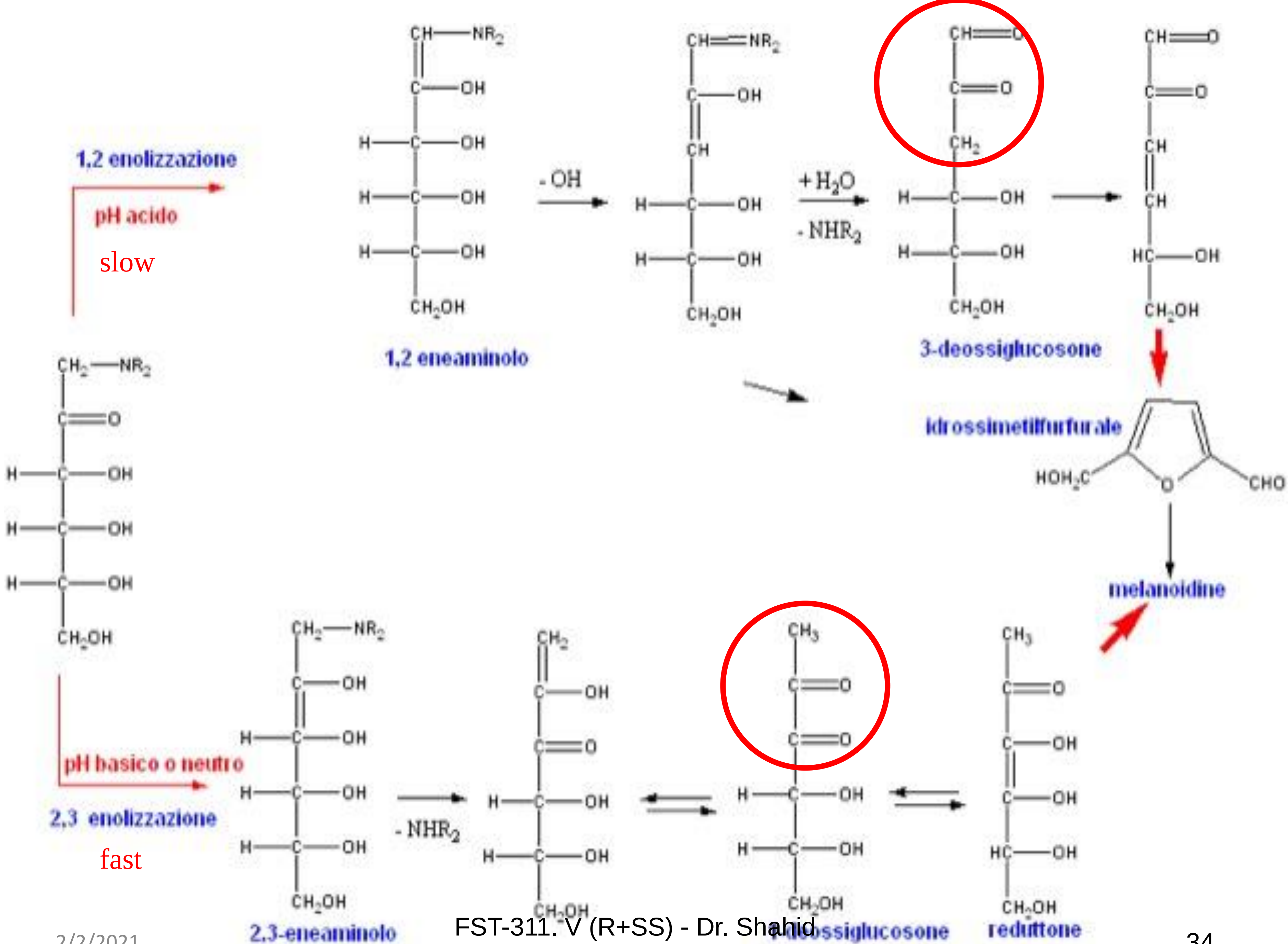


Hodge J E. Dehydrated foods: chemistry of browning reactions in model systems. *J. Agric. Food Chem.* **1**:928-43, 1953.

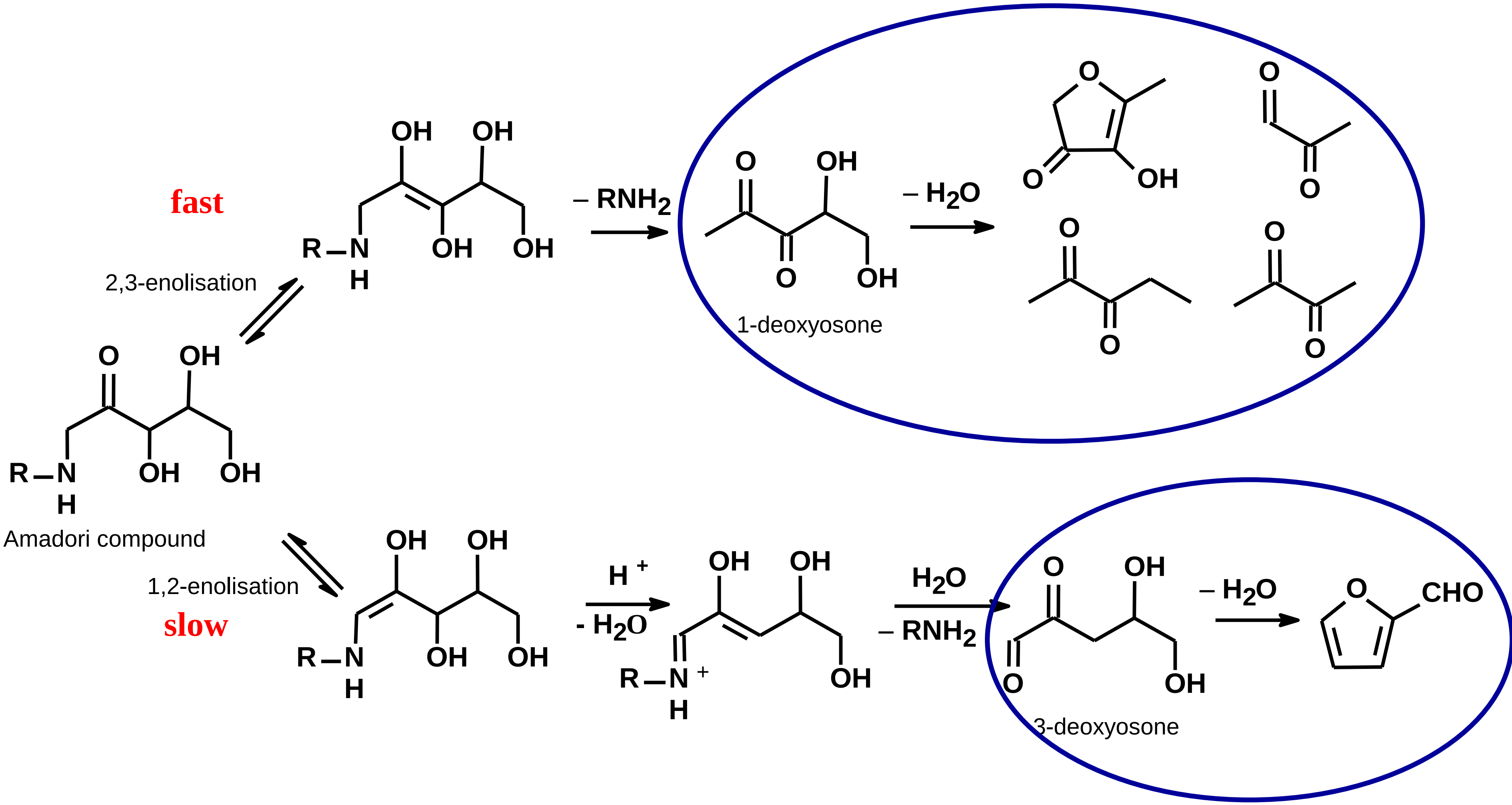

Aldose Sugar
+amino compound
N-substituted glycosylamine
+H$_2$O
Amadori rearrangement
Amadori rearrangement product (ARP)
1-amino-1-deoxy-2-ketose
-2H$_2$O
>pH 7
>pH 7
-3H$_2$O
≤pH7
Reductones
Fission products
(acetol, diacetyl, pyruvaldehyde, etc.)
Schiff's base of hydroxymethylfurfural (HMF) or furfural
-2H
+2H
Dehydroreductones
+H$_2$O
- amino compound
-CO$_2$
+α amino acid
Strecker degradation
+amino compounds
Aldehydes
HMF or furfural
Aldols and N-free polymers
+ amino compounds
+ amino compounds
Aldimines and Ketimes
Melanoidins (brown nitrogeneous polymers)

FORMATION OF AMADORI PRODUCT



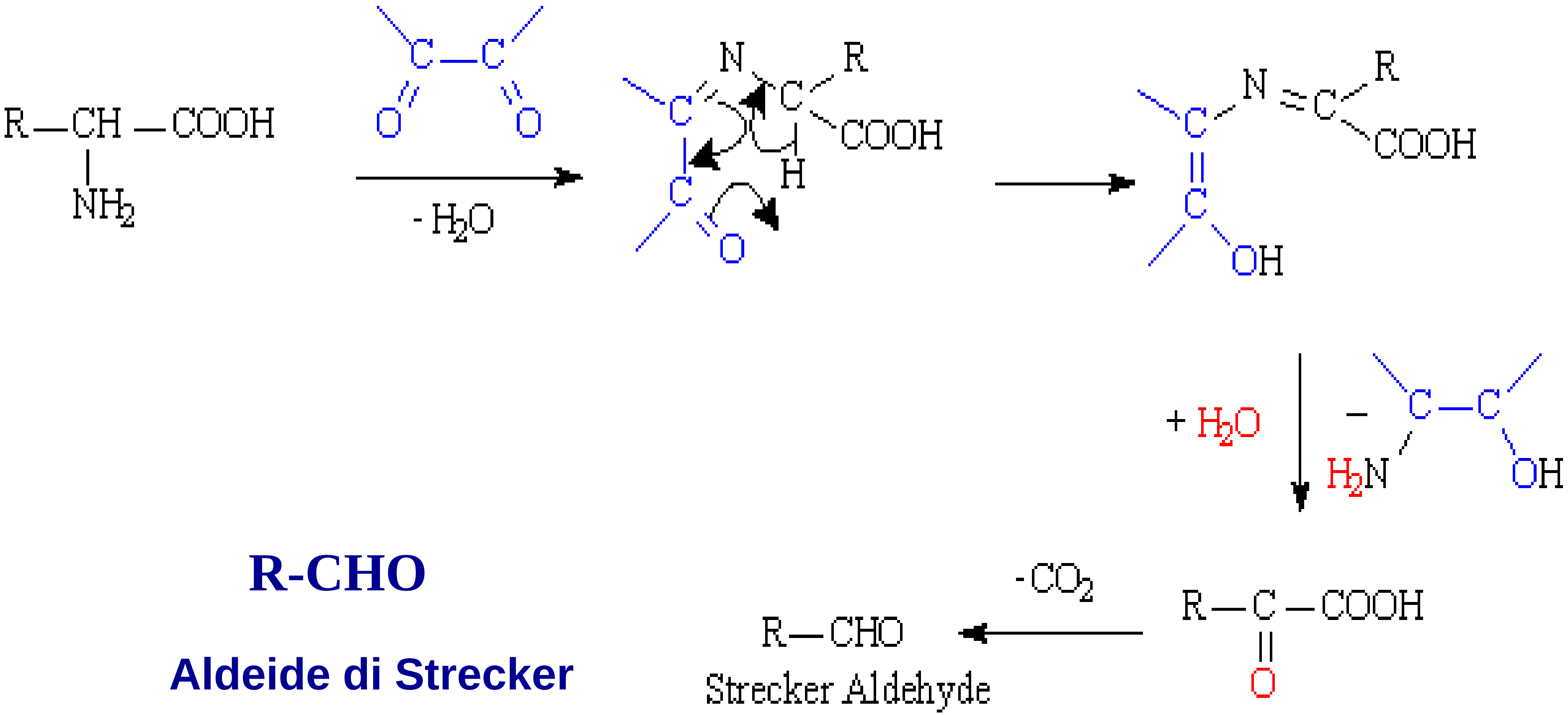

1,2 enolizzazione
pH acido
slow
1,2 eneaminolo
- OH
+ H2O
- NHR2
3-deossiglucosone
idrossimetilfurfurale
HOH2C
CHO
melanoidine
pH basico o neutro
2,3 enolizzazione
fast
2,3-eneaminolo
- NHR2
reduttone

FORMATION OF CARBONYL - MR



STRECKER DEGRADATION

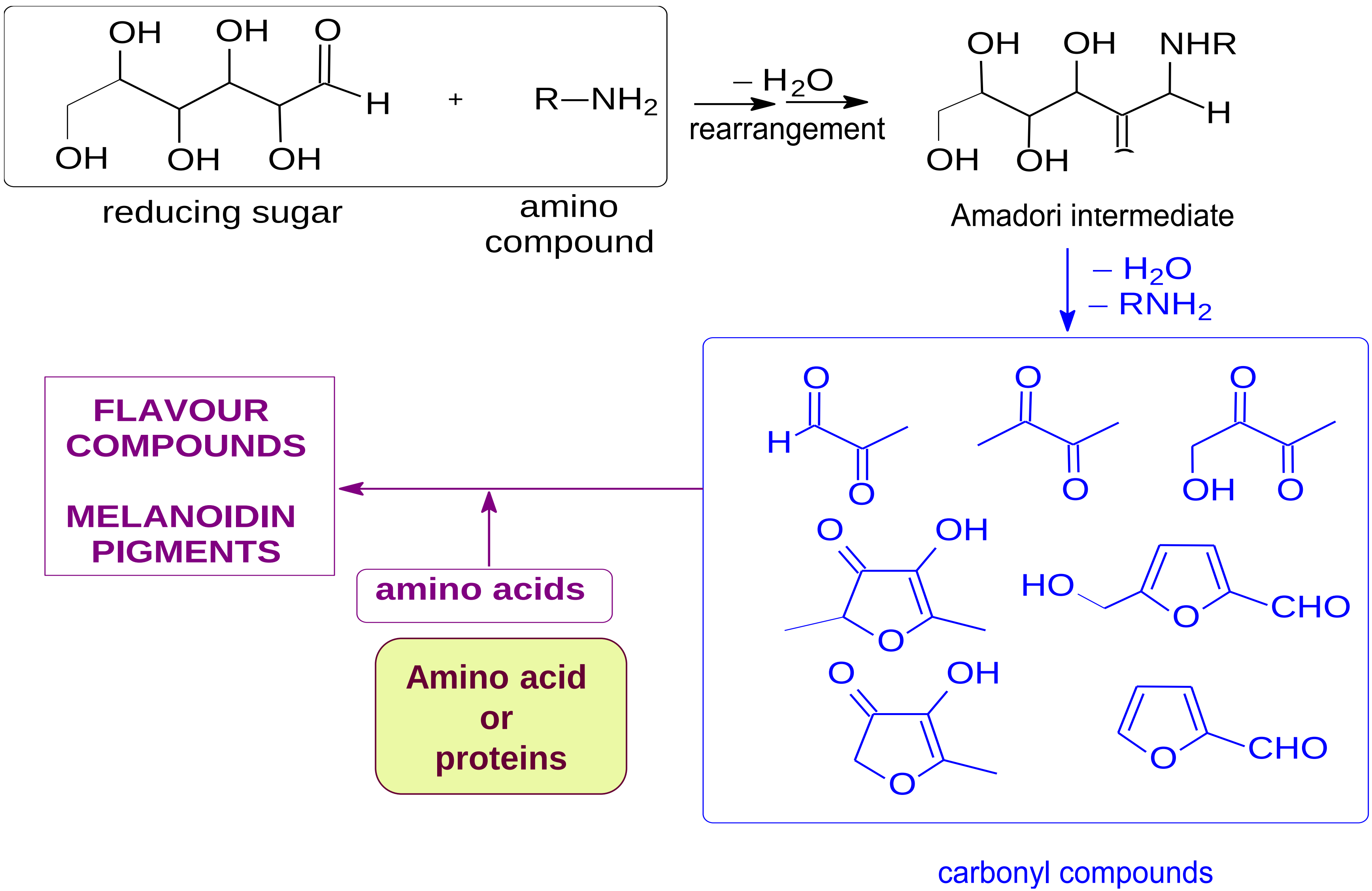
Free amino acids with dicarbonyl compounds



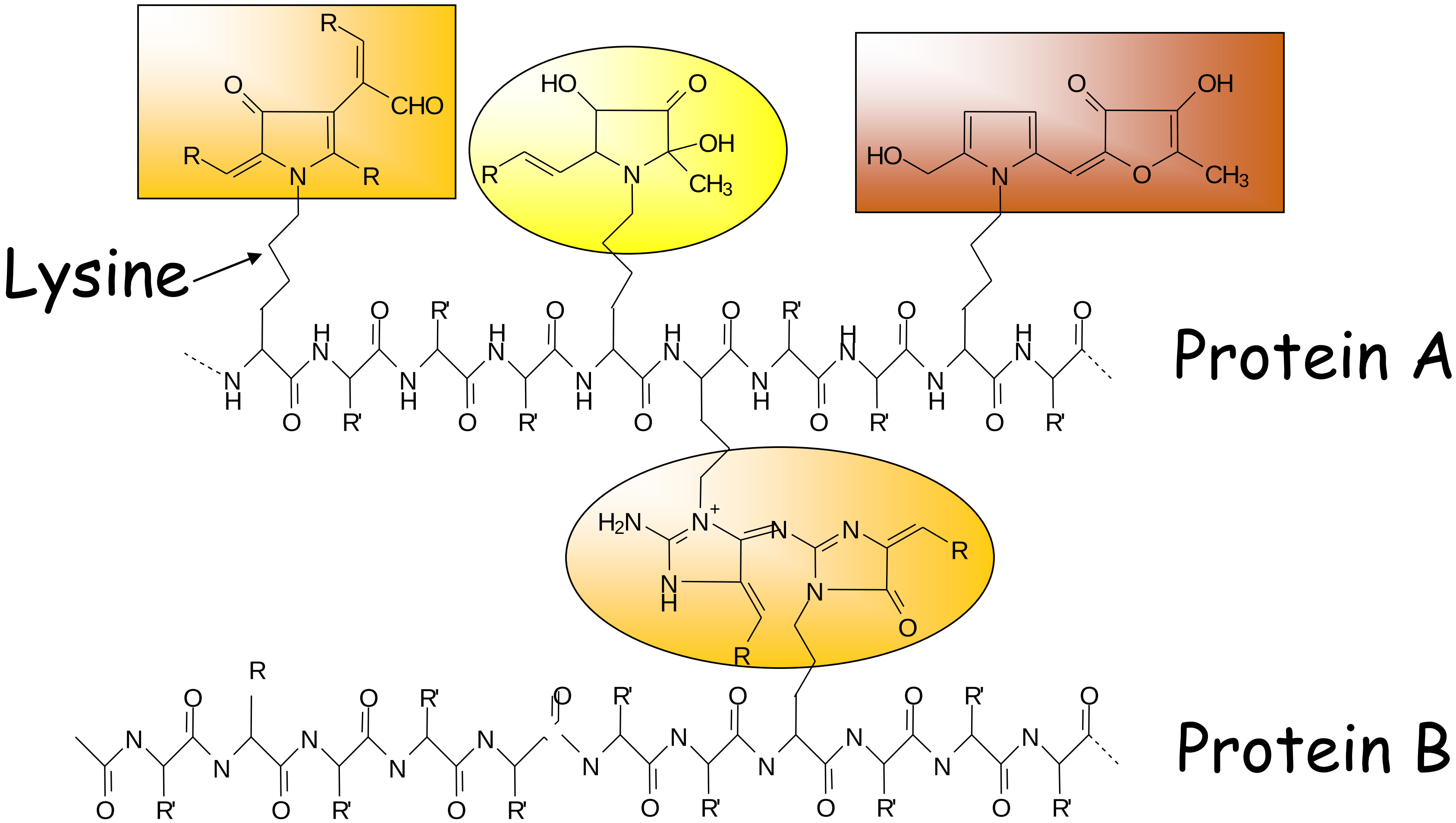
R-CHO

Aldeide di Strecker

FLAVOR AND COLOR - MR



FOOD "MELANOPROTEINS"



PRONYL-LYSINE

- THIS COMPOUND IS FORMED ON THE LATERAL CHAIN OF LYSINE RESIDUES
- PRONYL-LYSINE HAS A HIGH ANTIOXIDANT ACTIVITY