Handwritten Notes

On

Carbohydrates

Carbohydrates

→ all $C_x(H_2O)_y$ aren't carbs

→ all compounds, not following $C_x(H_2O)_y$ aren't necessarily non-carbohydrates (eg: Rhamnose($C_6H_{12}O_5$), deoxyribose($C_5H_{10}O_4$))

→ chemically, defined as optically active polyhydroxy ald./ketones or compounds which produce such units on hydrolysis.

→ All carbs giving Fehling's and Tollen's Test are reducing.

→ All monosacch. are reducing.

→ In disacch, if reducing grp of constituent monosacch are bonded, non reducing (Sucrose)

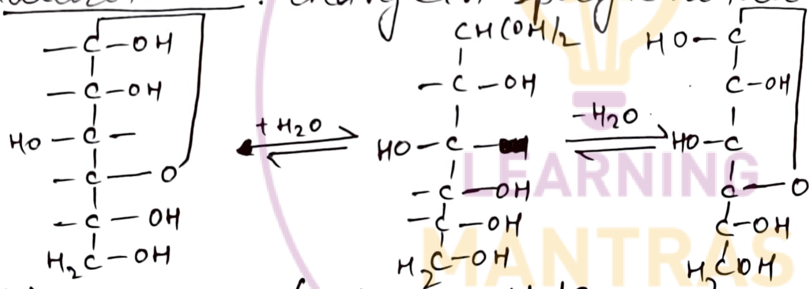
→ 'D' and 'L' refers to their relation with a particular isomer of glyceraldehyde.

→ Glycose (Two crystalline forms)

- α (mp - 419K)
  → obtained by crystallization from conc. solⁿ of glucose @ 303K (30°C)
- β (mp - 423K)
  @ 371K (≈ 50°C)

→ The word pyranose / furanose derived from:

→ **Mutarotation**: change in specific rotation value due to inter-conversion



α-D, $[\alpha]_D = +113$ — (intermediate aldehydrol form) — β-D, $[\alpha]_D = +19.5$

(36%) ——— $[\alpha]_D = +52.5$ ——— (64%)

→ If C at which epimer forms arise isn't specified, assume C_2

→ threose is a C_2 epimer of erythrose.

→ **Prepⁿ of Glucose**:

(a) from sucrose:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{boil}]{H^{\oplus}\text{(dil HCl/}H_2SO_4)} \underset{(50\%)}{\text{glu}} + \underset{(50\%)}{\text{fruct}}$$

(b) commercial method (from starch):

$$\underset{\text{(starch/cellulose)}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow[393K,\ 2\text{-}3\,atm]{H^{\oplus}} \underset{\text{glucose}}{n\,C_6H_{12}O_6}$$

Rxⁿs of glucose:

(1) glucose $\xrightarrow[HI/\Delta]{Red\ P}$  (n-Hexane) (suggests that all 6 carbons are linearly arranged)

(2) Rxⁿ of ald. grp.

$C_5H_{11}O_5-CHO$ (glucose)
- (i) $\xrightarrow{NH_2OH}$ (hydroxylamine) $C_5H_{11}O_5-CH=N-OH$
- (ii) $\xrightarrow{HCN}$ $C_5H_{11}O_5-CH(CN)(OH)$ (cyanohydrin)

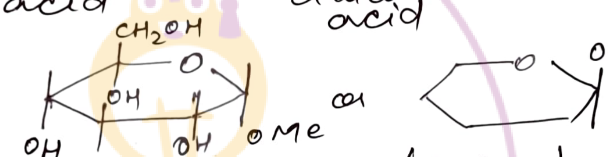
(confirmⁿ of ⊕ of carbonyl grp)

(3) $CHO-(CHOH)_4-CH_2OH$ $\xrightarrow[(eg\ Br_2)]{mild\ O.A.}$ $COOH-(CH(OH))_4-CH_2OH$ (Glucoronic acid) (indicates ⊕ of ald grp as carbonyl grp.)

(4) $CHO-(CHOH)_4-CH_2OH$ $\xrightarrow[(Acetic\ anhydride)]{Acetylation}$ $CHO-(CH-OCOCH_3)_4-CH_2-OCOCH_3$ } confirms ⊕ of 5-OH grps on diff carbons.

(5) $CHO-(CHOH)_4-CH_2OH$ $\xrightarrow[(oxidⁿ)]{HNO_3}$ $COOH-(CHOH)_4-COOH$ (Saccharic acid) ⟵ —"— $COOH-(CHOH)_4-CH_2OH$ (Glucomic acid) } indicates ⊕ of a 1° alcohol grp.

(6) Glucoside formⁿ

D glucose $\xrightarrow[HCl]{CH_3OH}$ 

(Acetal of ↑ aka Glucoside) (α methyl α-D glucopyranoside) or (β-D ‐‐)

} indicates ⊕ of ring str in glucose, where free -CHO reacts to form -CHOH grp at C_1.

* (7) Action of Phenylhydrazine:

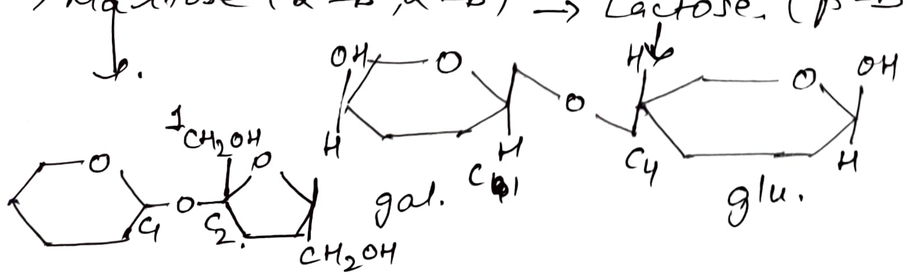
Glucose reacts with 3 mols/eq of Ph-hydrazine

$HC=O$, $H-C-OH$, $(CHOH)_3$, H_2C-OH (glucose) $\xrightarrow[(Ph-hy)]{H_2NNHC_6H_5}$ $HC=NNHC_6H_5$, $C-OH$ (Glucose Ph-hydrazone) $\xrightarrow[(oxidⁿ)]{Ph-Hy}$ $HC=NNHC_6H_5$, CO + (reduced) + NH_3 $\xrightarrow{Ph-Hy}$ (Ph-hydrazone of Glucosone) ⟶ $HC=NNHC_6H_5$, $C=NNHC_6H_5$ (Glucosazone)

→ Yellow crystalline,
→ Sparingly sol. in H_2O
→ sharp MP
→ test for ⊕ of glucose

Disacch: Done

→ Sucrose (α-D glu + β-D fruct)
→ Maltose (α-D, α-D) → Lactose (β-D gal, β-D glu)



Polysacch:
(i) Starch → amylose / → amylopectin

amylose	amylopectin
→ 15-20%	→ 80-85%
→ water soluble	Insoluble
→ linear, α-D (1,4)	→ branched, α-D (1,4 or 1-6)
→ 200-1000	→ ↑ high
→ I_2 test (blue-black) ✓	→ ×

Glycogen: ⊕ in liver, brain, muscles
→ animal starch (∥a to amylopectin but branching ↑)
→ also ⊕ in yeast, fungi
(Rest Done)

Amino acids: Depending on position of NH_2 grp wrt COOH grp (α, β, γ, δ - - -)
→ Proteins → α ⊕.
→ Glycine (as Glykos : sweet), tyrosine was first obtained from cheese (tyros : cheese)

How to Remember Amino acid Structures:

Let H_2N —(COOH)— H = (X)

① (X) — H (glycine)

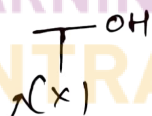
② (X) — CH_3 (Alanine).

③  (Valine)

④  (Leucine).

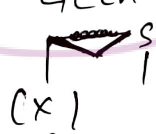
⑤  (Isoleucine) (inverted L)

⑥ CH_2-OH (X) (Serine)

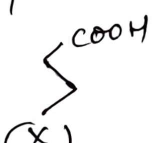
⑦  (Threonine) (4 C in 1 line)

⑧  (Tyrosine)

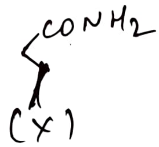
⑨ ┌SH (X) (Cysteine)

⑩  or  (Methionine)

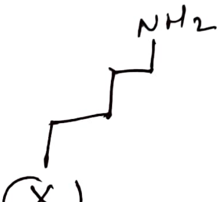
⑪ ┌COOH (X) (Aspartic acid)

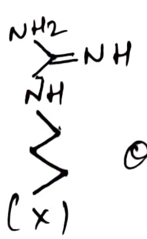
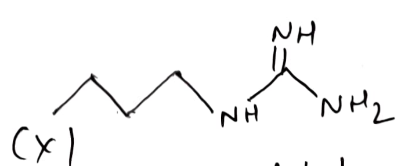
⑫  (Glutamic acid)

⑬ ┌$CONH_2$ (X) (Asparagine)

⑭  (Glutamine)

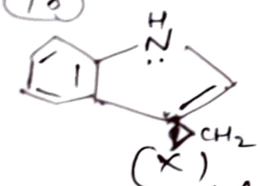
⑮  [(X)-CH_3-Ph] (Phenylalanine) ⊕ (Refer)

⑯  (Lysine) (2 'L's)

⑰  or  (Arginine) (almost 3 'A's)

Complex : (Just Remember)

(18)

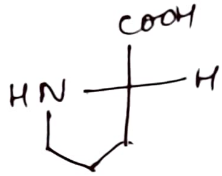


(Tryptophan)

(19)

(Histidine)

(20)



(Proline) (advanced/ahead of all) something diff.

[GAVe LIST ; TYRe CAM Age Age ; PLATy Helminths]

* Proline to be remembered) — Simple. — Advanced/Ahead → (WE LIT) (V)

TYRe → (TYRe, non-essential)

CAM → S-containing → M > C (α-betically) (so, essential) (My)

Acids. / their $CONH_2$ derivatives. → (non-essential)

PLATy Helminths → Pretty complex → (so all essential) (PLATy Helminths)

(we lit my platyhelminthes) → essential

Exceptions to one letter code:

1. Arginine → R
2. Lysine → K
3. Glutamic acid → E
4. Aspartic acid → D
5. Glutamine → Q
6. Aspargine → N
7. Ph-CH_3 (D—E) → F
8. Tyrosine → Y
9. Tryptophan (U — V) → W.

(3–6: all irregular)

As per the above seq:

- A. acid — D
- G. acid — E
- A — N
- G. — Q

(α-betically)

- Arg → R (as A was aldready used)
- Lysine → K (as after K, L comes)
- PhCH_3 (D — E) / F (as DE aldready used above)
- Tyr (as T was aldready used)
- Trp. U — V — W (to follow the trend, two skipped)

(KA) for others, blindly use the 1st letter.
(also, PLATy, acids and derivatives and TYRe are exceptions).

Exceptions to three letter code (very less):

1. Isoleucine — ILeu (Iso can't be used)
2. Glutamine } Gln
3. Aspargine } Asn (to indicate they are amides)
4. Tryptophan. — Trp (aldready learnt in Trp operon)

↳ I Got it. (I Got it)!

Chemical Properties: (show rxns of $-NH_2$, $-COOH$ and/or both)

$R-CH(\ddot{N}H_2)-COOH$ (amino acid)

- $\xrightarrow[\text{(acid-base)}]{NaOH}$ $R-CH(NH_2)-COO^{\ominus}Na^{\oplus}$
- $\xrightarrow[\text{(dry HCl)}]{C_2H_5OH}$ $H_3\overset{\oplus}{N}-CH(R)-COOC_2H_5$ $\xrightarrow{AgOH}$ $H_2N-CH(R)-COOC_2H_5$ (ethyl ester)
- $\xrightarrow[(Ba(OH)_2/\Delta)]{\text{deCO}_2}$ H_2N-CH_2-R (Amine)
- $\xrightarrow[4H]{LiAlH_4}$ $R-CH(NH_2)-CH_2OH$ (amino-alcohol)
- $\xrightarrow[CH_3-Br]{\text{Alkylation}}$ $R-CH(NHCH_3)-COOH$ (N-methyl derivative)
- $\xrightarrow[CH_3COCl]{\text{Acetylation}}$ $R-CH(NHCOCH_3)-COOH$ (N-acetyl derivative)
- $\xrightarrow{HNO_2}$ $R-CH(OH)-COOH$ (α-hydroxy acid)
- $\xrightarrow[\text{(acid-base)}]{HCl}$ $R-CH(\overset{\oplus}{N}H_3Cl^{\ominus})-COOH$
- $\xrightarrow{PCl_5}$ $R-CH(NH_2(HCl))-COCl$ (aminoacid chloride).

Action of heat on diff. types of A.As:

① α A.A.: (loose 2 mol H_2O/2 mol of AA to form cyclic amides

$R-CH(NH\boxed{H} \;\; \boxed{OH}OC)(CO\boxed{OH} \;\; \boxed{H}HN)CH-R \xrightarrow{\Delta} R-CH(NH-\overset{O}{\overset{\|}{C}})(\underset{\|}{\underset{O}{C}}-NH)CH-R + 2H_2O$

eg: R = H

(glycine) $\xrightarrow[(-2H_2O)]{\Delta}$ $\begin{matrix} CH_2-NH-CO \\ | \qquad\qquad | \\ CO-NH-CH_2 \end{matrix}$] Diketo piperazine.

② β A.A: (lose a molecule of NH_3/mol to yield α,β-unsaturated acids)

eg: $CH_2(\boxed{NH_2})-CH(\boxed{H})-COOH \xrightarrow[-NH_3]{\Delta} CH_2=CHCOOH$ (Acrylic acid)

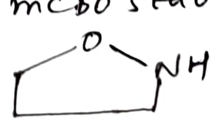
(β-amino proprionic acid)

$CH_3-CH(\boxed{NH_2})-CH(\boxed{H})-COOH \xrightarrow[-NH_3]{\Delta} CH_3-CH=CH-COOH$ (Crotonic acid)

(β-a-butyric acid)

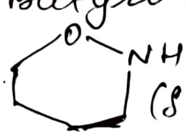
③ γ-AA and δ A.A $\xrightarrow{\Delta}$ intramolecular dehyd. → cyclic amides aka lactam (as 5/6 mem. so stable)

eg: $CH_2(NH\boxed{H})-CH_2-CH_2-CO\boxed{OH}$ $\xrightarrow{\Delta}$



(γ-amino butyric acid) (GABA) (γ-Butyro lactum)

$CH_2(NH\boxed{H})-CH_2-CH_2-CH_2-CO\boxed{HO}$ → δ-a-valeric acid $\xrightarrow{\Delta}$



(δ-valerolactum)

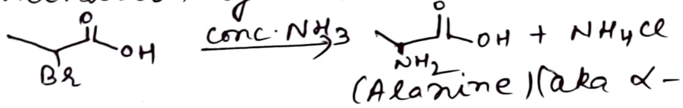
→ Amino acids: Usually colourless, crystaline solids, water soluble, high melting solids, behave as salts (rather as acid/amides) due to existence in zwitter ion form.

→ most naturally occuring A.A. are 'L' form, represented by writing NH_2 grp on LHS

Methods of Prepⁿ of A.A.:

① Amination of α-halo acids

eg:



(Alanine) (aka α-amino propeionic acid)

② Lab prepⁿ of glycine:

$ClCH_2COOH + 3NH_{3(l)} \xrightarrow{50°C} H_2NCH_2COONH_4 + NH_4Cl$

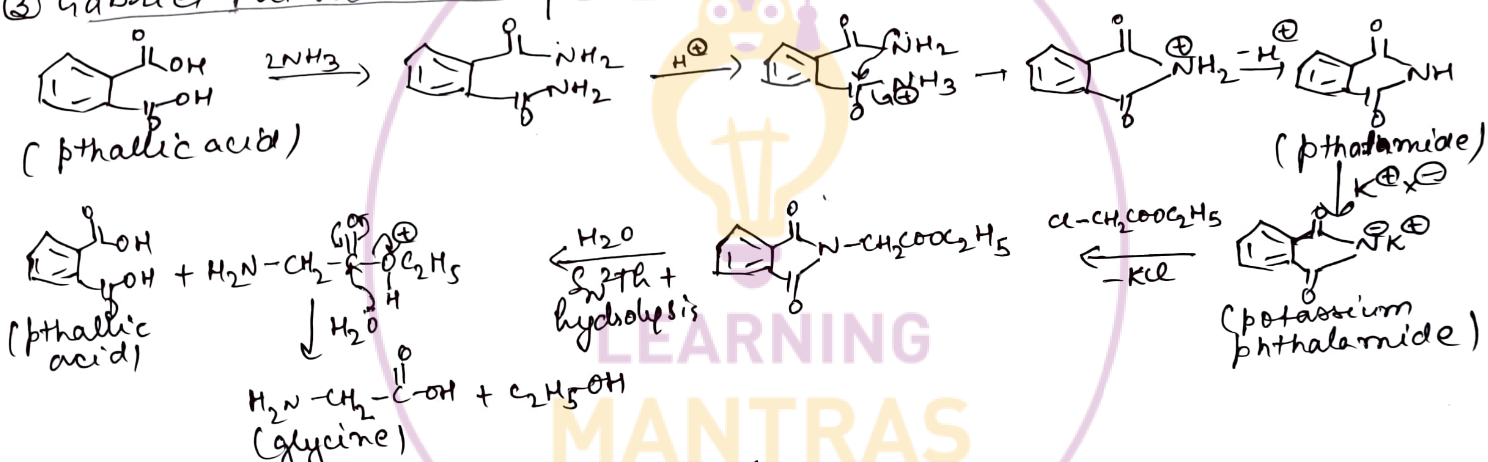
(α-cl acetic acid) (Amm. salt of glycine).

$\downarrow CuCO_3, \Delta$

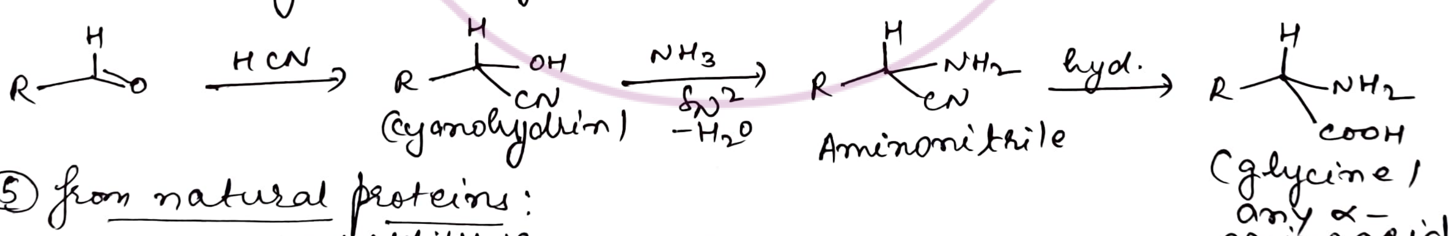
$CuS\downarrow + \text{glycine} \xleftarrow[H_2S]{H_2O} (H_2NCH_2COO)_2Cu + (NH_4)_2CO_3$

(blue needles on cooling)

③ Gabriel Phthalimide synthesis:



④ Strecker synthesis (from aldehyde)



⑤ from natural proteins:

Proteins $\xrightarrow[\text{250°C (hyd.) (autoclave)}]{\text{dil HCl / dil } H_2SO_4}$ mix. of α-A.A. $\xrightarrow{\text{esterification}}$ mix of esters → seperation via fractional distillation

(α A.A.) ← hyd of individual ester

Properties of A.A. (Physical)

① Colourless, crystalline, sweet taste, melt via decomposition @ >200°C. soluble in water but insoluble in organic solvents.

② In proteins, mostly L-conformation of A.A. found.

③ In neutral medium, 'inner salt' formed, aka bipolar ion/zwitter ion which is why - high melting solids (∵ charged, ionic)

④ Isoelectric point depends on nature of -R grp.

Proteins: (word proteios: primary / of prime importance)

peptide linkage:

H_2N-CH_2-COOH (glycine) $+$ $H_2N-CH(CH_3)-COOH$ (Alanine) $\longrightarrow$ $H_2N-CH_2-CONH-CH(CH_3)-COOH$ (Glycylalanine) [Gly-Ala]

Defining various levels of structures:

1° — ✓

2° → α-helix (all possible H-bonding b/w adj. amides (NH and CO) by coiling (RHS) (intramolecular))
→ β-pleated sheath (inter-molecular H-bonding)

3° → Fibrous (chains ||el to each other held by -S-S- and -H bond) (insoluble) (keratin, myosin)
→ Globular (chains coil around to give spherical shape) (soluble) (Insulin, albumins)
↓
Vanderwaal's, Electrostatic

4° ⟶ Two or more chains — subunits. (way of arrangement of ↗) ⟶ defined by 4° structure.

* Hb — 574 amino acids

Normal Hb: VHITPEEK (remember) (we hit Peek)

SCA: VHITPVEK (automatically ✓)

Composition (normally): ⟶ Con HSa?

C (50-53%) S (1%)
O (23-25%) Hb ⟶ Fe
N (16-17%) T_4 ⟶ I
H (6-7%) nucleic acids — P

native protein: Biologically active protein

Denaturation: Coagulation of egg white, curdling of milk.