Question 1:

A.

Which sugar(s) is/are (or contain) an aldose? i, iii

Which sugar(s) is/are (or contain) a ketose? ii, iii

Which sugar(s) is/are (or contain) a pentose? none

Which sugar(s) is/are (or contain) a D sugar? i, ii, iii

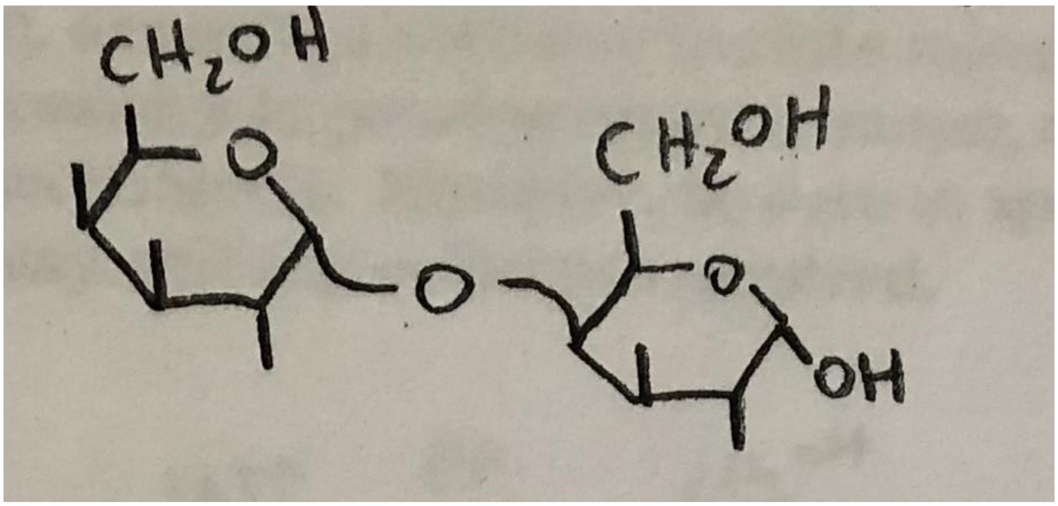
Which sugar(s) is/are a reducing sugar? i, ii

Which sugar(s) is/are (or contain) an epimer of glucose shown here : none

Which sugar(s) is/are drawn in the form most likely to be found in the organism? iii

B. β-D-talsopyranose-(1,2)- α-D-tagatofuranose

C.



D. Talsose ←→ galactose (epimerase)
Talsose ←→ tagatose (isomerase)

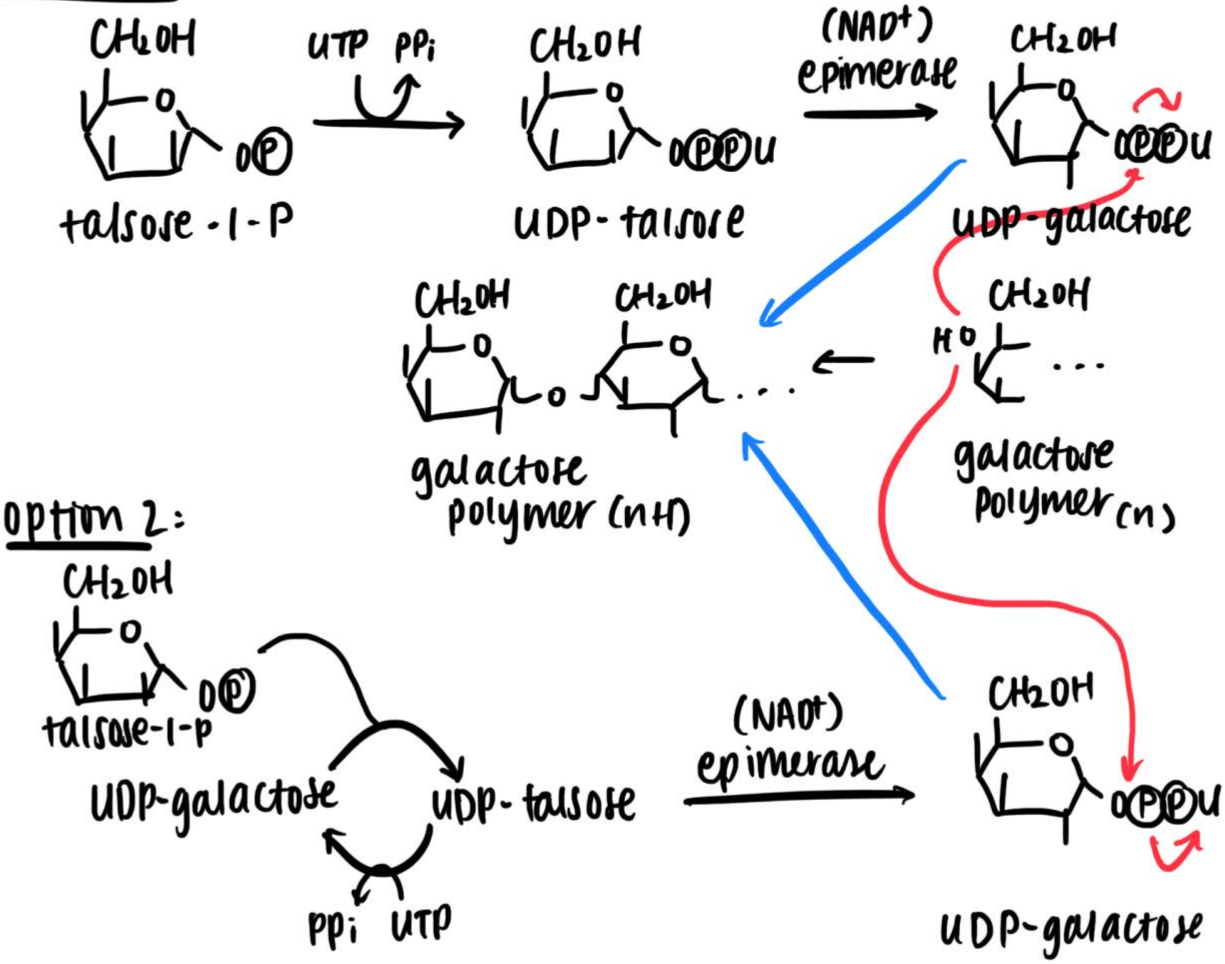
E.

1. Good storage sugars have one or more nonreducing ends, as the lack of free aldehyde/ketones makes the polymer less likely to be attacked and break the storage sugar apart. Thus, nonreducing ends increase the stability of storage sugars.
2. The Beta glycosidic bond prevents metabolism of this sugar by mammals because they lack the enzyme needed to break those down. Mammals generally only use and break down Alpha glycosidic bonds.

(+5 if both present, +3 if missing one)

F.

option 1:



CH2OH
talsose-1-P
UTP PPi
UDP-talsose
(NAD+)
epimerase
UDP-galactose
galactose
polymer (n+1)
galactose
polymer (n)
option 2:
talsose-1-P
UDP-galactose
UDP-talsose
PPi UTP
(NAD+)
epimerase
UDP-galactose

Question 2:

An enzyme, nucleotide diphosphate kinase (NDPK) catalyzes the following reaction:

$$CTP + GDP \leftrightarrow CDP + GTP \qquad \Delta G^{o\prime} = 0 \text{ kcal/mol}$$

A. (2 points) At equilibrium, which of the following will be true for the NDPK reaction? (circle your answer)

CTP < GTP CTP > GTP $\boxed{\text{CTP = GTP}}$ +2

Recall that succinic thiokinase catalyzes the following TCA cycle reaction:

$$\text{succinyl-coA} + GDP + P_i \leftrightarrow \text{succinate} + GTP + \text{coA} \qquad \Delta G^{o\prime} = -0.8 \text{ kcal/mol}$$

B. (2 points) At equilibrium, which of the following will be true for the succininc thiokinase reaction? (circle your answer)

+2

$\boxed{\text{GDP < GTP}}$ GDP > GTP GDP = GTP

If you mix 1 mM each of succinyl-coA, GDP, CDP, and P_i in a reaction with succinic thiokinase and NDPK:

C. (2 points) Will you have more CTP than GTP at equilibrium? Briefly explain your answer.

+1 No

+1 $\Delta G^{\circ\prime}$ of NDPK rxn will make $\boxed{[GTP]} = [CTP]$ in equilibrium

D. (2 points) Will you have more CTP than CDP at equilibrium? Briefly explain your answer.

+1 Yes

+1 Because Succinate Thiokinase makes $\boxed{[GTP]} > [CDP]$ & NDPK makes $\frac{[GTP]}{[GDP]} = \frac{[CTP]}{[CDP]}$

E. (2 points) If you add twice as much NDPK enzyme as succinic thiokinase, will you produce more CTP? Briefly explain why or why not.

+2 No. Enzymes do not alter K or ΔG but only the rate of a reaction

3pt: get correct ratio and proper explanation

F. (3 points) If you add 10 M CTP and 1 M CDP to a reaction with 1 mM each of succinyl-coA, GDP, and P_i where both succinic thiokinase and NDPK are present, approximate the ratio of GTP/GDP you expect to find when the reaction reaches equilibrium. Briefly explain your answer.

1pt: logical attempt but wrong ratio

10 because ratio of CTP/CDP = 10 and in 100x excess of GDP will make GTP/GDP ratio ~10 regardless of succinic thiokinase reaction

3pt: correct answer "yes favored"

4pt: proper explanation (with math or explain in words)

2pt: logical attempt but wrong answer

G. (7 points) If you add 10 M CTP and 1 M CDP to the reaction with 1 mM each of succinate, GTP, and coA where both succinic thiokinase and NDPK are present, will production of succinyl-coA be favored? Describe how you arrived at your answer. (Hint: the concentration of CTP and CDP added here are the same as in part F.)

ln(1000) = 6.9
ln(100) = 4.6
ln (10) = 2.3
ln (1) = 0
ln (0.1) = -2.3
ln (0.01) = -4.6
ln (0.001)= -6.9
RT = ~0.5 kcal/mol

From F know GTP/GDP ~ 10

$$\Delta G = \Delta G^{\circ\prime} + RT \ln \frac{[\text{Succ-CoA}][P_i]}{[\text{Succinate}][\text{CoA}]} \frac{[GDP]}{[GTP]}$$

$$= \underbrace{0 + 0.8}_{\text{from above } \Delta G^{\circ\prime}} + (0.5) \ln\left(\frac{0.001 \times 0.001}{0.001 \times 0.001} \times \frac{1}{10}\right)$$

$$= 0.8 + 0.5 \ln(0.1)$$

$$= 0.8 + 0.5(-2.3)$$

$$= 0.8 + -1.15$$

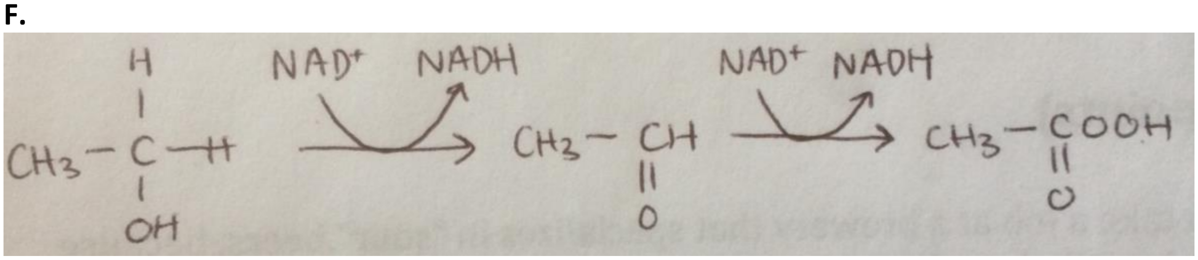
$$= -0.35$$ ← negative number ⇒ Succinyl-CoA synthesis favored

Question 3:

A. Citrate will inhibit PFK and inhibit the glycolysis so this needs to be added after fermentation. Explanations that included some description of how citrate might be metabolized before the end of the experiment were given some partial credit.
B. ATP consumption will mean a lower ATP/ADP ratio, driving glycolysis forward. Both energetic explanations and explanations that included the regulation of metabolic enzymes were accepted. Many assumed a higher consumption of ATP meant a higher ATP/ADP ratio. These were given partial credit.
C. An accurate drawing of lactate and an indication NADH was converted to NAD+ was required for full credit.
D. Both acetaldehyde and ethanol structures were required. The involvement of CO2, TPP, and NAD+/NADH were also required.

E. Yes. The presence of oxygen will favor oxidation of pyruvate via the citric acid cycle followed by regeneration of NAD+ and FAD by oxidative phosphorylation. Thus production of lactate and ethanol will decrease in the presence of oxygen. (Students were awarded 0.5 points if they said no because fermentation is an anaerobic process).

F.

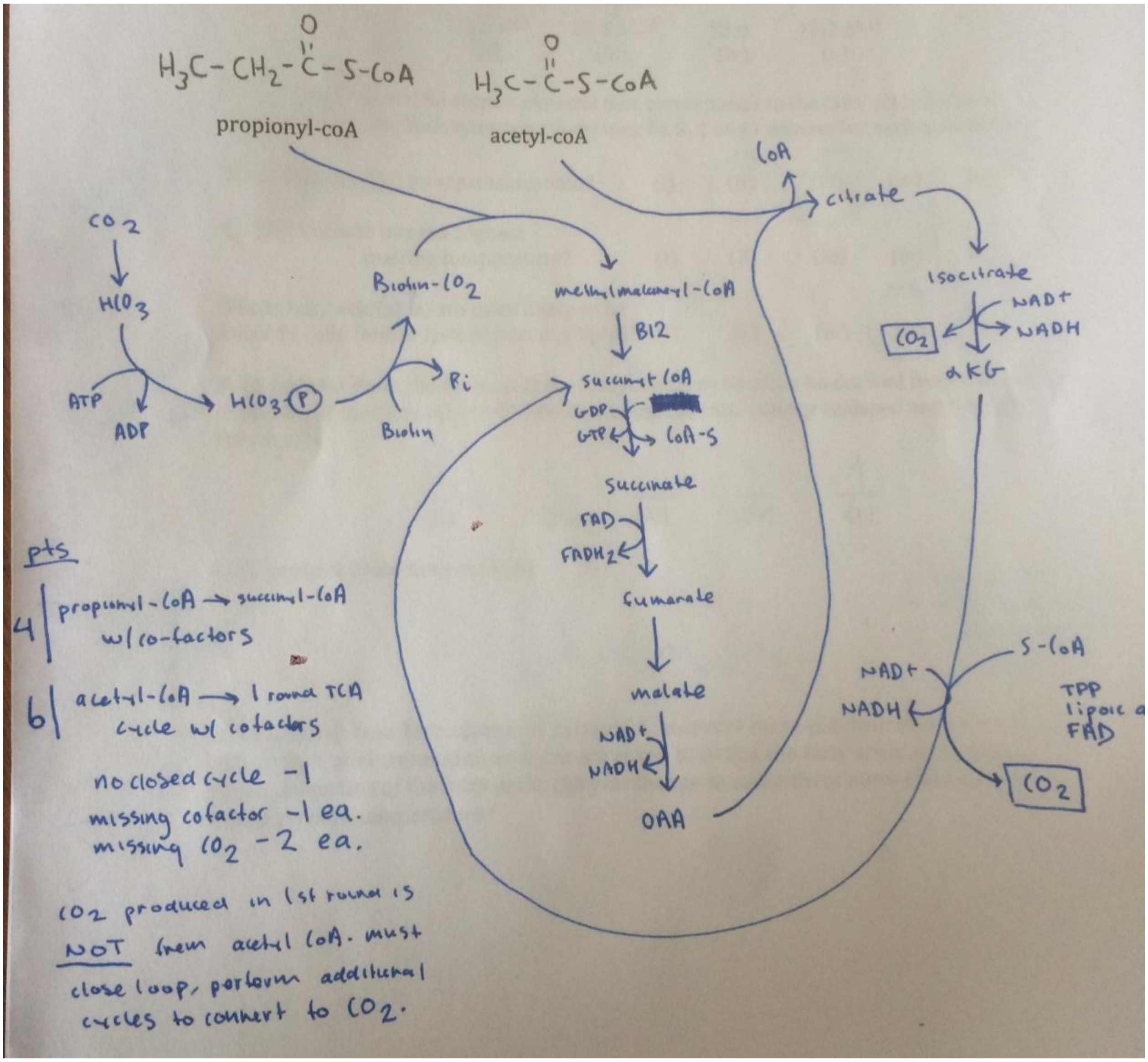


(1 point was awarded for marking each NAD+ reduction, with the third point awarded for drawing the correct structure for the acetaldehyde intermediate. 0.5 points were deducted if the structure of this intermediate was not drawn out).

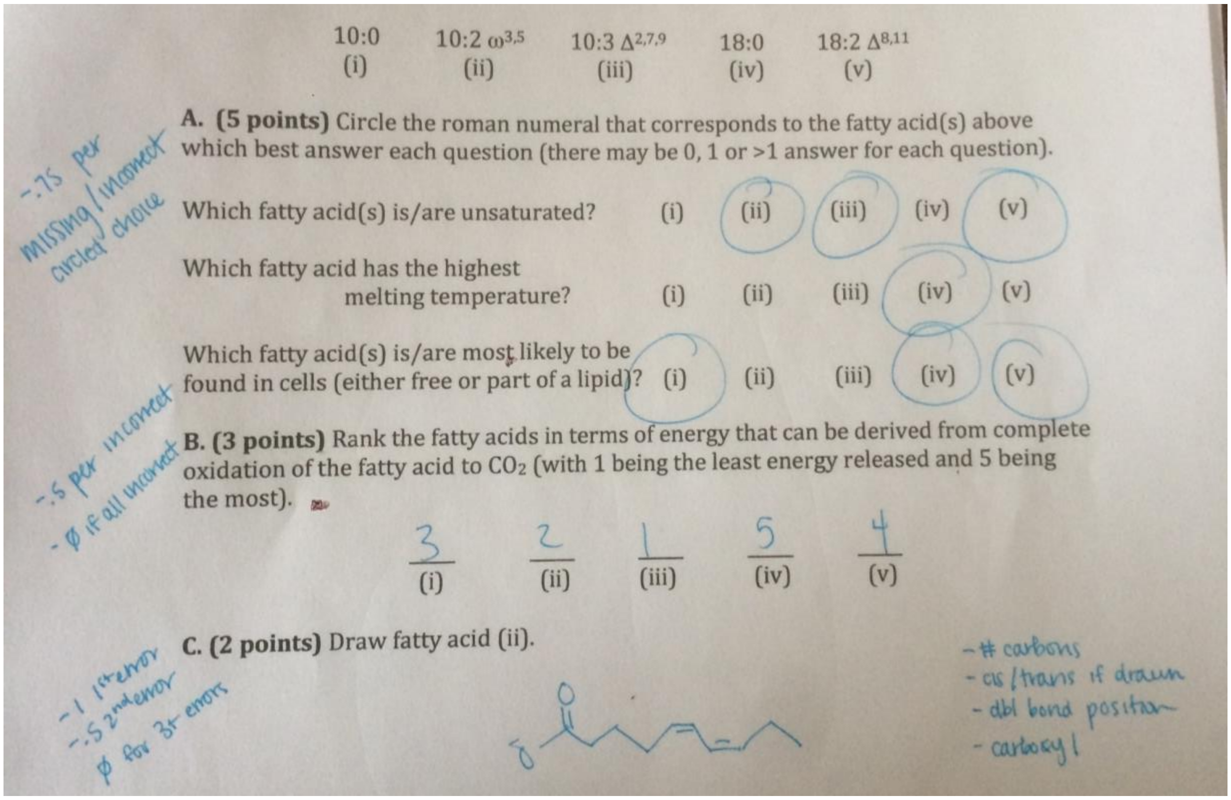
G. In the shown reaction, propionate is reduced to propionaldehyde. This reduction is coupled to oxidation of NADH to NAD+, which regenerates the cofactor required for production of acetate from ethanol. (1 point was awarded for correctly identifying that propionate is reduced. 2.5 points were awarded if the propionate reduction was coupled directly to ethanol oxidation instead of proceeding through the NADH/NAD+ cofactor).

H. To fully oxidize acetyl-coA from ethanol to CO_2, the yeast cell needs to run the TCA cycle. This requires OAA (which joins with the acetyl-coA in the first step of the cycle), and thus the yeast must generate OAA in some manner. The glyoxylate cycle can take 2 carbon species and convert them into 4 carbon species that are utilized in the TCA cycle. Specifically, glyoxylate and acetyl-coA react to generate malate, which can then be converted to the required OAA through a series of steps. This process, of generating species in the TCA cycle to allow the cycle to begin, is known as anaplerosis.

I.


H3C-CH2-C(=O)-S-CoA
H3C-C(=O)-S-CoA
propionyl-coA
acetyl-coA
CoA
citrate
isocitrate
NAD+
NADH
CO2
αKG
CO2
HCO3
ATP
ADP
HCO3-P
Biotin-CO2
Pi
Biotin
methylmalonyl-CoA
B12
succinyl CoA
GDP
GTP
CoA-S
succinate
FAD
FADH2
fumarate
malate
NAD+
NADH
OAA
S-CoA
NAD+
NADH
TPP
lipoic a
FAD
CO2
pts
4 | propionyl-CoA → succinyl-CoA w/ co-factors
6 | acetyl-CoA → 1 round TCA cycle w/ cofactors
no closed cycle -1
missing cofactor -1 ea.
missing CO2 -2 ea.
CO2 produced in 1st round is NOT from acetyl CoA. must close loop, perform additional cycles to convert to CO2.

Question 4:



10:0 (i) | 10:2 $\omega^{3,5}$ (ii) | 10:3 $\Delta^{2,7,9}$ (iii) | 18:0 (iv) | 18:2 $\Delta^{8,11}$ (v)

-.75 per missing/incorrect circled choice

A. (5 points) Circle the roman numeral that corresponds to the fatty acid(s) above which best answer each question (there may be 0, 1 or >1 answer for each question).

Which fatty acid(s) is/are unsaturated? (i) (ii) (iii) (iv) (v)

Which fatty acid has the highest melting temperature? (i) (ii) (iii) (iv) (v)

Which fatty acid(s) is/are most likely to be found in cells (either free or part of a lipid)? (i) (ii) (iii) (iv) (v)

-.5 per incorrect
-ϕ if all incorrect

B. (3 points) Rank the fatty acids in terms of energy that can be derived from complete oxidation of the fatty acid to CO_2 (with 1 being the least energy released and 5 being the most).

(i)	(ii)	(iii)	(iv)	(v)
3	2	1	5	4

-1 1st error
-.5 2nd error
ϕ for 3+ errors

C. (2 points) Draw fatty acid (ii).

- # carbons
- cis/trans if drawn
- dbl bond position
- carboxyl

D. Shorter chain length or increased number double bonds. These both will lower melting temperature and be more likely liquid at room temperature. (Mentioning any one of these gets full credits)

E.

① $10{:}3\ \Delta^{2,7,9}$

ATP → PPi ; S-CoA → AMP

→ (missing CoA has full credit).
(but need $\boxed{ATP}$)

$H_2C=CH-CH=CH-CH_2-CH_2-CH_2-CH=CH-\overset{O}{\overset{\|}{C}}-S-CoA$

Δ^9 Δ^7 Δ^2

(whether mentioning carnitine shuttle or not does not matter, all get full credit).

② $\downarrow H_2O$

$\ldots CH-CH-\overset{O}{\overset{\|}{C}}-S-CoA$
$\quad\ \ OH\quad H$

③ $\downarrow NAD^+ \rightarrow NADH$

$\ldots C-CH_2-\overset{O}{\overset{\|}{C}}-S-CoA$
$\quad \|$
$\quad O$

④ $\downarrow$ S-CoA → acetyl-CoA

$H_2C=CH-CH=CH-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-S-CoA$

⑤ $\downarrow H_2O \rightarrow SCoA$

$8{:}2\ \Delta^{5,7}$

missing co facters − 1 point.

missing steps − 2 points.