Final Examination
2017/2018 Academic Session

May/June 2018

JIK419 – Advanced Organic Chemistry
[Kimia Organik Lanjutan]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains **TEN** printed pages before you begin the examination.

Answer **FIVE (5)** questions. Answer the questions in English. You may also answer the questions in Bahasa Malaysia, but not a mix of both languages.

All answers must be written in the answer booklet provided.

Each question is worth 20 marks and the mark for each sub question is given at the end of that question.

In the event of any discrepancies in the exam questions, the English version shall be used.

*Sila pastikan bahawa kertas peperiksaan ini mengandungi **SEPULUH** muka surat yang bercetak sebelum anda memulakan peperiksaan ini.*

*Jawab **LIMA (5)** soalan. Jawab soalan-soalan dalam Bahasa Inggeris. Anda juga dibenarkan menjawab soalan dalam Bahasa Malaysia, tetapi campuran antara kedua-dua bahasa ini tidak dibenarkan.*

Setiap jawapan mesti dijawab di dalam buku jawapan yang disediakan.

Setiap soalan bernilai 20 markah dan markah subsoalan diperlihatkan di penghujung subsoalan itu.

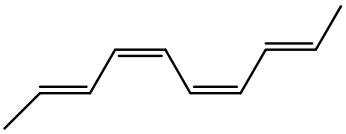
Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

...2/-

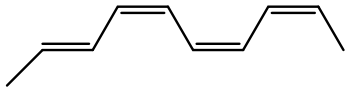
1. (a). Give the structure of the cyclic product formed when each decatetracene undergoes photochemical electrocyclic ring closure. Label each process as conrotatory or disrotatory and indicate the stereochemistry around the tetrahedral stereogenic centers.

Berikan struktur hasil siklik yang terbentuk apabila setiap dekatetrasena menjalani penutupan gelang elektrosiklik fotokimia. Labelkan setiap proses sebagai seputaran atau tak sepemutaran dan nyatakan stereokimia di pusat stereogenik tetrahedron.

(i).



(ii).

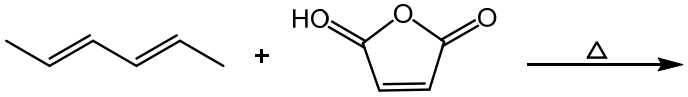


(8 marks/*markah*)

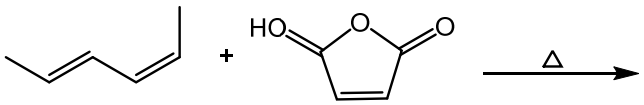
(b). Draw the product of each Diels-Alder reaction and indicate the stereochemistry at all stereogenic centers.

Lukiskan hasil untuk setiap tindak balas Diels-Alder dan tunjukkan stereokimia di semua pusat stereogenik.

(i).



(ii).



(6 marks/*markah*)

(c). A solution of 5-methylcyclopenta-1,3-diene rearranges at room temperature to a mixture containing 1-methyl-, 2-methyl-, and 5-methylcyclopenta-1,3-diene. Use curved arrows to show how both isomeric products are formed from the starting material by a sigmatropic rearrangement involving a C–H bond.

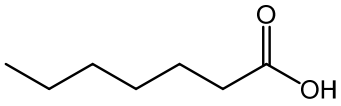
Suatu larutan 5-metilsiklopenta-1,3-diena menyusun semula pada suhu bilik kepada suatu campuran yang mengandungi 1-metil-, 2-metil-, dan 5-metilsiklopenta-1,3-diena. Gunakan anak panah lengkung untuk menunjukkan bagaimana kedua-dua hasil isomerik terbentuk daripada bahan permulaan dengan susunan semula sigmatropik yang melibatkan ikatan C-H.

(6 marks/*markah*)

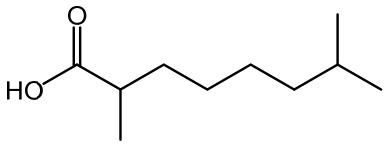
2. (a). Use the malonic ester synthesis to prepare each carboxylic acid below.

Gunakan sintesis ester malonik untuk menyediakan setiap asid karboksilik di bawah.

(i).



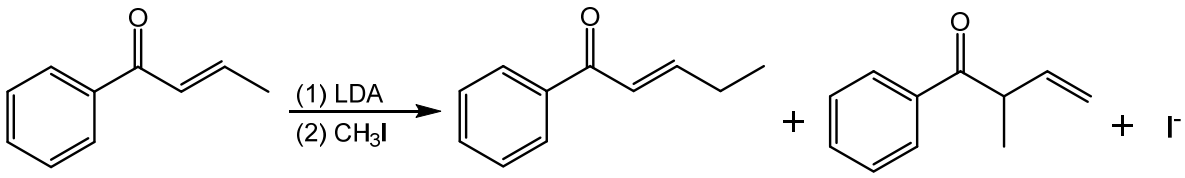
(ii).



(10 marks/*markah*)

(b). Draw a stepwise mechanism showing how two alkylation products are formed in the following reaction.

Lukiskan suatu mekanisme peringkat demi peringkat yang menunjukkan bagaimana dua hasil alkilasi terbentuk dalam tindak balas berikut.



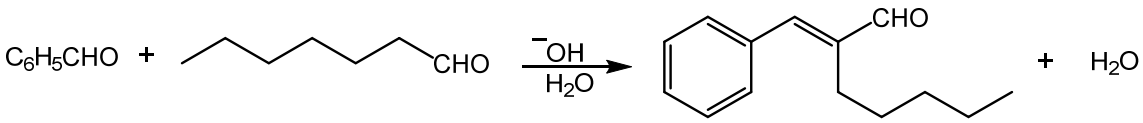
LDA = Lithium diisopropylamide

(10 marks/*markah*)

...4/-

3. (a). 2-Pentylcinnamaldehyde is an *α,β*-unsaturated aldehyde made by crossed aldol reaction between benzaldehyde and heptanal, followed by dehydration. Draw a stepwise mechanism for the following reaction that prepares 2-pentylcinnamaldehyde.

2-Pentilsinnamaldehid adalah suatu aldehid α,β-tak tepu yang dibentuk oleh tindak balas aldol silang antara benzaldehid dan heptanal, diikuti oleh pendehidratan. Lukiskan suatu mekanisme peringkat demi peringkat untuk tindak balas berikut yang menyediakan 2-pentilsinnamaldehid.

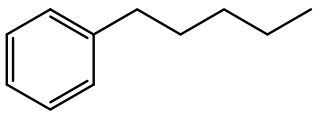


(10 marks/*markah*)

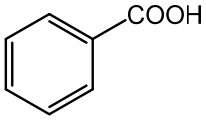
(b). Write out the two-step sequence (with appropriate reagents) that converts benzene to each of the following compound.

Tuliskan urutan dua langkah (dengan reagen yang sesuai) yang menukarkan benzena kepada setiap sebatian berikut.

(i).



(ii).



(10 marks/*markah*)

4. (a). For D-arabinose:

(i). Draw its enantiomer.

(ii). Draw an epimer at C3.

(iii). Draw an diastereomer that is not an epimer.

Untuk D-arabinosa:

(i). Lukiskan enantiomernya.

(ii). Lukiskan suatu epimer pada C3.

(iii). Lukiskan suatu diastereomer yang bukan epimer.

(6 marks/*markah*)

(b). A D-aldopentose **A** is oxidised with HNO_3 to an optically inactive aldaric acid **B**. **A** undergoes the Kiliani-Fisher synthesis to yield **C** and **D**. **C** is oxidised to an optically active aldaric acid. **D** is oxidised to an optically inactive aldaric acid. Identify compounds **A–D** by giving adequate explanation and give their respective structures.

*Suatu D-aldopentosa **A** dioksidakan dengan HNO_3 kepada asid aldarik tak aktif optik **B**. **A** menjalani sintesis Kiliani-Fisher untuk menghasilkan **C** dan **D**. **C** dioksidakan kepada asid aldarik aktif optik. **D** dioksidakan kepada asid aldarik tak aktif optik. Kenalpastikan sebatian **A**-**D** dengan memberikan penjelasan yang mencukupi dan berikan struktur masing-masing.*

(14 marks/*markah*)

5. (a). Draw the structure of the products formed when *α*-D-gulose is treated with each reagent below.

(i). CH_3I, Ag_2O

(ii). CH_3OH, HCl

(iii). $(CH_3CO)_2O$, pyridine

(iv). The product in (i)., then H_3O^+

(v). The product in (ii)., then $(CH_3CO)_2O$, pyridine

Lukis struktur hasil yang terbentuk apabila α-D-gulosa diolah dengan setiap reagen berikut.

(i). CH_3I, Ag_2O

(ii). CH_3OH, HCl

(iii). $(CH_3CO)_2O$, piridina

(iv). Hasil dari (i)., diikuti oleh H_3O^+

(v). Hasil dari (ii)., diikuti oleh $(CH_3CO)_2O$, piridina

(10 marks/*markah*)

(b). Draw the structure of the peptide shown below. Label the N-terminal and C-terminal amino acids and all amide bonds.

Lukiskan struktur peptida yang ditunjukkan di bawah. Labelkan hujung-N dan hujung-C asid amino dan semua ikatan amida.

Gly–His–Leu

(5 marks/*markah*)

(c). Explain why the pK_a of the $–NH_3^+$ group of an *α*-amino acid is lower than the pK_a of the ammonium ion derived from a 1° amine (RNH_3^+). For example the pK_a of the $–NH_3^+$ group of alanine is 9.87 but the pK_a of $CH_3NH_3^+$ is 10.63.

Jelaskan mengapa pK_a kumpulan $–NH_3^+$ asid α-amino adalah lebih rendah daripada pK_a ion ammonium yang diperoleh daripada 1° amina (RNH_3^+). Sebagai contoh, pK_a kumpulan $–NH_3^+$ daripada alanina adalah 9.87 tetapi pK_a $CH_3NH_3^+$ adalah 10.63.

(5 marks/*markah*)

...7/-

6. (a). What is the predominant form of each of the following amino acids at pH=11? What is the overall charge on the amino acid at this pH?

(i). Valine (pI=6.0)

(ii). Proline (pI=6.3)

(iii). Glutamic acid (pI=3.2)

(iv). Lysine (pI=9.7)

Apakah bentuk predominan untuk setiap asid amino berikut pada pH = 11? Apakah caj keseluruhan untuk setiap asid amino pada pH ini?

(i). Valina (pI=6.0)

(ii). Prolina (pI=6.3)

(iii). Asid glutamik (pI=3.2)

(iv). Lisina (pI=9.7)

(8 marks/*markah*)

(b). What *α*-halo carbonyl compound is needed to synthesise the following amino acids?

(i). Glycine

(ii). Isoleucine

Apakah sebatian karbonil α-halo yang diperlukan untuk mensintesis asid amino berikut?

(i). Glisina

(ii). Isoleusina

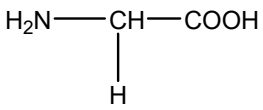
(4 marks/*markah*)

(c). Use the given experimental data to deduce the sequence (with adequate explanation) of an octapeptide that contains the following amino acids: Ala, Gly (2 equiv.), His (2 equiv.), Ile, Leu, and Phe. Edman degradation cleaves Gly from the octapeptide, and carboxypeptidase forms Leu and a heptapeptide. Partial hydrolysis forms the following fragments: Ile–His–Leu, Gly, Gly–Ala–Phe–His, and Phe–His–Ile.

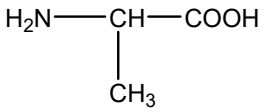
Gunakan data eksperimen yang diberikan untuk menyimpulkan urutan (dengan penjelasan yang mencukupi) untuk suatu oktapeptida yang mengandungi asid amino berikut: Ala, Gly (2 setara), Nya (2 setara), Ile, Leu, dan Phe. Pendegradasian Edman membelahkan Gly daripada oktapeptida, dan karboksipeptidas membentuk Leu dan suatu heptapeptida. Hidrolisis separa membentuk serpihan berikut: Ile-His-Leu, Gly, Gly-Ala-Phe-His, dan Phe-His-Ile.

(8 marks/*markah*)

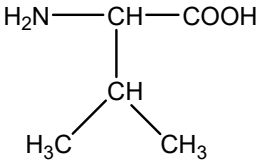
APPENDIX



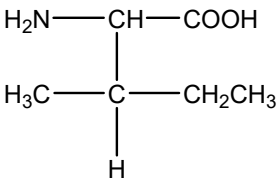
Glycine (Gly)



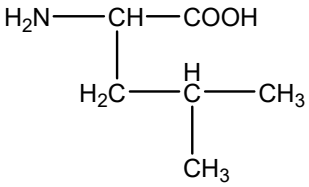
Alanine (Ala)



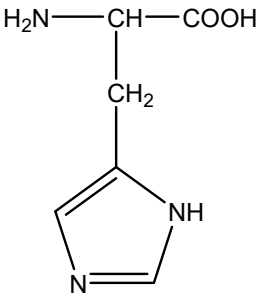
Valine (Val)



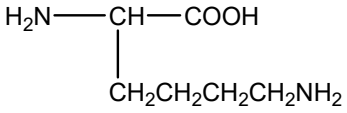
Isoleucine (Ile)



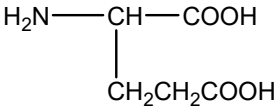
Leucine (Leu)



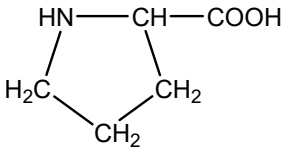
Histidine (His)



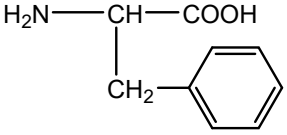
Lysine (Lys)



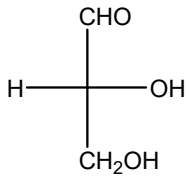
Glutamic acid (Glu)



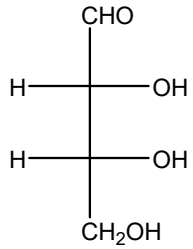
Proline (Pro)



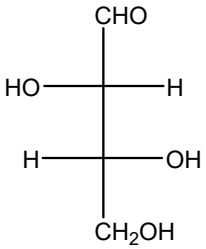
Phenylalanine (Phe)



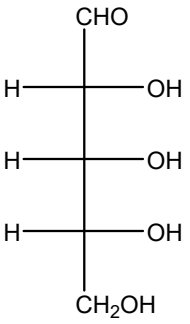
D-(+)-Glyceraldehyde



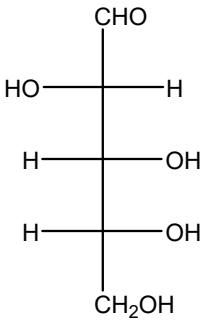
D-(-)-Erythrose



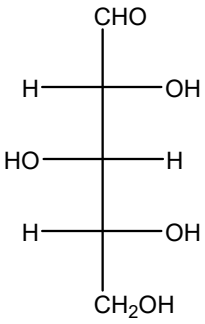
D-(-)-Threose



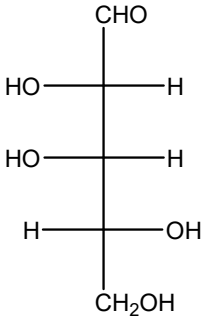
D-(-)-Ribose



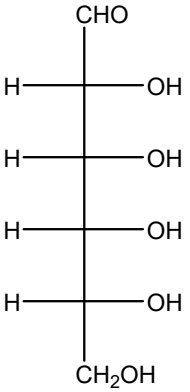
D-(-)-Arabinose



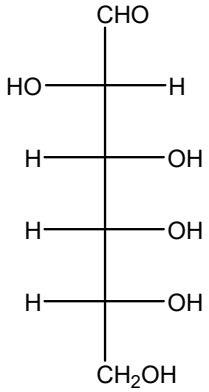
D-(+)-Xylose



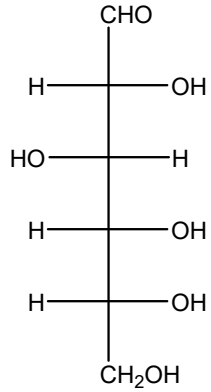
D-(-)-Lyxose



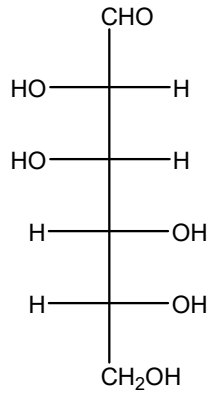
D-(+)-Allose



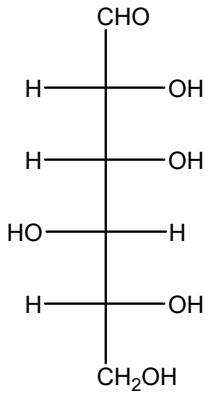
D-(+)-Altrose



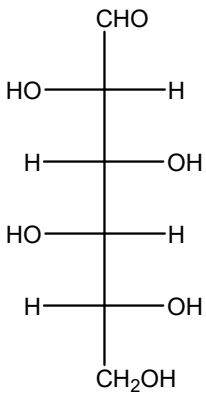
D-(+)-Glucose



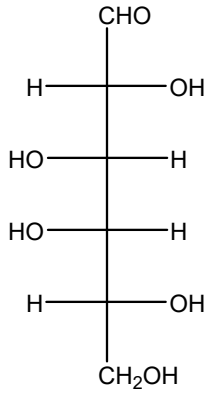
D-(+)-Mannose



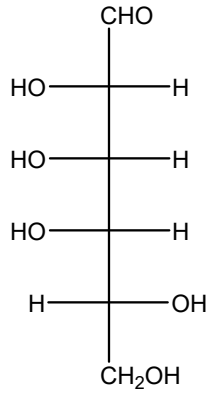
D-(-)-Gulose



D-(-)-Idose



D-(+)-Galactose



D-(+)-Talose

- oooOooo -