

University of Canterbury

Mid-Year Examinations, 2008

Prescription Number(s):	CHEM 325/BCHM 302
Paper Title:	Biological Chemistry

Time Allowed: 120 MINUTES

Number of pages: SIX

Answer **TWO** questions from Section A (60 marks).

Answer **ALL** question from Section B (60 marks).

Total marks = 120.

You should allocate about 1 minute per mark.

TURN OVER

SECTION A:**Answer TWO questions**

1. Discuss the role of model chemistry in developing understanding of the chemistry of biological systems. Provide detailed examples.

2. Many enzymes contain one or more metal ions at their active sites.
 - (a) What factors contribute to the suitability of a particular metal ion for use in an enzyme active site?

 - (b) What roles can such metal ions play in the mechanism of an enzymatic reaction?

 - (c) What roles are played by the protein in such systems?

3. Magnetic Resonance Imaging (MRI) is a technique that is widely used in medicine.
 - (a) Briefly outline the basis of the technique.

 - (b) Explain how metal ions can play a key role in MRI. Include comment on:
 - (i) which metal ions are used and why, and
 - (ii) what potential problems with their use have been overcome, and how this was achieved.

 - (c) Extend your answer to (b) to provide a discussion of possible improvements that could be made to the MRI technique.

TURN OVER

SECTION B:**Answer ALL questions**

4. (8 marks)

What structural features do you consider to be important in recognising the origins of the following classes of natural product?

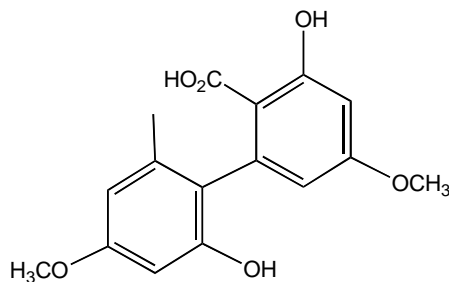
- (a) isoprenoid,
- (b) polyketide,
- (c) shikimate.

5. (12 marks)

For the polyketide compound below, identify the polyketide chain, show the starter unit, and indicate how the chain is folded.

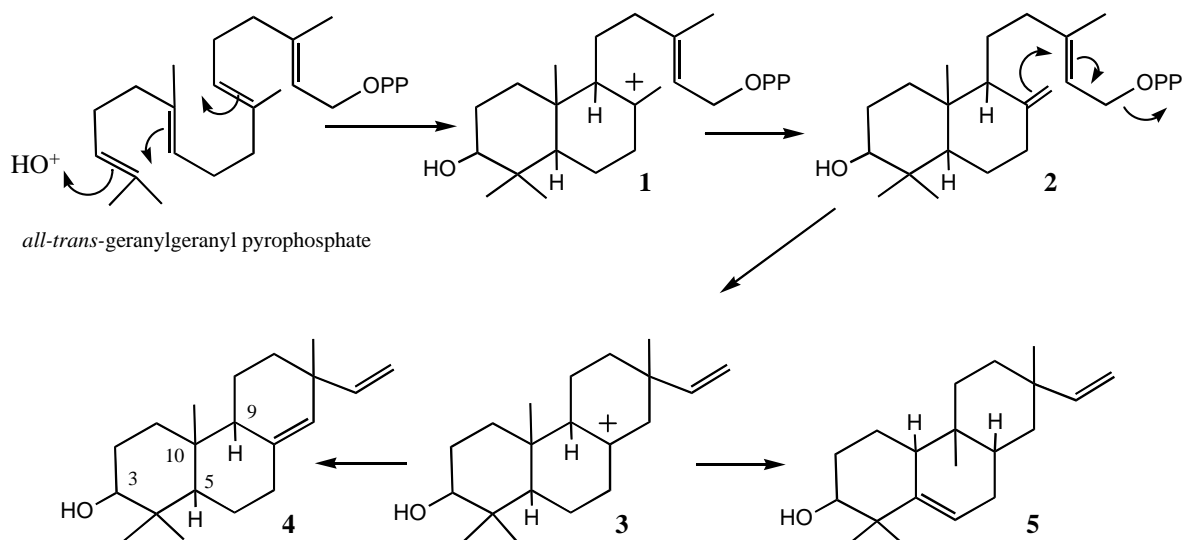
What reaction types are involved in:

- (a) the ring closures?
- (b) methylation?



6. (20 marks)

A portion of the biosynthesis of 3-hydroxypimaradiene (**4**), a diterpenoid, is shown in outline below. A direct precursor of 3-hydroxypimaradiene **4** is *all-trans*-geranylgeranyl pyrophosphate.

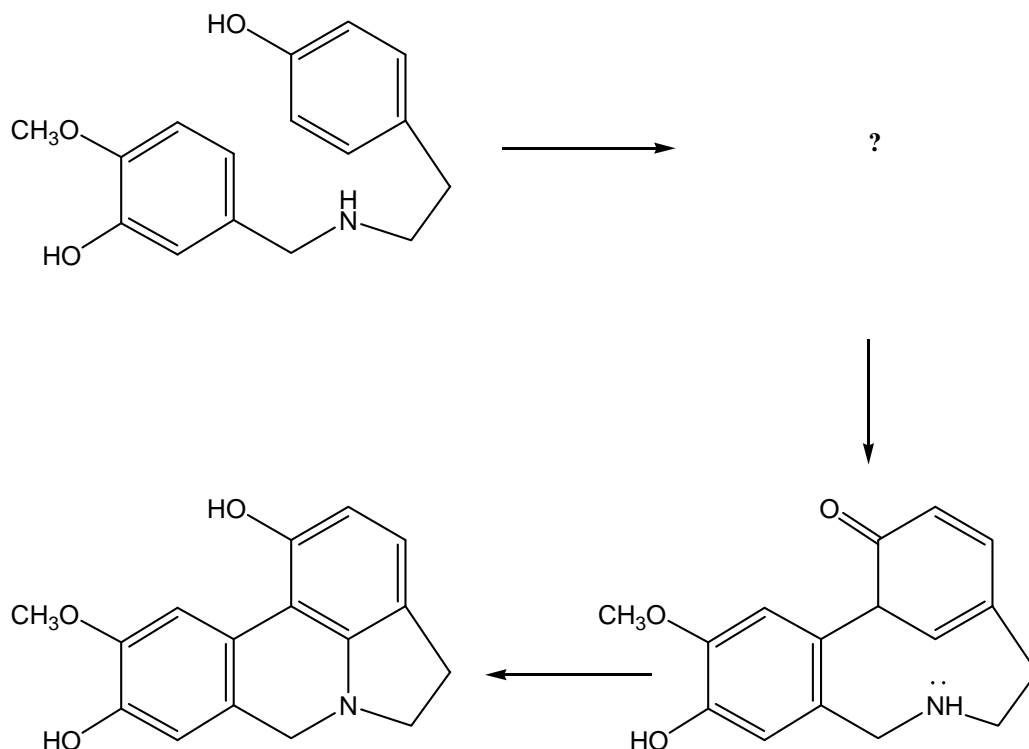


- (a) In poly-olefin cyclisation reactions what factors control the stereochemical configuration of the product?
- (b) *all-trans*-Geranylgeranyl pyrophosphate is cyclised by poly-olefin cyclisation to give products such as structure **4**. Draw a likely conformation for *all-trans*-geranylgeranyl pyrophosphate during cyclisation to form structure **1**.
- (c) Draw a diagram of structure **4** that shows the likely stereochemical configuration at C3, C5, C9 and C10 corresponding to your conformation in (b).
- (d) The unusual diterpenoid 3-hydroxyrimuene **5** is also found along with 3-hydroxypimaradiene **4**. Suggest how 3-hydroxyrimuene might be formed from structure **3**.

TURN OVER

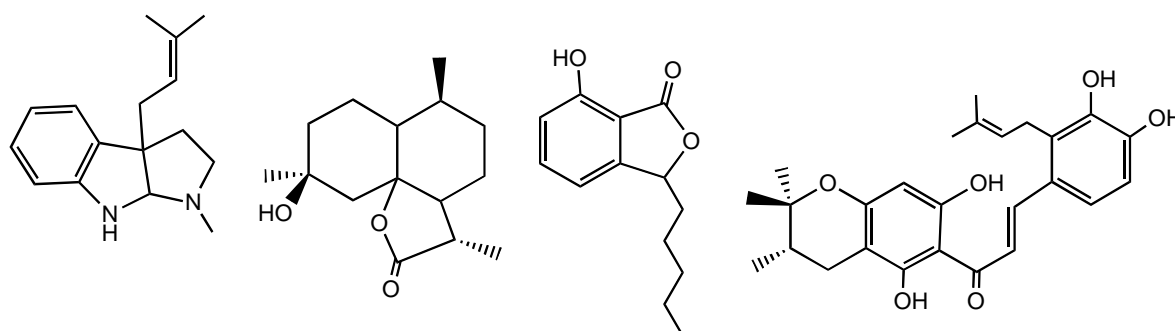
7. (10 marks)

The lycorine skeleton is formed by a pathway analogous for that for the biosynthesis of morphine. Suggest a structure for the missing intermediate. Show mechanisms, where possible, for the steps involved in formation of the lycorine skeleton.



8. (10 marks)

From the four compounds below select **TWO** and assign the biosynthetic origins. Note some compounds could be of "mixed" biosynthetic origin. For each compound indicate (delineate) the "building blocks" (*i.e.* the isoprene units, the polyketide chain, the starter unit, SAM, loss of O, amino acid *etc.*).

**END OF PAPER**