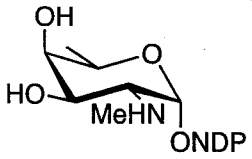
5.451 F2005
Problem Set 2.

(A) Chem Biol (2005) 12 293-302. (B) JACS (2000) 122 10493-503.

1. (30 pts) Draw a plausible biosynthetic pathway of the following sugars starting from glucose. Specific enzyme names and detailed mechanisms are not required, but iindicate the general type of enzyme along with any cofactor that is used.

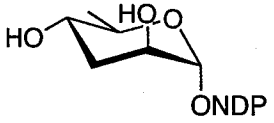
from neocarzinostatin

A

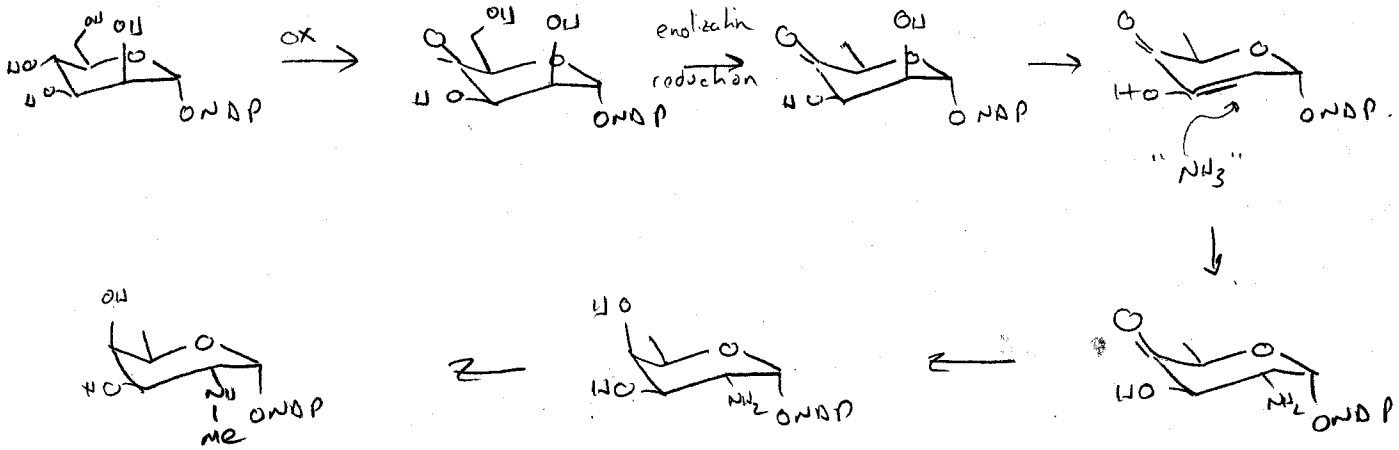


from. tyvelose.

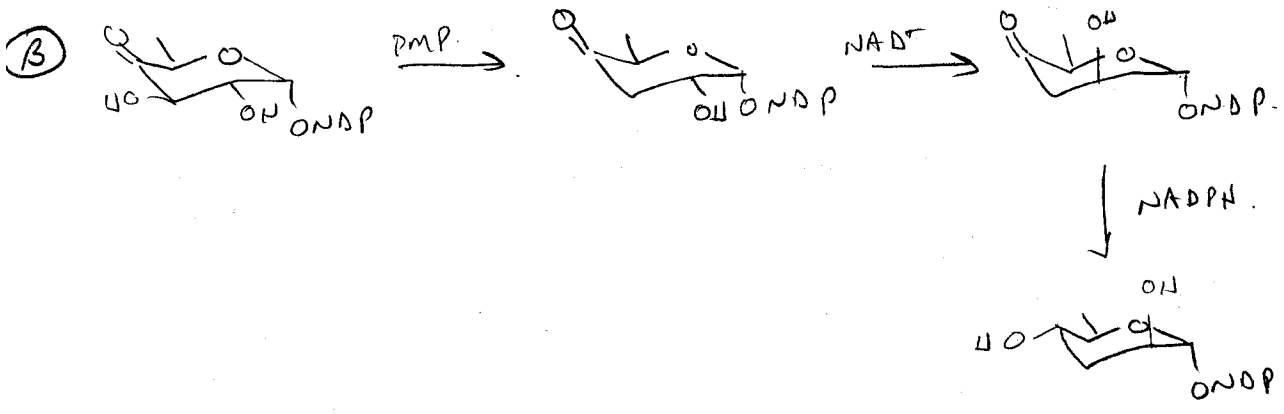
B



(A) In practice, starts from mannose. A mechanism starting w/ glucose is OK.



(B)



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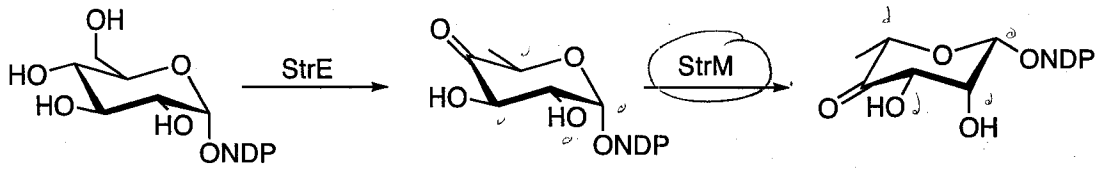
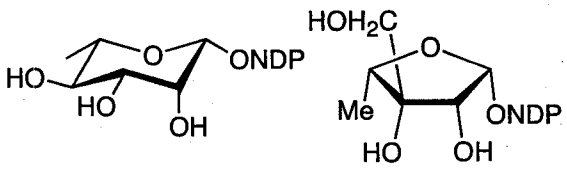
See Org Lett (1999) 1 133-136; JACS (2000) 122 12397-12398

5.451 F2005
Problem Set 2.

2. (30 pts) **A.** In a recent study, the "Des V" gene of the desosamine biosynthetic pathway was knocked ou of a desosamine producing organism (see page 15 of the sugar handout, 9/22). Draw the structure of the saccharide that would be expected to be formed from this knockout strain. **B.** A non-specific reductase is present in the producing organism,; draw the structure of the saccharide that would be expected to be formed under these conditions. **C.** The "Des I" gene was knocked out of the producing organism (containing the nonspecific reductase) and replaced with StrM from the streptosamine pathway (shown below). Predict the structure of the sugar that would be expected to be produced from the knockoutDesI/StrMstrain .

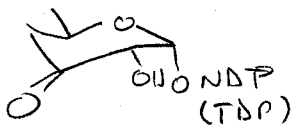


StrL

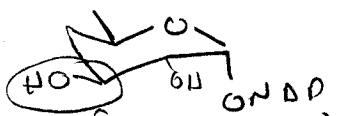


mixture of products

(A)

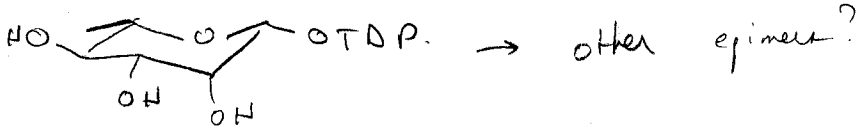


(B)

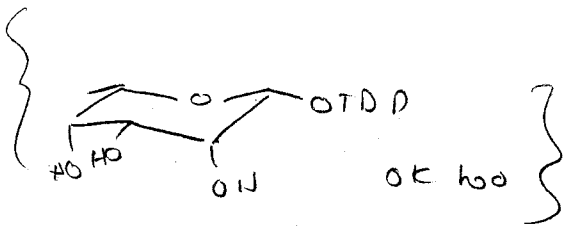


ok if epimerized

(C)



→ other epimers?



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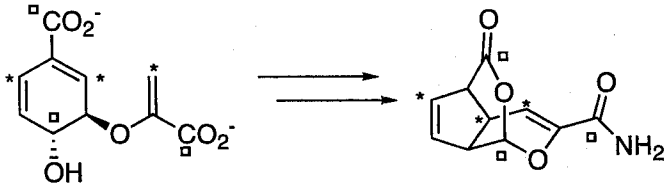
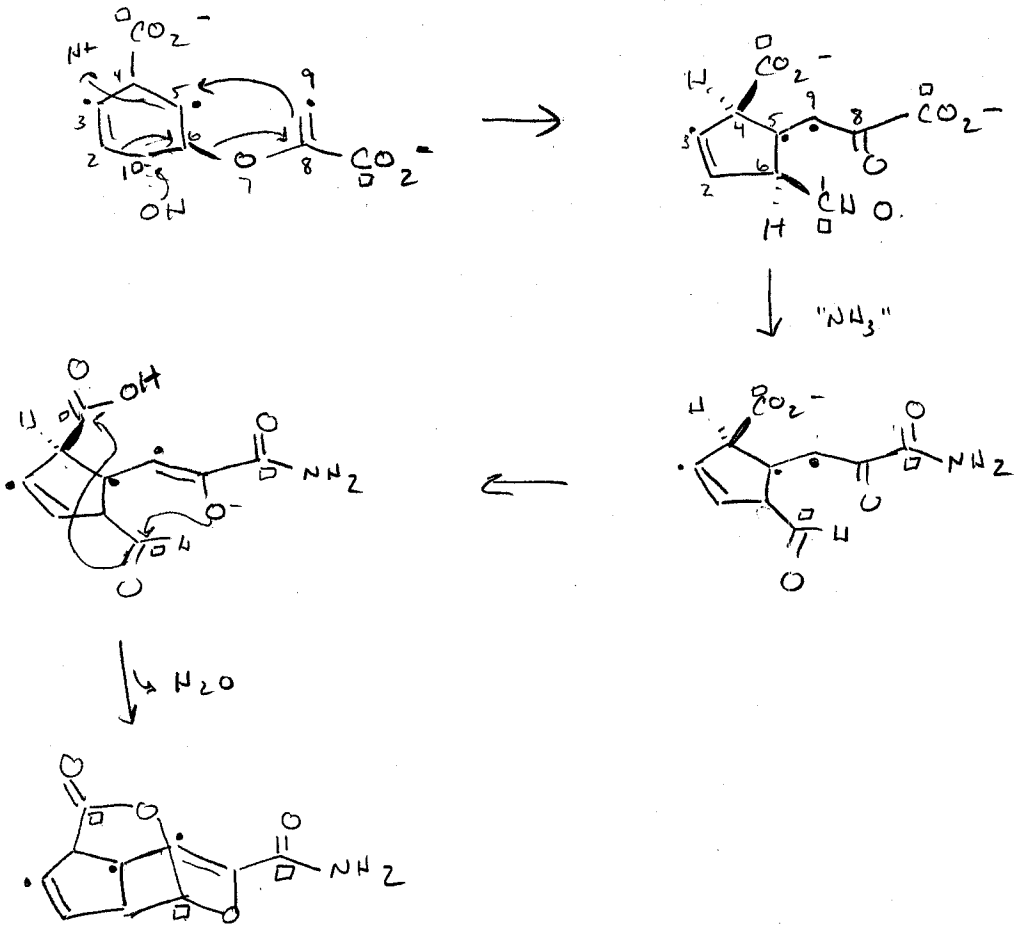
5.451 F2005
Problem Set 2.

See Eur. J Org Chem. (2002) 983-987.

3. (20 pts) The following compound is mde from the chorismate intermediate via a newly discovered branch of the shikimic acid biosynthetic pathway. Propose a mechanism for the conversion of chorismate to the product shown below taking into account the locations of the two sets of carbon isotopic labels. The mechanism and the source of the "NH2" moiety remains unclear. How you show the incorporation of ammonia into the product will not count for any points in the problem.





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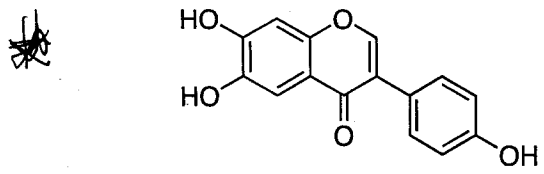
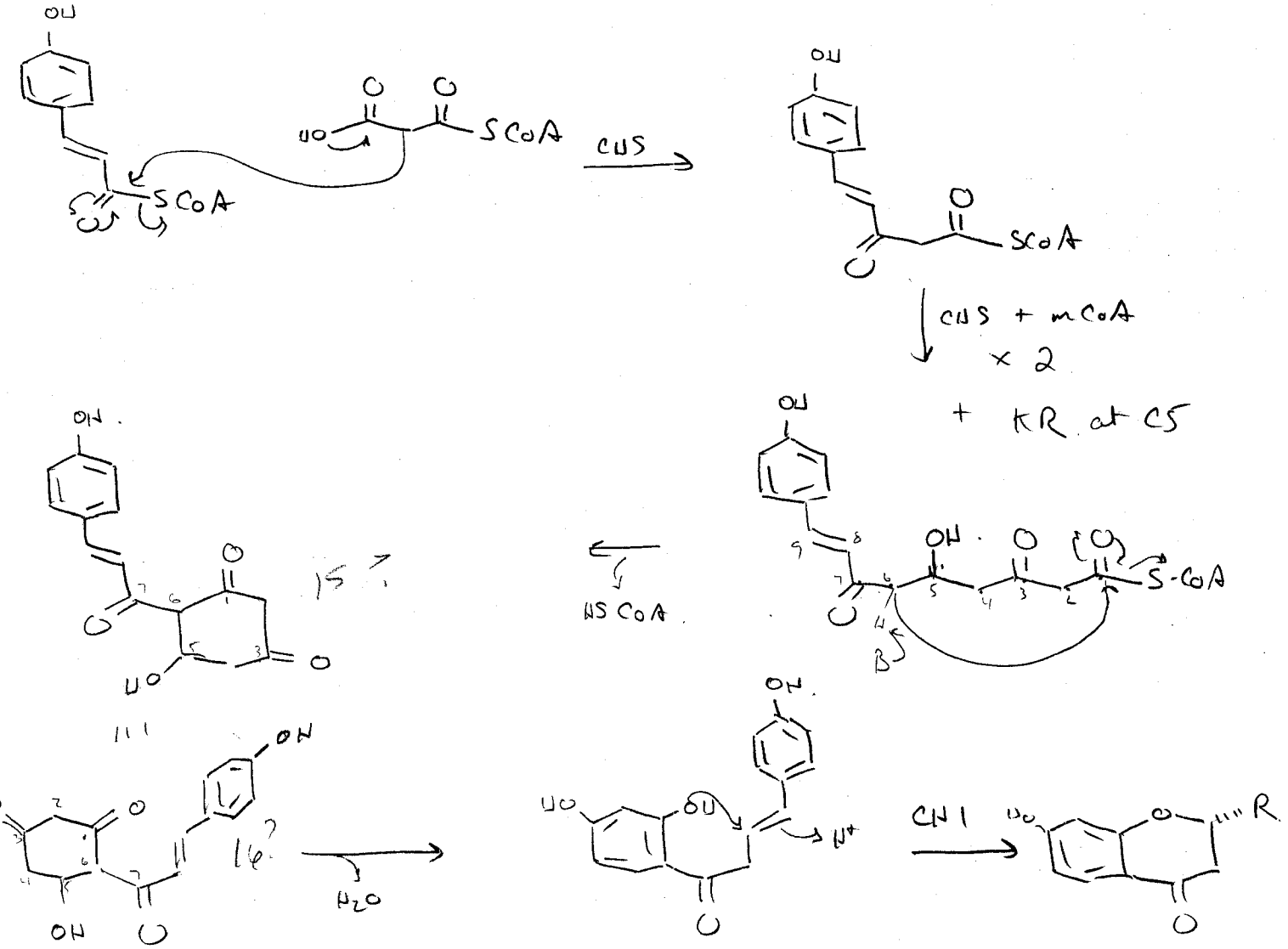
5.451 F2005
Problem Set 2.

See JBC (2001) 276 1688-1695

4. (20 pts) Draw a likely biosynthetic scheme for the following compound starting from coumaroyl CoA and 3 units of malonyl CoA. SHow all steps and indicate the general type of enzyme that would catalyze each transformation.





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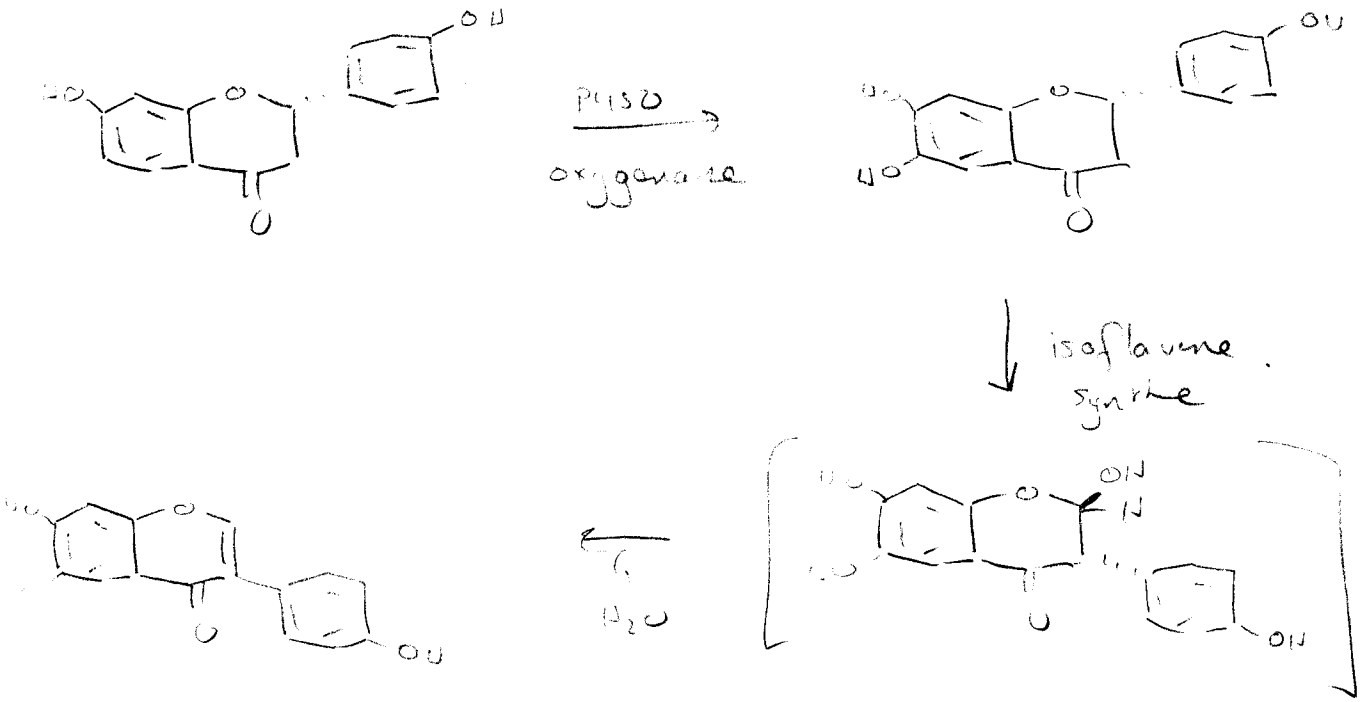

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