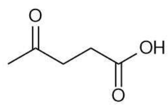
3. This question is about levulinic acid

In 2008 Arsenal F.C. midfielder Mathieu Flamini founded GF Biochemicals, which was the first company to mass produce levulinic acid. Levulinic acid is a versatile chemical that can be used to make pharmaceuticals, plastics and fuels. Levulinic acid can be made from renewable resources such as the sugar fructose.

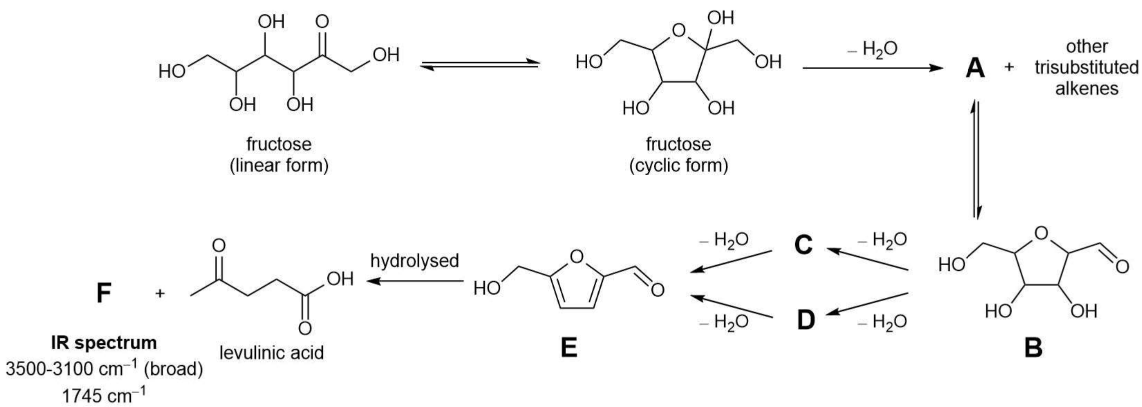


levulinic acid

(a) Tick the names of the functional groups present in levulinic acid in the answer booklet.

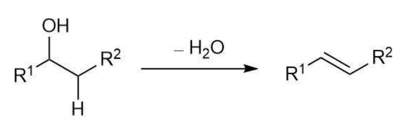
(b) Give the molecular formula for levulinic acid.

Fructose exists in equilibrium between its linear form and its cyclic form. This equilibrium mixture can be converted to levulinic acid as follows.



(c) Circle in the answer booklet the two atoms in the linear form of fructose which become bonded in the cyclic form.

Elimination of a molecule of water from the cyclic form of fructose forms compound **A** and several other trisubstituted alkenes. The alkene is formed due to loss of a hydrogen and a hydroxyl group (OH group) from adjacent carbon atoms as shown on the right.



If the alkene that is formed has an OH substituent, then it can isomerise as shown on the right.

(d) **(i)** Draw the structure of alkene **A**, which can isomerise to form **B.**

(ii) Draw the structure of the other trisubstituted alkenes that could also be formed.

Compound **B** can be converted into compound **E** via the elimination of two more molecules of water. This can occur via intermediate compounds **C** or **D**.

(e) Draw the structure of compounds **C** and **D**.

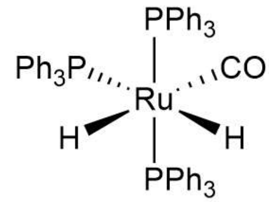
Compound **E** can by hydrolysed to levulinic acid and by-product compound **F**.

(f) Draw the structure of compound **F**.

The hydrogenation of levulinic acid gives a green and sustainable route to several different chemicals used in perfumes and flavouring. One catalyst for this hydrogenation is the octahedral complex of formula [$RuH_2(CO)(PPh_3)_3$]. This complex is named dihydridocarbonyltris(triphenylphosphine)ruthenium(**Z**), where **Z** is the oxidation state of ruthenium.

(g) State the value of **Z**.

The stereochemistry of the catalyst [$RuH_2(CO)(PPh_3)_3$] is shown.

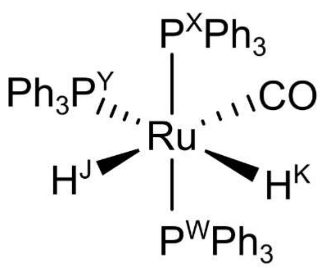


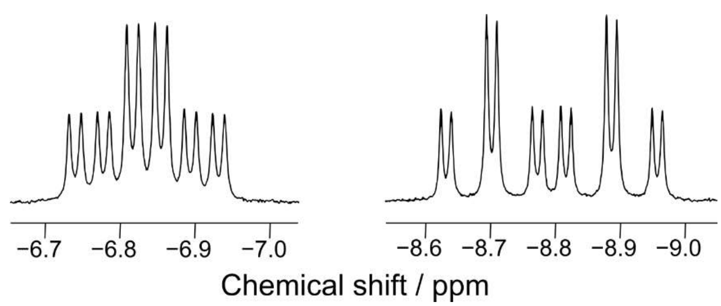
(h) Draw the other stereoisomers of this complex. Tick to indicate whether the stereoisomer shown and each stereoisomer you have drawn has an enantiomer. For a pair of enantiomers, only draw one of the pair.

This catalyst can be analysed by ^{31}P NMR. ^{31}P is 100% abundant and is a spin ½ nucleus like ^{1}H. The ^{31}P NMR is run in a way that means no coupling between ^{31}P and ^{1}H is observed. The only coupling which is observed is between ^{31}P nuclei in different environments.

(i) What is observed in the ^{31}P NMR spectrum of this catalyst? Tick the correct answer.

In the ^{1}H NMR spectrum, the two hydrides appear at negative chemical shifts and have complex coupling patterns. The couplings observed for these signals arise from coupling through two bonds to either ^{1}H or ^{31}P, (i.e. either ^{1}H–Ru–^{1}H, or ^{1}H–Ru–^{31}P) and are measured in Hz. The coupling constant between two nuclei that are *trans* is usually larger than between two nuclei that are *cis*.





The signal at −6.83 ppm is a 'triplet of doublets of doublets'. The signal is split into a triplet with the largest coupling constant of 31 Hz, further split into a doublet with coupling constant of 15 Hz, further split into a doublet with coupling constant of 6 Hz.

The signal at −8.80 ppm is a 'doublet of triplets of doublets'. The signal is split into a doublet with the largest coupling constant of 74 Hz, further split into a triplet with coupling constant of 28 Hz, further split into a doublet with coupling constant of 6 Hz.

(j) Complete the table to assign the values of the coupling constants in Hz to the following pairs of nuclei (H^J–H^K, H^J–P^W, H^J–P^X, H^J–P^Y, H^K–P^W, H^K–P^X, H^K–P^Y).