Tetrahedron Letters, Vol. 33, No. 24, pp. 3533-3536, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

Precursors of Damascenone in Fruit Juices

George K Skouroumounis,[A] Ralph A Massy-Westropp,*[A] Mark A Sefton,[B]
and Patrick J Williams[B]

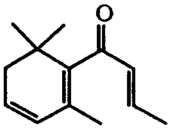
[A] Department of Organic Chemistry, University of Adelaide, GPO Box 498, Adelaide SA 5001.

[B] Australian Wine Research Institute, PO Box 197, Glen Osmond, SA 5064.

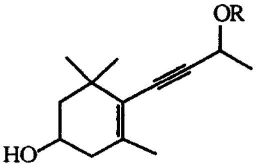
Abstract: *The acid catalysed reactions of 6,7-megastigmadiene-3,5,9-triol and the β-D-glucosides of 5-megastigmen-7-yne-3,9-diol and 3-hydroxy-β-damascone have been studied in relation to the formation of damascenone. The results show that hydrolysis of the allene triol could account for damascenone formation in the juices of grapes and other fruits.*

The potent aroma volatile damascenone **1** occurs in Riesling wine by hydrolysis of multiple percursors.[1] At least some of the precursors appear to be glycoconjugates with different conjugating moieties and non-glycosidic compounds are probably also precursors.[1] An aglycone that is found in grapes that is capable of generating **1** is the enyne diol **2a**, although this compound at pH 3 (wine pH) gives, in addition to **1**, 3-hydroxydamascone **3a** as the major product.[2]

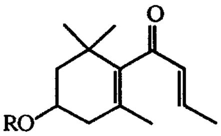
The observation in grape juice of the allenic ketones **4** and ketone **5** as aglycones along with enyne diol **2a**, led to the suggestion that allene triol **6a**, as a conjugate, may have been one of the additional precursors of **1** in grapes and wines.[1,2] An earlier scheme in which **1** was considered as being formed from **4** via **6a** and **3a**[3,4] formed the basis of this proposal. The recent finding of conjugate **6b** as a glucosidic precursor of damascenone in leaves of Lycium halimifolium Mil[5] has confirmed a role for **6a** in the biogenesis of damascenone **1**.



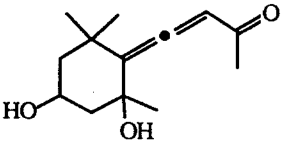
1



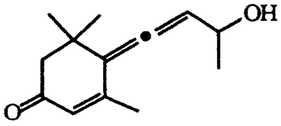
2a R = H
2b R = β-D-glucopyranosyl



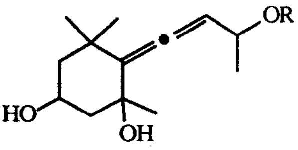
3a R = H
3b R = β-D-glucopyranosyl



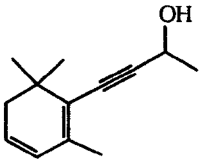
4



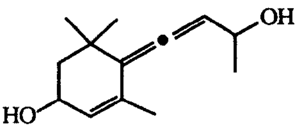
5



6a R = H
6b R = β-D-glucopyranosyl



7



8

To test the hypothesis that the allene triol **6a** can give damascenone **1** its hydrolysis at wine and juice pH has been studied. The results (Table 1) show that the allene triol **6a** prepared as described,[6] reacts rapidly at pH 3 at room temperature to give a small amount of damascenone **1** in addition to the major products, enyne diol **2a** and 3-hydroxy-β-damascone **3a**. It is already known that neither the enyne diol **2a** nor 3-hydroxy-β-damascone **3a** is a significant intermediate in the formation of damascenone under the conditions used.[2] Indeed, **3a** does not react at all and **2a** reacts very slowly at room temperature although it could be an intermediate when the hydrolysis is carried out at elevated temperatures and/or prolonged reaction times. These results are consistent with the observation of Olsson[7] that α-allenic alcohols rearrange much faster than α-acetylenic alcohols. It can be concluded that hydrolysis of the allene triol **6a** is fast enough to account for damascenone formation in the juices of grapes and other fruits. The recent observation[8] of products of allene triol in Chardonnay grape juices in proportions similar to those in Table 1 supports this hypothesis. The enyne diol **2a** is unlikely to be a source of damascenone in juices. However, it is a precursor during wine conservation.

Two intermediates, tentatively assigned as megastigma-3,5-dien-7-yn-9-ol **7** and megastigma-4,6,7-triene-3,9-diol **8**, were also observed in the hydrolysates of the allene triol **6a** under mild conditions. The evidence for the structures 7 and 8 comes from their mass spectra. The mass spectrum of 7 was the same as that reported.[9] The mass spectrum of 8 had significant ions at m/z 146 and 131 (100%) which were attributed to dehydration of the molecular ion, followed by loss of 44 (C9 and C10 carbons) and subsequent loss of a methyl group (these fragmentations have also been observed in the mass spectra of analogous allenic ketones[2,10]). A further ion at m/z 149 was attributed to M-44-15, without loss of water. Compound 7 could well be an immediate precursor of damascenone 1. It has been reported as a constituent of rum, a beverage which contains relatively high levels of damascenone.[9]

Because glycosides of the enyne diol 2a and 3-hydroxy-β-damascone 3a are known to be constituents of wines and grapes[11] the two glucosides, 2b and 3b, were synthesized and their hydrolyses studied.

The glucoside 3b of 3-hydroxy-β-damascone did not give damascenone under any of the conditions used (pH 1 and 3, 100°C, 8 h). However, the glucoside 2b gave a higher proportion of damascenone but hydrolysed approximately 8-10 times more slowly than the corresponding aglycone 2a. We have also noted this increased stability towards acid with the glucosides of other allylic alcohols.[12]

Possible pathways for the hydrolysis of the allene triol 6 are shown (Scheme 1).

Table 1 Hydrolysis of Allene **6a** at pH 3 in Water/Ethanol, 9:1.

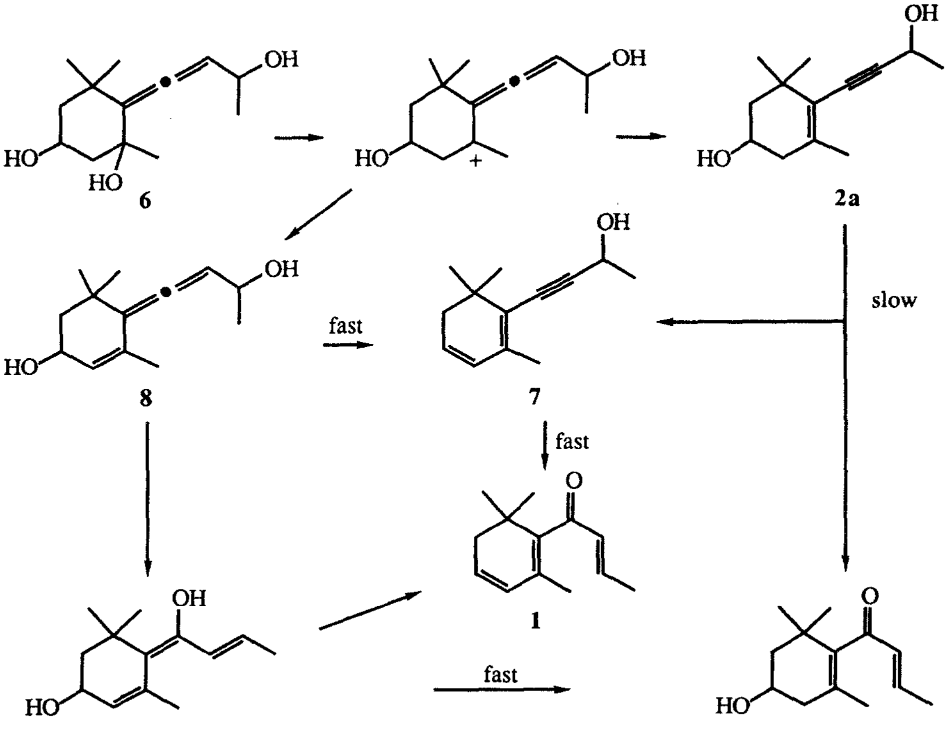
Conditions		Hydrolysis Products				
Temperature	**Reaction Time**	**1**	**2a**	**3a**	**7**	**8**[f]
24°C	4 h	trace[a]	2	13	trace[a]	1
	24 h	trace[b]	10	56	trace[b]	5
50°C	0.33 h	trace[c]	5	17	trace[c]	trace
	1 h	trace[d]	10	49	trace[d]	trace
	4 h	4	20	76	none	trace
80°C	0.33 h	5	24	70	2[e]	none
	1 h	7	21	72	trace	none
	4 h	8	21	71	none	none

Ratio of 1:7. [a] 1:2 ; [b] 3:1 ; [c] 3:1 ; [d] 7:1

[e] Response ratio of 1/mg internal standard was used.

[f] The ratio of compound 8 to internal standard appeared to vary with concentration of sample during GC and could not be determined accurately.

The figures are % yield, determined by GC/MS.



Scheme 1

References

1. Winterhalter, P.; Sefton, M.A.; Williams, P.J. *Am.J.Enol.Vitic.* **1990**, *41*, 277.
2. Sefton, M.A.; Skouroumounis, G.K.; Massy-Westropp, R.A.; Williams, P.J. *Aust.J.Chem.* **1989**, *42*, 2071.
3. Ohloff, G.; Rautenstrauch, V.; Schulte-Elte, K.H. *Helv.Chim.Acta* **1973**, *56*, 1503.
4. Isoe, S.; Katsumura, S.; Sakan, T. *Helv.Chim.Acta* **1973**, *56*, 1514.
5. Näf, R.; Velluz, A.; Thommen, W. *Tetrahedron Lett.* **1990**, *31*, 6521.
6. Hlubucek, J.R.; Hora, J.; Russell, S.W.; Toube, T.P.; Weedon, B.C.L. *J.Chem.Soc., Perkin I*, **1974**, 848.
7. Olsson, A.; Claesson, A.; Bogentoft, C. *Acta Chem.Scand.* **1973**, *27*, 1629.
8. Sefton, M.A.; Francis, I.L.; Williams, P.J. *Vitis*, submitted.
9. Heide, R.; Schaap, H.; Wobben, H.J.; De Valois, P.J.; Timmer, R. (Res.Dep. Naarden International N.V., N.L-1400 Narden, Neth.) *Qual. Foods Beverages: Chem. Technol., [Proc.Symp.Int. Flavor Conf.]*, 2nd **1981**, *1*, 183-200 Edited by G. Charalambous, G. Inglett, Academic: New York N.Y.; Mass spectrum received as personal communication.
10. Tan, S-T.; private communication.
11. Sefton, M.A.; Williams, P.J. *J.Agric.Food Chem.* **1991**, *39*, 1994.
12. Skouroumounis, G.K., Ph.D Thesis, University of Adelaide, **1991**.

(Received in UK 16 March 1992)