

1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN): A Possible Degradation Product of Lutein and beta-Carotene*

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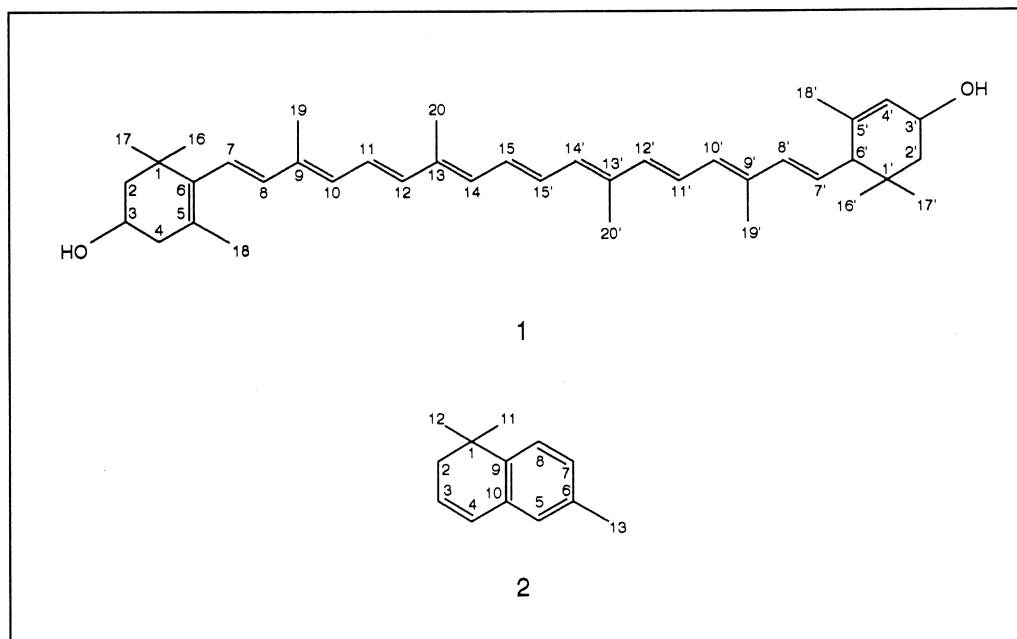
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Lutein and beta-carotene were heated in H₂SO₄ and ethanol/tartaric acid media adjusted to pH 1 and 3, respectively. Various products were formed, but 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), responsible for the kerosene-like flavour of aged Weisser Riesling wines, derived from lutein only.

Carotenoids are unstable compounds and are easily degraded to a variety of products in the presence of oxygen and light as well as at elevated temperatures. Ohloff (1972) hypothesised that carotenoids are precursors of aromatic compounds such as C₁₃-norisoprenoids. Recently, several C₁₃-norisoprenoids have been identified upon liberation from their bound forms in grapes and wines (Sefton *et al.*, 1989; Winterhalter, Sefton & Williams, 1990). One of these, 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) (**2**), is regarded as an important contributor to the bottle-aged kerosene-like character of aged Weisser Riesling wines (Simpson, 1978; Simpson & Miller, 1983; Marais, Van Wyk & Rapp, 1992). In general, when this flavour is present at high intensities it has a detrimental effect on wine quality. The degradation products of the following carotenoids have been investigated: beta-carotene (Day &

Erdman, 1963; Mader, 1964; La Roe & Shipley, 1970; Isoe *et al.*, 1972; Schreier, Drawert & Bhiwapurkar, 1979; Kawakami, 1982; Hohler, Nitz & Drawert, 1988; Kanasawud & Crouzet, 1990a), violaxanthin (Burden & Taylor, 1970), zeaxanthin (Isoe *et al.*, 1972), lycopene (Kanasawud & Crouzet, 1990b) and canthaxanthin (Roshdy & Daun, 1990).

The Ohloff (1972) hypothesis mentioned above, the formation of a small quantity of TDN (**2**) as a degradation product of beta-carotene (Hohler *et al.*, 1988), and the presence of relatively large quantities of beta-carotene and lutein (**1**) in grapes (Razungles *et al.*, 1987; Razungles *et al.*, 1988; Marais, Van Wyk & Rapp, 1990) prompted further investigation of the degradation products of these two carotenoids.



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MATERIALS AND METHODS

Lutein (**1**) (approximately 5 mg) was suspended in a 2 ml H₂SO₄ solution, previously adjusted to pH 1 with distilled H₂O. The solution was placed in a tinfoil-covered glass tube, filled with nitrogen before sealing, and then heated at 50°C for 4 hours in a waterbath. Lutein (**1**) was also treated at pH 3 under the same conditions. Degradation products obtained were extracted three times by 3 ml distilled pentane/dichloromethane (2:1) and the extracts concentrated.

Lutein (**1**) (approximately 5 mg) was also suspended in 10 ml of a simulated wine medium, consisting of 10% ethanol (EtOH), previously adjusted to pH 3 with tartaric acid (TA). The solution was placed in a tinfoil-covered glass tube, filled with oxygen before sealing, and then heated at 60°C for 3 hours in a waterbath. Degradation products obtained were extracted by Freon 11 and concentrated (Marais, 1986).

beta-Carotene was treated similarly to lutein.

Concentrated extracts were kept at 0°C until analysis by capillary gas chromatography (Hewlett Packard 5880A) and coupled gas chromatography-mass spectrometry (Finnigan 4600). The capillary columns and gas chromatographic conditions used were described by Marais *et al.*

(1992). The identities of the compounds were confirmed, either by comparing their mass spectra and retention times with those of authentic standards, or tentatively assigned by comparing their mass spectra with those obtained from the literature.

RESULTS AND DISCUSSION

The major compounds, identified as degradation products of lutein (**1**) and beta-carotene in H₂SO₄ (pH 1, 50°C, 4 hrs, N₂ atm.) and EtOH/TA (pH 3, 60°C, 3 hrs, O₂ atm.) media, are listed in Tables 1 and 2, respectively. A relatively large quantity of TDN (**2**) was produced as a degradation product of lutein (**1**) in a H₂SO₄ medium at pH 1 (Table 1) and also at pH 3 (data not shown). This compound was not produced from beta-carotene under the same conditions or when both carotenoids were individually heated in an EtOH/TA medium (Tables 1 and 2). Hohler *et al.* (1988) reported the formation of a small quantity of TDN (**2**) from beta-carotene in a N,N-dimethylformamide solution under photo-oxidative conditions. Their method is not comparable to those used in this study and this could account for the difference in TDN (**2**) production from beta-carotene.

TABLE 1
Major thermal degradation products of lutein (**1**).

Degradation product and mass spectral data (m/z, %)	Media		Identity assignment
	H ₂ SO ₄ *	EtOH/TA**	
1. 1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN) (2): 172(21), 158(7), 157(100) , 143(3), 142(50), 141(24), 129(4), 128(7), 115(11), 77(6), 76(2), 51(3), 39(2)	x		A
2. 2,3-Dehydro-alpha-ionone (2 isomers): 190(6), 175(8), 147(25), 133(7), 132(6), 131(14), 119(15), 117(7), 115(6), 107(8), 105(40), 93(7), 91(30), 84(6), 79(13), 77(14), 69(7), 65(10), 55(13), 53(9), 51(6), 43(100) , 41(21), 39(16)	x	x	B(a)
3. 3,4-Dehydro-beta-ionone: 190(7), 175(43), 157(4), 147(10), 142(5), 133(5), 131(13), 119(6), 117(4), 115(9), 105(11), 91(13), 79(7), 77(7), 65(5), 53(4), 43(100) , 41(9), 39(7)	x		B(a)
4. 3-Oxo-alpha-ionone: 191(3), 150(9), 149(9), 121(4), 109(7), 108(94), 107(9), 91(6), 79(10), 77(12), 53(6), 43(100) , 41(9), 39(9)	x	x	A
5. 3-Hydroxy-beta-ionone: 208(2), 194(8), 193(84), 175(19), 149(7), 147(8), 133(9), 131(12), 123(7), 121(10), 119(6), 109(14), 107(6), 105(19), 93(7), 91(18), 81(5), 79(13), 77(12), 65(6), 55(10), 53(9), 43(100) , 41(23), 39(12)	x	x	B(b)

* Lutein heated in nitrogen at 50°C for 4 hours in a H₂SO₄ solution, adjusted to pH 1 with distilled water.

** Lutein heated in oxygen at 60°C for 3 hours in a 10% ethanol solution, adjusted to pH 3 with tartaric acid.

A = Identities confirmed by comparing mass spectra and retention times with those of authentic standards; B = Identities tentatively assigned by comparing mass spectra with those obtained from the literature; (a) = Yamazaki *et al.* (1988); (b) = Winterhalter & Schreier (1988).

TABLE 2

Major thermal degradation products of beta-carotene.

	Degradation product and mass spectral data (m/z,%)	Media		Identity assignment
		H ₂ SO ₄ *	EtOH/TA**	
1.	6-Methyl-2-heptanone: 110(6), 95(7), 85(5), 71(14), 69(9), 67(7), 59(7), 58(78), 55(8), 43(100) , 41(17), 39(8)	x		B(a)
2.	6-Methyl-5-hepten-2-one: 111(7), 108(22), 93(8), 83(6), 71(13), 69(28), 68(8), 67(13), 58(18), 56(6), 55(33), 53(7), 43(100) , 41(57), 39(15)	x		B(a)
3.	beta-Cyclocitral: 153(7), 152(70), 138(8), 137(95), 124(8), 123(85), 119(17), 110(10), 109(85), 107(24), 105(8), 95(32), 93(28), 91(37), 81(81), 79(43), 77(33), 69(17), 67(100) , 65(20), 60(7), 57(10), 55(42), 53(38), 51(15), 43(52), 41(84), 39(50)	x	x	B(a)
4.	beta-Ionone: 192(4), 178(13), 177(100) , 159(5), 149(8), 135(14), 133(7), 121(9), 119(8), 107(11), 105(10), 95(10), 93(16), 91(17), 81(6), 79(13), 77(14), 71(7), 67(7), 55(11), 53(8), 43(80), 41(24), 39(11)	x	x	A
5.	5,6-Epoxy-beta-ionone: 135(8), 124(7), 123(100) , 109(6), 107(5), 95(5), 91(5), 79(8), 55(7), 43(55), 41(14), 39(7)	x	x	A
6.	Dihydroactinidiolide: 180(15), 152(8), 137(37), 124(12), 111(100) , 110(27), 109(43), 95(14), 93(8), 91(7), 81(13), 79(14), 77(10), 69(15), 67(43), 65(8), 55(15), 53(15), 51(7), 43(76), 41(32), 39(22)	x	x	B(b)
7.	4-Oxo-beta-ionone: 206(28), 191(5), 164(14), 163(64), 150(12), 149(17), 136(12), 135(20), 122(20), 121(37), 119(15), 107(15), 105(15), 93(20), 91(24), 79(15), 77(15), 65(13), 55(22), 53(14), 43(100) , 41(28), 39(20)	x	x	A

* beta-Carotene heated in nitrogen at 50°C for 4 hours in a H₂SO₄ solution, adjusted to pH 1 with distilled water.

** beta-Carotene heated in oxygen at 60°C for 3 hours in a 10% ethanol solution, adjusted to pH 3 with tartaric acid.

A = Identities confirmed by comparing mass spectra and retention times with those of authentic standards; B = Identities tentatively assigned by comparing mass spectra with those obtained from the literature; (a) = McLafferty & Stauffer (1989); (b) = Schreier, Drawert & Junker (1976).

One of the main degradation products of lutein (**1**) was 3-oxo-alpha-ionone (Table 1). This compound may be an intermediate in the formation of TDN (**2**), since in aqueous solutions of organic acids, it cyclised to 4,4,7-trimethyl-3,4-dihydro-2(1H)-naphthalenone, which upon reduction and dehydration yielded TDN (**2**) (Davis, Stevens & Jurd, 1976). Although 3-oxo-alpha-ionone was formed from lutein (**1**) in both media (Table 1), the absence of TDN (**2**) in the EtOH/TA medium could not be explained. A combination of factors such as temperature, pH and the medium used probably affected the development of TDN (**2**) from its precursor(s). Since the H₂SO₄ medium was not sparged with N₂, traces of O₂ probably occurred and could account for the similarity in some of the degradation products between the two media. Another degradation product of lutein (**1**), 3,4-dehydro-beta-ionone, found only in the H₂SO₄ medium (Table 1), has also been proposed as a precursor of TDN (**2**) (Enzell, Wahlberg & Aasen, 1977). Other major compounds also occurred, but could not be identified due to the lack of reference compounds. In view of the abovementioned results and proposals, lutein (**1**) in grapes could be an original precursor of TDN (**2**) in wine.

CONCLUSIONS

This study presents the first evidence that lutein (**1**) may be an original precursor of TDN (**2**). Further studies are needed to elucidate the biosynthetic relationship between lutein (**1**), TDN (**2**) and its precursors occurring mainly in Weisser Riesling grapes and wine.

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