Carotenoid Levels in Maturing Grapes as Affected by Climatic Regions, Sunlight and Shade*

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The effect of climatic region, degree of ripeness, sunlight and shade on carotenoid concentrations in Weisser Riesling and Chenin blanc grapes was investigated. Lutein and beta-carotene concentrations were higher in grapes from hot regions than grapes from cooler regions. In general, decreases in carotenoid concentrations were observed with an increase in ripeness. Also, grapes exposed to sunlight generally had lower carotenoid concentrations than shaded grapes. Both lutein and beta-carotene concentrations varied little between Weisser Riesling and Chenin blanc grapes at comparable ripening stages.

Recent investigations revealed that lutein, beta-carotene, 5,6-epoxylutein, violaxanthin and neoxanthin commonly occur in grapes and that the former two are consistently present at the highest levels (Gross, 1984; Razungles *et al.*, 1987; Razungles *et al.*, 1988; Marais, Van Wyk & Rapp, 1990). These carotenoids are regarded as the precursors of various degradation products, such as C_{13}-norisoprenoids (Day & Erdman, 1963; Sanderson, Co & Gonzales, 1971; Enzell, Wahlberg & Aasen, 1977; Wahlberg *et al.*, 1977; Ohloff, 1978; Kawakami, 1982; Hohler, Nitz & Drawert, 1988; Marais *et al.*, 1990; Kanasawud & Crouzet, 1990). For example, under acidic conditions lutein and beta-carotene spontaneously give rise to the formation of C_{13}-norisoprenoids like 3-oxo-alpha-ionone, 4-oxo-beta-ionone and 5,6-epoxy-beta-ionone (Marais *et al.*, 1990). Steps in the pathways for the formation of 3-oxo-alpha-ionone from violaxanthin and zeaxanthin were also proposed (Burden & Taylor, 1970; Isoe *et al.*, 1972; Strauss, Wilson & Williams, 1987). Stevens, Lundin & Davis (1975), as well as Davis, Stevens & Jurd (1976) proposed pathways for the transformation of the abovementioned ionones to another C_{13}-norisoprenoid, namely 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN). It is possible that TDN could derive from carotenoids. Traces of TDN were in fact produced during the photo-oxidation of beta-carotene (Hohler *et al.*, 1988).

The presence of TDN in white wines is of a particular significance, since at low concentrations it can be beneficial to wine quality, whereas at high concentrations it is the major contributor to the undesirable "kerosene-like" bottle-aged odour, which occurs uniquely in Weisser Riesling wines (Simpson, 1978a, 1978b; Simpson & Miller, 1983; Rapp, Güntert & Ullemeyer, 1985; Marais *et al.*, 1990). It does not occur in varietal wines with similar terpene levels as Weisser Riesling or varietal wines containing virtually no terpenes, such as Chenin blanc. It is also well-known that this characteristic "kerosene-like" odour normally develops much faster in Weisser Riesling wines produced from grapes cultivated in hot wine-producing regions than in those from cool climates.

Since some carotenoids appear to be the precursors of C_{13}-norisoprenoids, including TDN, this investigation was aimed at determining the variation in the levels of such carotenoids of Weisser Riesling and Chenin blanc grapes at different ripening stages, in different climatic regions, and exposed to sunlight and shade.

MATERIALS AND METHODS

In 1989 grape samples of *Vitis vinifera* L. cv. Weisser Riesling (Rhine Riesling) and Chenin blanc were harvested at a single ripening stage between 19 and 20 degrees Balling (°B) in five grape-growing regions, namely Elgin (1503 degree-days), Constantia (1745 degree-days), three localities in Stellenbosch (1945 degree-days), Robertson (2178 degree-days) and Lutzville (2229 degree-days). In 1990 grape samples were harvested from the same vineyards, with the exception of Lutzville and Stellenbosch, at ripening stages varying between 11°B and 22°B. The 1990 samples from Stellenbosch were harvested from three Weisser Riesling clones, namely W1,37 and 239. The grapes of the former two clones, exposed to direct sunlight and to shade, were sampled at ripening stages between 13°B and 20°B. Clones were not considered in grapes from

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other regions. All grape samples (approximately 2 kg each) were precooled immediately after harvesting and then transported to a cold storage room at -30°C until lyophilised. The berries (200 g per sample) were lyophilised, pulverised, extracted with acetone and the extracts analysed for carotenoids by HPLC according to the technique used by Razungles *et al.* (1987). An ultrasphere ODS reversed-phase column (25 cm x 4,6 mm) was used. Beta-apo-8'-carotenal (0,05 mg per sample) was used as internal standard to determine the relative concentrations of the carotenoids.

RESULTS AND DISCUSSION

Effect of different climatic regions on carotenoid concentrations: Figure 1 shows the concentration of lutein and beta-carotene in Weisser Riesling grapes from different regions and vintages.

In general, the highest carotenoid levels occurred in grapes produced in hot regions (Robertson and Lutzville), whereas the lowest levels occurred in grapes from cool regions (Constantia and Elgin). With few exceptions the concentrations of lutein and beta-carotene in the grapes from three localities (1989 vintage) and of three clones (1990 vintage) in the Stellenbosch region varied between these two extremes. It is clear that locality within a region, as well as clone, may also have a marked effect on carotenoid levels.

The fact that the carotenoid contents of the 19-20°B grapes were higher in 1990 than in 1989 can probably be attributed to the effect of the vintage. In most cases, lutein occurred in higher concentrations than beta-carotene at the same sugar content (Fig. 1).

The relative concentrations of other grape components with spectra characteristic of carotenoids followed the same trends as lutein and beta-carotene. Based on the premise that carotenoids are the precursors of norisoprenoids, higher levels of these compounds may be anticipated in grapes from hot regions.

A comparison between carotenoid levels of Weisser Riesling and Chenin blanc grapes at similar ripening stages is illustrated in Figure 2.

Generally, both lutein and beta-carotene occurred in higher concentrations in the grapes of Chenin blanc than in Weisser Riesling grapes at comparable ripening stages. The

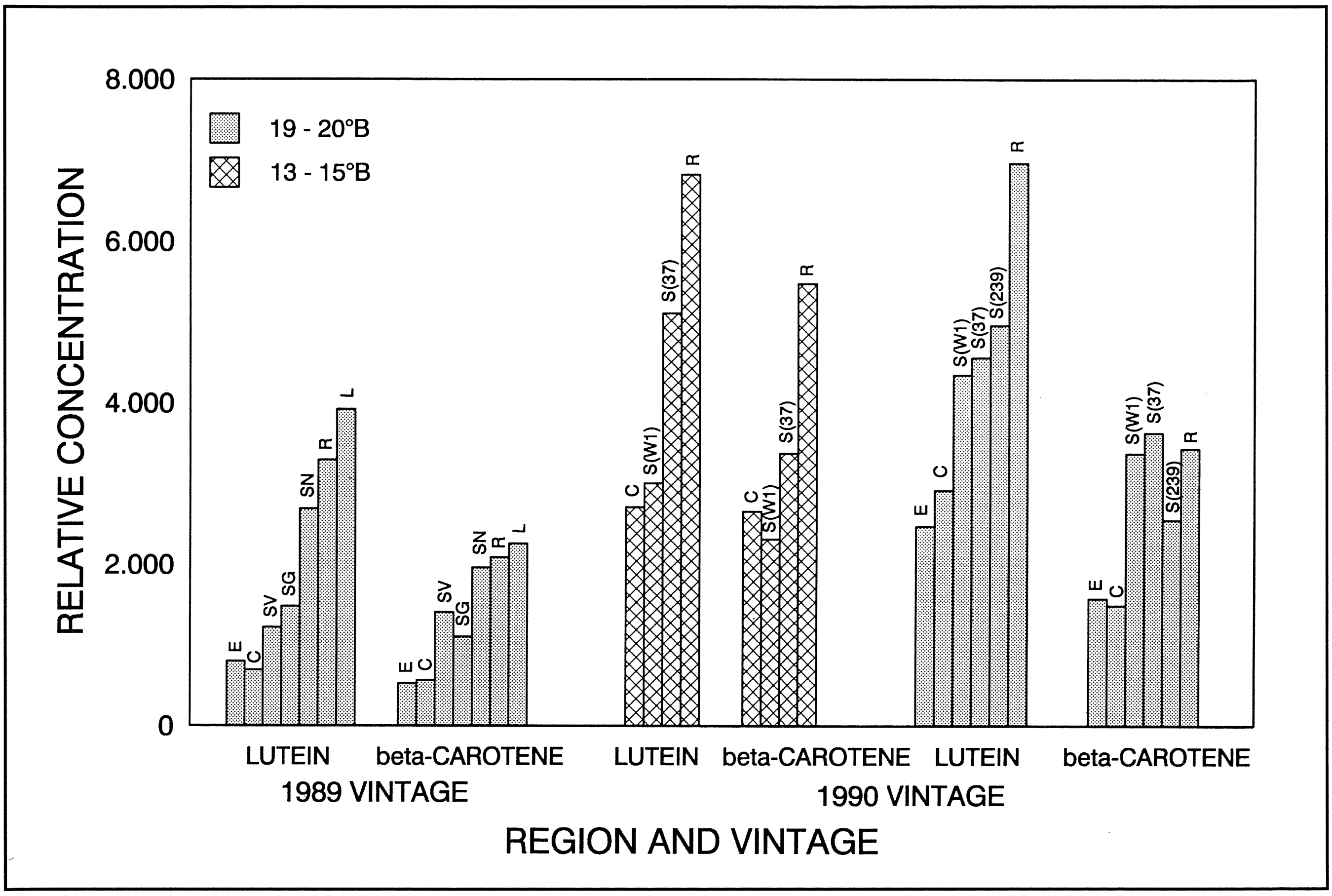

FIGURE 1

Lutein and beta-carotene concentrations in Weisser Riesling grapes from different grape growing regions (1989 and 1990 vintages). E = Elgin, C = Constantia, SV = Stellenbosch (Verdun), SG = Stellenbosch (Groenhof), SN = Stellenbosch (Nietvoorbij), S(W1) = Stellenbosch (clone W1)*, S(37) = Stellenbosch (clone 37)*, S(239) = Stellenbosch (clone 239), R = Robertson and L = Lutzville.

* Average of grapes exposed to sunlight and shade.

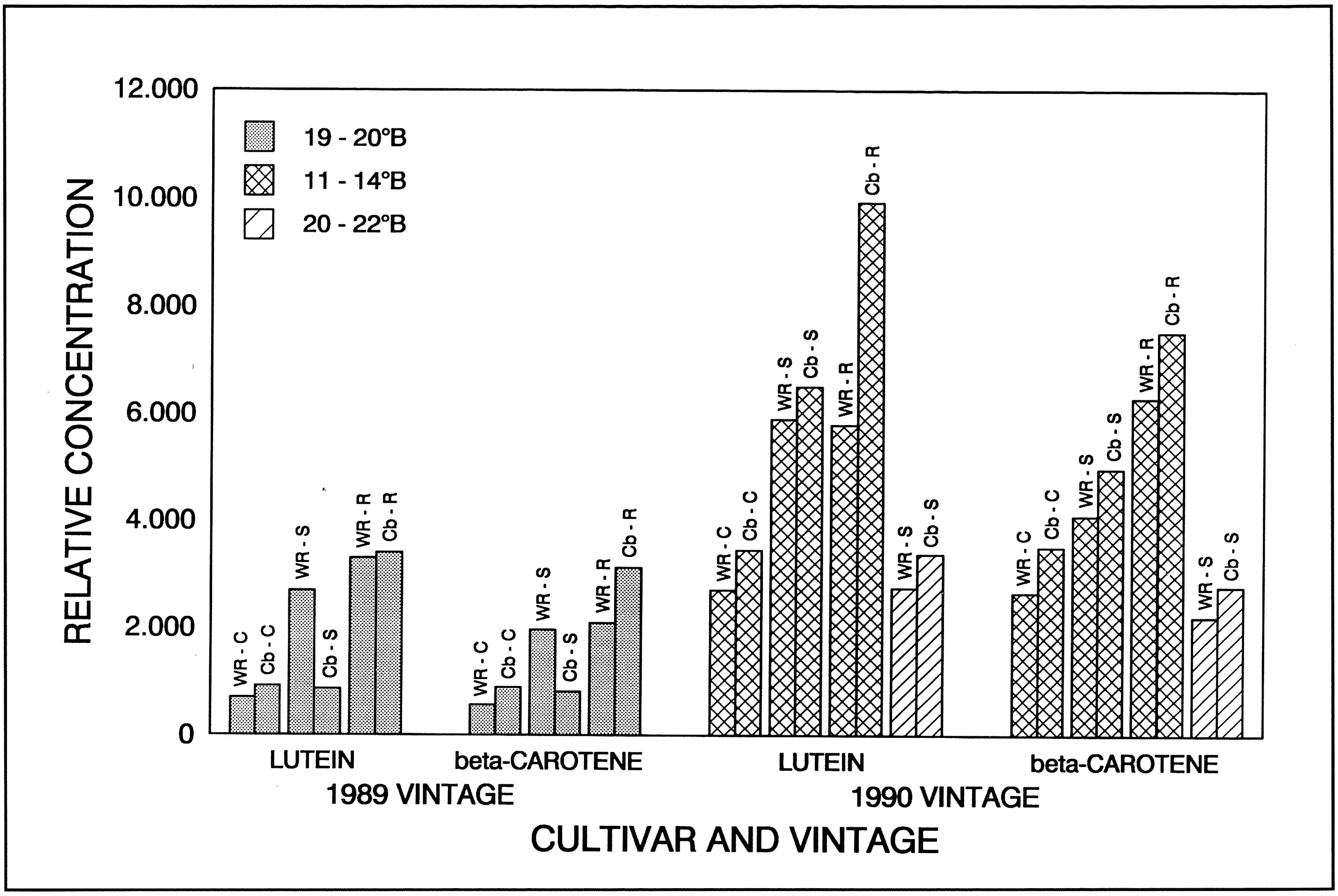

FIGURE 2

Lutein and beta-carotene concentrations in Weisser Riesling and Chenin blanc grapes from different grape growing regions (1989 and 1990 vintages). WR = Weisser Riesling; Cb = Chenin blanc; C = Constantia; S = Stellenbosch; R = Robertson.

warmer the region, the higher the carotenoid concentrations in the grapes of both cultivars. Razungles *et al.* (1987) also found higher lutein and beta-carotene concentrations in ripe grapes of Chenin blanc than in Weisser Riesling grapes. Since substantial amounts of TDN are produced almost exclusively in Weisser Riesling wine during ageing, it appears reasonable to expect that this unique property may be reflected by the concentrations of the carotenoids, which have been claimed to be the precursor compounds (Ohloff, 1978; Simpson & Miller, 1983; Rapp *et al.*, 1985). This, however, was not the case with lutein and beta-carotene. On the other hand, this finding does not necessarily preclude the possibility that these and other carotenoids could be precursors of TDN, since their degradation may also be affected by other factors. It has, for example, been shown that the formation of degradation products from carotenoids can be influenced by the presence of phenols and lipoxygenases (Sanderson *et al.*, 1971; Schreier, 1984).

Effect of degree of ripeness on carotenoid concentrations: Figure 3 shows the development of beta-carotene during ripening of Weisser Riesling grapes from different clones and regions. The effect of sunlight and shade on beta-carotene levels is discussed in the next section.

With few exceptions, beta-carotene concentration decreased with an increase in ripeness. A similar trend was observed in the development of lutein. Razungles *et al.* (1988) also reported decreases in carotenoid concentrations during ripening with a sharp decrease during véraison. The effect of ripeness on the concentration of an unknown compound with absorption maxima typical of carotenoids (423, 447 and 475 nm) is illustrated for Weisser Riesling and Chenin blanc grapes from two regions in Figure 4 and for two Weisser Riesling clones in Figure 5. According to the absorption maxima given by Razungles *et al.* (1987) and Ng & Tan (1988), this compound appears to be an epoxide of lutein or beta-carotene.

It is clear that this proposed carotenoid compound also decreased in concentration with an increase in ripeness. These decreases were more prominent at sugar concentrations below approximately 15°B, as was the case in the warmer region of Robertson (Fig. 4). In all probability the same tendency could be expected in the cooler Constantia region.

Various other researchers also studied carotenoid behaviour in different fruit and vegetables during ripening and different trends were reported. Carotenoid concentrations increased in tomatoes (Cabibel & Ferry, 1980) and decreased in apples (Mussini, Correa & Crespo, 1985). In mangos, carotenoid concentrations increased initially and then decreased (Ashraf *et al.*, 1981), while in bananas decreases up to colour break and subsequent increases were reported (Gross & Flügel, 1982). An increase in carotenoid concentrations in oranges after colour break is primarily due to the synthesis of xanthophylls (Spurgeon & Porter, 1983).

The proposed carotenoid compound occurred in higher concentrations during the early stages of ripening and also decreased at a slightly faster rate in Weisser Riesling than in Chenin blanc grapes (Fig. 4). Whether the difference in concentration and behaviour of this compound is substantial enough to account for the differences in concentration of degradation products between Weisser Riesling and Chenin blanc, remains to be proved.

Effect of sunlight and shade on carotenoid concentrations: The effect of sunlight and shade on carotenoid concentrations in Weisser Riesling grapes is illustrated for beta-carotene in Figure 3 and for the proposed carotenoid compound in Figure 5. With few exceptions the carotenoid levels were consistently higher in grapes exposed to shade or low light intensity than grapes exposed to direct sunlight or high light intensity. The sugar concentrations were consistently lower (between 0,8°B and 2,6°B) in shaded grapes than those more directly exposed to sunlight. Decreases in the proposed carotenoid compound levels per °B over the sampling period varied between 10% and 13% in shaded grapes, contrary to approximately 18% in the sunlight-exposed grapes of both clones (Fig. 5). Therefore, the tendency, namely lower carotenoid levels in grapes at higher sugar concentrations, appears to be more pronounced in grapes exposed to sunlight and higher temperature than in shaded grapes. Studies on the effect of light on carotenoid stability in model solutions demonstrated that both photodegradation and photo-isomerisation of beta-carotene occur, the former being the predominant reaction (Pesek & Warthesen, 1987, 1988, 1990). The rate of these reactions increased with an increase in temperature (Kanasawud & Crouzet, 1990) and may account for the observed lower carotenoid levels in grapes exposed to sunlight.

CONCLUSIONS

Factors such as region, degree of ripeness, sunlight and shade have a fairly prominent effect on lutein and beta-carotene concentrations in Weisser Riesling and Chenin blanc grapes. Grapes produced in hot regions contained higher carotenoid concentrations than those produced in cooler regions. In general it was found that lower sugar concentration and shady conditions were associated with higher carotenoid concentrations. Both lutein and beta-

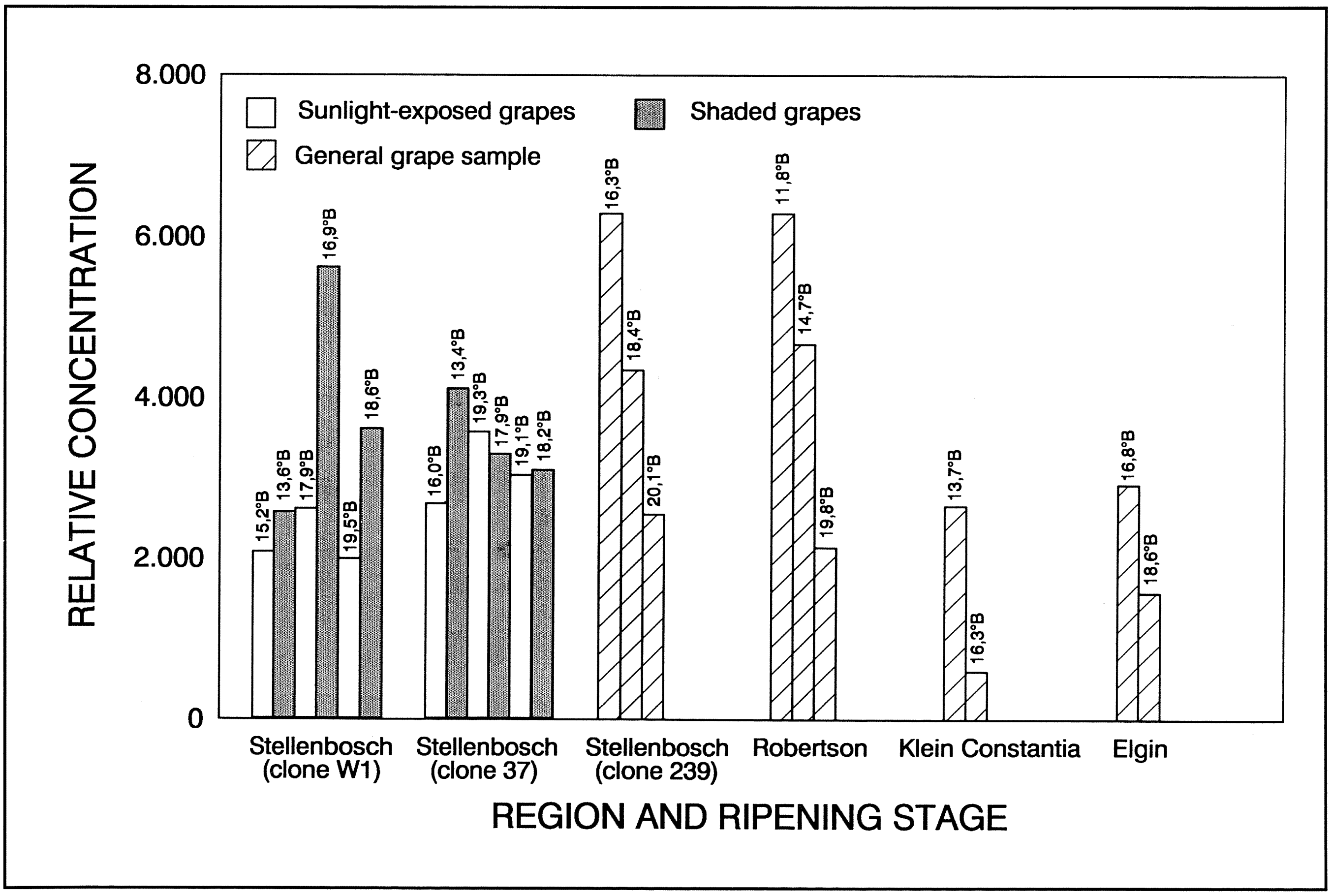

FIGURE 3

The effect of degree of ripeness, sunlight and shade on the beta-carotene concentration in Weisser Riesling grapes from different clones and grape growing regions (1990 vintage).

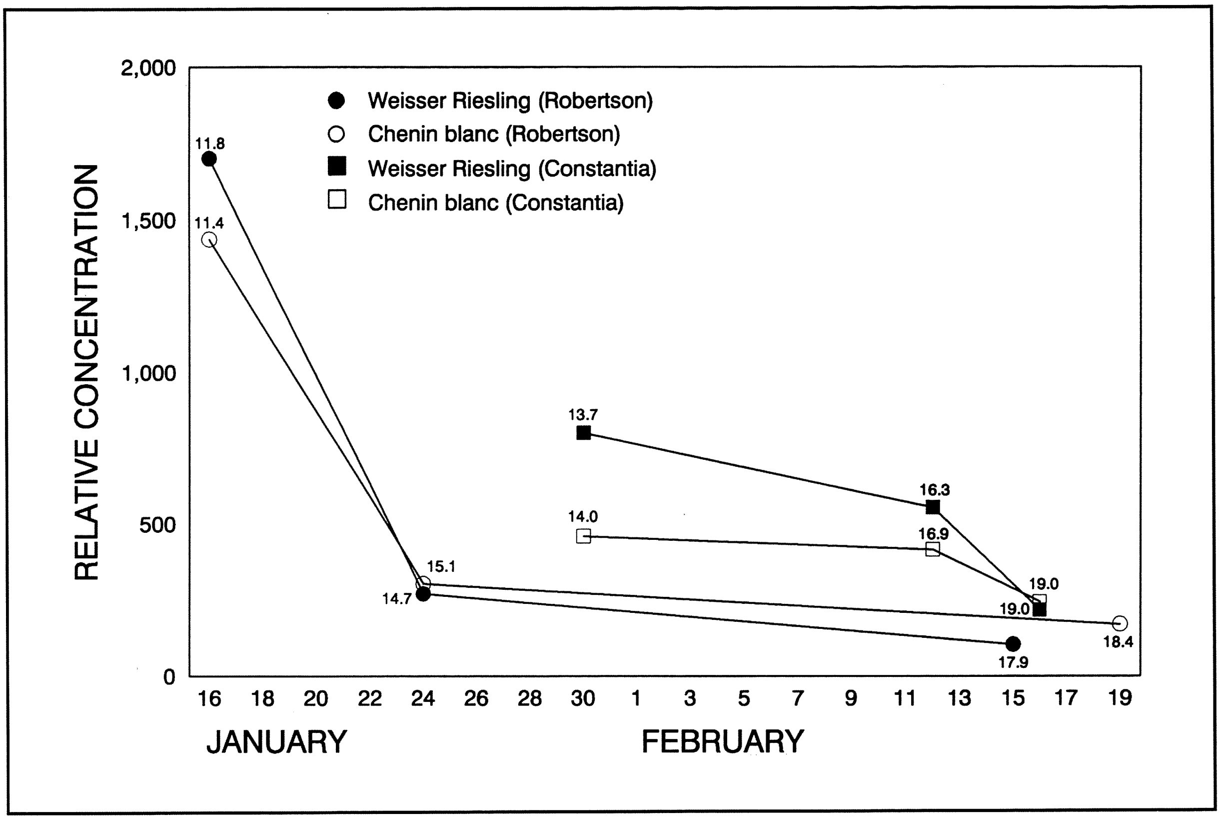

FIGURE 4

The effect of degree of ripeness on the concentration of a proposed carotenoid compound in Weisser Riesling and Chenin blanc grapes from different grape growing regions (1990 vintage). Sugar concentration (°B) is indicated at each sampling date.

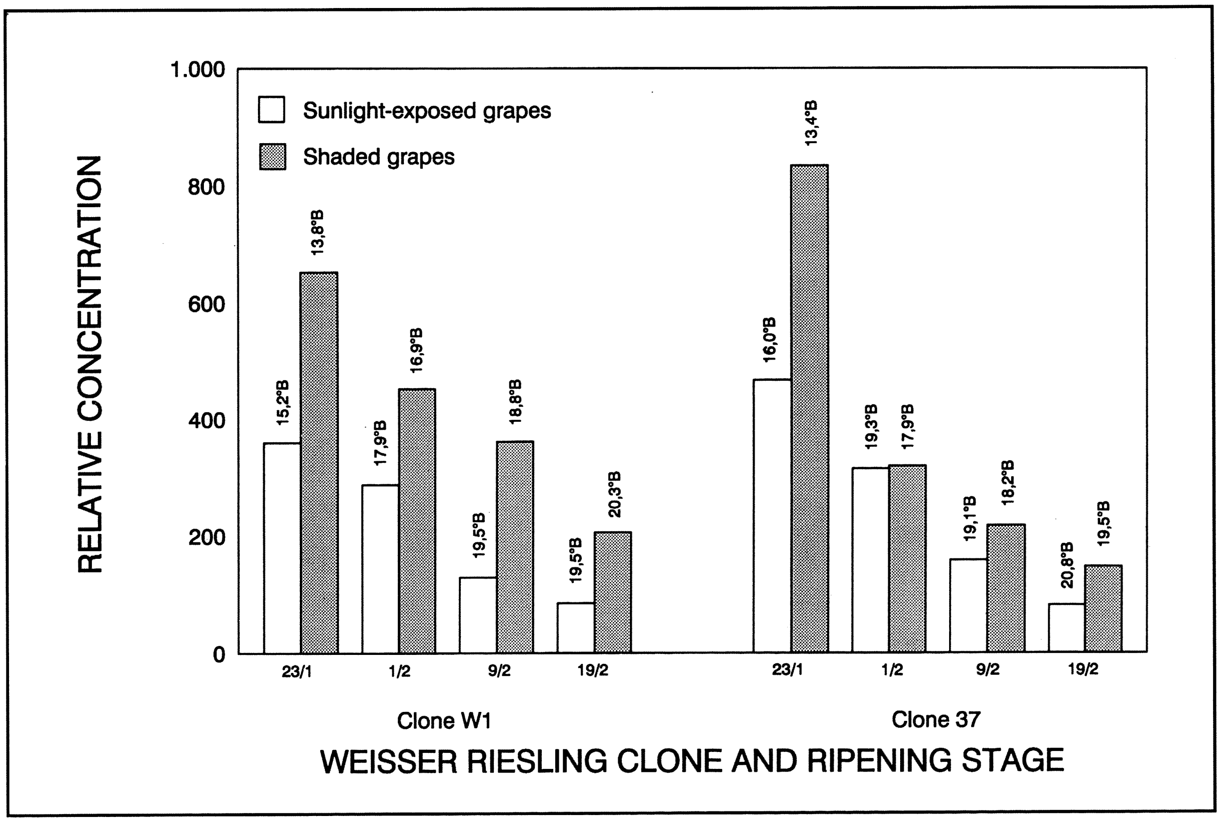

FIGURE 5

The effect of degree of ripeness, sunlight and shade on the concentration of a proposed carotenoid compound in Weisser Riesling grapes from different clones (1990 vintage).

carotene concentrations varied little between Weisser Riesling and Chenin blanc grapes at comparable ripening stages. A proposed carotenoid compound was of interest, since it may act as a precursor of norisoprenoids typical of the aroma of Weisser Riesling. Further investigations are necessary to clarify the relationship between carotenoids and TDN formation.

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