Hydroxylated Linalool Derivatives as Precursors of Volatile Monoterpenes of Muscat Grapes

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Thermal induction of volatile monoterpenes in juices of muscat grapes (sp. *Vitis vinifera* cv. Muscat of Alexandria and Muscat à Petits Grains) was studied by GC and GC–MS of headspace samples. The roles of the four recently discovered grape polyols 3,7-dimethylocta-1,5-diene-3,7-diol (1), 3,7-dimethylocta-1,7-diene-3,6-diol (2), 3,7-dimethyloct-1-ene-3,6,7-triol (3), and 3,7-dimethyloct-1-ene-3,7-diol (4) are interpreted in this process. Heating juice for 15 min at 70 °C significantly increased the concentration of the furan linalool oxides, nerol oxide, hotrienol, and α-terpineol. Also 2,6,6-trimethyl-2-vinyltetrahydropyran, *cis*- and *trans*-5-isopropenyl-2-methyl-2-vinyltetrahydrofurans, 2,2-dimethyl-5-(1-methylpropenyl)tetrahydrofuran, myrcenol, and *cis*- and *trans*-ocimenols, all previously unrecognized as grape products, became prominent constituents of heated juice headspace composition. Under mild acid conditions at grape juice pH, polyols 1–4 rearranged nonenzymatically, to give all of the above volatile products.

Muscat grapes are the most aromatic of all the *Vitis vinifera* varieties, and several studies, reviewed by Terrier and Boidron (1972), have been made into the nature of the components giving rise to the aroma. Early in the course of these investigations it was recognized that a relationship existed between muscat character and the presence of monoterpenoid compounds in the fruit. Subsequent research has demonstrated a firm correlation between linalool and geraniol content and the degree of muscat character of the grapes (Wagner et al., 1977). A similar but less clearly defined relationship exists for other aromatic, nonmuscat varieties.

Those monoterpenes which have been positively identified as naturally present in muscat grapes are linalool, α-terpineol, nerol, geraniol, hotrienol, and the furan and pyran forms of the linalool oxides (Ribéreau-Gayon et al., 1975). While many of these compounds are fragrant and are doubtless important to the general aroma enhancement of the fruit, it is apparent that none is responsible for the specific muscat flavor. However, the presence of hotrienol and the linalool oxides suggests that the class of monoterpenoids with a higher oxidation level than that of linalool may contain compounds with characteristic muscat aromas. Accordingly, the genesis and progress of development of oxidized terpenes with berry ripening, as well as transformations of these compounds in the fruit, are of interest in the search for possible minor, but potent, aroma substances of the grape.

In addition to volatile monoterpenes, the existence of bound, nonvolatile terpenoids in muscat grapes has also been suggested (Cordonnier and Bayonove, 1974). These bound compounds release supplementary quantities of volatile terpenes under certain conditions and hence could be important in the development of muscat aroma. The chemistry and biochemistry of these proposed conjugated products remain largely unknown.

Recent investigations have been made in this laboratory into the nature of the nonvolatile monoterpenoids of "Muscat of Alexandria" grapes (Williams et al., 1980). During the course of this work four new hydroxylated linalool derivatives, 1, 2, 3, and 4 (see Scheme I), were isolated from the fruit. The fact that three members of this group have a higher oxidation level than that of linalool added further stimulus to our interest in these

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hydrophilic compounds as possible precursors of other volatile products of the grape.

This paper examines the thermal induction of volatile monoterpenes in juices of ripe muscat grapes and interprets the roles of terpene polyols 3,7-dimethylocta-1,5-diene-3,7-diol (1), 3,7-dimethylocta-1,7-diene-3,6-diol (2), 3,7-dimethyloct-1-ene-3,6,7-triol (3), and 3,7-dimethyloct-1-ene-3,7-diol (4) in the process.

EXPERIMENTAL SECTION

Grape Samples. Grapes were harvested from the Waite Agricultural Research Institute vineyard, Glen Osmond, South Australia. The *Vitis vinifera* L. varieties used for the study were "Muscat of Alexandria" (syn. "Muscat Gordo Blanco") and a red variant of "Muscat à Petits Grains" (syn. "Muscat de Frontignan"). At picking, the "Muscat of Alexandria" had a sugar level of 18.5 °brix. Immediately after harvesting, this fruit was held at -20 °C until required.

The "Muscat à Petits Grains" sample was prepared for headspace analysis directly after picking; it had a sugar level of 14.4 °brix.

Sample Preparation. Frozen "Muscat of Alexandria" berries were partially thawed and were homogenized in a Waring blender. The homogenate was warmed to room temperature, and after 1 h it was rehomogenized with solid NaCl to saturate it. After filtering off the skins and seeds through a muslin cloth, the NaCl-saturated juice was centrifuged at 10 000 rpm for 15 min. The pH of the juice was 3.2. The clarified juice was divided into two portions; one-half was heated on a steam bath at 70 °C and held at this for 15 min, then rapidly cooled back to room temperature. The second portion of juice was left untreated.

"Muscat à Petits Grains" samples were prepared in the same manner except that the NaCl-saturated total homogenate was not filtered or centrifuged.
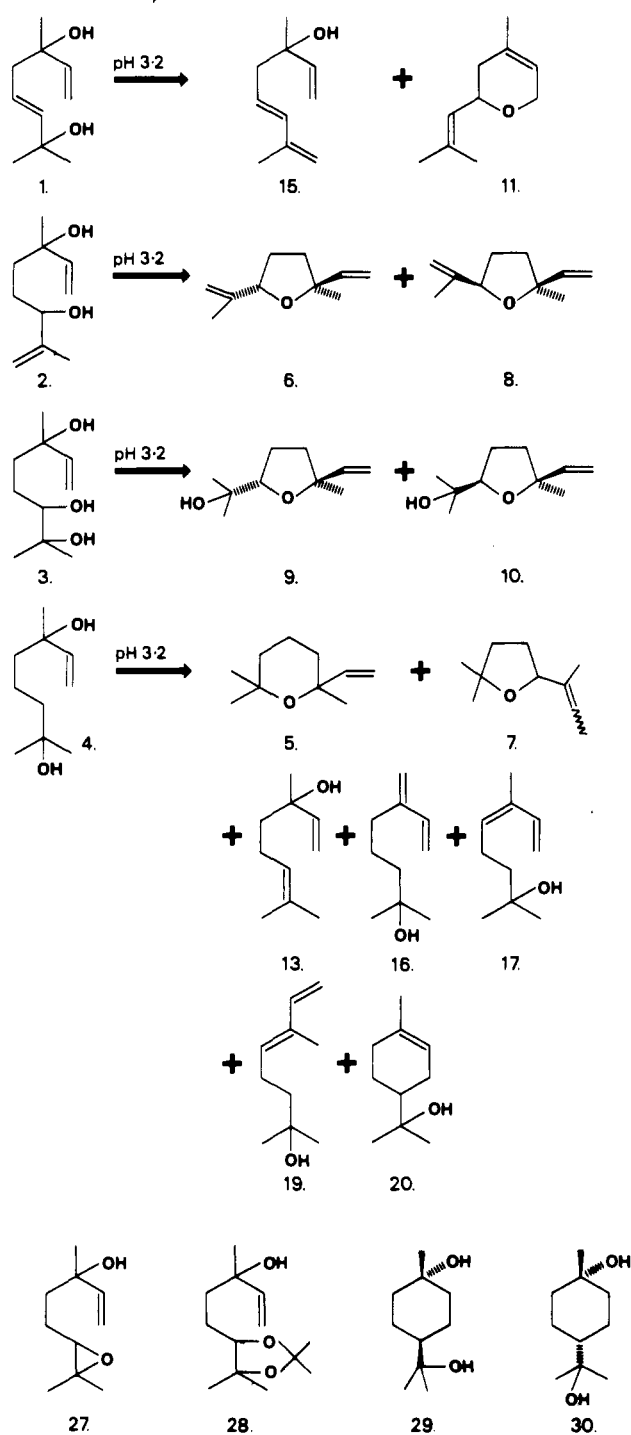
2-Phenethyl alcohol (1.0 mL of 5.54 mM solution in ethanol) was added to each sample prior to headspace extraction. Control experiments demonstrated that 2-phenethyl alcohol was not a significant headspace component of either natural or heated muscat grape juice.

Headspace Extraction. Headspace extraction into freon F11 was carried out according to the procedure of Rapp and Knipser (1978). Juice or homogenate samples of 400 mL were swept with N_2 at 50 mL/min for 24 h. At completion of the extraction period, the freon solution of the juice volatiles was concentrated to ca. 60 mL and stored at -20 °C prior to gas chromatography (GC).

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Scheme I. Acid Hydrolysis Products of Grape Polyols 1-4 (Structures 27-30 Show Other Compounds Referred to in the Text)

prepared as follows: To 400-mL portions of the NaCl-saturated buffer solution were added 3-5-mL aliquots of standard aqueous solutions of polyols 1, 3, and 4 to give a final concentration of 1 μg/mL. Dienediol 2 was diluted to 0.1 μg/mL in the pH 3.2 buffer. One solution of each of the polyols 1-4 was heated to 70 °C for 15 min and then rapidly cooled to room temperature. 2-Phenethyl alcohol internal standard was added and then each sample was headspace extracted as described for the juice. Blank headspace extractions were performed on the NaCl-saturated buffer solution.

Analysis of Polyols. The polyols 1-4 were extracted from both heated and unheated juice and then were partitioned as described by Williams et al. (1980). After addition of an external standard (benzyl alcohol, 2 mg), the partitioned extracts were diluted to 5 mL with $CHCl_3$ and analyzed by GC.

Portions (2 mL) of the standard $CHCl_3$ solutions above were evaporated with a stream of N_2, and the residue was treated with acetone (1 mL), 2,2-dimethoxypropane (0.5 mL), and anhydrous $CuSO_4$ (120 mg). After stirring each reaction mixture at room temperature for 1 h, a small portion was injected into the GC for analysis of the acetonide (28).

Gas Chromatography and Mass Spectrometry. Analytical GC was carried out on a Carbowax 20M SCOT column, and the conditions for this and GC-MS have been described (Williams et al., 1980).

Reference Compounds. Materials other than those mentioned below were obtained as commercial chemicals or as donated samples.

Oxides 5 and 7 (see Table I) were synthesized according to Strickler and Kovats (1966). Hotrienol (15) was prepared from dienediol 1 by large-scale acid-catalyzed rearrangement. Similarly, isomers 6 and 8 were synthesized from dienediol 2. Products 5, 6, 7, 8, and 15 were all isolated and purified by preparative GC, and their structures were confirmed by comparison of ¹H NMR, MS, and IR spectra with published data (Strickler and Kovats, 1966; Yoshida et al., 1969; Ohloff et al., 1964).

The ocimenols 17 and 19 were prepared by NaOCH₃-catalyzed deacetylation of *cis*- and *trans*-ocimenyl acetate. Product identity and stereochemistry were assigned on the basis of GC retention times (Ter Heide, 1976) and GC-MS (Sakaguchi et al., 1972).

Epoxide 27 was synthesized by dropwise addition of diastereoisomeric 6,7-epoxydihydrolinalyl acetate (1.0 g in 15 mL of dry ether) to a stirred suspension of LiAlH₄ (0.2 g) in dry ether (5 mL) over 30 min. The mixture was stirred at room temperature for 3 h and cooled in an ice bath, the LiAlH₄ complex was decomposed, and the product was worked up and distilled, affording 27 as a colorless oil (0.6 g), bp 87–90 °C (2 mm). The product had ¹H NMR spectral characteristics consistent with the epoxide structure and similar to those reported by Felix et al. (1963).

RESULTS AND DISCUSSION

Headspace Composition of Muscat Grape Juices. The terpenoids identified here in the headspace composition of "Muscat of Alexandria" grape juice are listed in Table I. Some of these compounds have been positively or tentatively identified in other muscat grape varieties (Terrier and Boidron, 1972; Ribéreau-Gayon et al., 1975).

Nerol oxide (11) and 4-terpinenol (14) have been recognized previously as wine volatiles (Schreier and Drawert, 1974), and the former compound has also been identified in extracts of some nonmuscat grape varieties (Schreier et al., 1976a). However, the anhydrofuran linalool oxides
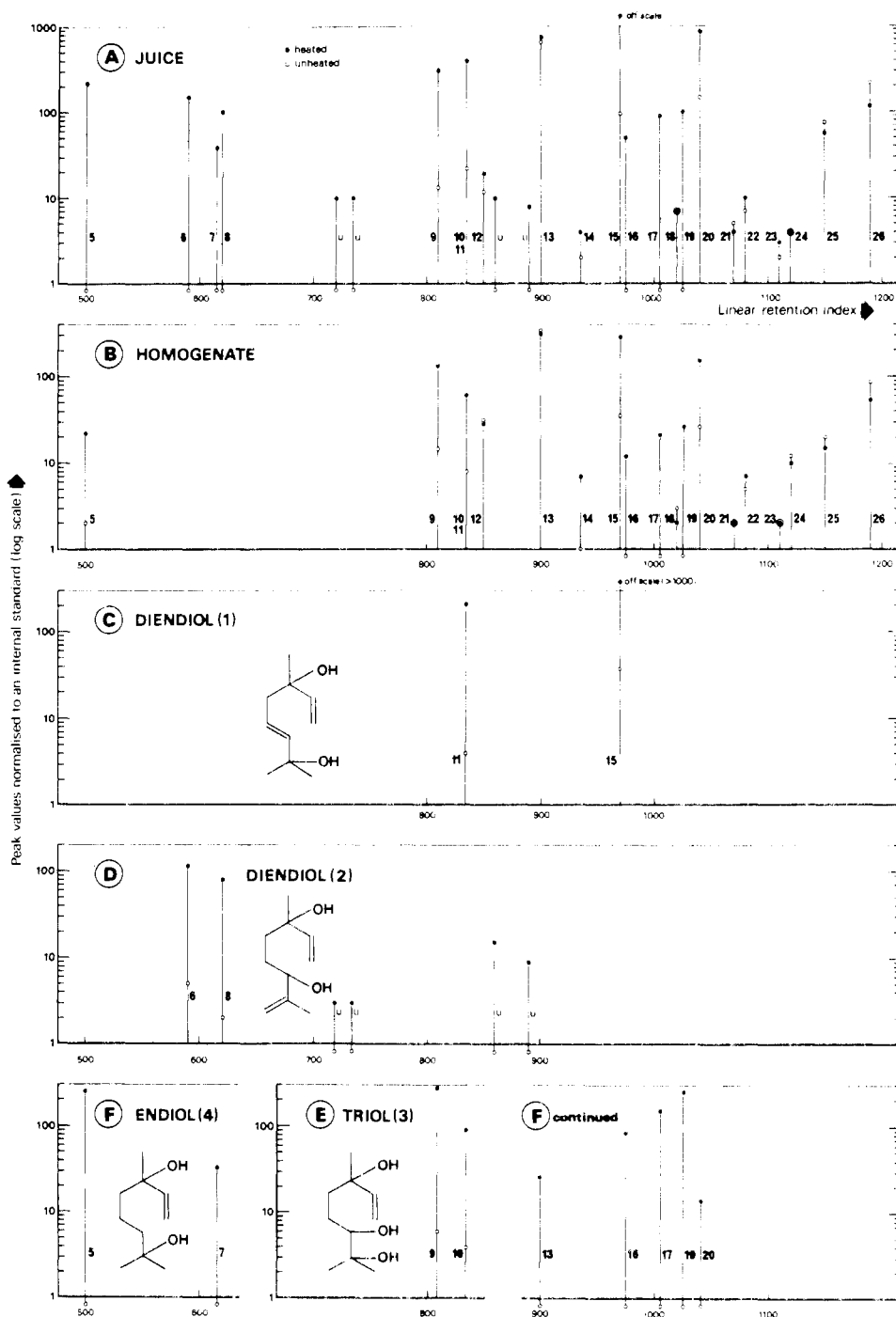
For analysis, 10 mL of the freon extract in a sharply tapered flask was concentrated by distillation of the solvent through a glass column (1 × 15 cm) of Fenske's helices (bath temperature 35 °C). The residue was then cooled and injected into the GC.

Model Solutions. Triol 3 and enediol 4 were prepared and purified as described (Williams et al., 1980). Dienediols 1 and 2 were donated samples; only diol 1 required purification and this was carried out according to the method of Kjøsen and Liaaen-Jensen (1973).

A potassium hydrogen tartrate (saturated)–tartaric acid (0.1 M) buffer solution was saturated with NaCl and then adjusted to pH 3.2 with KOH.

Two separate solutions of each of the polyols 1-4 were

Figure 1. Monoterpene components in headspace composition of heated and unheated samples: (A) "Muscat of Alexandria" grape juice, (B) "Muscat à Petits Grains" total homogenate, (C–F) model solutions of grape polyols 1–4, respectively. For peak assignments see Table I. Peaks labeled u are unknown.

6 and 8, the oxides 5 and 7, myrcenol (16), and the isomeric ocimenols 17 and 19 have not previously been identified as grape or wine products. These compounds were usually not observed in fresh grape juice but were significant constituents of heated juices.

Figures 1A and 1B respectively show the monoterpenoid components recognized in headspace compositions of clarified salt-saturated juice of "Muscat of Alexandria" and salt-saturated total homogenate of "Muscat à Petits Grains". Compound retention index (Van Den Dool and Kratz, 1963) and peak height normalized to that of an internal standard comprise the absissa and the ordinate. The log scale shows monoterpene peak heights in the juice or homogenate at room temperature (unheated) and after

heating at 70 °C for 15 min.

From Figure 1A it can be seen that heating the juice for a short period had a significant effect on the concentration of some of the monoterpenes. The changes can be summarized as follows: (a) The furan linalool oxides 9 and 10, nerol oxide (11), hotrienol (15), and α-terpineol (20) were induced to greatly enhanced concentrations over those originally found in the juice. (b) 2,6,6-Trimethyl-2-vinyltetrahydropyran (5), the isomeric anhydrofuran linalool oxides 6 and 8, the oxide 7, and myrcenol (16) together with the isomeric ocimenols 17 and 19 were induced from almost nonexistent levels in the fruit to become prominent constituents of the heated juice headspace. (c) The levels of citronellal (12), linalool (13), 4-terpinenol (14),

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Table I. Compounds Identified in the Headspace Composition of Muscat of Alexandria Juice

compd no.[a]	compd	evidence for assign-ment[b]	reference for id	as a grape prod
5	2,6,6-trimethyl-2-vinyl-tetrahydropyran	MS, A	c	
6	trans-5-isopropenyl-2-methyl-2-vinyltetra-hydrofuran (trans-anhydrofuranlinalool oxide)	MS, A	d	
7	2,2-dimethyl-5-(1-methyl-propenyl)tetrahydro-furan	A	c	
8	cis-5-isopropenyl-2-methyl-2-vinyltetra-hydrofuran (cis-anhy-drofuranlinalool oxide)	MS, A	d	
9	trans-α,α,5-trimethyl-5-vinyltetrahydrofur-furyl alcohol (trans-furanlinalool oxide)	MS, A	e	f
10	cis-α,α,5-trimethyl-5-vinyltetrahydrofur-furyl alcohol (cis-furanlinalool oxide)	MS, A	e	f
11	nerol oxide	MS, A	d	g
12	citronellal	A		
13	linalool	MS, A		f
14	4-terpinenol	A		g
15	hotrienol	MS, A		h
16	myrcenol	MS, A	i, j, k	
17	cis-ocimenol	MS, A	i, j, k	
18	neral	A		l
19	trans-ocimenol	MS, A	i, j, k	
20	α-terpineol	MS, A		f
21	geranial	A		l
22	trans-2,2,6-trimethyl-6-vinyltetrahydropyran-3-ol (trans-pyran-linalool oxide)	A	e	f
23	cis-2,2,6-trimethyl-6-vinyltetrahydropyran-3-ol (cis-pyranlinalool oxide)	A	e	f
24	citronellol	A		f
25	nerol	MS, A		f
26	geraniol	MS, A		f

[a] Also refers to peak numbers in Figure 1. [b] MS = mass spectrum of the component was identical with that of the reference compound when recorded under similar cond-itions; A = the peak was enhanced by the reference com-pound when cochromatographed on the Carbowax column. [c] Strickler and Kovats (1966). [d] Ohloff et al. (1964). [e] Felix et al. (1963). [f] Terrier and Boidron (1972). [g] Schreier and Drawert (1974). [h] Schreier et al. (1974). [i] Klein and Rojahn (1963). [j] Sakaguchi et al. (1972). [k] Ter Heide (1976). [l] Bayonove and Cordonnier (1971).

the isomeric citrals 18 and 21, the isomeric pyran linalool oxides 22 and 23, citronellol (24), nerol (25), and geraniol (26) were not affected to any significant extent by heating.

These heat-induced changes are typical of those seen in both clear juices and total homogenates of "Muscat of Alexandria" grapes, and the fact that each responds in a similar manner to heating demonstrates that the skins and pulp of the grape are not responsible for the changes seen. However, it has been found that total homogenates of grapes give less concentrated headspace compositions than clear juice for both heated and unheated samples.

Figure 1B shows the heat-induced changes in the headspace composition of a total homogenate of "Muscat à Petits Grains" grapes. These changes are similar to those

discussed above for "Muscat of Alexandria" and demon-strate that the phenomenon is not limited to a single muscat grape variety. Comparison of Figure 1A with Figure 1B shows that with the exception of the oxides 6, 8, and 7 and the four unknown components, all of the terpenoid compounds present in the "Muscat of Alexandria" juice were also present in the "Muscat à Petits Grains" homogenate. These seven components may have been present as minor constituents in the latter sample, but as they could not be unequivocally assigned, they have not been included in Figure 1B.

In an effort to rationalize the many compositional changes observed on heating juices and total homogenates, a study of the chemistry of polyols 1, 2, 3, and 4 was carried out.

Mild Acid Hydrolysis of the Terpene Polyols 1, 2, 3. and 4. Figures 1C–1F depict headspace compositions of model solutions of the four polyols 1, 2, 3, and 4 in NaCl-saturated tartrate buffer at pH 3.2. This was the pH of the juice studied in Figure 1A. The headspace compositions were obtained with and without heating the model solutions at 70 °C for 15 min and after normalizing the peak heights relative to that of the internal standard. They are presented in the same manner as those for the juice and homogenate in Figures 1A and 1B.

The reactions leading to the products shown in Figures 1C–1F are illustrated in Scheme I. Some of these reactions, as well as close analogues, have been investigated previ-ously. Klein and Rojahn (1963) demonstrated that acid hydrolysis of enediol 4 gave 2,6,6-trimethyl-2-vinyltetra-hydropyran (5), myrcenol (16), and the isomeric ocimenols 17 and 19 as major products. Ohloff et al. (1964), in an extensive study of monoterpene allyldiols, showed that acid hydrolysis of diols isomeric with 1 and 2 produced nerol oxide (11) and the anhydrofuran linalool oxides 6 and 8, respectively. The chemistry of triol 3 has not been pre-viously reported.

It can be seen from Figures 1C–1F that the four hy-droxylated linalool derivatives 1, 2, 3, and 4 rearrange smoothly under mild conditions of acid hydrolysis to give products, all of which were found in muscat grape juice. With the exception of the enediol 4, the polyols rearranged even at room temperature under the conditions of the headspace analysis. Significantly, the levels of oxidized terpenoids, hotrienol (15), and the isomeric furan linalool oxides 9 and 10 seen in the unheated juice can be ac-counted for in terms of a simple, nonenzymatic, acid-catalyzed rearrangement of the dienediol 1 and triol 3 which were present in the juice. When heated to 70 °C at pH 3.2, the four hydroxylated linalool derivatives re-arranged extensively to products seen in the heat-induced juice. With the exception of α-terpineol (20), all of the heat-induced terpenoids of the juice can be attributed to rearrangement products of the grape polyols 1, 2, 3, and 4.

The model solutions used for the experiments illustrated in Figures 1C–1F were made up with concentrations of polyols 1, 2, 3, and 4, approximating those of the juice. These solutions then gave rearrangement products in relative proportions and absolute abundance which mir-rored fairly faithfully the distribution of these compounds in the heated and unheated juice samples.

In the model hydrolysis of dienediol 1, the distribution of nerol oxide (11) and hotrienol (15) varied considerably with small changes in reaction conditions. At room tem-perature and pH 2.2, dienediol 1 gave ten times the yield of products 11 and 15 than that obtained at pH 3.2, with 15 predominant. However, after heating at 70 °C for 15

min, the ratio of nerol oxide (11) to hotrienol (15) altered from 1:10 at pH 3.2 to 10:1 at pH 2.2 although the extent of the reaction was about the same at both pH values. This implies that hotrienol (15) also rearranged to nerol oxide (11) under these conditions.

Dienediol 2 was the only polyol giving significant quantities of products which have not yet been identified. While the anhydrofuran linalool oxides 6 and 8 were the major products when dienediol 2 was heated at pH 3.2, four other, as yet unidentified, terpenoids were also produced. These four could also be seen in the heated juice headspace, and each peak enhanced in the gas chromatogram when coinjection of the heated dienediol 2 model solution headspace was made into the heated juice headspace.

The triol 3 rearranged readily at pH 3.2 to give exclusively the furan linalool oxides 9 and 10. Rather unexpectedly, no trace of the pyran linalool oxides 22 and 23 was obtained from this compound. Cyclization of the triol 3 under a variety of conditions always gave unequal proportions of the two furan linalool oxides 9 and 10, with the trans isomer 9 predominant. This is the ratio of these two isomers often seen in homogenates of muscat grapes (see Figure 1B). However, this proportion was sometimes apparently altered by the presence of nerol oxide (11) which cochromatographed with the *cis*-furan linalool oxide (10) on the Carbowax column.

The major products obtained from enediol 4 under conditions of mild acid hydrolysis were similar to those reported by Klein and Rojahn (1963) with the exceptions that the oxide 7 was observed in place of monoterpene hydrocarbons.

The heat-induced products of the juice, viz., oxides 5 and 7, myrcenol (16), and the isomeric ocimenols 17 and 19, could have arisen directly from linalool (13) as they share the same oxidation level. Earlier workers have indeed produced some of these compounds by strong acid-catalyzed rearrangement of linalool (13) (Strickler and Kovats, 1966). However, when linalool (13) was subjected to similar mild acid hydrolysis and headspace analysis as that used for enediol 4, a very different product distribution from that shown in Figure 1F was observed. This procedure returned much unreacted linalool (13) with α-terpineol (20) as the main rearrangement product; no oxides 5 and 7, myrcenol (16), or ocimenols 17 and 19 were found.

Felix et al. (1963) found that 6,7-epoxydihydrolinalool (27), with acid, afforded linalool oxides 9, 10, 22, and 23. The ratio of furanoid to pyranoid products was 10:1 and the distribution of the furanoid oxides 9 and 10 was nearly equal. In this work, epoxide 27 was cyclized under mild acid conditions in tartrate buffer at room temperature. The furanoid to pyranoid product ratios were then 2:1 and within each isomeric pair the cis to trans distributions remained about equal. This product distribution contrasts with that from the triol 3 and highlights a difference in cyclization mechanism operating for the compounds 3 and 27. The small and variable presence of pyran linalool oxides 22 and 23 observed in headspace compositions of sequential samples of maturing "Muscat of Alexandria" grapes suggests the presence in the fruit of a very small pool size of 6,7-epoxydihydrolinalool (27) or a derivative thereof. It has been postulated that the four polyols 1, 2, 3, and 4 could all come from 6,7-epoxydihydrolinalool (27) by a series of enzyme-mediated transformations (Williams et al., 1980). The feasibility of this proposal is demonstrated by the formation of small amounts of 1, 2, and 3 from the above reaction of epoxide 27 in tartrate buffer.

Influence of Heating on the Content of the Grape Terpene Polyols 1, 2, 3, and 4. Studies of the grape polyols 1, 2, 3, and 4 in "Muscat of Alexandria" have shown a wide variation in their relative proportions at different stages of fruit maturity. No attempt was made here to establish a rigorous analytical method for the polyols in grape juice, and accordingly no value for the absolute concentration of these four in the juice was available. However, analyses of polyol fractions from "Muscat of Alexandria" juices both before and after heating by use of parallel extraction and GC techniques allowed observation of the effect of heating on the diols. Similarly, conversion of triol 3 in the polyol fractions to the more volatile acetonide 28 (Williams et al., 1980) facilitated GC analysis and enabled an estimate of the relative proportion of the triol 3 to be assessed. Analyses for the unheated juice in Figure 1A showed the ratio of diols 1, 4, and 2 to be 35:7:1 and triol 3 was present in about the same proportion as enediol 4. During studies on these compounds, dienediol 1 was isolated from mature "Muscat of Alexandria" fruit at levels of approximately 2 ppm, and on these bases the model solutions of 1, 3, and 4 used for the study illustrated in Figures 1C, 1E, and 1F were made up at 1 ppm. The model solution of dienediol 2 was prepared at one-tenth the concentration of substrate as that used for the other three.

The polyol fraction isolated from the heated juice was found to have the concentrations of 1, 2, and 3 clearly depleted, with each reduced to less than half its original concentration in the juice. The effect of heating on the concentration of enediol 4 was less clearly visible and this diol was obviously not affected to the same extent as the more sensitive polyols 1, 2, and 3.

Another feature brought out by this GC analysis of the polyol fraction was the appearance of *cis*- and *trans*-1,8-terpins 29 and 30 in the heated juice. These two compounds were present as only trace constituents in the unheated juice, but were enhanced to significant concentrations by the heating process. This heat-induced formation of the 1,8-terpins 29 and 30 is still under investigation.

CONCLUSION

The experiments detailed here indicate that many of the volatile monoterpenoids of "Muscat of Alexandria" grapes arise by mild acid-catalyzed rearrangements of the polyols 1, 2, 3, and 4. Three of these hydroxylated linalool derivatives 1, 2, and 3 rearrange even at room temperature and juice pH to give the products shown in Scheme I at levels observed in juice. Heating induces extensive rearrangement of all four polyols. Thus the almost odorless compounds 1–4 are precursors of many grape volatiles with quite low odor threshold values.

Recognition of this phenomenon should give some insight into flavor changes taking place in grape juice during processing or handling. Therefore, pH adjustment of juices, heat-treatment for pasteurization purposes, or even extensive storage periods will induce changes in the concentration of important volatile terpenoid aroma components of the juice by the mechanisms discussed.

The findings have implications for the interpretation of data from analytical surveys of volatile monoterpenoids of grapes. Such analyses have been made to observe terpenoid development with berry maturation (Terrier et al., 1972) or for the assignment of varietal characteristics of grapes (Schreier et al., 1976b). In most cases, vigorous solvent extraction and lengthy workup procedures have been employed in these analyses. In view of the sensitivity of grape constituents 1–4, reproducibility of these workup procedures would be difficult to control. Thus it would be expected that variable and often spuriously high con-

centrations of constituents like nerol oxide (11), hotrienol (15), and the isomeric furan linalool oxides 9 and 10 would ensue. For these reasons very mild and high precision isolation techniques are recommended. For example, headspace sampling of juice will minimize, but may not necessarily totally eliminate, artefactual enhancements of volatile terpenoids in the juice. Nevertheless, headspace sampling will give a profile more representative of juice composition than that obtained by solvent extraction.

The results here could also help to explain earlier experimental observations in this field of research. Cordonnier and Bayonove (1974) reported the production of numerous new terpene substances when juice of "Muscat of Alexandria" was acid hydrolyzed. These authors rationalized their findings in terms of a degradation of derivatives of linalool and geraniol. It seems probable that rearrangement of the polyols 1–4 occurred with liberation of the products shown in Scheme I, thus making the results of the acid hydrolysis difficult to interpret.

Nevertheless, the enzymatic production of geraniol and nerol from "Muscat of Alexandria", as reported by Cordonnier and Bayonove (1974), and also the heat inducement of α-terpineol observed in this study, cannot be presently explained. Investigations into these latter aspects are being carried on.

Finally, recognition of the sensitivity of the hydroxylated linalool derivatives 1–4 may have relevance to other fruit products where terpene composition is influenced by processing conditions. The enhancement in concentration of hotrienol (15) and the isomeric furan linalool oxides 9 and 10 recently observed in peaches after canning (Souty and Reich, 1978) may be accounted for by thermal breakdown of dienediol 1 and triol 3 possibly present in the fruit.

ACKNOWLEDGMENTS

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Volatiles of Corn Tassels: Possible Corn Ear Worm Attractants

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The vacuum steam volatile oil of sweet corn tassels has been analyzed by capillary gas–liquid chromatography–mass spectrometry. A total of 35 components were identified in this volatile oil. Major components included ethyl and methyl phenylacetates, nonanal, heptanal, and decanal. The most unusual components are the ethyl and methyl phenylacetates (benzeneacetic acid ethyl and methyl esters).

The volatile compounds associated with the corn plant have been thought to be involved in the attraction of the corn ear worm (*Heliothis zea*) moth to the corn plant (McMillian and Wiseman, 1972). Volatile components of sweet corn silk, husk, and kernels have already been studied (Flath et al., 1978; Buttery et al., 1978; Buttery, 1979). The tassel is a characteristic part of the corn plant

and is thought (cf. Sparks, 1979) to also possibly play a role in the behavior of the corn ear worm moth. This paper reports the identification of volatile components of the sweet corn tassel.

EXPERIMENTAL SECTION

Materials. Corn tassels were cut (at the base of the tassel) from sweet corn plants (Golden Jubilee variety) grown on an experimental farm at Gilroy, CA. No insecticide or other sprays were used in the growing of the corn. The main study was carried out with tassels heavily loaded with pollen, but studies were also made on immature and

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