

## Iso-geraniol (3,7-dimethyl-3,6-octadien-1-ol): A novel monoterpene in *Vitis vinifera* L. cv. Muscat Roy

by

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### Isogeraniol (3,7-Dimethyl-3,6-octadien-1-ol): Ein neues Monoterpen bei der Sorte Muscat Roy (*Vitis vinifera* L.)

**Zusammenfassung:** Der Monoterpengehalt im Most der Neuzüchtung *Vitis vinifera* L. cv. Muscat Roy und ihrer Elternsorten Muscat Frontignan und Dabuki wurde untersucht. Das Monoterpenprofil von Muscat Roy ist dem von Muscat Frontignan sehr ähnlich. Trotzdem enthält es wesentlich höhere Konzentrationen an Geraniol und  $\alpha$ -Terpineol. Im Most von Muscat Roy wurde ein neuer Monoterpenalkohol, 3,7-Dimethyl-3,6-octadien-1-ol (Isogeraniol) identifiziert; im Most der Elternsorten ist jedoch kein Isogeraniol nachweisbar.

**Key words:** iso-geraniol, terpene, flavour, constituent, must, new breeding, variety of vine.

### Introduction

The selection of new varieties for better fruit flavor is one of the most difficult goals plant breeders ever aspired to. Since flavor compounds are secondary metabolites, their formation depends on many gene products and therefore the 'inheritance of flavor' is not well understood. The role of the monoterpenes in flavor of musts and wines has been reviewed (MARAIS 1983; RAPP *et al.* 1984; STRAUSS *et al.* 1986). It has been established that Muscat varieties contain more monoterpenes, such as linalool (RIBÉREAU-GAYON *et al.* 1975), as compared to Sauvignon blanc (AUGUSTYN *et al.* 1982) and Chardonnay (SIMPSON and MILLER 1984). Sauvignon blanc and Chardonnay contain lower concentrations of monoterpenes with different flavor compound profiles.

Muscat Roy (Muscat Frontignan  $\times$  Dabuki) is a new wine grape cultivar developed by Prof. SPIEGEL-ROY (Volcani Institute, Israel). The delicate Muscat flavor and lack of bitterness of its wine (unpublished data) encouraged us to study the monoterpene content of this promising cultivar.

We report the identification of iso-geraniol, a new monoterpene alcohol in grapes and the comparison of the monoterpene content between Muscat Roy and its parental cultivars.

### Materials and methods

#### Monoterpene extraction and identification

Grapes of Dabuki, Muscat Frontignan, and Muscat Roy (*Vitis vinifera* L.) were obtained from the Shfela region of Israel. The grapes were processed immediately after

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the harvest and 250 ml of musts were extracted by freon 11 according to RAPP *et al.* (1976). Freon samples were concentrated to 100  $\mu$ l and injected into either a Finnigen MAT 4600 GC-MS system or to a GC Varian-3700 equipped with 60 m 0.32 mm i.d. Supelcowax-10 column (Supelco). Helium served as carrier gas and GC temperature was programmed as follows: 5 min at 60 °C, then increased to 230 °C at 2 °C/min. Ionization energy was 70 eV. All MS identifications were confirmed by injecting authentic standards.

#### Iso-geraniol (3,7-dimethyl-3,6-octadien-1-ol) preparation

Iso-geraniol was prepared according to ARPINO *et al.* (1977), except sodium dichromate was substituted as the oxidizer. 15 ml of 16.8 mM sodium dichromate in sulfuric acid (2.5 g sodium dichromate were dissolved in 1.9 ml concentrated sulfuric acid, then 12.5 ml H<sub>2</sub>O were added) were added dropwise to 10 ml of 50 mM geraniol in ether in a round bottom flask at a rate of 1 ml/min. The mixture was stirred for 2 h at room temperature, at which time the organic phase was separated, washed twice with an equal volume of water, once with 5% sodium carbonate solution, and again with water. Dehydrated magnesium sulfate was added to the organic phase (to remove water trace) and filtered after 15 min. The ether was removed by vacuum. The oily residue was dissolved in freon 11 and subsequently injected into GC-MS.

### Results and discussion

In the course of our work we identified a new monoterpene alcohol in the grapes of Muscat Roy. The new monoterpene was identified as 3,7-dimethyl-3,6-octadien-1-ol, which is also known as iso-geraniol. The mass spectrum shown in Fig. 1 as well as the retention time of grape iso-geraniol (Fig. 2) were identical to the data of the synthetic compound. The partial oxidation of geraniol resulted in the formation of citral (geranial) as a major product and iso-geraniol as a minor constituent (Fig. 2, peaks no. 1 and 2, respectively), coinciding with the results of ARPINO *et al.* (1977). The concentration of iso-geraniol in the must was 50  $\mu$ g/l (Table). Iso-geraniol was previously identified in the flowers of the small evergreen tree Zinchoge (*Daphne odora* THUNB.) by WATANABE *et al.* (1982) and in the essential oil of Petitgrain Eureka lemon fruit by BAALIOUAMER *et al.* (1985). Since no sensing threshold value for iso-geraniol is available, its effect on the flavor of Muscat Roy remains in question. However, the fact that no one has ever reported its presence in grapes led us to examine the monoterpene content of the parental cultivars of Muscat Roy (Muscat Frontignan and Dabuki). Both cultivars are *Vitis vinifera* L., the latter cultivar is a local white table grape. The table summarizes the GC-MS must data of the three cultivars. As expected, Muscat Frontignan contains more monoterpenes, such as linalool and citronellol, compared with Dabuki (a non-muscat cultivar). Muscat Roy shows a profile similar to Muscat Frontignan regarding most monoterpenes, thus explaining its Muscat flavor. However, iso-geraniol was found only in Muscat Roy. It seems odd to find in a cultivar a compound that is undetectable in its parental cultivars. The relatively high concentration of  $\alpha$ -terpineol in Dabuki and Muscat Roy has very little contribution to the flavor due to its high sensing threshold (MARAIS 1983), but is indicative of higher oxidative conditions in both cultivars. One may speculate that Dabuki inherited oxygenase and isomerase genes resulting in monoterpenes of a high oxidative state. In such biochemical conditions when monoterpenes are present in high concentrations (inherited by Muscat Frontignan), a new monoterpene, such as iso-geraniol, could be formed.

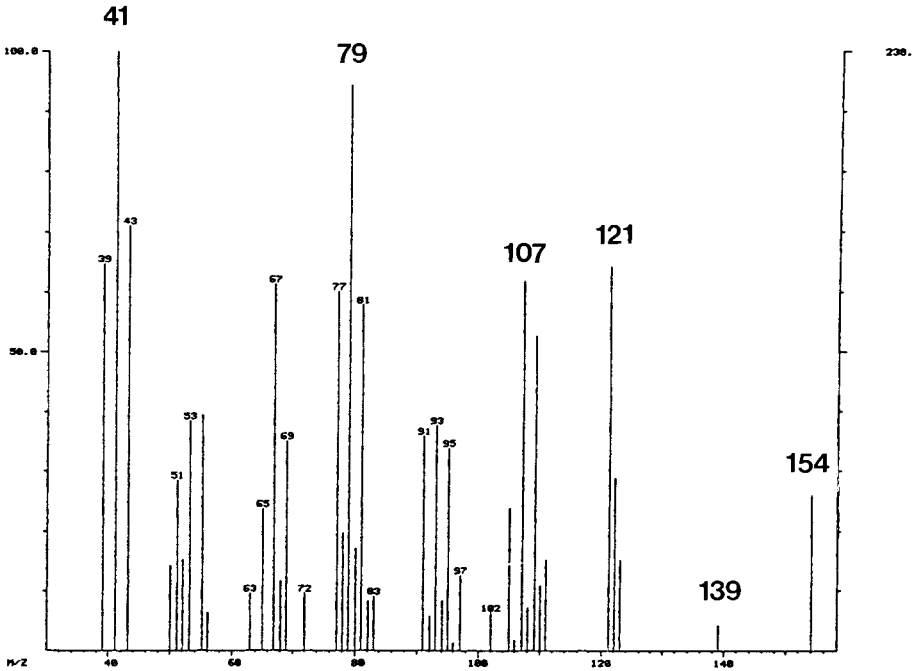


Fig. 1: Mass spectrum of iso-geraniol (3,7-dimethyl-3,6-octadien-1-ol).  
 Massenspektrum von Isogeraniol (3,7-Dimethyl-3,6-octadien-1-ol).

The monoterpene content of Muscat Frontignan, Dabuki and their progeny Muscat Roy  
 Monoterpengehalt von Muscat Frontignan, Dabuki und ihrem Abkömmling Muscat Roy

Monoterpene ( $\mu\text{g/l}$ )	Muscat Frontignan	Dabuki	Muscat Roy
cis-furan-linalooloxide	20	20	30
trans-furan-linalooloxide	30	15	15
linalool	210	20	350
$\alpha$ -terpineol	20	200	180
cis-pyran-linalooloxide	190	50	230
trans-pyran-linalooloxide	5	5	5
citronellol	120	30	110
nerol	40	5	60
iso-geraniol	—	—	50
geraniol	50	20	150

In conclusion, prediction of the flavor of a given cultivar by evaluating its parental cultivars is presently unreliable. The mechanism by which various monoterpenes are inherited is not fully understood and when breeding for flavor compounds a high rate of diversity is to be expected.

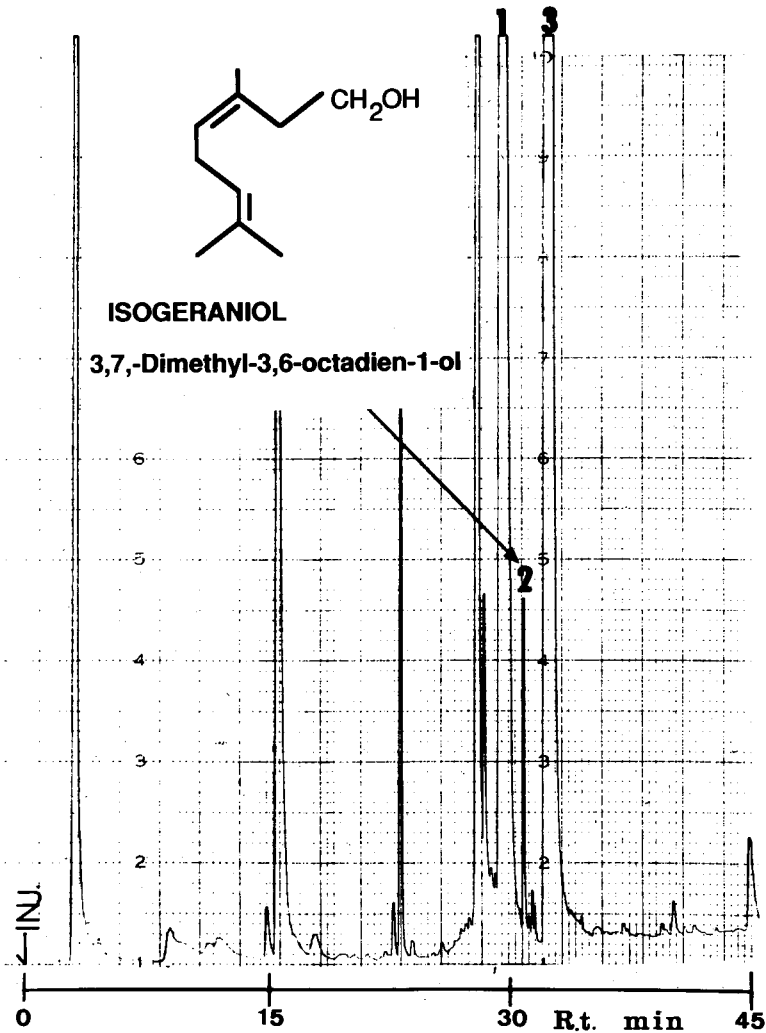


Fig. 2: GC analysis of geraniol that was partially oxidized with sodium dichromate. 1 = geranial (citral), 2 = iso-geraniol (3,7-dimethyl-3,6-octadien-1-ol), 3 = geraniol.

GC-Analyse von mit Natriumdichromat partiell oxidiertem Geraniol. 1 = Geranial (Citral), 2 = Iso-geraniol (3,7-Dimethyl-3,6-octadien-1-ol), 3 = Geraniol.

### Summary

The must monoterpene content of the new *Vitis vinifera* L. cultivar Muscat Roy and its parental cultivars, Muscat Frontignan and Dabuki, was studied. The monoterpene profile of cv. Muscat Roy is very similar to that of Muscat Frontignan. However, it contains significantly higher concentrations of geraniol and  $\alpha$ -terpineol. A new monoterpene alcohol, 3,7-dimethyl-3,6-octadien-1-ol (iso-geraniol), was identified in the must of Muscat Roy, but not in the musts of its parental cultivars.

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