Volatile amines in *Vitis vinifera* varieties and changes during maturation

by

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**Zusammenfassung.** — Bei den *Vitis-vinifera*-Sorten Cabernet Sauvignon und Chenin blanc wurden die Konzentrationsänderungen der flüchtigen Amine vom Weichwerden der Beeren bis zur Beerenreife in wöchentlichen Intervallen bestimmt. Diese Veränderungen wiesen bei beiden Sorten grundsätzlich die gleiche Tendenz auf. Zu Beginn der Beerenreife waren die Methylamin- und 2-Phenäthylaminkonzentrationen hoch; während der Reife fielen sie auf erheblich niedrigere Werte ab. Die Äthylaminkonzentration stieg beträchtlich an. Dimethylamin und Isoamylamin zeigten keine klare Tendenz. Die Diäthylkonzentration war bei Cabernet Sauvignon in der Mitte der Reifeperiode am höchsten, bei Chenin blanc dagegen über den ganzen Untersuchungszeitraum recht konstant. Bei der Beerenreife lagen im nichtgepreßten Most von Cabernet Sauvignon, Chenin blanc, Weißem Riesling und Pinot noir folgende Aminkonzentrationen (in µg/l) vor: Methylamin — 500, 180, 850 und 145; Dimethylamin — 45, 10, 25, 35; Äthylamin — 610, 150, 1900, 4900; Diäthylamin — 30, 25, <1, 30; Isoamylamin — 2, 5, 700, 160; 2-Phenäthylamin — 4, <1, 200, 25; 2-Methyl-1-butylamin (α-Amylamin) — <1, <1, <1, 3; n-Propylamin — <1, <1 (für Riesling und Pinot noir nicht bestimmt).

**Introduction**

Very little work has been done in amine estimations in wines and none, to our knowledge, has been reported for grapes. Several authors (3, 9) reported in beer that amines are not formed during fermentation, but come from malt, hops, etc. In wines there is no such study with reference to grapes.

According to SMITH (12) the lower aliphatic monoamines are widely distributed in the plant kingdom. They are often produced in flowers at anthesis or by fruiting bodies of fungi. Insects which carry pollen or spores are attracted by the smell of these amines, which may simulate rotting meat. In the Araceae, several aliphatic and aromatic amines are produced as part of a complex mechanism to attract flies which effect pollination.

Among the plants already studied for the presence of volatile amines, no reference is made by SMITH (12) to grapes of *Vitis* spp. In the present study, amine content of four cultivars of grape (*V. vinifera*) var. Cabernet Sauvignon, Chenin blanc, White Riesling and Pinot noir were examined at maturity, and changes occurring during the maturation of the first two varieties were also monitored.

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Materials and methods

Two V. vinifera varieties, Chenin blanc and Cabernet Sauvignon (both from University of California vineyards at Davis), were harvested weekly from early July till the 1st week of October, 1980. Two other V. vinifera varieties (Pinot noir and White Riesling) were selected at full maturity for analysis.

About 20—24 pounds (9—11 kg) of grapes were stemmed, then crushed in a small electrical screw press at standard conditions. The juice (free of skins) was allowed to settle at 0 °C. Only the clean, particle-free juice was used for analysis. One exception was the Pinot noir sample where the whole crushed grapes, juice and seeds were used for analysis.

The extraction method, derivation and GC method for qualitative analysis were those of DAUDT and OUGH (2). Recovery, standard deviation of measurements and retention times of the TFA derivatives were given. Variations from that report for these grape juice measurements were: 1. The amount of TFA was increased (because of large amounts of ammonia in grapes) to 10—12 ml, first as a 6 ml increment, than as 2 or 3 ml increments; 2. 10—15 ml of 8 % sodium bicarbonate solution were added to neutralize the great amount of acid formed and then dry sodium bicarbonate added until the solutions were completely neutralized.

Fig. 1: Ethylamine changes during grape maturation with two varieties of V. vinifera. Starting date was 18 July, 1980, represented by 1 on the harvest scale.

The trifluoroacetamides were analyzed by GC with capillary column (25M, fused silica, 0.20 mm I.D., coated with Carbowax 20M) separation and N/P detector determination. Three internal standards were used for the quantification (7).

The sample amines were verified by comparing the retention times and mass spectra on two fused silica capillary columns (Carbowax 20M and SE-54) to those of known synthesized amine TFA derivatives (8).

Results and Discussion

There is a great variation in the amount of amines with degree of maturity (the ripening period from the time the berries reach full size until the sugar accumulation reaches the desired level). Ethylamine (Fig. 1) increased slowly during maturation of Chenin blanc and Cabernet Sauvignon. In the latter variety, however, ethylamine increased and then dropped in the 9th week, remaining at that level for 1 week and increasing towards the end of maturation. Free-run juice of Cabernet Sauvignon was higher in this amine, at maturation, then in the Chenin blanc sample.

For Chenin blanc the methylamine was present in high amounts at the start of the picking scheme. Although methylamine increased in the 4th week, dropping between

Fig. 2. Methylamine changes during grape maturation for two varieties of V. vinifera. Starting date was 18 July 1980, represented by 1 on the harvest scale.

Maturity levels and volatile amines determined during and at the end of the maturation period in four *V. vinifera* vars.

Reifezustand sowie Konzentration der flüchtigen Amine während und am Ende der Reifeperiode bei vier *V. vinifera*-Sorten

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\(^1\) 2-Methyl-1-butylamine. — \(^2\) Not detected. — \(^3\) In this case the whole grapes were destemmed then crushed and the skins, juice and seeds all distilled. —

\(^4\) Not measured.
Volatile amines and changes during maturation

the 1st and 2nd week of harvest, it never attained the high levels of the 1st week. The
shape of the methylamine curves for both varieties, with the exception of the first three
samples is very similar. The extreme variations in both figures may be partially due to
sampling or analytical variation, or possibly changes in pool concentrations of the
amines in the grapes. From the table, it can be seen that the concentration of the other
amines also varied during maturation. This non-uniform concentration might be tenta-
tively explained by a reaction that may happen between an amine and an amino acid
with subsequent amide formation. For example, Suzuki (13) and Takeo (14) showed
that 4-glutamylethylamide (theanine) and 4-glutamylmethylamide were formed in the
roots of the tea plant by condensation of ethylamine or methylamine, respectively with
 glutamic acid.

Two other V. vinifera varieties measured at maturity were White Riesling and
Pinot noir. The table also lists the amine concentration found for these juice samples.

In the grapes, the amines are probably either formed by the decarboxylation of the
respective amino acid as in some plants (1) or by aldehyde amination through a trans-
aminase enzyme system as in other plants (4). In higher plants, Hartmann et al. (5, 6)
and Preussier (10) reported that, although some similar amines are known to be pro-
duced by amino acid decarboxylation, aldehyde amination appears to be a more com-
mon biosynthetic pathway. The amounts of these and other amines found in the raw
material will vary with the variety of the grapes. As with beer (3, 9), the amines found
in wine are present in the raw product before fermentation. Comparably, barley, malt
and hop varieties used in brewing also greatly determine the kind of amine and gen-
eral concentration in beer.

Summary

Changes in the volatile amines of Vitis vinifera var. Cabernet Sauvignon and var.
Chenin blanc during maturation were measured at weekly intervals from veraison to
maturity. The amine concentration changes during maturation for both varieties fol-
lowed the same general trends. Methylamine and 2-phenethylamine were high early in
the season and dropped to much lower levels during maturation. Ethylamine concen-
tration showed substantial increases. The dimethylamine and isoamylamine showed
no significant trends in concentration during the sampling period. The diethylamine
concentration increased midseason for Cabernet Sauvignon samples and then
decreased, but remained fairly constant for Chenin blanc samples. At maturity, free-
run juice of Cabernet Sauvignon, Chenin blanc, White Riesling and Pinot noir had 500,
180, 850, and 145 µg/l of methylamine, 45, 10, 25 and 35 µg/l of dimethylamine, 610, 150,
1900 and 4900 µg/l of ethylamine, 30, 25, < 1 and 30 µg/l of diethylamine, 2, 5, 700 and
160 µg/l of isoamylamine, 4, < 1, 200 and 25 µg/l of 2-phenethylamine, < 1, < 1, < 1, and
3 µg/l of 2-methyl-1-butylamine (α-amyl) and < 1, < 1 µg/l n-propylamine (Cabernet
Sauvignon and Chenin blanc only), respectively.

Literature cited

   of ethylamine. Phytochemistry 9, 537—540.


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