CHAPTER 1

Carbonic Maceration Wines: Characteristics and Winemaking Process

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Contents

Abstract

Invented by Michel Flanzy in 1934, carbonic maceration involves placing the intact grape clusters into a closed tank with a carbon dioxide-rich atmosphere. The berries subsequently undergo an intracellular fermentation without yeast intervention. Complex changes occur during this process which entail the transformation

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of a small amount of sugar into alcohol (1.5–2% alcohol), the reduction of malic acid content by about half, and the generation of secondary products.

Compared with wines produced by conventional techniques, carbonic maceration produces wines of distinctive character of superior quality possessing a harmonious balance. It can be used to generate a wide range of wines (red as well as rosé), to be drunk young or aged.

The process is composed of four steps: vatting of intact berries, "maceration–fermentation," pumping off, and pressing, followed by a second fermentation phase. Exchanges and interactions occur between grape berries, the gaseous atmosphere, and the must present at the bottom of the tank during the first step of the carbonic maceration winemaking process. Yeast fermentation starts at this stage, in the liquid phase, and continues throughout the second step as well, with the malolactic fermentation.

The specific conditions required for a good handling of carbonic maceration are presented.

I. INTRODUCTION

Winemaking by carbonic maceration (CM) is a process exploiting the adaptability of intact grape berries to an oxygen-deprived medium enriched with carbon dioxide (CO_2). This adaptation is reflected almost instantly inside each berry by the transition from a respiratory to fermentative anaerobic metabolism (AM).

The CM winemaking process is different from all other processes due to the role played by berry fermentation. Grape berries, being living entities, can act as agents of their own transformation, before any action of exogenous microorganisms. For this, though, the anatomic integrity of the berries must be preserved as much as possible. In this, CM also differs from other technologies in that the harvesting mechanism is a crucial aspect in the process, where rough handling must be avoided. CM may be used not only in the production of red wines and young wines but also rosé wines, fortified, and sparkling wines.

II. HISTORICAL DEVELOPMENT

In the 1930s, the French scientist Michel Flanzy (1902–1992) performed an experiment concerning the preservation of dessert grapes in an atmosphere limited in oxygen content. The first experiments involved the immersion of grapes in a carbon dioxide-rich atmosphere. They were performed in a cellar of the Narbonne district (France) in 1934. Although a partial failure in preserving the fruit, they proved interesting. The grapes, when vinified, produced qualitatively distinctive wines. It was then that Flanzy imagined using the capacity of the self-transformation of the grape berry. When compared organoleptically with conventionally produced (CP) wines, using the same varieties, wines resulting from this new process were considered original and of superior quality.

These results, presented to the French Academy of Agriculture (Flanzy, 1935), intrigued the assembly and triggered many comments. The members of the assembly, while recognizing the originality of the process, remained reserved as to its significance, stating: ''. . .it is a true revolution in the winemaking world you have initiated. You may be right. . .''; ''. . .it is a totally new method in opposition with those followed in the Mediterranean region and elsewhere.'' In addition, misunderstanding and winemaker skepticism generated for important obstacles to the diffusion of these new ideas.

In response to academic and professional skepticism, Flanzy extended his trials. He was supported in his views by Swiss researchers (Gallay and Vuichoud, 1938) who confirmed his results. Support was also obtained in the views of Pasteur. Sixty years earlier, Pasteur had expounded the hypothesis, without verifying it, of the possible enologic interest of the grape immersion in carbon dioxide. Pasteur urged winegrowers ''. . . to find some new application that can be useful, commercially speaking'' (Pasteur, 1872). The term ''carbonic maceration'' itself was first used about 1940.

In the 1960s, Michel Flanzy created a working group called ''Carbonic Maceration.'' Under his leadership, a series of experiments were conducted both on the biological phenomena occurring during the process and on mastering the technique. The results, together with those of other studies performed in Spain, Italy, and Romania, were presented during the International Days (INRA Montfavet-Avignon, 1971), and published in 1973 and 1987 in two books entitled ''The winemaking by Carbonic Maceration'' (Flanzy *et al*., 1987). An update overview was published in 1998 (Flanzy, 1998).

Research in France continued until 2001 (Flanzy *et al*., 2001), focusing on the underlying mechanisms of the grape-berry AM, with its impact on fruit ripening, and on the comprehensive exploitation of this winemaking process.

III. DISTINCTIVE SENSORY CHARACTERISTICS

When tasted, wines resulting from CM are often characterized by their aromatic richness, softness, and harmonious balance. Density, dry extract, fixed acidity, and residual sugar contents are generally lower in CM wines than in conventionally produced (CP) wines (obtained from crushed grapes). Color depth and tannic sensation depend strongly on the temperature–time parameters of the first (carbonic maceration) winemaking step. During this step, for a given temperature, phenolic compound indexes of CP wines are generally higher than those of CM wines. These results can be, however, reversed by changing the duration of storage at a given temperature or by increasing exchanges between the solid and liquid phases during the process.

During aging and shelflife, parallel evolutions between CM and traditionally wines occur at the polyphenol and polysaccharide levels, where the contents of both decrease.

The aroma compounds that uniquely characterize CM wines have not been clearly identified to date (Dubois *et al.*, 1977; Versini and Tomasi, 1983; Dell'Oro and Di Stefano, 1991; Salinas *et al.*, 1996). Nonetheless, these compounds likely originate from two different processes. With some cultivars, such as Muscat and Shiraz, their varietal aspects are enhanced (Bitteur *et al.*, 1996). In the second instance, aromatic compounds formed during CM are dominant, especially with varieties producing aromatically neutral wines (e.g., Carignan). AM generates flavors of the CM type, starting from precursors involved in their biosynthesis. Moreover, intact berries that rise to the upper part of the tank, are enriched in aroma compounds generated by yeast fermentation at the bottom of the tank (Tesnière *et al.*, 1989; Fondville *et al.*, 1996). In addition, alcohol and C_6 aldehyde contents (which generate herbaceous flavors) are lower in juice produced by berries after AM than from controls.

Initially, the dominant aroma is generated by esters, such as isoamyl acetate and ethyl cinnamate. These are produced at the end of fermentation and possess floral and intense fruity notes typical of young wines. These features disappear within a few months, being replaced by other aromatic aspects typical of aged wines. As Charnay (1958) noted ''The floral or exotic bouquets, that developed so characteristically in their youth, disappear quickly, exposing a regional aspect, but significantly improved, much more delicate and richer in bouquet.'' For Chauvet (1971) ''what distinguishes the overall CM wine aroma is inherent to the harmonious articulation of joint components, whereas in classic wines, it appears discontinuous because of variations in the components' intensity.''

During the aging of CM wines, a sharp increase in volatile phenol content has sometimes been noted (Etiévant *et al.*, 1989). It is likely that this observation is due to an inappropriate handling and the result of contamination by *Brettanomyces* and various bacteria subsequent to alcoholic fermentation.

CM reduces the foxy and raspberry aromas of hybrid direct producers (Gallay and Vuichoud, 1938), Concord grapes (Fuleki, 1974), and *Muscadinia rotundifolia* cultivars (Carroll, 1986).

IV. ECONOMIC INTEREST AND IMPORTANCE OF CARBONIC MACERATION IN THE WORLD

The selective use of CM depends on the intentions and quality percepts of the producer. However, realizing its benefits depends on grape quality (appropriate ripening stage, state of health, etc.).

The applicability of CM to a wide range of styles, all starting from the same raw materials, increases its economic desirability. This also permits the producer to respond quickly to changing market demands. Moreover, it is applicable globally, in all wine-growing regions.

Traditionally, methods related to (but different from) CM have been and are still used in Beaujolais (France), Rioja (Spain), and Georgia. In Georgia, grape clusters are poured into large, earthen-ware vessels (*kvevri*), half-buried in the ground, and sealed with cork. In Rioja, the grape harvest was also poured in *vinaira* (lagares) made of various materials, usually stone. In these practices, there is no flushing out of the air with carbon dioxide. At present, wine growers more or less follow the CM protocol described in Section V.

After a period of rapid adoption in many regions in Europe, North and South America, Australia, and Japan (Flanzy *et al.*, 1987), many producers have abandoned CM or use it with only a fraction of the harvest. This relates primarily to the high costs associated with manual harvesting. Nonetheless, renewed interest in the use of CM has developed in regions such as in Rioja (2008), in Burgundy (2009), and in other prestigious appellations, such as in Riceys in Champagne (2008).

V. CARBONIC MACERATION WINEMAKING PROCESS

The CM winemaking technique can be divided into four steps (Fig. 1.1):

the vatting of intact, healthy, grape clusters in a tank whose atmosphere is already mainly composed of carbon dioxide (CO_2);
the ''maceration–fermentation'' step, where a changing proportion of the grapes are submerged either in a gaseous or in a liquid phase (the latter corresponding to the must generated by berries crushed during or subsequent to vatting);
the free escape or pumping of the juice and pressing of the grapes that respectively generate the slightly fermented juice and press-run juice; and
the second fermentation stage, during which yeast and malolactic fermentation occur (if the latter is desired).

After the completion of fermentation, racking, clarifying, and stabilization, the wine may be bottled (if early commercialization is desired), or

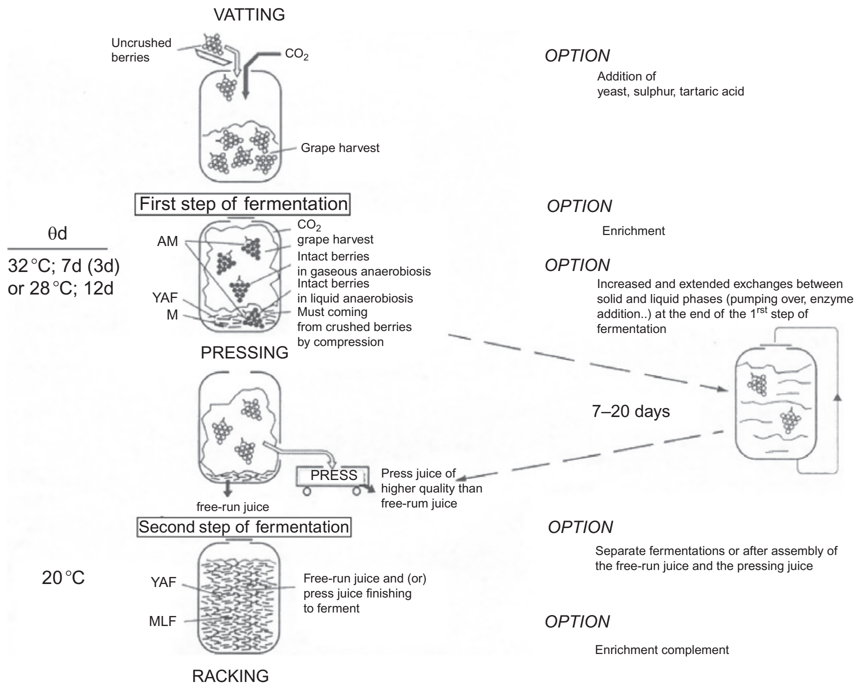

FIGURE 1.1 *Scheme of carbonic maceration winemaking.* AM, anaerobic metabolism of grape berries; YAF, yeast alcoholic fermentation; M, maceration; qd = pair: temperature (q°C); action duration (days). (Figure from "Œnologie—fondements scientifiques et techniques." Flanzy *et al*. collection "Sciences & Techniques Agroalimentaires." © Technique & Documentation, 1998, p. 780. Reproduced with the permission of the Editor.)

matured for several years (if aging is desired). The latter may or may not involve the use of oak barrels.

A. Grape harvesting, transportation, and vatting

The harvest must arrive at the cellar with the least possible physical damage. AM occurs only when the anatomical integrity of the berries is maintained. For example, berries detached from their pedicel under anaerobiosis synthesize less alcohol than do berries still attached to the stalk. This limits the use of mechanical harvesting to varieties with tough skins. In addition, must flowing out of damaged or crushed fruit is rapidly fermented by yeasts present on berry skin. Under these situations, AM development is very limited or nonexistent, depending on the degree to which the integrity of the berry is altered.

Correspondingly, from picking to vatting, handling of the fruit with the least physical alteration is required for maximal development of CM. For example, the pressure exerting by the grape mass on the fruit at the bottom of the vat increases considerably, when tank height is doubled. This increases the quantity of harvest immersed in the must from 15% to 25%.

At harvest, the grapes must be transferred with caution into a tank, previously filled up with CO_2. The gas may come from a carbon dioxide cylinder or from another tank containing fermenting must. After vatting, an exogenous supply of CO_2 must be provided until berry and yeast fermentation produces this gas in sufficient quantities. Initially, the berries absorb variable amounts of CO_2, depending on the harvest temperature, for example, 50% of the tank volume at 35 °C. This results in an infusion of outside air, delaying the onset of AM.

Tanks can be made of wood, concrete, fiberglass, metal, or synthetic resins. Short-sided tanks are preferred to limit the pressure exercised on the grape harvest. Several trapdoors are required for a better vatting. A directional gutter allows for improved grape distribution in the vat. Intact grapes could also be placed in polyethylene bags, closed and released at the vine, or placed in rooms with controlled temperature.

B. Maceration–fermentation step

In the tank, grape berries exist in three environments: intact berries immersed in a CO_2-rich atmosphere; berries crushed during loading or subsequently due to the accumulated weight of the grape mass—the must that flows out undergoes yeast fermentation; and intact fruit clusters immersed in the must released from crushed berries.

Three phenomena occur simultaneously during this step: AM of intact berries in the gaseous atmosphere and liberated juice—AM is highly altered when berries are submerged in fermenting juice; yeast fermentation of the must at the bottom of the tank (sometimes associated with the onset of malolactic fermentation); and exchanges through diffusion between intact or crushed berries and stalks with the gaseous atmosphere and the fermenting must.

The temperature at which this first step is performed is very important. In general, the best wine structure is obtained when this occurs at 30–32 °C. The duration of this step depends on both the type of the wine expected and the temperature of the grapes when harvested. The duration is inversely proportional to the temperature. For example, the duration at 32 °C will be between 5 and 8 days, where it will be between 15 and 20 days at 15 °C. When conducted at 15–20 °C, CM yields a wine with a very subtle aroma that only lasts a few months.

Consequently, it is recommended to search for the optimal temperature in relation to the type of wine desired. For instance, harvesting may be performed during the hottest part of the day or an external heat source may be placed in the vat. Although this last option is not easy to perform, because of heterogeneity between the liquid and solid phases, equipment and techniques exist to overcome the heat deficit: vats with double walls, bottoms permitting the circulation of a heated fluid, or short immersion of the harvest in warm must.

The duration of this phase also significantly influences the final characteristics of the wine. Thus, the wine maker must consider the temperature-duration interaction as both direct the development of the wine toward an early or late maturing style.

At present, there is increasing interest in the use of CM for the production of wines with long aging potential, involving maturation in oak. Thus, at the end of the first step, contact between the wine, pomace, and the lees may be extended from a few days to months. When the effects of AM are considered to be appropriate, relative to the nature of the product expected (e.g., color or tannin extraction) some wine producers use pumping over, combined with the addition of macerating enzymes. The latter facilitate is improved extraction of quality-related compounds.

Wine producers may also wish to adjust for harvest deficiencies or modify the development of the natural phenomena. This may involve acidification of the must or fermentation with selected yeasts. The amount added depends on the potential must volume (produced at the bottom of the tank after vatting plus must released from intact berries). Such adjustments can improve the protective action of SO_2, but may also limit yeast development. However, a compromise is often preferred to reduce its concentration at the must at the bottom of the tank.

C. Devatting, pressing

In CM, press-run juice produces a wine of higher organoleptic quality than that from free-run juice. Press-run juice is more concentrated in residual sugars and total potential alcohol. Berries not immersed in must absorb, through diffusion, some volatile compounds (alcohol, aromas, etc.) from the gaseous phase. This is itself enriched in vapors coming from the yeast fermentation at the bottom of the tank (Fig. 1.2). An example of these differences is provided in Table 1.1 where the concentration of alcohol and residual sugars obtained at pressing differ widely between the wine obtained from crushed grapes and two CM wines. The data are derived from an experiment with Carignan in 110 hl tanks.

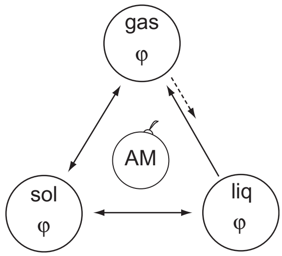

FIGURE 1.2 *Exchanges between different phases during the first step of fermentation of the carbonic maceration winemaking process*. AM, anaerobic metabolism of the grape berries; gas ϕ, gaseous phase (tank atmosphere); sol ϕ, solid phase (harvest: stems, intact or crushed berries); liq ϕ, liquid phase (must). Arrows with straight lines: efficient exchanges. Arrows with dotted lines: supposed exchanges. (Figure from "Œnologie—fondements scientifiques et techniques." Flanzy *et al*. collection "Sciences & Techniques Agroalimentaires." © Technique & Documentation, 1998, p. 783. Reproduced with the permission of the Editor.)

TABLE 1.1 Total potential alcohol

	CP			CM1			CM2		
	F	P	F + P	F	P	F + P	F	F + P	P
Produced alcohol	10.72	10.98		11.32	10.66		10.98	10.08	
Sugars (g l^{-1})	10.3	10.7		2.5	31.2		5.75	64.4	
Total potential alcohol	11.29	11.57	11.34	11.45	12.42	11.59	11.3	12.65	11.65

Carignan tanks (110 hl) of conventionally produced (CP) wines vinified with crushed grape harvest and carbonic maceration (CM) wines. After pressing: F, free-run juice, P, pressing juice; FP, assembly of F and P. Total potential alcohol = produced alcohol + alcohol corresponding to the residual sugars (André *et al*., 1967).

D. Second step of fermentation

Given the tendency of microorganisms to grow in the juice released during CM (Barre, 1969), it is essential to stop yeast fermentation before lactic acid bacteria induce a lactic *piqure*. There are ample residual sugars to favor such bacterial growth. Consequently, it is not always a good idea to mix CM press- and free-run juice. It is important to limit malolactic fermentation prior to pressing. If malolactic fermentation has commenced, it is necessary to vinify the free-run juice (low sugar content) separately from the press-run juice (rich in sugars).

In most cases, the second step proceeds very rapidly: 2–7 days for yeast fermentation and a few additional days for the malolactic fermentation. Sometimes, the two phenomena end simultaneously. This explains the remarkable ability of CM wines to be elaborated and drunk early. It is, however, a mistake to limit these CM wines to a single style.

Indeed, some wine makers and experimenters have introduced changes to the usual CM scheme to enhance its aging potential. For example, in a blind tasting (Flanzy, 1998), wine from Châteauneuf-du-Pape were still considered in excellent condition after 20 years.

Numerous refinements to the initial technique (Flanzy, 1935) have been proposed: extended maceration after fermentation has ended at the bottom of the tank; racking off the fermented free-run juice and replacing it with fresh must; *délestage* (a mild pumping over) after the initial CM phase, followed by additional maceration; and the use of rotary fermentation tanks (at low speeds) at the end of the second phase.

Trials performed on Shiraz for several years have allowed the comparison of wines produced under three winemaking protocols: CM for 8 days (C); CM for 8 days, followed by a 10-day period with a daily pumping over—to maintain contact between harvest and free-run juice (P); same protocol as in P, but with the addition of pectolytic enzymes, before the first pumping over (P) (Flanzy *et al*., 2001).

Tasting results of these wines after 16 and 53 months are presented in Fig. 1.3. The data illustrate changes in preference for E and P wines at the

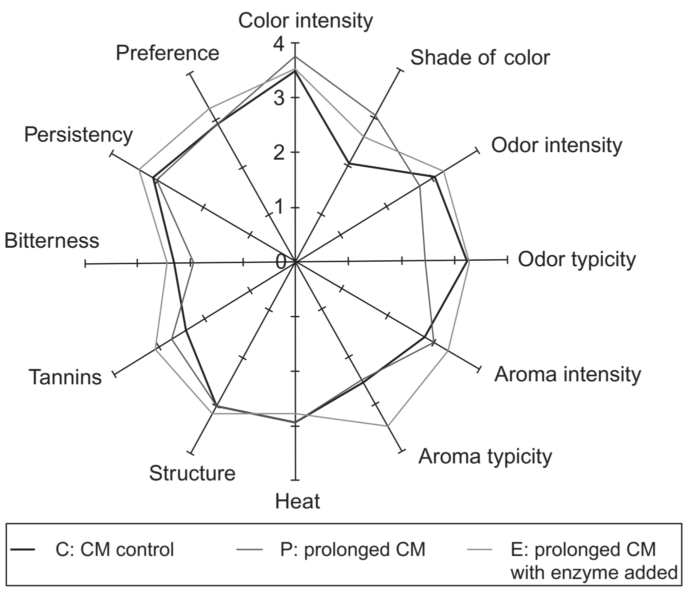

FIGURE 1.3 *Sensory profiles of three carbonic maceration (CM) wines from Shiraz in 1995, after 16 months.* (Figure from Flanzy *et al*., 2001. Reproduced with the permission of the Editor.)

second tasting. Similar preferences were found with the varieties Carignan, Grenache, and Mourvedre. C winemaking protocol (CM for 8 days) is preferred up to the 12–18 months, after which the other E and P protocols were considered more complete and complex.

E. Exchange by diffusion, fermentations

During the first step of CM, exchanges and interactions occur between the fruit, the gaseous atmosphere, and the must at the bottom of the tank (Fig. 1.2).

AM greatly modifies the composition of the basic medium (must coming from the berries progressively crushed during the first step). It likely stimulates and modifies yeast and bacterial metabolisms, probably affecting the organoleptic characteristics of the wine.

During the initial step of CM, yeasts develop in a medium that progressively increases in volume and changes in composition; this variation is due not only to microbial action but also to the continuous supply of juice modified by berry-cell fermentation.

Subsequent yeast and lactic bacteria metabolism in the press-run juice occurs in a medium rich in sugars and with a high potential for microbial growth (Barre, 1969). This helps explain the speed of the second fermentation phase, the early ''biologic stability'' of the wines, and the possible yeast and bacterial competition.

VI. SPECIFIC CHARACTERISTICS OF GRAPE BERRIES IN CARBONIC MACERATION: ANAEROBIC METABOLISM

The distinctive feature of CM is the exploitation of grape-cell AM. Intact berries quickly shift from oxidative to fermentative metabolism under anaerobic conditions (atmospheres with oxygen contents $<1\%$).

Under such conditions, AM is easily characterized by intracellular fermentation, with the production of small amounts of ethanol (1.5–2%); the accumulation of secondary by-products, such as glycerol and acetaldehyde; the evolution of organic acids; the catabolism of malic acid (without the generation of lactic acid but with the formation of ethanol and succinic acid); the absence of tartaric acid degradation; changes in organic nitrogen content (involving an increase in the amino acid content, especially in γ-aminobutyric acid combined with decreases in glutamic and aspartic acids); and the diffusion of phenolic, and of some aromatic compounds, from the skin to the pulp.

The activities of cytoplasmic enzymes, such as aspartase, glutamate, oxaloacetate, malic enzyme, and alcohol dehydrogenase (ADH) decrease at the onset of anaerobiosis, with occasional transient increases on the fourth day (at 35 °C) (Flanzy, 1998). On the contrary, the total malate dehydrogenase activity (cytoplasmic and mitochondrial) remains at a high level, even after 10 days.

The marked absorption of ambient CO_2 by berries (50% of their volume at 15 °C) is accompanied by the incorporation of a small proportion of the CO_2 by phosphoenolpyruvate (β-carboxylation) and by malic acid synthesis. Malic acid is a key molecule during AM since it is also catabolized to ethanol, and γ-aminobutyric and succinic acids.

A suggested sequence grape-cell AM is given in Fig. 1.4.

Tolerance of the fruit to anoxia is evidenced by the maintenance of a high energy charge (an index of the cell energy status), very close to that of berries in air for 4–7 days. In addition, mitochondria retain much of their ability to return to respiratory metabolism on exposure to air after

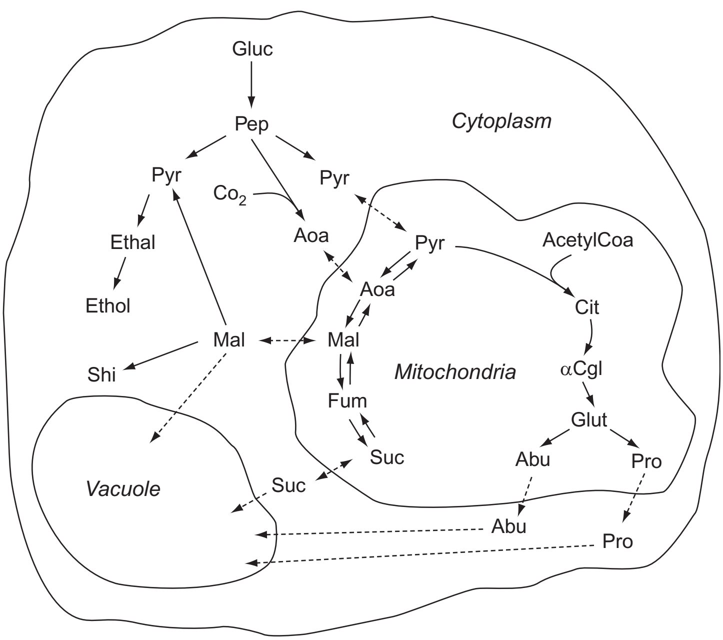

FIGURE 1.4 *Anaerobic metabolism (AM) of the cell of a grape berry*. Arrows with straight lines: likely pathways of the AM of the grape berries in hypoxia. Arrows with dotted lines: exchanges between cellular compartments. Abu, Aoa, αCgl, Cit, Fum, Glut, Mal, Pep, Pyr, Shi, Suc = acids: γ-aminobutyric, oxaloacetic, α-cetoglutaric, citric, fumaric, glutamic, malic, phosphoenolpyruvic, pyruvic, shikimic, succinic; Ethal, Ethol = acetaldehyde, ethanol; Gluc = glucose; Pro = proline. (Figure from "Œnologie—fondements scientifiques et techniques." Flanzy *et al*. collection "Sciences & Techniques Agroalimentaires." © Technique & Documentation, 1998, p. 566. Reproduced with the permission of the Editor.)

5 days of hypoxia. The adaptation to anaerobiosis is also observed in polypeptide synthesis, in the presence of proteins characteristics of hypoxic shock (Tesnière *et al*., 1993).

Hypotheses concerning the activation and termination of AM have been suggested. An in-depth study of the phenomenon has generated information on changes during the first stages of fruit development. In particular, characterization of the genes encoding alcohol dehydrogenase (ADH) (directly related to AM) was performed. ADH RNAs were induced as early as véraison (the onset of ripening), and expression continued throughout fruit ripening (Tesnière and Abbal, 2009). These data suggest that mature fruit are somehow ''prepared'' for a switch from aerobiosis to anaerobiosis.

VII. ORIGINALITY OF GRAPE-BERRY RIPENING

The ability of grape berries to cope with anaerobiosis and initiate AM is mainly related to the characteristics of grapevine (*Vitis vinifera*) alcohol dehydrogenase (VvADH). The enzyme transforms sugar into ethanol and CO_2 (similar to yeast ADH). What is remarkable is that VvADH activity (encoded by several grapevine genes, see Tesnière and Abbal, 2009) is quite high in ripe berries, where there is no apparent oxygen deficiency. Among these different ADH isoenzymes, VvADH2 is unique in being a ripening-related isogene particularly involved in this phenomenon. Berry integrity is pivotal to the activity of VvADH2.

Despite the action of VvADH, grape-cell fermentation generates no more than 2% ethanol. The reason for such a limitation is unknown, but one hypothesis suggests that, at this level, ethanol may disrupt cell membrane integrity, resulting in a loss of metabolic control due to the loss of essential cellular components (Flanzy, 1998).

Studies on VvADH activity in ripe grapes indicate that its activity is a normal aspect of fruit development. Its presence is detected only at the onset of ripening (véraison), increasing gradually thereafter. Thus, the ability of grapes to undergo AM is an inherent aspect of the grape-berry ripening. This point seems to be characteristic of fruits which belong to the class of the ''nonclimacteric'' fruit (Tesnière and Verriès, 2001).

VIII. CONCLUSIONS

CM imposes specific constraints: anatomic integrity of the berries and healthy fruit as well as special requirements for harvesting, transportation, and temperature control. It also requires a CO_2 saturated atmosphere at the beginning and throughout the first step of fermentation.

This winemaking process is applicable to a range of wine styles. In addition, its flexibility allows winemakers to adjust it to his/her particular needs and economical objectives.

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