The quantum-dimensional Periodic Table of Elements identified bio-energetic reverse oxidation. This new process is shown to also control wine fermentation

Revision of Wine-Fermentation Chemical Equations by Quantum Reverse Oxidation Correctly Identifies Wine Aging Process

SUMMARY: The conventional chemical formulas for the fermentation of grape sugars to alcohol are incompletely given. This can be corrected by supplying quantum-dimensional reverse oxidation to the formulas. Wine fermentation is similar to the bio-energetic conversion of sugars to carbon dioxide in living cells. Bio-energetic cellular conversion is a component of the animal/plant energy symbiosis revealed by quantum geometry[1] . Its application to wine fermentation is proved by the fact that fermentation also proceeds by a partial of the Krebs cycle ATP "burning" which supplies cell energy. However, the fermentation of sugar to alcohol requires much less oxygen than is consumed by cellular bio-energetic reverse oxidation. Only a half-molecule of oxygen is required by fermentation. This oxygen is supplied by a polyphenol oxidase converted to a proto-protein from which the yeast extracts needed amino acids. Since only one proto-protein is needed to oxidize two sugar molecules, excessive amounts will be remaindered in the wine as a sensory deficiency.

Wine Fermentation Chemical Equations[2]
(Revised by the Quantum-Dimensional Reverse Oxidation Model [3])

$C_6H_{12}O_6 = Dextrose$

$2CH_3 - CH_2 - OH = Alcohol$

$CO_2 = carbon\ dioxide$

$OH = Hydroxyl\ radical$

$H_2O = water$

QUANTUM - DIMENSIONAL FERMENTATION CHEMICAL EQUATION

$$C_6H_{12}O_6 + O* \xrightarrow{Reverse\ Oxidat.} (2CH_3 - CH_2 - OH) + (2CO_2) + (C - OH) + (H_2O) + (heat)$$

** From partial reduction of a polyphenol oxidizer*

Initial Krebs Cycle ATP Enzymic Burning of Dextrose by Yeast Cell (revised)[4]

$C_6H_{10}O_6P_2 = Dextrose\ 1{,}6\text{-}\ diphosphate$ (*product of ATP reverse oxidation*)

$$C_6H_{12}O_6 + P_2^* + O \xrightarrow{\text{reverse oxidation}} C_6H_{10}O_6P_2 + H_2O + heat$$

* *Provided by ATP (Adenosine triphosphate) from yeast cell*

The Oxygen Required by Yeast Fermentation is Supplied by a Polyphenol Oxidizer (PPO)

The must from broken grapes seldom, if ever, can hold free oxygen in solution. Free

[1] *Four Dimensional Atomic Structure.* L. Dawson, Paradigm Publishing , 2013. See *Tab 4*

[2] Quantum dimensional modification (from reverse oxidation discovery) of fermentation chemical equation presented in *"The Chemistry of Winemaking;"* Jason Mumm, p. 4.

[3] See *The Four Dimensional Atomic Structure;* "TAB 4'

[4] Modification of Mumm equation. Op. cit.

atmospheric oxygen is incorporated by polyphenol oxidases when the membrane separating juice-bearing grape pulp from grape skins is ruptured:

> *The enzymic oxidation of phenols, particularly in the presence of atmospheric oxygen and polyphenoloxidase (PPO), takes place in the early stages of processing and is well known to be a cause of browning in foodstuffs (Wang,1990). In the intact cells of fresh fruit or vegetable tissues, phenols located predominantly in the vacuole and oxidoreductases located in cytoplasm cannot meet due to different cell membrane systems, whereas enzymic browning will arise once the cells are bruised or wounded in air (Wang, 1990)*[5]

It is a known fact of winemaking that the must from crushed and pressed white grapes acquires a browning and that this browning intensifies at the later stages of pressing— for juice which has been under longer contact with the air before being extracted from the pulp. This browning of the grape juice disappears as the juice undergoes fermentation. Fermentation clears the wine of the brown discoloring.

As noted, the browning is caused by the further oxidation of PPOs which have been made available to the grape must by rupture of the grape skins. The distinction between phenols from grape skins (and seeds) and polyphenol oxidases (PPOs) is somewhat arbitrary since both are composed of hydroxyls (the "OH" radical) bound to "aromatic rings[6] ." These aromatic phenols give smell and taste characteristics to wine. Oxidation binds a second hydroxyl radical to the aromatic ring to produce a "polyphenol oxidases." PPOs share these bound hydroxyl radicals with the phenols which are tracked by winemakers during the winemaking process. The distinction between winemaking phenols and the chemist's PPOs is somewhat arbitrary. The main difference between a winemaker's "phenol" and a chemist's "PPO" is that the winemaking monophenol becomes a polyphenol with a second hydroxyl radical via oxidation.

Further, a spanish study compared winemaking phenolic content with PPOs. The study was conducted on two grape varieties which were followed from grape maturation through winemaking. It showed that the PPOs consistently tracked total phenols throughout the process[7] .

A Second Oxidation of the PPO Molecule Produces an "o-quinone" Oxidizer

A monophenol which is oxidized to produce a second bound hydroxyl radicals becomes a polyphenol oxidases "o-diphenol." When the PPO is oxidized a second time, it becomes an "o-quinone." An o-quinone is an oxidizer which can combines with amino acids to become a "proto-protein" and provide a browning of the grape must.

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[5] Food Chemistry 108 (2008) 1–13 *Review Mechanisms of oxidative browning of wine* Hua Li *, Anque Guo, Hua Wang College of Enology, Northwest A&F University, Yangling, Shaanxi 712100, PR China Received 5 June 2007; received in revised form 6 October 2007; accepted 22 October 2007

[6] An aromatic hydrocarbon or arene (or sometimes aryl hydrocarbon) is a hydrocarbon with alternating double and single bonds between carbon atoms forming rings. The term 'aromatic' was assigned before the physical mechanism determining aromaticity was discovered, and was derived from the fact that many of the compounds have a sweet scent. The configuration of six carbon atoms in aromatic compounds is known as a benzene ring, after the simplest possible such hydrocarbon, benzene. Aromatic hydrocarbons can be monocyclic (MAH) or polycyclic (PAH). SOURCE: *"Aromatic hydrocarbon"*; Wikipedia, the free encyclopedia

[7] *"Evolution of grape polyphenol oxidases activity and phenolic content during maturation and vinification;"* Valero, E., Sanchez-Ferrer, A., Varon, R., and Garcia-Carmona, F. . Vitis 28, 85-95(1989)

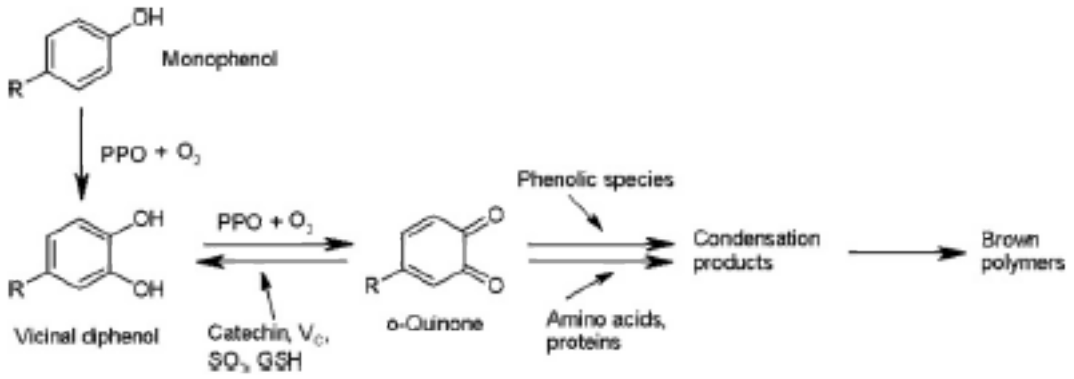

Fig. 1. Enzymic browning process in grape must.

"The produced quinones can also polymerize and condensate with many other compounds[8] (including phenolic and non-phenolic species), and finally forms brown pigments."

The yeast fermentation of grape must can easily break down the browning proto-proteins and cause them to revert to PPO o-quinone oxidizers (see illustration above). This is possible because the yeast needs access to the amino acids with which the PPO o-quinone has compounded. The amino-acid PPO compound is an unstable protein which obviously can provided the yeast cell with the needed alpha amino acids it requires for yeast cell division and to avoid a "stuck" fermentation:

"Some winemakers will, however, deliberately expose their white wine musts to oxygen, allowing oxidation of many of the phenolic compounds in what is called "oxidative juice handling." The must turns dark, but from then on the wine is handled reductively. The resulting white wine is actually longer-lived and more resistant to oxidation."[9]

We have seen that this deliberate darkening of the grape-must is the result of the a PPO o-quinone oxidation reaction with an amino acid to produce a browning "proto-protein" pigment. The browning is reversed during the fermentation of the grape-must to gain access to the original PPO o-quinone oxidizer. An oxygen source is required by the yeast to reverse oxidize or to "phosphatase burn" the dextrose molecule into alcohol and carbon dioxide residuals. This reversal of the browning requires that the fermenting yeast extract the amino acid from the compound to reveal the original PPO o-quinone oxidizer (see illustration above). The compounded amino acid is obviously a form of the alpha amino acid[10] which the yeast requires.

The Rule Fermenter and Control of Phenolic Content during Fermentation in the Presence of Grape Skins

A new system for the fermentation of grape-must in the presence of skins was invented by engineer David Rule. The new "pump under" system keeps the grape-must in contact with the skins more consistently than the conventional "punch down" system which requires that a cap of compacted skins— which rises out of the grape must— be re-submerged by "punching" the cap down.

Matched pair tests between the Rule "pump under" fermenter and the standard "punch down" red fermentation method were conducted over three fermentation seasons. Four

[8] "*Review Mechanisms of oxidative browning of wine .*" Op. cit.

[9] *Wine Flaws: Oxidation* , Jamie Goode; Sommelier Journal, p.p. (47-51) June 2008

[10] An "alpha amino acid" is one in which the amine is in the alpha position of the molecule.

vintages from the same varieties and from the same vineyards were comparatively fermented in the Rule fermenter and by the punch down method:

> *"A series of comparative fermentations between the pump-under fermenter developed by Pasco Poly, Inc. and the conventional punchdown method has revealed that the pump under fermenter significantly increases skin-born polyphenols in red wines.*
>
> *The tests were conducted over three years and over three different climates and over two different varieties of grape. The same comparative results were indicated in all cases. The results were not restricted by climate, season or even grape variety. Skin-born polyphenols increased by an average of 47% across the board [for the pump under vs. punch down]. The lowest increase in skin-born polyphenols was recorded at 33% and it occurred in the test of the grape with the highest number of natural polyphenols in the study."*[11]

Using a "t" test for matched pairs, the Rule advantage in phenolic content was well below the scientific threshold of the "0.01" probability level[12]. The explanation of the greater Rule phenolic content is the fact that the Rule fermenter kept the grape skins in constant contact with the fermenting grape-must while the "punch down" skin-cap often floated above the must and had to be reintroduced by "punch down." A greater number of phenols were introduced by greater juice-skin contact.

Comparative phenolic contents for the matched pairs were provided by a commercial wine lab using a suite of 12 phenolic compounds. Each phenol in the suite was measured as the number of milligrams per liter of wine which allowed a direct comparison with its matched pair in the study. There was no testing of polyphenol oxidase (PPO) activity since such tests presented measuring difficulties beyond the capacities of a commercial wine lab[13]. However, the spanish study of polyphenol oxidases (PPOs) and phenolic content demonstrated that the PPOs (and presumably PPO activity when skins were broken) tracked phenolic content[14]. Therefore, it may be assumed that PPOs accurately tracked phenolic content in the Rule matched pair tests as well. The Rule fermenter presented more polyphenol oxidases to the grape-must than did the "punch down" method.

The PPO o-quinone— with a half-life of only 1400 seconds (23.3 minutes)[15]— rapidly develops into a browning agent "proto-protein." This browning agent is reduced back to the PPO o-quinone by the fermenting yeast cell's acquisition of the proto-protein's alpha amino acid. The reacquired PPO o-quinone becomes an oxygen source for the fermentation and is further reduced to become a stable PPO o-diphenol. It may be assumed that the Rule fermenter has the capacity to provide the wine-must an estimated average of 43% more o-quinones— as converted to proto-proteins— than does the punch down method.

The Problem of Excess *o-quinone* "Proto-Proteins"

The deliberate browning of the grape-must during white-wine production demonstrates that

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[11] "*The Control of Antioxidants in Red Wine by the Pump-Under Fermenter (a comparison with punch down fermentation)"* Dawson, Lawrence. Snake River N-Radiation Lab report.

[12] *t= 6.700970746 > t= 5.8408 for .01 level of confidence (3 degrees of freedom). Statistically, even a lower probability than the "0.01" level of probability for the empirical differences in phenolic content.*

[13] Catalytic PPO activity must be measured spectro-photometrically – after extensive centrifuging— and realized rather quickly since the half-life of the o-quinone is only 1400 seconds. ; SOURCE: *Evolution of grape polyphenol oxidases activity and phenolic content during maturation and vinification;"* Op. cit.

[14] Ibid.

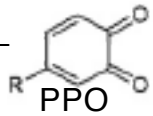
[15] Ibid.

the o-quinone "proto-proteins" thus made can be reduced by the yeast to the originating PPO o-quinone to provide an oxidation source for the fermentation. However, the skin contact with the grape-must is restricted to crushing and pressing. Afterwards, the skins are thrown away and the fermentation proceeds outside their presence. The extraction of o-quinone proto-proteins is restricted by this limited skin-to-juice contact.

What happens, however, when this skin-to-juice contact is not restricted— as with red fermentation in the presence of the skins? In this case, o-quinone proto-proteins can build to an excess— to a greater population than is needed to oxidize the conversion of dextrose sugar to alcohol and carbon dioxide during fermentation. The reason that o-quinone proto-proteins can easily build an excess is explained by the oxygen needs of the fermentation.

The proto-protein reduced back to an o-quinone makes two oxygen atoms available:

$$(O_2) + (\text{PPO } o-diphenol) \longleftarrow$$



PPO
o-quinone

$$\xleftarrow[\text{amino acid reduction}]{} \text{proto - protein}$$

The reduction of a proto-protein back to an o-quinone releases two oxygen atoms to a further oxidation. However, the reverse oxidation or "phosphatase burning" of the dextrose sugar molecule is only a partial Krebs cycle.[16] The conversion of dextrose to alcohol and carbon dioxide requires only one oxygen atom, not the many required by Krebs burning during cell energy production. The reduction of one proto-protein can oxidize two molecules of sugar:

Complete Fermentation phosphatase Burning

$$C_6H_{12}O_6 + O* \xrightarrow{\textit{Reverse Oxidat.}} (2CH_3 - CH_2 - OH) + (2CO_2) + (C - OH) + (H_2O) + (heat)$$

** From partial reduction of a polyphenol oxidizer*

Only one oxygen atom required to oxidize hydrogen to water (outputting heat) and totally reduce dextrose to alcohol, CO_2 and a yeast carbon hydroxyl .

Initial phosphatase Enzymic Burning of Dextrose by Yeast Cell

$$C_6H_{12}O_6 + P_2^* + O \xrightarrow{\text{reverse oxidation}} C_6H_{10}O_6P_2 + H_2O + heat$$

** Provided by ATP (Adenosine triphosphate) from yeast cell*

Only one oxygen atom required in initial ATP oxidation of hydrogen to water (outputting heat) and to convert dextrose to 1,6-diphosphate dextrose

The phosphatase burning of a sugar molecule to provide alcohol, carbon dioxide and certain residuals used in yeast cellular construction requires one oxygen atom to accomplish. However, the reduction of one o-quinone proto-protein releases two oxygen atoms. Therefore, one proto-protein reduction can oxidize two sugar molecules. The continuous release of o-quinone proto-proteins, as is the case for skin-contact fermentation, threatens to provide an excess of the proto-proteins. For red wines, however, this situation is not destructive. Excess proto-proteins provide an aging potential to the wine.

The o-quinone proto-protein is unstable. Over time, it is naturally reduced back to the originating o-quinone which again becomes an active oxidizer. The naturally occurring phenols, caffaric acid and p-courmaric acid, can acquire these active oxidizers to produce positive aging characteristics for the wine:

"Caftaric acid or p-coumaric acid is oxidized by PPO to produce caffeoyltartaric acid

[16] "ATP and ADP are made in the Krebs cycle to give cells energy." P.4, *The Chemistry of Winemaking,* J. Mumms, p. 4. Op. cit.

o-quinones (CTAQ), which are powerful oxidants and able to oxidize other compounds in wine to cause great changes in wine tone and colour intensity depending on the phenols and the reactive situations."[17]

Excess o-quinone proto-proteins when "aged" back to simple PPO o-quinones interact with caffaric acid to produce oxidants which are available to other phenols which can impact flavor and colour intensity in a positive way. That is, excess o-quinone proto-proteins are the initiating source of wine aging.

Control of o-quinone Proto-Proteins simultaneously with Phenolic Content controls Wine Aging Potential

The matched pair fermentations comparing the Rule device with the standard "punch down" fermentation technique gave a skin-born phenolic content advantage to Rule for all samples. However, wine superiority for the Rule fermentations could not be recognize at the time of vinification because— as proved by the spanish study— the 43% increase in phenolic content was accompanied by a similar increase in o-quinone PPOs. The phenolic content advantage was disguised by increases in o-quinone proto-proteins.

Only 1/2 of the oxygen released by yeast's amino acid reduction of proto-proteins is necessary for fermentation of dextrose sugar molecules. The partial oxidation potential of each proto-protein reduction left a residue of o-quinone proto-proteins in the wine after fermentation was completed. These excess o-quinone proto-proteins disguised the Rule wine advantage and would do so until they could be aged to CATQ o-quinones and change *"wine tone and color intensity."*[18]

The existence of excess o-quinone proto-proteins and their aging requirements were revealed in another test of the Rule fermenter. The Rule skin-contact fermenter was applied to several white varieties[19]. The skin-contact fermentation of white grapes proved that the characteristic off odor/flavor of o-quinone proto-proteins could be disguised by the coloring phenols known as *anthocyanins*[20] . The characteristic o-quinone proto- protein off odor/ flavor appeared in the Rule fermented white wines, but not the Rule fermented red wines. The only phenolic difference between whites and reds are anthocyanin phenols:

"Although there is significant genetic variation between varieties, the only major difference between red grapes and white grapes is anthocyanins."[21]

The characteristic off odor/flavor of o-quinone proto-proteins are easily recognized and may be reproduced by the simple expedient of exposing wine (primarily white wine) to the air for extended periods of time[22]. This occurs because atmospheric oxygen combines with o-diphenol PPOs in the wine to produce o-quinone PPOs. These newly created o-quinone polyphenol oxidases combine with alpha amino acids to produce the proto-protein. The half-life of of the o-quinone PPOs is 1400 seconds (23.3 minutes). That is, most of the o-quinones are converted proto-proteins within an hour, rendering their characteristic odor/flavor to the wine. It was this characteristic odor/flavor which was detected in all white wines which had been completely fermented on their skins in imitation of a red wine fermentation.

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[17] *"Review Mechanisms of oxidative browning of wine."* Op. cit.

[18] Ibid.

[19] By the St. Regulus Winery, Weiser, Idaho, in 2008 and 2009 for Riesling, Chardonnay and Gewurztraminer.

[20] Anthocyanins are flavoring agents as well as a coloring agents since all phenols are composed of hydroxyls bound to "aromatic rings."

[21] *"Phenolic Analysis in White Wines and Juices at ETS Laboratories"* Steven F. Price . SOURCE: http://locale.mannlib.cornell.edu/gsdl/collect/wiwp/index/assoc/HASHf2df.dir/Phenolic_analysis_in_white_wines.pdf

[22] *Wine Flaws: Oxidation* , Jamie Goode; Sommelier Journal. Op. cit.

Experiments with white wine grapes in the Rule fermenter identified the wine aging process. With newly made wines, off flavors produced by o-quinone proto-proteins were detectable in the white wines while they were largely masked by the anthocyanins in red wines. Detectable o-quinone proto-proteins could be monitored as the wines aged. Those aging characteristics have now been identified. A 2008 Riesling and a 2008 Chardonnay have bottle aged the o-quinone proto-proteins to CATQ o-quinones which then oxidized other phenols to new levels of complexity[23] . This aging process is further identified by the bottle aging of a 2009 Riesling which is tending towards, but has not completely reached, the 2008 stage of complexity. These taste change could not be monitored using red wines because the o-quinone proto-proteins are masked.

CONCLUSION: The Rule Fermenter may have the capacity to control wine-aging characteristics for economic and esthetic purposes

According to David Rule, his fermenter has the capacity to mechanically control the amount of skin-juice contact. He states that *"it controls the juice rate uniformly past each skin.*[24] *"* If this means that the contact between juice and skin can be reduced to "0" so that no skin polyphenol oxidases are exchanged with the juice, then the fermenter can mechanically control excess o-quinone PPOs and subsequent excess o-quinone proto-proteins from entering the grape-must. For grapes of maximum phenolic quality, the fermenter can be used to maximize aging characteristics. Premium wines— requiring long bottle aging before release— will result.

However, for grapes producing wines which need to be marketing rapidly for economic reasons, the fermenter could provide restricted o-quinone proto-proteins (and restricted phenolic content) for wines of restricted bottle aging requirements. These would be pleasant young wines without the "masked" off odors/flavors of excess o-quinone proto-proteins.

The key is making the fermenter operate to provide separation or exposure of juice to skins in order to control the contribution which polyphenol oxidases and resultant proto-proteins provide to wine aging potential. More skin contact with the juice for more proto-proteins and greater aging requirements. Less skin contact with the juice for less proto-proteins and younger, early release wines. Machine design and operation must follow function in this matter.

Lawrence Dawson
The Snake River N-Radiation Lab

[23] Tasting conclusions of the St. Regulus winery.

[24] From a private email.