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Study of the antiradical activity of wine polyphenols using UV–VIS and DFT methods

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Abstract. This study investigates the antiradical activity of the wine polyphenols catechin (Cat) and quercetin (Que) in ethanol and wine-model solution, combining experimental DPPH$^\bullet$ scavenging assays with Density Functional Theory (DFT) calculations. Quercetin exhibited similar activity in both media, one mol of polyphenol scavenging approximately 3.4 moles of DPPH$^\bullet$, whereas catechin showed enhanced performance in wine-model solution, neutralizing up to 4 moles of DPPH$^\bullet$ compared to 2.8 moles in ethanol. Theoretical and experimental correlations indicate that catechin predominantly follows a SET-PT mechanism in wine-model solution, while quercetin likely undergoes alternative pathways, including possible dimerization.
Keywords: catechin, quercetin, DPPH, DFT, antiradical activity.

Studiul activității antiradicalice a polifenolilor din vin utilizând metode UV–VIS și DFT

Rezumat. Acest studiu investighează activitatea antiradicalică a polifenolilor din vin, catechina (Cat) și quercetina (Que), în etanol și în matricea de vin, prin combinarea testelor experimentale – metoda DPPH$^\bullet$, cu calcule bazate pe teoria funcționalului densității (DFT). Quercetina a prezentat o activitate comparabilă în ambele medii, un mol de polifenol neutralizând aproximativ 3.4 moli de DPPH$^\bullet$, în timp ce catechina a demonstrat o activitate antiradicalică îmbunătățită în matricea de vin, neutralizând până la 4 moli de DPPH$^\bullet$ comparativ cu 2.8 moli în etanol. Corelarea rezultatelor teoretice cu cele experimentale sugerează că, în matricea de vin, catechina acționează predominant printr-un mecanism de tip SET-PT, în timp ce quercetina poate urma căi alternative de reacție, inclusiv posibile procese de dimerizare.
Cuvinte-cheie: catechină, quercetină, DPPH, DFT, activitate antiradicalică.

1. Introduction

The study of wine antioxidants, their redox behaviour, and underlying mechanisms of action represents a highly relevant and dynamic research field from both scientific and practical perspectives. Phenolic compounds play a crucial role in determining the sensory quality, stability, and health-related properties of wines [1]. Among these, catechin

and quercetin are two representative polyphenols widely present in wine, contributing significantly to its organoleptic characteristics as well as to its antioxidant potential [1], [2].

Previous investigations have addressed the antioxidant activity of these compounds, their mechanisms of action in various solvents, and possible synergistic effects in combination with other antioxidants [3], [4]. These studies provide a solid foundation for understanding their behaviour in simplified model systems. However, a comprehensive understanding of the antiradical activity of catechin and quercetin within the complex wine-model solution remains insufficiently explored, both experimentally and through theoretical approaches.

Our earlier research on antioxidant compounds ascorbic acid and dihydroxyfumaric acids demonstrated that the reaction environment significantly influences antiradical activity [5]. In particular, rate constants measured in wine-model solution were found to be substantially higher than those in ethanol, with increases of approximately one order of magnitude for dihydroxyfumaric acid and about twofold for ascorbic acid [5]. These findings highlight the critical importance of medium effects when evaluating antioxidant behaviour.

Applying the same methodological framework, the aim of the present work is to perform a comparative study in ethanol and wine-model solution to investigate the antiradical potential of catechin and quercetin. To gain deeper mechanistic insight, Density Functional Theory calculations are employed to evaluate possible hydrogen atom transfer and electron transfer mechanisms involved in their radical scavenging activity. Beyond providing mechanistic insight, the obtained insights may also have practical relevance for winemaking by improving the understanding of how individual phenolic compounds contribute to oxidative stability in different wine matrices, thereby supporting strategies for managing phenolic composition and preserving wine quality during storage.

2. Results and Discussions

The antioxidant activity of the investigated wine polyphenols — quercetin (Que) and catechin (Cat), was evaluated using 2,2-diphenyl-1-picrylhydrazyl ($DPPH^{\bullet}$) assay, a widely applied spectrophotometric method based on the ability of antioxidants to donate hydrogen atoms or electrons to stabilize the DPPH radical [6]. The experimental investigations were conducted at room temperature (25 °C) in 96% ethanol (EtOH) and in a wine-simulated model (WM), composed of a 12% (v/v) hydroalcoholic solution containing 5 g/L tartaric acid, adjusted to pH 3.2 [7].

Complementarily, Density Functional Theory (DFT) calculations were employed to gain molecular-level insight into the antioxidant mechanisms. The geometry of neutral

state and radicals of Que and Cat in the gas and solvent medium was optimised using the DFT method with hybrid exchange-correlation functional, B3LYP and 6-311G(2d,2p) basis set [8]. The electronic structure calculations were performed using Gaussian 09 program package.

Figure 1 presents the dose–response behaviour of quercetin and catechin, evaluated in ethanolic and wine model media. The plotted data indicate a concentration-dependent antiradical activity of wine polyphenols; the decrease in the measured response reflects a lower percent of the remaining DPPH•, correspondingly, the increase in the antioxidant efficiency.

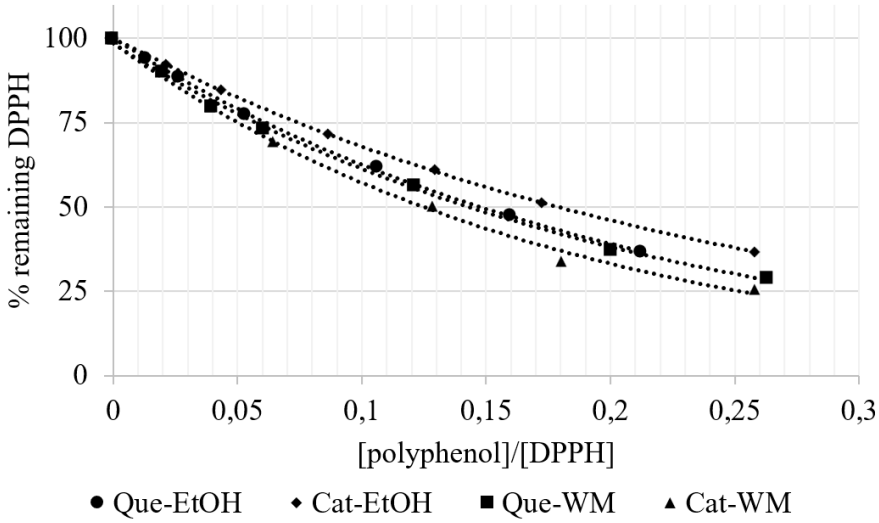


Figure 1. Dose–response curves illustrating the antiradical activity of quercetin and catechin in ethanolic (EtOH) and wine-model solution (WM) after 1 h of reaction with 25 mg/L DPPH•. Data are presented as mean ± standard deviation (SD) of three independent experiments (n = 3)

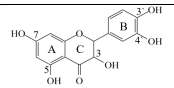
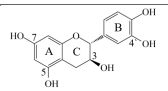
Quercetin exhibits similar antioxidant efficiency in both ethanolic and wine model media (Figure 1), suggesting that the solvent environment does not influence the reactivity of this polyphenol. In contrast, catechin exhibited enhanced antiradical activity in the wine model medium compared to 96% ethanol (Figure 1), scavenging 75% of the free radical at the 0.25 [Cat]/[DPPH] molar ratio.

The quantitative parameters derived from the dose–response curves are summarized in Table 1. The IC_{50} and IC_{100} values represent the concentrations of the scavenger required to inhibit 50% and 100% of the free radical, respectively. For quercetin, similar IC_{50} values were observed in EtOH (0.148) and WM (0.146), indicating comparable antiradical

efficiency in both media. Likewise, IC_{100} values for quercetin showed minimal variation between EtOH (0.296) and WM (0.292). The corresponding stoichiometric values (n) were 3.378 in EtOH and 3.425 in WM, suggesting that, in both media, one mol of polyphenol reduces ≈ 3.4 moles of $DPPH^{\bullet}$.

In contrast, catechin exhibited a more pronounced medium-dependent behaviour. In ethanol, catechin showed higher IC_{50} (0.179) and IC_{100} (0.358) values compared to quercetin, corresponding to a lower stoichiometric value (n = 2.793). However, in the wine model medium, catechin demonstrated enhanced antiradical activity, with reduced IC_{50} (0.125) and IC_{100} (0.250) values and a notably higher stoichiometric value (n = 4.000), meaning that in WM one mol of Cat scavenges up to 4 moles of the free radical. These findings are in agreement with the previously reported data for a wide range of phenolic compounds reacting with the DPPH radical [5], [9].

Table 1. Antiradical activity parameters (IC_{50} and IC_{100}) and total stoichiometric values n of selected wine polyphenols in different media

Compound	Media	IC_{50}	IC_{100}	n^*	Number of –OH groups	Molecular structure
Que	EtOH	0.148	0.296	3.378	5	
	WM	0.146	0.292	3.425		
Cat	EtOH	0.179	0.358	2.793	5	
	WM	0.125	0.250	4.000		

$^*n = 1/IC_{100}$. Data are presented as mean ± standard deviation (SD) of three independent experiments (n = 3)

Table 1 indicates the number of hydroxyl (–OH) groups available in the molecular structures of the compounds, both quercetin and catechin possessing five hydroxyl groups and two aromatic rings. These structural features are directly associated with their antiradical capacity, as hydroxyl groups and conjugated double bounds play a critical role in hydrogen atom donation and radical stabilization [10].

In this regard, the DFT results provide valuable molecular-level insight into the antiradical behaviour of catechin and quercetin by evaluating the thermodynamic feasibility of three principal radical scavenging mechanisms: hydrogen atom transfer (HAT), single-electron transfer followed by proton transfer (SET–PT), and sequential proton loss electron transfer (SPLET) [8], [11]. The above mechanisms are characterized by the following thermochemical parameters: bond dissociation enthalpy (BDE), adiabatic ionization potential (IP), proton dissociation enthalpy (PDE), proton affinity (PA), and electron transfer enthalpy (ETE), which were analysed in the gas phase, water, and ethanol (Equations

(1)–(5)) [8], [12].

$$BDE = H(ArO)^{\bullet} + H(H^{\bullet}) - H(ArOH) \quad (1)$$

$$IP = H(ArOH^{\bullet+}) + H(e^{-}) - H(ArOH) \quad (2)$$

$$PDE = H(ArO^{\bullet}) + H(H^{+}) - H(ArOH^{\bullet+}) \quad (3)$$

$$PA = H(ArO^{-}) + H(H^{+}) - H(ArOH) \quad (4)$$

$$ETE = H(ArO^{\bullet}) + H(e^{-}) - H(ArO^{-}) \quad (5)$$

Table 2 summarizes the DFT-calculated thermodynamic parameters for both polyphenols, covering the three antioxidant mechanisms – HAT, SET-PT, and SPLET – evaluated in the gas phase as well as in water and ethanol. Lower energy values correspond to higher intrinsic reactivity of the respective hydroxyl (–OH) groups.

In the gas phase, catechin exhibits the lowest BDE values at the 5-OH and 7-OH positions, indicating that these A-ring hydroxyl groups are the most effective hydrogen donors. This observation differs from previous reports identifying the 3′-OH and 4′-OH groups of the catechol moiety as the most reactive sites [10]. However, in aqueous and ethanolic media, the present results align with the literature across all investigated mechanisms. Therefore, in water and ethanol, the catechin's hydroxyl groups can be ranked in increasing order of energy (i.e., decreasing reactivity) as follows: 4′-OH < 3′-OH < 5-OH < 7-OH < 3-OH. This is consistent with the structural features of catechin, in which the conjugated double bonds in rings A and B enhance the reactivity of the hydroxyl groups, compared to the 3-OH group located in the C ring.

For quercetin, the hydroxyl groups at the C3′ and C4′ positions of the B ring consistently exhibit the highest reactivity, independent of the reaction phase (gas or solvent) and the antioxidant mechanism considered (HAT, SET-PT, or SPLET). This is reflected by their comparatively low bond dissociation enthalpy (BDE) values in the HAT pathway, favourable proton dissociation enthalpy (PDE) in the SET-PT mechanism, and proton affinity (PA) and electron transfer enthalpy (ETE) parameters in the SPLET mechanism.

In contrast to the results obtained for Cat, where the 3-OH group was found to be the least reactive one, the data for quercetin indicate that the 3-OH group represents a thermodynamically favoured reactive site, characterized by relatively low reaction enthalpies. This behaviour may be attributed to the nearby carbonyl (keto) group, which can influence the stability of the corresponding radical or ionic species [13]. Therefore, in water and ethanol the quercetin's hydroxyl groups can be ranked in increasing order of energy as follows: 3′-OH < 3-OH < 4′-OH < 5-OH < 7-OH.

By correlating the DFT results with the experimental data, it can be proposed that, in the case of quercetin, the 3 hydrogen atoms or electrons donated by the polyphenol

to scavenge the DPPH radical most likely originate from the 3′-OH, 3-OH, and 4′-OH groups, both in ethanol and in the wine model solution. For catechin, the hydroxyl groups involved in DPPH radical scavenging are predicted to be 4′-OH, 3′-OH, and 5-OH in ethanol, while in the WM solution — which can be more reliably correlated with the DFT data obtained in water due to its high water content (88%) of the WM, the reactive sites extend to include also 7-OH group.

The data from Table 2 clearly demonstrate that the reaction medium influences the thermodynamics of the antioxidant mechanisms for both catechin and quercetin. For the HAT mechanism, the solvent effect is relatively small. Bond dissociation enthalpy values vary only slightly between the gas phase and solution, ranging from 257 to 275 kcal/mol for Cat and from 227 to 238 kcal/mol for Que.

A much stronger solvent dependence is observed for the SET-PT and SPLET mechanisms. In the gas phase, the IP, PDE, and PA values are significantly higher, whereas in solution these thermodynamic parameters decrease substantially – by approximately 53 kcal/mol, 216 kcal/mol and 289 kcal/mol, respectively. As a result, the overall SET-PT and SPLET reaction enthalpies decrease by more than 200 kcal/mol in polar media, demonstrating that these pathways become markedly more favourable in solution.

The ionization potential and electron transfer enthalpy, which describe the electron transfer steps in SET-PT and SPLET mechanism, are consistently lower in water than in ethanol for both Cat and Que. This behaviour can be attributed to the higher polarity and dielectric constant of water ($\varepsilon \approx 78$) compared to ethanol ($\varepsilon \approx 24$), which leads to more efficient stabilization of charged and highly polar species, such as radical cations and polarized transition states formed during electron transfer, therefore, indicating that electron transfer is thermodynamically more favourable in aqueous solution.

In contrast, proton dissociation enthalpy (PDE) and proton affinity (PA), which characterize proton transfer steps, are generally lower in ethanol than in water. This indicates that deprotonation is marginally more favourable in ethanol under the modelled conditions. Although water is more polar, ethanol can form strong, directional hydrogen bonds with phenolic and phenolate species while providing a less tightly structured solvation shell. This can stabilize the deprotonated form without excessively stabilizing the neutral precursor, leading to slightly lower PA and PDE values.

The theoretical observations align with the experimentally registered antiradical activity of catechin in ethanol and wine model media. More probably, in wine model solution (pH $\approx$ 3.2, 5 g/L tartaric acid), the acidic environment suppresses deprotonation of catechin, making the SPLET mechanism less favourable. Under these conditions, antioxidant activity is more likely to proceed through SET-PT pathways, which do not require prior

Table 2. Bond dissociation enthalpy (BDE), ionisation potential (IP), proton dissociation enthalpy (PDE), proton affinity (PA) and electron transfer enthalpy (ETE) values of Que and Cat in the gas and solvent phase (kcal/mol)

Phase	Position	HAT	SET-PT			SPLET		
		BDE	IP	PDE	IP+PDE	PA	ETE	PA+ETE
Cat								
Gas	3-OH	273.696	348.748	240.804	589.552	537.531	52.021	589.552
	5-OH	257.559		224.667	573.415	513.626	59.789	573.415
	7-OH	258.696		225.804	574.552	516.895	57.657	574.552
	3′-OH	261.463		228.571	577.319	510.830	66.489	577.319
	4′-OH	260.676		227.784	576.532	524.652	51.880	576.532
Water	3-OH	275.127	292.146	28.112	320.257	244.311	75.946	320.257
	5-OH	259.008		11.992	304.138	227.567	76.571	304.138
	7-OH	259.104		12.088	304.234	229.599	74.635	304.234
	3′-OH	257.981		10.966	303.111	226.003	77.109	303.111
	4′-OH	257.729		10.713	302.859	233.567	69.292	302.859
Ethanol	3-OH	275.032	299.280	24.533	323.813	243.236	80.578	323.813
	5-OH	258.856		8.358	307.638	226.125	81.513	307.638
	7-OH	261.737		11.238	310.518	228.221	82.297	310.518
	3′-OH	258.129		7.630	306.910	223.808	83.102	306.910
	4′-OH	257.821		7.322	306.602	232.788	73.814	306.602
Que								
Gas	3-OH	236.075	319.441	232.489	551.931	496.227	55.704	551.931
	5-OH	236.835		233.249	552.691	481.406	71.284	552.691
	7-OH	236.913		233.328	552.769	477.316	75.453	552.769
	3′-OH	227.779		224.194	543.635	484.712	58.923	543.635
	4′-OH	234.970		231.385	550.826	491.034	59.792	550.826
Water	3-OH	231.044	261.343	14.830	276.173	202.878	73.295	276.173
	5-OH	235.360		19.147	280.490	194.409	86.081	280.490
	7-OH	238.158		21.945	283.288	193.427	89.861	283.288
	3′-OH	229.757		13.544	274.887	197.284	77.603	274.887
	4′-OH	231.453		15.240	276.582	200.489	76.093	276.582
Ethanol	3-OH	231.309	268.493	11.598	280.091	201.919	78.172	280.091
	5-OH	235.438		15.727	284.220	193.077	91.142	284.220
	7-OH	238.042		18.331	286.824	192.425	94.398	286.824
	3′-OH	229.575		9.864	278.357	195.825	82.532	278.357
	4′-OH	231.577		11.865	280.358	199.312	81.046	280.358

deprotonation. At the same time, the hydroalcoholic medium provides a highly polar environment that efficiently stabilizes radical and charged intermediates formed after the first oxidation step. This stabilization enables further sequential oxidation of catechin, allowing more hydroxyl groups to participate in DPPH scavenging.

Taking into consideration the structural similarities between Cat and Que, as well as the obtained DFT data, it was expected that Que would follow the same DPPH$^\bullet$ scavenging mechanism as Cat. However, the experimental results show that Que has the same IC_{50} value (0.15) in both EtOH and WM, indicating that the influence of the medium is negligible. Other processes, such as dimerization, may still occur in WM and could significantly influence the antiradical activity of wine polyphenols, which might also apply to Que [14].

3. Conclusions

The present study demonstrates that the polyphenols catechin and quercetin exhibit different antiradical behaviours depending on the reaction medium. Quercetin showed consistent activity in both ethanol and wine-model solution, with one mole scavenging approximately 3.4 moles of DPPH$^\bullet$. In contrast, catechin displayed enhanced antiradical capacity in wine-model solution, neutralizing up to 4 moles of DPPH$^\bullet$ compared to 2.8 moles in ethanol. The DFT calculations revealed that the most reactive hydroxyl groups in quercetin are located at positions 3′-OH, followed by 3-OH and 4′-OH, whereas in catechin the order of reactivity is 4′-OH > 3′-OH > 5-OH > 7-OH. The correlation of theoretical and experimental results suggests that catechin primarily follows a SET-PT mechanism in wine-model solution, while the SPLET pathway is likely inhibited due to the high concentration of tartaric acid. For quercetin, the observed behaviour cannot be fully explained by the evaluated reaction pathways alone. Secondary processes, including quercetin dimerization previously reported in the literature, may contribute to its lower radical scavenging activity in the wine-model solution; however, these processes were not directly investigated in the present study.

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References

[1] EL RAYESS, Y.; NEHME, N.; AZZI-ACHKOUTY, S.; JULIEN, S.G. Wine phenolic compounds: Chemistry, functionality and health benefits. *Antioxidants*. 2024, vol. 13, no. 11, 1312. DOI: 10.3390/antiox13111312.

[2] GUTIÉRREZ-ESCOBAR, R.; ALIAÑO-GONZÁLEZ, M.J.; CANTOS-VILLAR, E. Wine polyphenol content and its influence on wine quality and properties: A review. *Molecules*. 2021, vol. 26, no. 3, 718. DOI: 10.3390/molecules26030718.

[3] VICOL, C.; DUCA, G. Synergistic, Additive and Antagonistic Interactions of Some Phenolic Compounds and Organic Acids Found in Grapes. *Acta Chimica Slovenica*. 2023, vol. 70, no. 4, pp. 654–665. DOI: 10.17344/acsi.2023.8214.

[4] BOŽOVIĆ, M.; PETROVIĆ, D.; CAKOVIĆ, D.; MLADENOVIĆ, M.; RAGNO, R. Phenolic content and antioxidant potential of wine extracts. *Natural Product Communications*. 2025, vol. 20, no. 3. DOI: 10.1177/1934578X251327227.

[5] VICOL, C.; CIMPOIU, C.V.; DUCA, G. Investigation of synergic/anti-synergic interactions of dihydroxifumaric acid and ascorbic acid with DPPH. *Studia Universitatis Babes-Bolyai Chemia*. 2021, vol. 66, no. 2, pp. 49–58. DOI: 10.24193/subbchem.2021.2.04.

[6] BRAND-WILLIAMS, W.; CUVELIER, M.E.; BERSET, C.L.W.T. Use of a free radical method to evaluate antioxidant activity. *LWT-Food science and Technology*. 1995, vol. 28, no. 1, pp. 25–30. DOI: 10.1016/S0023-6438(95)80008-5.

[7] COMUZZO, P.; BATTISTUTTA, F.; VENDRAME, M.; PÁEZ, M.S.; LUISI, G.; ZIRONI, R. Antioxidant properties of different products and additives in white wine. *Food chemistry*. 2015, vol. 168, pp. 107–114. DOI: 10.1016/j.foodchem.2014.07.028.

[8] ANITHA, S.; KRISHNAN, S.; SENTHILKUMAR, K.; SASIREKHA, V. Theoretical investigation on the structure and antioxidant activity of (+) catechin and (-) epicatechin–a comparative study. *Molecular Physics*. 2020, vol. 118, no. 17, e1745917.

[9] VILLAÑO, D.; FERNÁNDEZ-PACHÓN, M.S.; MOYÁ, M.L.; TRONCOSO, A.M.; GARCÍA-PARRILLA, M.C. Radical scavenging ability of polyphenolic compounds towards DPPH free radical. *Talanta*. 2007, vol. 71, no. 1, pp. 230–235. DOI: 10.1016/j.talanta.2006.03.050.

[10] XIANG, Y.; XIANG, M.; MAO, Y.; HUANG, L.; HE, Q.; DONG, Y. Insights into structure-antioxidant activity relationships of polyphenol-phospholipid complexes: The effect of hydrogen bonds formed by phenolic hydroxyl groups. *Food Chemistry*. 2025, 144471. DOI: 10.1016/j.foodchem.2025.144471.

[11] GORINCIOI, E.; VICOL, C.; BOLOCAN, N.; CIMPOIU, C.V.; BARBA, A.; NICA, S.L.; DUCA, G. Harnessing Synergy: Investigation of the Antioxidant Interactions between trans-Resveratrol and L-Ascorbic Acid by Spectroscopic and DFT methods. *Acta Chimica Slovenica*. 2025, vol. 72, pp. 654–665. DOI: 10.17344/acsi.2025.9292.

[12] ZHENG, Y.Z.; DENG, G.; LIANG, Q.; CHEN, D.F.; GUO, R.; LAI, R.C. Antioxidant activity of quercetin and its glucosides from propolis: A theoretical study. *Scientific reports*. 2017, vol. 7, no. 1, 7543. DOI: 10.1038/s41598-017-08024-8.

[13] GULCIN, İ.; ALWASEL, S.H. DPPH radical scavenging assay. *Processes*. 2023, vol. 11, no. 8, 2248. DOI: 10.3390/pr11082248.

[14] LATOS-BROZIO, M.; MASEK, A. Structure-activity relationships analysis of monomeric and polymeric polyphenols (Quercetin, Rutin and Catechin) obtained by various polymerization methods. *Chemistry & Biodiversity*. 2019, vol. 16, no. 12, e1900426. DOI: 10.1002/cbdv.201900426.

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