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Antioxidant properties of xanthones extracted from the pericarp of *Garcinia mangostana* (Mangosteen): A theoretical study

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ABSTRACT

A theoretical study on antioxidant properties of fourteen xanthones extracted from the pericarp of *G. Mangostana* has been performed. Three main reaction mechanisms are investigated: hydrogen atom transfer (HAT), single electron transfer–proton transfer (SETPT) and sequential proton loss electron transfer (SPLET). The O—H bond dissociation enthalpy (BDE), ionization energy (IE), proton affinity (PA) and electron transfer energy (ETE) parameters were computed in gas phase and water. The results show that HAT would be the most favorable mechanism for explaining antioxidant activity of xanthones in gas phase, whereas the SPLET mechanism is thermodynamically favored in water.

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1. Introduction

Garcinia mangostana, known as mangosteen [1] is considered as 'the queen of fruits'. Mangosteen is widely grown in Southern Viet Nam and Southeast Asian countries. The mangosteen-fruit is dark purple or reddish, with white, soft and juicy edible pulp with a slightly acid, sweet flavor and a pleasant aroma. Moreover, the fruit pericarp has been used for long time as a traditional medicine for treatment of abdominal pain, diarrhea, dysentery, infected wound, suppuration and chronic ulcer [2]. The major active substances in mangosteen pericarp are xanthones and their derivatives. They are classified in polyphenolic compounds commonly found in higher plant families [3,4], some of which have been reported to have high antioxidant activity [2,5,6], anti-inflammatory activity [7,8], anti-bacterial activity [9], anti-atherosclerotic activity [8] and anti-malarial activities [10]. Therefore, xanthones from mangosteen have been also recently used to produce various dietary supplement products as well as antiseptic goods.

Kinghorn et al. [2] used the chromatography to isolate two new highly oxygenated prenylated xanthones and twelve well-known xanthones from the pericarp of mangosteen as shown in Figure 1. In addition, the antioxidant activities of all isolated compounds were determined using authentic and morpholinosydnonimine-derived peroxynitrite methods. Although experimental results concerning the antioxidant capacity of xanthones are well reported in literature, there are rarely theoretical investigations neither analyzing the free radical scavenger capacity of these molecules, nor determining the reaction mechanisms. Thus, the purpose of this study was to determine whether natural components from mangosteen act as antioxidants by analyzing the electron transfer power and hydrogen atomic transfer and to identify those that are more efficient for scavenging free radicals.

Compounds **1–14** were identified as 8-hydroxycudraxanthone G (**1**), mangostingone [7-methoxy-2-(3-methyl-2-butenyl)-8-(3-methyl-2-oxo-3-butenyl)-1,3,6-trihydroxyxanthone] (**2**), cudraxanthone G (**3**), 8-deoxygartanin (**4**), garcimangosone B (**5**), garcinone D (**6**), garcinone E (**7**), gartanin (**8**), 1-isomangostin (**9**), α-mangostin (**10**), γ-mangostin (**11**), mangostinone (**12**), smeathxanthone A (**13**), and tovophyllin A (**14**) [2].

2. Theoretical and computational methods

Three mechanisms are commonly proposed to explain radical scavenging processes of phenolic antioxidants [11–14], as shown in Figure 2.

The bond dissociation enthalpy (BDE), the proton affinity (PA), the ionization energy (IE), the electron transfer enthalpy (ETE) from
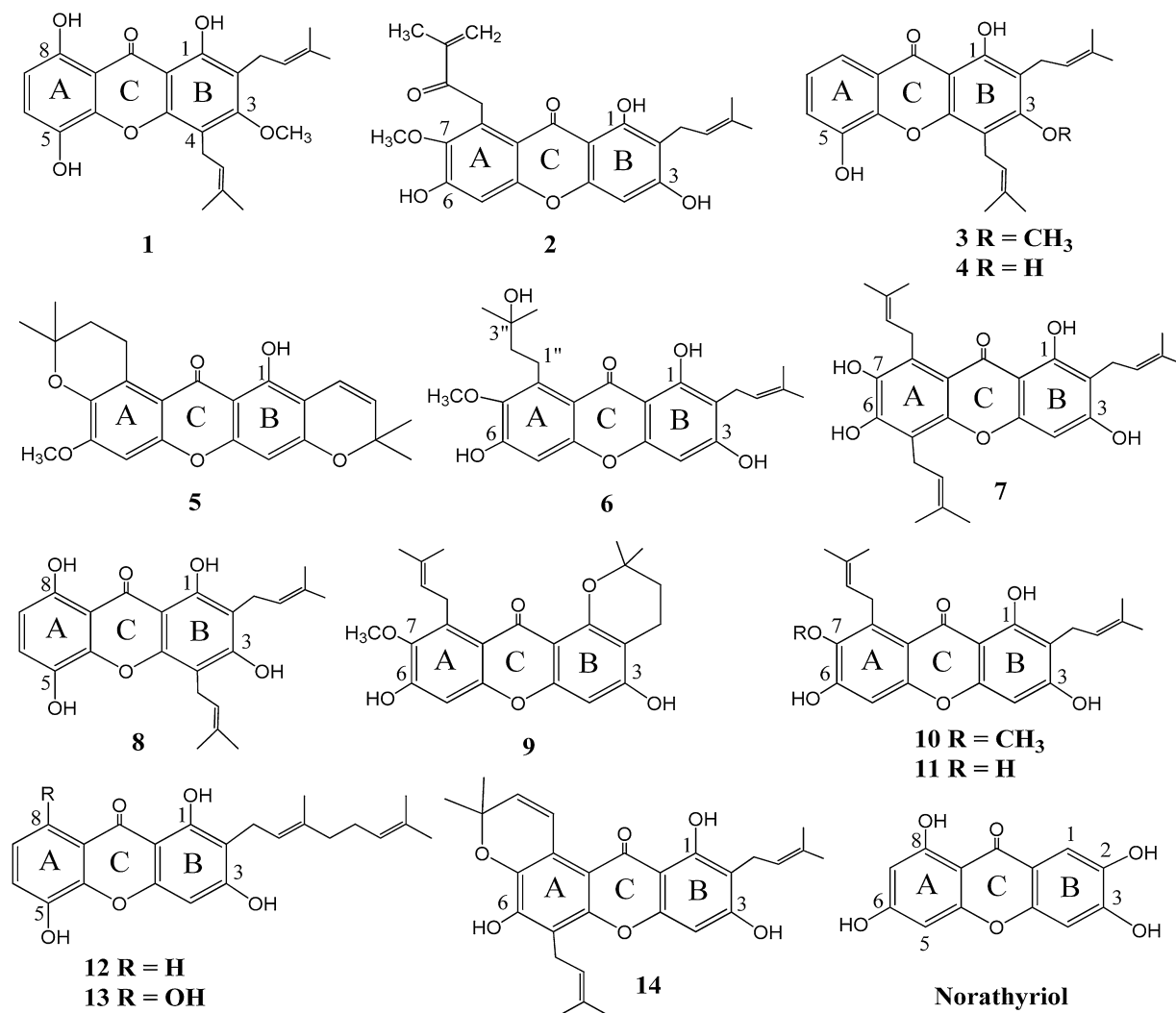
Figure 1. Structures of compounds isolated from the pericarp of *G. mangostana* and related compound.
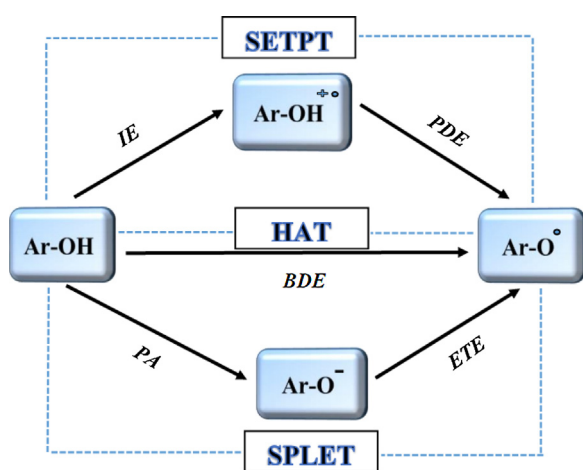
Figure 2. Scheme of the analyzed mechanisms of antioxidant activity.

antioxidant, ArOH, respectively. These values allow analyzing the relevance of each of three proposed antioxidant activity mechanisms. The first mechanism is called hydrogen atom transfer (HAT) quantified by the BDE; the second is single-electron transfer followed by proton transfer (SETPT) quantified by the IE and the PDE, and the last is the sequential proton loss electron transfer (SPLET) governed by the PA and ETE.

Total enthalpies of the studied species X, $H(X)$, at the temperature T are usually estimated from the usual expression: $H(X) = E_0 + ZPE + H_{trans} + H_{rot} + H_{vib} + RT$. The H_{trans}, H_{rot}, and H_{vib} are the translational, rotational, and vibrational contributions to enthalpy, respectively; E_0 is the total energy at 0 K and ZPE is the zero-point vibrational energy. The enthalpy value for the hydrogen atom in the gas phase was calculated at 298 K based on its exact energy of −0.5 Hartree at 0 K and thermal correction (2.5RT). The reaction enthalpy values were determined from total enthalpies of the individual species in the gas-phase, as follows:

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

$$IE = H(ArOH^{\bullet+}) + H(e^-) - H(ArOH) \qquad (2)$$

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

the anion and the proton dissociation enthalpy (PDE) from the radical cation were calculated as differences between the heat of formation (ΔH_f^0) of the products and the reactants (Figure 2), where Ar—O$^\bullet$ and Ar—O$^-$ are the radical and the anion derived from the

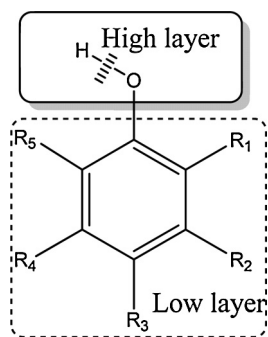**Figure 3.** Schematic description of two-layer proposed ONIOM model.

$$PA = H(ArO^-) + H(H^+) - H(ArOH) \qquad (4)$$

$$ETE = H(ArO^\bullet) + H(e^-) - H(ArO^-) \qquad (5)$$

The hydration enthalpies of the hydrogen atom ($H^\bullet$), proton (H^+) and electron (e^-) were taken from the literature [15–17]. All reaction enthalpies defined in Eqs. (1)–(5) were calculated for 298.15 K and 1.0 atmosphere pressure.

Geometry optimizations and vibrational frequency calculations were conducted using the semi-empirical PM6 method. Vibrational frequencies obtained at the PM6 level were subsequently scaled by a factor of 1.078 [18] for estimating the zero-point vibrational energies (ZPE). The enthalpy values at higher level were evaluated from the calculated single-point electronic energy based on PM6 optimized structures. To estimate the solvent effect on the studied enthalpies, we performed the IEF-PCM method [19,20]. All computations were performed using the GAUSSIAN 09 suite of programs [21].

According to our previous letters, it was demonstrated that the two-layer ONIOM method [22–26] with the high layer treated by ROB3LYP/6-311++G(2df,2p) that consists only of the hydrogen and oxygen atoms was a good choice to predict the BDE(O—H) with the accuracy within 1–2 kcal/mol [27,28]. Therefore, we continued to develop this partitioning scheme using the DFT restricted open-shell (RO)B3LYP/6-311++G(2df,2p) for the high layer and the semi-empirical PM6 method for the lower layer with the aim to further shed light on the structural and electronic

properties of compounds extracted from mangosteen and their radicals.

In our previous letters, several partitioning schemes for choosing the high and the low layer of the two-layer ONIOM were studied in detail. By improving the results of these letters [28], a partitioning scheme for the two-layer-ONIOM as described in Figure 3 is chosen that generates an accurate estimation of BDE(O—H) within 1–2 kcal/mol deviation. According to this, each molecule is divided into two layers, the atoms located at the breaking bond is treated as the high layer while the leftover atoms of the molecule belong to the second layer, which is treated as a lower one. The (RO)B3LYP/6-311++G(2df,2p) method is thus applied for the atoms in the high layer, whereas the PM6 procedure is applied for the low one. In the model shown in Figure 3, the core layer has only one oxygen atom and one hydrogen atom related to the target bond for estimating BDE at the high level. The rest are defined as the low layer.

3. Results and discussion

3.1. The H atom transfer (HAT) mechanism – bond dissociation enthalpies

The HAT mechanism is characterized by the BDE values which showed the abilities of donating a hydrogen atom and forming the radical form of a wide class of phenolic compounds. The BDE corresponds to the O—H bond breaking (hydrogen abstraction), thus this parameter describes the stability of the hydroxyl bonds. The lower the BDE, the easier the O—H bond dissociation, and the more important its role in the antioxidant reactivity. To reduce computation time, we used the PM6 method to calculate preliminarily the BDE(O—H) at any position to find out the weakest bond, PM6 results are showed Table S1. Then, the weakest bond was continued to be calculated at high level using ONIOM(ROB3LYP/6-311++G(2df,2p):PM6) with our partitioning model described in Figure 3. The calculated results in gas phase and in water are given in Table 1.

On the basis of the calculated BDEs values in Table 1, the hydrogen donating ability of xanthone compounds in gas phase follows the order: **11 > 10 > 7 > 1 > 9 ≈ Norathyriol > 8 > 13 > 6 > 14 > 2 > 3 > 4 > 12 > 5**. For all studied neutral molecules, the lowest BDEs can be found for OH groups in A ring (excepted **5** and Norathyriol). The scavenging activities on ONOO⁻ of 13 isolated compounds (**1** and **3–14**) have experimentally tested by Kinghorn

Table 1
ONIOM(ROB3LYP/6-311++G(2df,2p):PM6)-computed BDE(O—H) of fourteen xanthone compounds extracted from *G. mangostana* at 298 K.

Compounds	O—H position	BDE (O—H) kcal/mol		ΔBDE[a]	IC$_{50}$[b] μM	
		Gas phase	Water		Authentic ONOO⁻	SIN-1-derived ONOO⁻
1	5 (ring A)	84.1	84.3	0.2	4.6	10.0
2	6 (ring A)	86.3	86.7	0.4	N/A	N/A
3	5 (ring A)	86.4	86.1	−0.3	>30	3.2
4	5 (ring A)	86.6	86.3	−0.3	>30	11.9
5	1 (ring B)	99.1	93.2	−5.9	15.9	>30
6	6 (ring A)	85.7	86.2	0.5	26.4	15.1
7	6 (ring A)	83.8	86.4	2.6	14.1	>30
8	5 (ring A)	84.3	84.4	0.1	9.1	9.3
9	6 (ring A)	84.2	85.9	1.7	19.2	24.1
10	6 (ring A)	82.8	85.7	2.9	12.2	<0.49
11	6 (ring A)	82.3	85.9	3.6	8.0	3.1
12	5 (ring A)	87.2	87.4	0.2	>30	>30
13	5 (ring A)	85.2	85.6	0.4	2.2	9.7
14	6 (ring A)	86.1	85.9	−0.2	>30	>30
Norathyriol	2 (ring B)	84.2	86.0 (86.6[c])	1.8 (2.4)		N/A

[a] ΔBDE = ΔBDE$_{water}$ − ΔBDE$_{gas}$.

[b] Ref. [2].

[c] Ref. [29].

Table 2
Ionization energies at 298 K of fourteen xanthone compounds extracted from the pericarp of *G. mangostana* using the PM6 method.

Compounds	IE kcal/mol		IE[a] kcal/mol
	Gas phase	Water	
1	189.79 (172.73)	124.70 (117.72)	N/A
2	209.16 (178.72)	136.32 (126.33)	N/A
3	190.48 (174.80)	129.66 (121.68)	135.53
4	193.25 (176.65)	130.59 (122.56)	134.95
5	187.95 (168.35)	127.79 (116.70)	130.82
6	206.86 (180.57)	136.43 (126.55)	139.05
7	190.48 (173.42)	127.57 (120.12)	135.02
8	191.41 (174.34)	125.08 (118.24)	130.23
9	198.56 (177.11)	132.23 (118.48)	137.27
10	191.64 (173.65)	136.46 (121.42)	139.26
11	188.41 (178.95)	127.55 (120.62)	136.68
12	203.40 (181.95)	135.54 (126.75)	138.02
13	193.71 (178.95)	125.86 (118.97)	130.64
14	187.26 (172.73)	125.80 (117.22)	132.64
Norathyriol	201.32 (192.10)	132.49 (125.00)	N/A

Data in parentheses are adiabatic values.
[a] Vertical IE values were calculated in water Ref. [30].

et al. [2] via IC_{50} values given in Table 1. Five species out of 13 xanthones (**1**, **8**, **10**, **11** and **13)** were demonstrated to possess potent antioxidant activity in both assays tested. The most remarkable case is compounds 10 and 11, in which 6-OH BDEs are lower than other OH groups, 82.3 and 82.8 kcal/mol, respectively. This indicates that H atom transfer from the 6-OH of compounds **11** and **10** are easier than from other OH groups, homolytic cleavage of 6-OH happens most possibly to transfer H atom to free radical. Therefore, 6-OH of compound **10** and **11** play a very important role in HAT antioxidative mechanism, and this is confirmed by previous experimental research [2].

As can be observed in Table 1, the influence of water on BDE values was slight. For example, the largest deviation between the BDE in the gas phase and in water is 5.9 kcal/mol. The order of BDE values in water is quite different: **1 < 8 < 13 < 10 < 9 < 11 < 14 < Norathyriol < 3 < 6 < 4 < 7 < 2 < 12 < 5**.

3.2. The sequential electron transfer proton transfer (SETPT) mechanism

3.2.1. Ionization energies

According to SETPT mechanism, IE is the first step of this mechanism which is an important factor representing the ability of electron donation. The lower the IE value, the easier the electron transfer and the higher the antioxidant activity. In this part, we use PM6 method for calculating the IE value. The accuracy of this method was studied by our previous letter [28]. The calculated IE values of investigated compounds in the gas phase as well as in water are presented in Table 2.

The calculated data in Table 2 permits to conclude that the sequence of IE values in gas phase is **14 < 5 < 11 < 1 < 3 < 7 < 8 < 10 < 4 < 13 < 9 < Norathyriol < 12 < 6 < 2**, whereas the tendency of IE values in water is quite different: **1 < 8 < 14 < 13 < 11 < 7 < 5 < 3 < 4 < 9 < Norathyriol < 12 < 2 < 6 < 10**. In increasing the solvent polarity, a remarkable decrease in IE values of investigated compounds is observed. This indicates that cation radicals are charged and quite sensitive to the solvent polarity and the production of cation radicals is enhanced in aqueous solution but the formation of neutral species is unfavorable in aqueous solution. Therefore, the water solution would promote the electron-donating capacity but reduce the electron-accepting capacity of xanthone compounds extracted from the pericarp of *G. mangostana*.

3.2.2. Proton dissociation enthalpies

The second step of SETPT mechanism was described by the O—H proton dissociation enthalpy (PDE) which showed thermodynamically preferred OH group for deprotonization of radical cation formed (Figure 2). The calculated results are given in Table 3. In compound **5**, position 1 of ring B had the lowest PDE value, i.e. 253.15 kcal/mol. Similarly, in **Norathyriol**, the PDE value of 2-ring B is the lowest PDE value, i.e. 212.43 kcal/mol. The lowest PDE is obtained at position 5 of ring A for compounds **1**, **3**, **4**, **8**, **12** and **13** which are estimated to be about 225.54, 230.42, 229.26, 225.06, 226.87 and 222.38 kcal/mol, respectively. The PDE values at position 6 of ring A for compounds **2**, **6**, **7**, **9**, **10**, **11** and **14** which are lower than the ones obtained at other positions are estimated to be about 237.29, 228.09, 233.59, 231.89, 233.33, 227.47 and 242.45 kcal/mol, respectively. The order is in line with the one of BDE. In accordance with the result of PDE calculations, for all the studied compounds except to the compound **5** and **Norathyriol**, the lowest PDEs have been found at the position 5 and 6 of ring A. PDEs reached in water are significantly lower than the corresponding gas phase values, because the solvation enthalpies of proton are high. This indicates that proton dissociation ability in water is more promoted than in gas phase.

3.3. The sequential proton loss electron transfer (SPLET) mechanism

3.3.1. Proton affinities

In the first step of SPLET mechanism, the heterolytic bond dissociation of a phenolic hydroxyl group leads to the formation of phenolate anion and the release of a proton. The proton loss process is the important step of this mechanism which can be described by the PA values. The obtained proton affinities are summarized in Table 3. For each molecule, the lowest PA is set in bold.

The effect of solvent on the enthalpies has been studied by several groups [15,29,31,32], using the IEF-PCM model for investigating solvent effect on the BDE, IE, PA, ETE and PDE parameters of polyphenolic compounds. The results showed that the water solvent affects hugely on PA and PDE values.

Because the proton loss process is the important step of the SPLET mechanism which can be described by the PA values, therefore the investigated compounds with the lower PA act as the antioxidants in this mechanism. As can be seen from comparison with data in gas phase in Table 3, the water has remarkable influence on PAs due to the high solvation enthalpy of proton. The difference between PA in the gas phase and aqueous solution ranges from −295.75 to −378.23 kcal/mol. This means to favor the deprotonating process in water solvent. In gas phase, PA values are significantly higher than BDE and IE values. However, the PA values in water are remarkably lower than the corresponding values of BDE and IE. Therefore, obtained results indicate that in water, SPLET mechanism may be preferred from the thermodynamics point of view.

3.3.2. Electron transfer enthalpies

In gas phase and in water, ETE values are always lower than those of IE. This indicates that the single electron transfer process from the anionic form is more preferable than that from the neutral form, which agrees with the results obtained by other studies [33–35]. From the ΔETE values in Table 3, it can be seen that the water effect induces a significant increase in ETEs of phenolate anions; it means that water solvent is unfavorable for the following electron transfer process. The average difference between ETEs in the gas phase and water solvent is approximately 19.07 kcal/mol.

Table 3

B3LYP/6-31+G(d,p)//PM6 – computed PA, ETE and PDE at 298 K of fourteen xanthones extracted from the pericarp of *G. mangostana* in gas phase and in water.

Compounds	PA kcal/mol		ΔPA[a]	ETE kcal/mol		ΔETE[b]	PDE kcal/mol		ΔPDE[c]
	Gas phase	Water		Gas phase	Water		Gas phase	Water	
1									
5 (ring A)	**336.75**	**33.47**	−303.28	**56.49**	**69.74**	13.25	**225.54**	**−6.25**	−231.79
8 (ring A)	347.64	40.67	−306.97	58.45	73.12	14.67	238.39	4.33	−234.06
1 (ring B)	340.68	35.84	−304.84	67.35	78.94	11.59	240.33	5.32	−235.01
2									
6 (ring A)	**324.08**	**22.28**	−301.80	75.86	99.04	23.18	**237.29**	5.82	−231.47
1 (ring B)	343.91	37.05	−306.86	**67.14**	**81.43**	14.29	248.4	**2.97**	−245.43
3 (ring B)	328.70	27.52	−301.18	79.58	91.77	12.19	245.64	3.79	−241.85
3									
5 (ring A)	**330.96**	**31.02**	−299.94	67.96	**77.44**	9.48	**230.42**	**−3.00**	−233.42
1 (ring B)	341.68	37.61	−304.07	**67.44**	77.71	10.27	240.61	3.87	−236.74
4									
5 (ring A)	336.22	30.97	−305.25	63.17	77.69	14.52	**229.26**	**−3.65**	−232.91
1 (ring B)	345.61	36.78	−308.83	65.12	80.09	14.97	240.59	4.56	−236.03
3 (ring B)	**327.43**	**26.28**	−301.15	77.01	98.39	21.38	234.30	12.36	−221.94
5									
1 (ring B)	**348.47**	**37.49**	−310.98	**60.60**	**77.59**	16.99	**253.15**	**13.00**	−240.15
6									
6 (ring A)	**324.38**	**23.98**	−300.40	74.79	87.03	12.24	**228.09**	**−4.28**	−232.37
1 (ring B)	343.26	35.57	−307.69	67.52	**82.75**	15.23	239.70	3.03	−236.67
3 (ring B)	328.37	26.96	−301.41	79.63	92.45	12.82	236.91	4.12	−232.79
3 (ring B)	376.17	57.40	−318.77	**43.47**	119.12	75.65	248.56	61.22	−187.34
7									
6 (ring A)	**323.55**	**23.54**	−300.01	71.24	84.12	12.88	**233.59**	**−0.93**	−234.52
7 (ring A)	342.26	34.78	−307.48	**54.61**	**71.74**	17.13	235.67	**−2.09**	−237.76
1 (ring B)	349.16	38.86	−310.3	62.86	79.55	16.69	250.83	9.82	−241.01
3 (ring B)	331.96	27.85	−304.11	74.56	90.09	15.53	245.32	9.30	−236.02
8									
5 (ring A)	338.49	33.06	−305.43	55.09	69.95	14.86	**225.06**	**−47.38**	−272.44
8 (ring A)	347.10	40.44	−306.66	59.01	72.99	13.98	237.60	−36.97	−274.57
1 (ring B)	341.18	34.88	−306.30	69.08	82.11	13.03	241.74	−33.41	−275.15
3 (ring B)	**327.96**	**29.38**	−298.58	80.43	92.69	12.26	239.86	−28.33	−268.19
9									
6 (ring A)	335.96	**27.85**	−308.11	**63.99**	**83.15**	19.16	231.89	−41.44	−273.33
3 (ring B)	**331.88**	28.20	−303.68	70.92	88.90	17.98	234.74	−35.34	−270.08
10									
6 (ring A)	**325.98**	**23.61**	−302.37	70.78	85.96	15.18	**232.09**	**0.96**	−231.13
1 (ring B)	347.55	36.91	−310.64	**64.57**	**80.64**	16.07	247.44	8.94	−238.5
3 (ring B)	330.64	26.66	−303.98	76.02	90.13	14.11	241.99	8.18	−233.81
11									
6 (ring A)	**320.79**	**17.20**	−303.59	73.75	87.93	14.18	**227.47**	−41.69	−269.16
7 (ring A)	339.34	29.45	−309.89	**56.54**	**72.78**	16.24	228.82	**−44.59**	−273.41
3 (ring B)	331.34	24.13	−307.21	75.46	90.23	14.77	239.74	−32.46	−272.20
1 (ring B)	348.40	34.66	−313.74	63.62	80.06	16.44	244.96	−32.10	−277.06
12									
5 (ring A)	337.60	29.20	−308.40	**61.80**	**80.45**	18.65	**226.87**	**−43.88**	−270.75
1 (ring B)	344.59	35.41	−309.18	67.97	83.07	15.10	240.02	−35.04	−275.06
3 (ring B)	**327.01**	**25.40**	−301.61	79.44	92.77	13.33	233.92	−35.35	−269.27
13									
5 (ring A)	340.23	31.07	−309.16	**53.48**	**72.66**	19.18	222.38	**−49.14**	−271.52
8 (ring A)	**323.94**	**24.56**	−299.38	82.38	93.35	10.97	235.00	−34.95	−269.95
3 (ring B)	346.21	36.32	−309.89	60.50	76.62	16.12	235.40	−39.93	−275.33
1 (ring B)	340.04	33.48	−306.56	76.14	93.97	17.83	244.86	−25.41	−270.27
14									
6 (ring A)	334.33	28.83	−305.50	66.96	81.34	14.38	**242.45**	**−30.01**	−272.46
1 (ring B)	345.98	38.17	−307.81	65.52	80.12	14.60	252.67	−21.89	−274.56
3 (ring B)	**331.87**	**28.00**	−303.87	75.26	94.35	19.09	248.30	−17.82	−266.12
Norathyriol									
2 (ring B)	**327.56**	**25.49**	−302.07	65.08	**79.88**	14.80	**212.43**	**−10.46**	−222.89
3 (ring B)	331.15	25.63	−305.52	71.99	87.08	15.09	222.93	−3.12	−226.05
6 (ring A)	403.04	25.69	−377.35	**0.75**	90.85	90.10	223.59	0.71	−222.88
8 (ring A)	413.97	35.74	−378.23	**0.75**	84.84	84.09	234.52	4.74	−229.78

a ΔPA = PA$_{water}$ − PA$_{gas}$.
b ΔETE = ETE$_{water}$ − ETE$_{gas}$.
c ΔPDE = PDE$_{water}$ − PDE$_{gas}$.

4. Conclusions

In this letter, the antioxidative activities of fourteen xanthones extracted from the pericarp of *G. Mangostana* in gas phase and water have been studied through HAT, SETPT and SPLET mechanisms, respectively. We have calculated the parameters of BDE, IE, PA, ETE and PDE according to the mechanism proposed in the literature for the radical scavenging activity. On the basis of the obtained results in the gas phase and water, the conclusions can be drawn as follows:

- Among the three mechanisms, HAT is thermodynamically preferred in gas phase and SPLET is more favored in water.
- Significant differences between gas phase and water enthalpies are characteristic for the reactions involving charged species.
- Among the studied fourteen xanthones, compound **10** and **11** are predicted to be potential antioxidants, this agrees with the results obtained from other studies [2,36].

Therefore, this study contributes to the ongoing interest on understanding of the antioxidant activity of xanthones extracted from the pericarp of *G. Mangostana* and their future exploitation for food or pharmaceutical applications.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2015.02.033.

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