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Thermodynamics of potential antioxidant action of Δ^5-sterols

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Abstract

In this work, we have calculated bond dissociation enthalpies of selected C–H and O–H bonds in sterols using two semi–empirical quantum chemistry methods AM1 and PM3.

Keywords: sterols, BDE, hydrogen atom transfer, AM1, PM3

Introduction

Phytosterols are triterpene compounds. They are structural components of plant membranes and stabilize phospholipid bilayers in plant cell membranes. In last 10 years, they received considerable attention because of their cholesterol–lowering properties, anticancer and antioxidant activity (Moreau et al. 2002; White and Armstrong 1986). In this work, we have studied following phytosterol: Δ^5–sitosterol, Δ^5–campesterol, Δ^5–avenasterol, Δ^5–brassicasterol, Δ^5–stigmasterol (Fig 1). We have studied also cholesterol present in animal cell membranes. Published works indicate that major targets of O_2 attack during sterol oxidation are C7–H and O–H bonds (Smith, 1996).

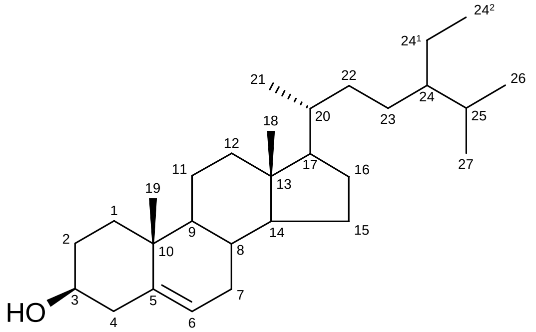

Figure 1: Atom numbering in sterols

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Materials and methods

Geometry optimization of parent molecules and corresponding radicals was performed using PM3 and AM1 semiempirical quantum chemistry methods using Hyperchem program package (Hyperchem, USA). These are specially designed to obtain enthalpies of formation of chemical systems. Dewar et al. (1985) AM1 method (Austin Model 1) represents a standard tool for both theoretical and experimental organic chemists. Later, Stewart (1989) proposed a mathematical re-parameterization called PM3 (Parameterized Model 3). Bond dissociation enthalpies (BDE) were calculated using the formation enthalpies of the molecule, M, radical, R, and hydrogen atom, H

$$\mathrm{BDE} = \Delta_f H(\mathrm{R}) + \Delta_f H(\mathrm{H}) - \Delta_f H(\mathrm{M})$$

Results and Discussion

Table 1 summarizes obtained results for C7–H and O–H bonds homolytic dissociation. These show that C7–H bond cleavage requires less energy than O–H bond. C7 carbon is in α–position to C5=C6 double bond.AM1 method predicts identical BDEs for all sterols. PM3 predicts BDE(C7–H) and BDE(O–H) values in 23 kJ mol^{-1} and 9 kJ mol^{-1} range, respectively. Since all sterols have identical structure of the rings, very close or identical BDEs can be expected. The results indicate that different tails in the studied molecules, attached at C17, do not affect BDEs. BDE(C7–H) are similar to O–H BDEs found for four tocopherols (Klein et al. 2007) that represent most powerful natural antioxidants.

Table 1: Bond dissociation enthalpies of studied sterols

Δ^5-sterol	BDE(C7–H) kJ mol^{-1}		BDE(O–H) kJ mol^{-1}	
	PM3	AM1	PM3	AM1
Sitosterol	330	336	421	466
Campesterol	330	336	422	466
Avenasterol	322	336	430	466
Brassicasterol	323	336	430	466
Stigmasterol	345	336	422	466
Cholesterol	330	336	421	466

Conclusion

In accordance with experimental works (Lampi et al. 2002; Smith 1996), we can conclude that most important site of oxidation of studied sterols is hydrogen at C7 atom.

Acknowledgement

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