PRELIMINARY COMPARATIVE STUDY OF THERMAL BEHAVIOR OF PURE CHOLESTEROL AND CHOLESTANOL

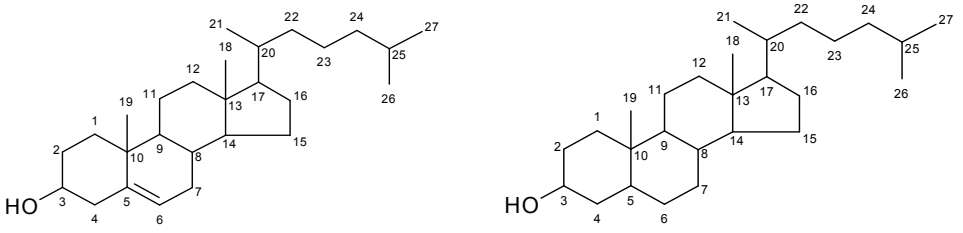
Mihaela Manea*, Valentina Chiosa and Cristina Mandravel

abstract: In this paper the thermal behaviour of the cholesterol and cholestanol, UCB Belgium and Aldrich p.a. products are studied by simultaneous TG/DTG-DTA thermal analysis. Experiments were realised in the same conditions, in inert and oxidative atmosphere. Obtained data are explained comparatively making judgements on the thermal reactivity of the two sterols.

key words: TG-DTA, cholesterol, cholestanol

Introduction

Cholesterol (Fig. 1a), the most abundant sterol in human body, is the subject of different spectral [1÷5], thermodynamic [6÷8] and modelling [9÷13] studies for the last years in pure state and artificial and natural mixtures. It is a major component of lipoproteins, a structural moderator of cell membranes permeability and a precursor in the biochemical synthesis of steroid hormones and D_3 vitamins. His important role in metabolism is not completely elucidated [6÷8].



a) b)

Fig. 1 *Molecular formula of cholesterol (a) and cholestanol (b).*

Cholestanol (Fig. 1b) is a minor, but very toxic sterol constituent in the human body; increase of cholestanol in serum concentration induces a pathological condition *cerebrotendinous xanthomatosis* (CTX) [14].

Conversion of the cholesterol in cholestanol injected in humans was reported in literature by Rosenfeld and all. in 1967, via a 3-ketonic intermediate [15].

* Department of Physical Chemistry, Faculty of Chemistry, University of Bucharest, bd. Elisabeta 4-12, sect. 3, 030018, Bucharest, Romania

Aim of this preliminary study is the comparison of thermal behaviour for these two sterols by TG/DTG and DTA methods.

Experimental part

Materials. In thermodynamic study were used UC Belgium p.a. cholesterol and Aldrich p.a. cholestanol products.

Methods. The instrumentation consisted in Simultaneous Thermal Analyzer STA 409 PC Luxx, manufactured by Netzsch Geratebau GmbH, using TG-DTA sample carrier with type S thermocouple (temperature range 20ºC ÷ 1300ºC) and mass resolution of 2 µg. The experiments were made using 0.3 ml Al_2O_3 crucibles.

All TG-DTA experiments were performed in oxidative (synthetic air 99.999%) and inert (N_2 99.999%) atmosphere with a carrier gas flow rate of 20 mL/min, protective gas flow rate of 10ml/min, at a heating rate of 2.5K/min in the temperature range 45°C ÷ 600°C and with the sample mass ranging between 5 and 7 mg cholesterol / cholestanol.

Results and Discussion

Preliminary analysis of the thermal behaviour of the both sterols can be interpreted as follows:

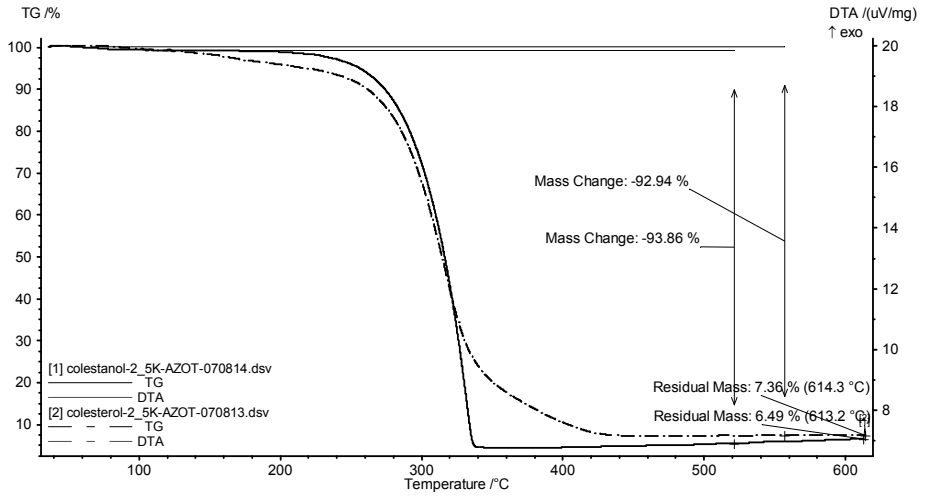


Fig. 2 *TG -cholesterol/cholestanol (N_2)*

In inert atmosphere the shape of the TG curve (Fig. 2) shows a one step decomposition process which is quite similar until 333ºC. After this temperature the decomposition process becomes very fast for cholestanol and significantly much slower for cholesterol, fact also

confirmed by the presence of DTA exothermal peaks in the same temperature region with the 332ºC (cholestanol) and 318ºC (cholesterol) DTG peaks, as it can be seen in Fig. 3.

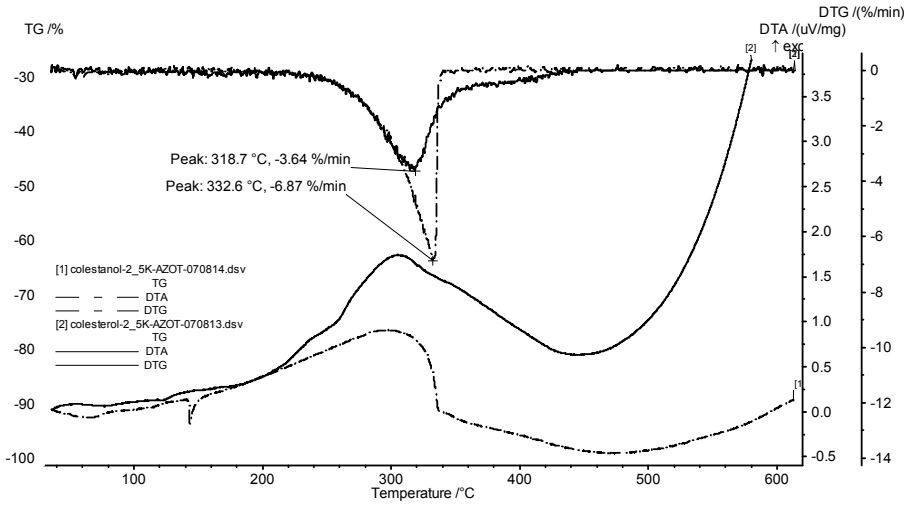


Fig. 3 *DTA/DTG-cholesterol/cholestanol* (N_2).

From the TG curves we can conclude that the two sterols are thermally stable both in inert and oxidative atmospheres under 200ºC. The decomposition of cholesterol and cholestanol in nitrogen seems to start around 250ºC which is an important hint for further investigations by GC-MS in the sense that derivatization is necessary to avoid thermal degradation and the induced degradation products.

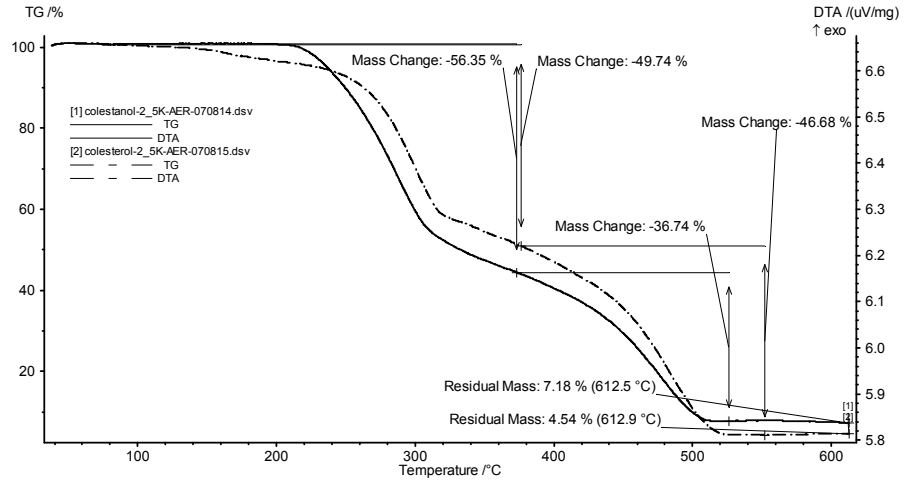


Fig. 4 *TG-cholesterol/cholestanol (air)*

In air atmosphere the shape of the TG curve (Fig. 4) shows a two step decomposition process. The decomposition process confirmed by the presence of DTA exothermal peaks in

the same temperature region with the 286ºC/477ºC (cholestanol) and 302ºC/482ºC (cholesterol) DTG peaks as it can be seen in Fig. 5.

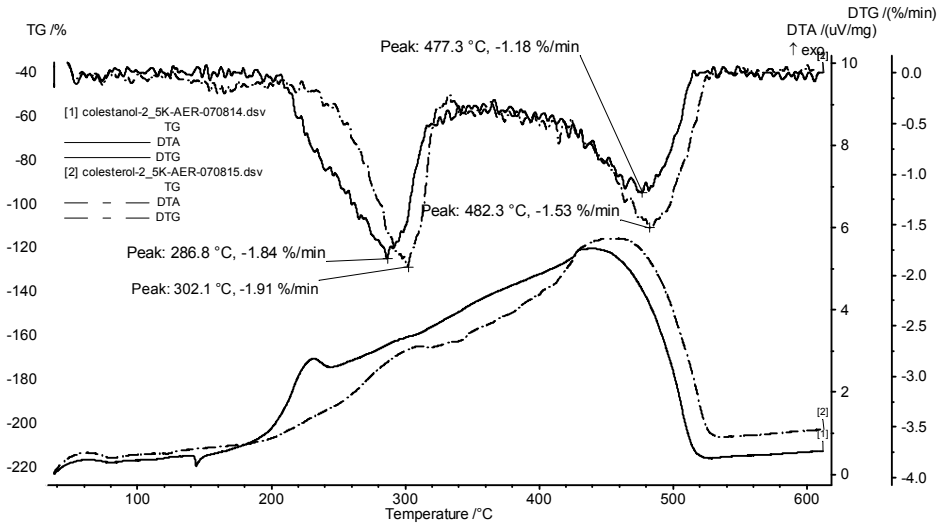


Fig. 5 *DTA/DTG-cholesterol/cholestanol (air)*

Thermal behaviour in air and inert atmosphere can be summarised by the data comprised in Tables 1 and 2 for TG/DTG and DTA measurements.

Table 1. Results of TG measurements

TG	Air atmosphere			Inert atmosphere	
	Mass change (%)		Residual mass(%)	Mass change (%)	Residual mass(%)
Cholesterol	49.74	46.68	4.54	92.94	7.36
Cholestanol	56.35	36.74	7.18	93.86	6.49

Table 2. Results of DTA measurements

DTA	Air atmosphere (2 peaks)		Inert atmosphere (1 peak)
Cholesterol	302.1°C (1.91%/ min)	482.3°C (1.53%/min)	318.7°C (3.64%/min)
Cholestanol	286.8°C (1.84%/min)	477.3°C (1.18%/min)	332.6°C (6.87%/min)

In the domain of temperatures and conditions corresponding to mass spectroscopy experiments from literature studies [16÷18] results that for studied sterols, process of parent peak formation (corresponding to M=386, respectively 388) is succeeded by numerous fragmentation stages. From analysis of 10 largest peak (see table 3) obtained on the mass spectrogram for both sterols results that the most probable process is lost of propane radical (M=43) from C_{24}. Reduced intensity of the peak corresponding to M=17 (radical hydroxyl), absent in Table 3 for both sterols, can be explained by the great tendency for recombination of OH radical, lost from position C_3.

Table 3. The 10 largest peaks in MS of studied sterols

Cholesterol	43.99	55.90	81.80	107.80	95.77
Cholestanol	215.99	233.9	81.69	107.67	55.66
Cholesterol	41.67	57.66	106.64	145.62	275.58
Cholestanol	95.64	43.63	165.58	108.54	234.53

Conclusions

In this preliminary study we observed firstly TG/DTG and DTA in the same conditions for pure cholesterol and cholestanol. These data show a larger thermal reactivity of cholesterol than cholestanol in accord with some modelling studies [9÷12].

REFERENCES

1. Senegacnik, N. and Klofutar, C. (1997) *Spectrochimica Acta* A **53**, 1495-505.
2. Senegacnik, N. and Klofutar, C. (1998) *Spectrochimica Acta* A **54**, 709-17.
3. Popescu Teodoreanu, C., Chiosa, V., Chivu, M. and Mandravel, C. (2002) *J. Univ. Chem. Technol. Metall* Sofia **34**, 115-20.
4. Chivu, M. (2002) *PhD Thesis*, Bucharest University.
5. Mandravel, C., Chiosa, V., Teodoreanu, C.L. and Stanculescu, I. (2005) *Rev. Roum. Chim* **50**(7-8), 683-8.
6. Kaloustian, J., Pauli A. N., Lechene de la Porte, P., Lafont, H. and Portugal, H. (2003) *Journal Termal Analysis Calorimetry* **71**, 341-51.
7. Teodoreanu, C.T. (2005) *Ph. D. Thesis***,** Bucharest University
8. Kaloustian, J., Lechene de la Porte, P., El-Moselhy, T., Lafont, H. and Portugal, H. (2003) *Journal Termal Analysis Calorimetry* **71**, 331-8.
9. Bendic, C., Popescu, C., Chiosa, V., Stanculescu, I. and Mandravel, C. (2001) *Anal Univ Buc*., anul **X** (serie noua)**,** 19-25.
10. Weinberg, J., Olteanu, M. and Lerner, D.A. (2005) *Rev. Roum. Chim*. **50**(6), 479-84.
11. Stanculescu, I., Manea, M., Chiosa, V. and Mandravel, C. (2006) *Anal. Univ. Buc*., anul **XV** (serie noua) vol. **I**, 101-5.
12. Manea, M., Chiosa, V., Raju, G. and Stanculescu, I. (2006) *Anal. Univ. Buc-Chimie*, anul **XV** (serie noua) vol. **II,** 43-8.
13. Chiosa, V., Manea, M., Stanculescu, I. and Mandravel, C. (2007) *Revue Roumaine de Chimie*, in press.
14. Seyama, Y. (2003) J. Med. Fool. **6**, 217-24.
15. Rosenfeld, R.S., Youmof, B. and Hellman, L. (1967) *J. Lipid. Res*. **8**, 16-23.
16. Tokuda, H., Saitoh, E., Kimura, Y. and Takano, S J. (1988) *Chromatogr*. **454**, 109-20.
17. Van Gelder,W.M.J., Jonker, H.H., Huizing, H.J. and Scheffer, J.J.C. (1988) *J. Chromatogr*. **442**, 133-45.
18. Japp, M., Gill, R. and Osselton, M.D (1987) *J. Forensic Sci*. **32**(6), 1574-86.