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Thermo-oxidative evaluation of new cardol derivatives as antioxidants for mineral oils

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Abstract In this study, the thermo-oxidative stability of two new phosphorylated derivatives of cardol, a compound from the cashew (*Anacardium occidentale* L.) industry waste CNSL (cashew nutshell liquid), were evaluated. The antioxidant capacity of these new molecules upon two mineral oils, NH10 and NH20 were also studied by thermogravimetric analysis (TG/DTG), observing the onset and offset temperatures variation. The results showed that both MP and DP Cardol increased considerably the onset and offset temperatures of NH10 and NH20 oils.

Keywords Cashew nutshell liquid · Cardol · Antioxidant · Thermogravimetry

Introduction

Mineral oils are products derived from crude oil by various refining methods. An average oil molecule may contain several different structures, e.g., straight and branched-chain saturated hydrocarbons (paraffins), closed-ring saturated hydrocarbons (naphthenes), and unsaturated, aromatic hydrocarbons [1].

Naphthenic oils have a wide variety of applications where they are used as process oils. Differently from paraffinic oils, they are composed basically by closed-ring saturated hydrocarbons; possess lower viscosity, lower flash point, lower pour point, and lower resistance to oxidation. Owing to these properties, naphthenic mineral oils are generally used in process with narrow temperature ranges and where a low pour point is required.

To increase their performance and extend their application range, the utilization of additives, such as antioxidants, is of great value. In this way, our group evaluated in a previous article the use of phosphorylated cardanol, the main constituent of technical CNSL (Cashew Nutshell Liquid), as a new potential antioxidant for naphthenic oils NH10 and NH20 [2].

Cashew nut shell liquid (CNSL), a byproduct obtained during the processing of cashew nuts, the pseudo-fruit from *Anacardium occidentale* L., is a brownish viscous oil rich in phenolic compounds. Vietnam, Nigeria, India, Brazil, and Indonesia are the largest producers/exporters of cashew of the world representing more than 90% of the global production. World-wide CNSL production is estimated to be 360,000 tons per year, and as the production of cashew nuts is rising, the availability of up to 600,000 tons/year of CNSL should be reached soon [3, 4].

Depending on the basis of the mode of extraction from cashew nut shell, CNSL is classified into two types, solvent-extracted CNSL and technical CNSL. Commercially available technical CNSL is obtained by roasting shells, and contains mainly cardanol and cardol (Fig. 1), both having degrees of saturation of the C15 alkyl side chain varying from complete saturation to partial unsaturation, as shown in Fig. 1 [5, 6].

Although cardanol and its derivatives have been well studied, demonstrating many different applications, e.g., polymers [7], antioxidants [8], surfactants [9], flame-retardants [10], gum inhibitors for gasoline [11], and many others [12], cardol remains as a forgotten molecule.

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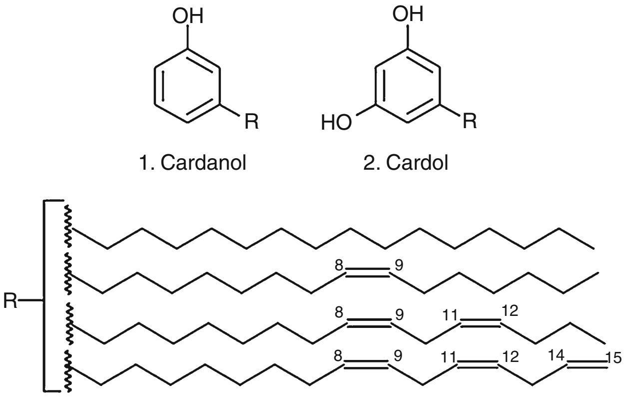


Fig. 1 The main constituents of technical CNSL

Owing an orcinol-like structure, cardol is the minor constituent of technical CNSL, representing 15–20% (w/w) of it. Many biological activities have been related to cardol, such as molluscicidal [13], larvicidal [14], antifilarial [15], and acetyl cholinesterase inhibitors [16], but almost no fine chemicals with industrial applications derived from cardol are found in the scientific literature [5].

Knowing that CNSL is considered a byproduct from the cashew industry and Brazil produces more than 17.000 tons of CNSL every year, our laboratory is continually working on to develop new products and processes related to cardol and cardanol, in the sense to aggregate more value to CNSL.

In this study, our continued effort to create new CNSL derivatives as potential *bioadditives* was considered worthwhile, preparing new phosphorylated additives derived from cardol, mono (MP) and di (DP) phosphorylation of hydrogenated cardol, respectively (Fig. 2), and evaluating their thermo-oxidative stability. As well, their antioxidant capacities upon mineral oils (NH10 and NH20) were evaluated by thermogravimetric analysis (TG/DTG). Phosphorylated products from cardol have been patented [17] based on the present study results.

Experimental procedure

Materials

The NH10 and NH20 oils were supplied by Petrobras S/A, technical CNSL was supplied by Amêndoas do Brasil LTDA. Reagents and solvents were supplied by Aldrich and Vetec Química. Column chromatography was run using silica gel 60 (70–230 mesh, Vetec Química), while TLC was conducted on precoated silica gel polyester sheets (Kieselgel 60 F254, 0.20 mm, Merck).

Measurements

The samples obtained were analyzed by GC–MS on a Hewlett-Packard Model 5971 using a (5%-phenyl)-methylpolysiloxane (DB-5) capillary column (30 m × 0.25 mm) with film thickness 0.1 mm; carrier gas helium, flow rate 1 mL min^{-1} with split mode. The injector temperature and detector temperature were 250 and 200 °C, respectively.

Melting points were determined using a digital Mettler Toledo FP90 apparatus.

NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz for ^{1}H, 125 MHz for ^{13}C and 202.5 MHz for ^{31}P NMR) using $CDCl_3$ as solvent for phosphorylated cardol derivatives and acetone-d6 for cardol.

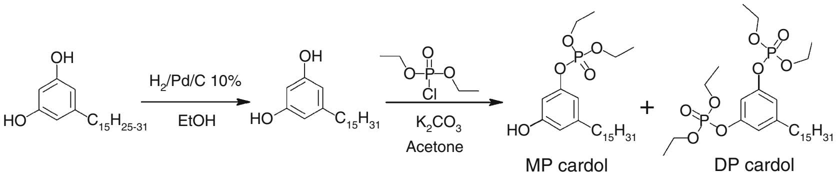
Thermoanalytical measurements were carried out using a Mettler-Toledo TGA/SDTA851e thermogravimetric analyzer. The measurements were performed at scanning rate of 10 °C min^{-1}. Samples of 10 mg were heated from 25 to 800 °C. The measurements were carried out at synthetic air atmosphere (50 mL min^{-1}). The initial degradation temperature, called onset temperature, is not so easy to identify. Therefore, a better definition of start of reaction is the extrapolated onset temperature, T_e, which is basically the intersection of the tangents of the curve at the upper horizontal baseline and the steepest part of the curve. The same definition could be applied to the extrapolated offset temperature, T_o, but in this case the intersection is made between the tangents of the curve at the lower horizontal baseline and the steepest part of the curve [18].

Methods

Isolation of cardol

Cardol (2.1 g) was isolated from technical CNSL (20.0 g) through column chromatography eluted with a stepwise gradient of *n*-hexane/ethyl acetate (from 9:1 to 7:3 by volume). The fractions obtained in the column

Fig. 2 Reaction scheme for the synthesis of Cardol derivatives



chromatography were analyzed through thin layer chromatography (TLC), reunited according to their retention factors and then characterized by GC/MS and ^{1}H NMR as pure cardol (Fig. 1a).

Cardol: brownish oil; ^{1}H NMR (acetone-d6, δ): 0.80 (t, 3H); 1.26 (m); 1.51 (m); 2.05 (m); 2.39 (t); 2.75 (m); 4.94 (m); 5.31 (m); 5.77 (m); 6.05 (t, 1H); 6.09 (d, 2H). MS: $m/z = 314$ (M^+) and 316 (M^+).

Hydrogenation of cardol

Cardol (3.0 g) was dissolved in 10 mL of ethanol (previously purged with H_2), and 10% Pd/C (0.3 g) was added. The mixture was magnetically stirred under a H_2 atmosphere (2 bar) for 72 h at room temperature in a 100 mL Glass reactor connected with a manometer. The resulting solution was filtered through a Celite bed to remove the catalyst, and then evaporated under reduced pressure, 2.56 g (85.3%) of a solid material was obtained and then characterized by GC/MS and ^{1}H NMR as the hydrogenated cardol.

Hydrogenated cardol: white solid (m.p.: 94.5–95 °C); ^{1}H NMR (acetone-d6, δ): 0.88 (t, 3H); 1.28 (m); 1.56 (m, 2H); 2.43 (t, 2H); 6.17 (s, 1H); 6.18 (s,2H). MS: $m/z = 320$ (M^+).

Mono-phosphorylation of hydrogenated cardol (MP Cardol)

Phosphorylated cardol derivatives were synthesized according to the modifications of a previous published procedure [2]. The stoichiometric ratio of the reactants (cardol, diethyl chlorophosphate, and potassium carbonate) was changed based on the degree of substitution of the desired product, mono or di-phosphorylated (Fig. 2).

Hydrogenated cardol (3.125 mmol), diethyl chlorophosphate (3.125 mmol), and potassium carbonate (3.5 mmol) were added to a 250-mL round-bottom flask containing acetone (150 mL). The mixture was magnetically stirred under reflux temperature for 10 h. The removal of the solvent left an oily residue, which was then purified by column chromatography on silica gel (hexane/ethyl acetate 5:5) to give 884 mg (62%) of a yellowish oil, characterized by GC/MS and NMR (^{1}H, ^{13}C, and ^{31}P) as the mono-phosphorylated cardol derivative (MP Cardol).

Compound MP Cardol: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.881$ (t, 3H); 1.257 (s); 1.359 (t, 6H); 1.556 (m, 2H); 2.492 (t, 2H); 4.203 (m, 4H); 6.464 (s, 1H); 6.501 (s,1H); 6.751 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.25$; 16.15; 22.85; 29.44; 29.52; 29.69; 29.78; 29.86; 31.18; 32.09; 36.00; 65.05; 104.92; 111.24; 112.87; 145.91; 151.11; 157.98. ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = -5.72$. MS: $m/z = 456$ (M^+).

Di-phosphorylation of hydrogenated cardol (DP Cardol)

The procedure for di-phosphorylation of cardol was the same as mentioned above; the only modifications were the stoichiometric ratio and reaction time. Hydrogenated cardol (3.125 mmol), diethyl chlorophosphate (6.3 mmol), and potassium carbonate (6.5 mmol) were added to a 250-mL round-bottom flask containing acetone (150 mL). The mixture was magnetically stirred under reflux temperature for 18 h. The removal of the solvent left an oily residue, which was then purified by column chromatography on silica gel (methanol/ethyl acetate 2:8) to give 747 mg (41%) of a brownish oil, characterized by GC/MS and NMR (^{1}H, ^{13}C, and ^{31}P) as the di-phosphorylated cardol derivative (DP Cardol).

Compound DP Cardol: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.873$ (t, 3H); 1.259 (s); 1.373 (t, 12H); 1.578 (m, 2H); 2.570 (t, 2H); 4.186 (m, 8H); 6.888 (s, 2H); 6.919 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.27$; 16.20; 22.86; 29.41; 29.54; 29.64; 29.88; 31.16; 32.11; 35.96; 64.92; 109.73; 116.77; 146.38; 151.24. ^{31}P NMR (202 MHz, $CDCl_3$): $\delta = -6.62$. MS: $m/z = 592$ (M^+).

Results and discussion

Thermal analyses

Phosphorylated cardol derivatives

The thermogravimetric analyses (TG/DTG) of mono and di phosphorylated Cardol are shown in Figs. 3 and 4, respectively. TG curves are plotted as continued strong lines and their first derivatives as dashed lines.

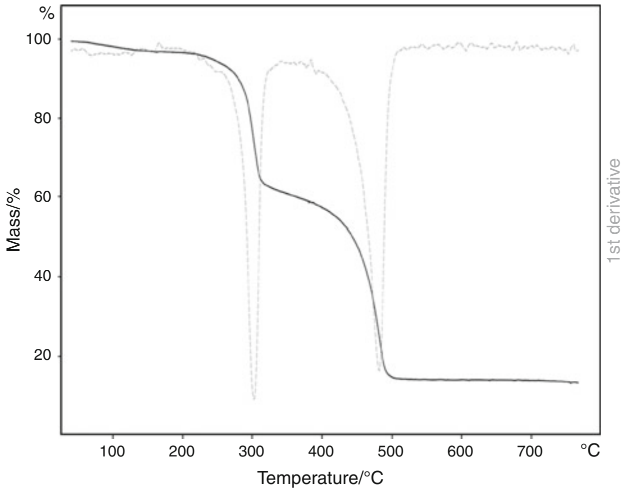


Fig. 3 TG analysis of MP Cardol

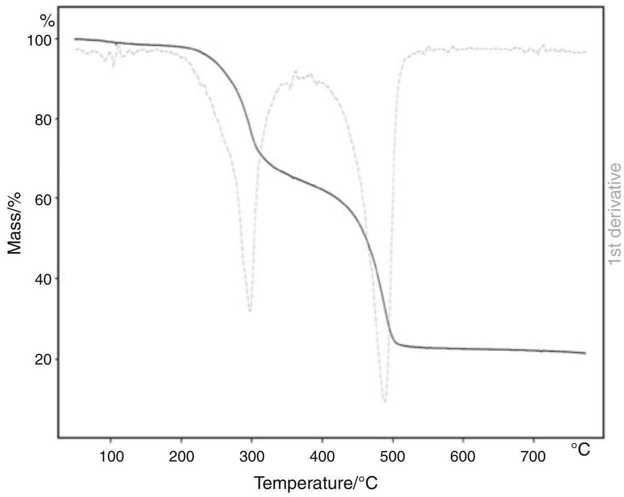


Fig. 4 TG analysis of DP Cardol

Although the graphics, in a more general evaluation, are very similar, it is interesting to observe the shapes of the first event derivatives in both analyses. In monophosphorylated (MP) cardol this event is very thin and well defined, while in the diphosphorylated (DP) cardol this event is much broader and the derivatives of the second event are very similar in shape. This behavior probably indicates the replacement of the hydroxyl group, present in mono substituted derivative, for the phosphate group present in the di substituted one. Table 1 summarizes the temperatures observed during each event.

Mineral oils

The minerals oils, NH10 (Fig. 5) and NH20 (Fig. 6), were first analyzed without addition of the *bioadditives* for comparison purposes.

The main difference between these two mineral oils is their thermal capacity. NH10 is more thermal sensible with onset temperature (T_e) about 181 °C, while NH20 is required for higher temperature applications, since its onset temperature is about 208 °C.

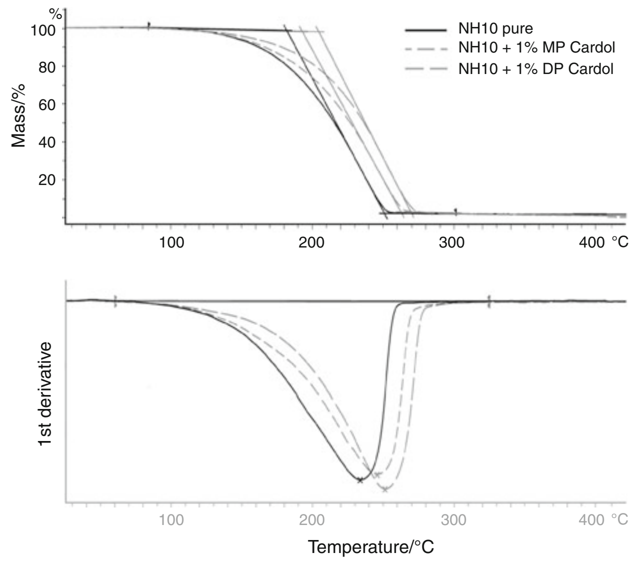


Fig. 5 TG and DTG analysis of additivated NH10 samples

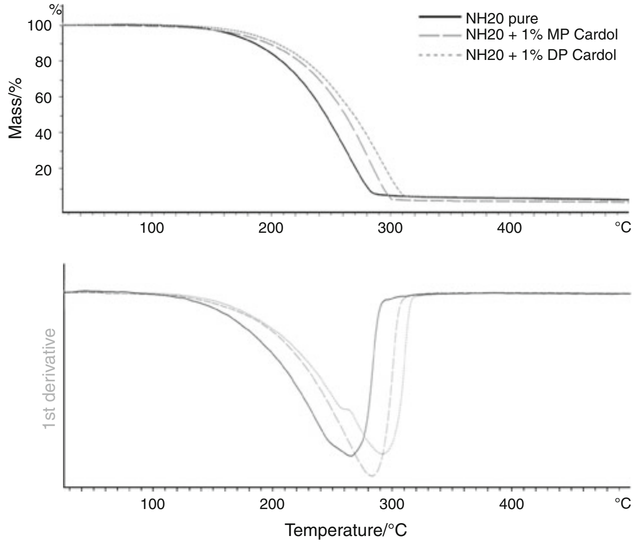


Fig. 6 TG and DTG analysis of additivated NH20 samples

Additivated NH10 oil

As the main purpose of this study was to evaluate the antioxidant properties of new phosphorylated cardol derivatives, NH10 oil was additivated with 1% MP Cardol and with 1% DP Cardol, separately.

In Fig. 5, the additivation of NH10 with 1% MP Cardol resulted in an increase of 6.4% in the onset temperature (T_e), from 181.1 to 192.7 °C, and a 5.0% increase in the offset temperature (T_o), from 250.6 to 263.2 °C. The peak

Table 1 Temperatures observed during cardol derivatives thermal analyses

Sample	First event			Second event			Residue
	T_e/°C	T_o/°C	Peak/°C	T_e/°C	T_o/°C	Peak/°C	%/weight
MP Cardol	286.67	308.72	302.00	457.13	488.57	481.33	14
DP Cardol	268.58	308.33	296.33	457.72	495.85	487.17	22.5

Table 2 Temperatures observed during additivated NH10 oil thermal analyses

Sample	T_e/°C	T_o/°C	Peak/°C
NH10 oil (pure)	181.10	250.68	233.67
NH10 oil + 1% MP Cardol	192.71	263.29	245.67
NH10 oil + 1% DP Cardol	203.69	268.31	251.33

Table 3 Temperatures observed during additivated NH20 oil thermal analyses

Sample	T_e/°C	T_o/°C	Peak/°C
NH20 oil (pure)	207.94	283.19	265.17
NH20 oil + 1% MP Cardol	228.70	299.58	283.00
NH20 oil + 1% DP Cardol	230.79	310.18	291.83

of maximum degradation temperature was also increased, rising from 233.6 to 245.6 °C.

The addition of 1% DP Cardol produced better effects to the thermal properties of NH10 oil than MP Cardol. The T_e and T_o rose to 203.6 and 268.3 °C, respectively. The peak of maximum degradation temperature went to 251.3 °C, against 245.6 °C from MP Cardol additivation. This characteristic permitted to conclude that the second phosphate group has a very important function, giving more thermal stability to the NH10 oil, if compared with the hydroxyl group from mono substituted cardol. Table 2 shows the results obtained from both MP Cardol and DP Cardol additivation.

Additivated NH20 oil

The additivation of NH20 oil with 1% phosphorylated cardol derivatives also improved its thermo-oxidative stability. Figure 6 shows the TG/DTG analyses for NH20 oil pure and additivated with 1% MP Cardol and 1% DP Cardol.

The analysis for the additivation with 1% MP Cardol, showed an increase of 10% in T_e, rising from 207.9 to 228.7 °C. This effect was not so pronounced in the T_o, which increased from 283.1 to 299.5 °C. An improvement in the peak of maximum degradation temperature was also observed, rising from 265.1 to 283.0 °C.

For the additivation with 1% DP Cardol, NH20 oil showed a better thermo-oxidative stability, as expected, than with MP Cardol. The presence of a second phosphate group in the molecule resulted in an improvement of onset and offset temperatures in greater values, which rose to 230.7 and 310.1 °C, respectively. Table 3 summarizes the results obtained from NH20 oil additivated with both MP and DP Cardol products.

Conclusions

In this study, the authors synthesized, evaluated the thermo-oxidative stability, and analyzed the antioxidant effect upon mineral oils of two new phosphorylated cardol derivatives, MP Cardol and DP Cardol. The syntheses were successful and the new products were fully characterized. The evaluations of their antioxidant activity upon mineral oils, NH10 and NH20, were made through TG/DTG analyses which showed excellent results for both new molecules.

The first product, MP Cardol, showed a great antioxidant activity upon mineral oils as 1% additive, increasing the onset temperature of NH10 and NH20 oils in 6 and 10%, respectively, and the offset in 5 and 5.7%, respectively. For DP Cardol, the analyses showed better results, the onset/offset temperatures for NH10 and NH20 rose 12%/7% and 11%/9.5%, respectively. This behavior suggested that the presence of a second phosphate group was essential to improve the thermo-oxidative stability of the mineral oils studied.

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References

1. Levin M, Redelius P. Determination of three-dimensional solubility parameters and solubility spheres for naphthenic mineral oils. Energ Fuel. 2008;22:3395–401.
2. Rios Façanha MR, Mazzetto SE, Carioca JOB, Barros GC. Evaluation of antioxidant properties of a phosphorated cardanol compound on mineral oils (NH10 and NH20). Fuel. 2007;86: 2416–21.
3. Gedam PH, Sampath Kumaran PS. Cashew nut shell liquid: extraction, chemistry and applications. Progr Org Coat. 1986;14:115–57.
4. Attanasi OA, Berretta S, Fiani C, Filippone P, Mele G, Saladino R. Synthesis and reactions of nitro derivatives of hydrogenated cardanol. Tetrahedron. 2006;62:6113–20.
5. Mazzetto SE, Lomonaco D, Mele G. Cashew nut oil: opportunities and challenges in the context of sustainable industrial development. Quim Nova. 2009;32:732–41.
6. Kumar PP, Paramashivappa R, Vithayathil PJ, Rao PVS, Rao AS. Process for isolation of cardanol from technical cashew (*Anacardium occidentale* L.) nut shell liquid. J Agric Food Chem. 2002;50:4705–8.
7. Yadav R, Srivastava D. The effect of CTBN concentrations on the kinetic parameters of decomposition of blends of cardanol-based epoxidized novolac resin modified with carboxyl-terminated liquid copolymer. J Appl Polym Sci. 2009;114:1694–701.
8. Lomonaco D, Cangane FY, Mazzetto SE. Thiophosphate esters of cashew nutshell liquid derivatives as new antioxidants for poly(methyl methacrylate). J Therm Anal Calorim. 2011;104:1177–83.
9. Scorzza C, Nieves J, Vejar F, Bullón J. Synthesis and physicochemical characterization of anionic surfactants derived from cashew nut shell oil. J Surfactants Deterg. 2011;13:27–31.

10. Ravichandran S, Bouldin RM, Kumar J, Nagarajan R. A renewable waste material for the synthesis of a novel non-halogenated flame retardant polymer. J Clean Prod. 2011;19:454–8.
11. Castro Dantas TN, Dantas MSG, Dantas Neto AA, D'Ornellas CV, Queiroz LR. Novel antioxidants from cashew nut shell liquid applied to gasoline stabilization. Fuel. 2003;82:1465–9.
12. Mele G, Vasapollo G. Fine chemicals and new hybrids materials from cardanol. Mini-Rev Org Chem. 2008;5:243–53.
13. Stasiuk M, Kozubek A. Biological activity of phenolic lipids. Cell Mol Life Sci. 2010;67:841–60.
14. Lomonaco D, Santiago GMP, Ferreira YS, Arriaga AMC, Mazzetto SE, Mele G, Vasapollo G. Study of technical CNSL and its main components as new green larvicides. Green Chem. 2009;11: 31–3.
15. Ghisalberti EL. Secondary metabolites with antinematodal activity. Stud Nat Prod Chem. 2002;26:425–506.
16. Stasiuk M, Bartosiewicz D, Kozubek A. Inhibitory effect of some natural and semisynthetic phenolic lipids upon acetylcholinesterase activity. Food Chem. 2008;108:996–1001.
17. Patent 013100000095, deposit 03/08/2010 - under sigil.
18. Heal GR. Thermogravimetry and Derivative Thermogravimetry. In: Haines PJ, editor. Principles of thermal analysis and calorimetry. Cambridge: Royal Society of Chemistry; 2002. p. 10–53.