Lyoluminescence Dosimetry of L-Proline Incorporated of Sensitizer Dependence on the Temperature and pH of Solution

Qahtan Adnan Abdulqader[1], Ammar Alhasan*[2]

[1]Department of Physics, College of Science, Al-muthanna University, Iraq
[2]College of Pharmacy, Al-Muthanna University, Al-Muthanna, Iraq

Abstract

To increase the sensitivity of dosimeter, it has to improve the properties that are required to increase its sensitivity. It was proven that the dependence of lyoluminscence (LL) of irradiated amino acid (L-prolin) incorporated with chemiluminscence reagent (luciginine) on the pH and temperature of the solution. LL means the emission of light from dissolved material in a suitable solvent, which is previously exposed to ionizing radiation. When the incorporated phosphor irradiated to gamma rays an electronically excited species are trapped within the solid matrix, this extra energy will be emitted in the form of light ($\lambda = 420\text{-}500nm$), on dissolving the material in water in this test. The LL intensity increases with increasing pH of the solution. The best reproducible and optimum LL intensity is at (pH=8.5-9) of the solution, However, LL intensity will be decreased when the PH is higher than 12. In this value of pH the stability of free radicals is optimum. The same is found for solvent temperature dependence, the optimum LL intensity is at 45-48 ^{o}C. LL intensity will increase up to 70 ^{o}C,it was found that the total glow increased because of increasing the self-glow of luciginine , but LL intensity will decrease because of dissociation of phisphore structure. In addition to the self-glow of the sanitizer will increase too at temperate up to 70 ^{o}C , however, that will cause self-glow to the dosimeter material.

Keywords: lyoluminscence; amino acid; gamma rays; pH; solvent

<div dir="rtl">

تأثير درجة الحرارة ودرجة الاس الهيدروجيني على التقنين الاشعاعي بطرية التالق الاذابي لل (L– proline) الممزوج بلمتحسس الكيميائي

قحطان عدنان عبد القادر[1] ، عمار محمد جعاز الحسن[2]*

[1] قسم الفيزياء ،كلية العلوم ،جامعة المثنى ، المثنى ، العراق

[2] كلية الصيدلة ، جامعة المثنى ، المثنى ، العراق

الخلاصة

الزيادة حساسية المقنن الاشعاعي, لا بد من تحسين العوامل والصفات التي تحدد حساسيتة. و التألق الاذابي (LL). تم اختيار الحامض الاميني (L–prolin) كمقنن اشعاعي وتم تطعيمه بمادة التألق الكيميائي كمحفز لاشارة التألق الاذابي. حيث سيزداد عدد الجذور الحرة المتكونة بسبب الاشعاع. وعند ذوبان مادة المقنن ,فأن المذيب سيوفر طريقا سهلا لاتحاد الجذور الحرة .يشير هذا البحث الى العوامل التي تعتمد عليها عملية انبعاث الضوء اثناء اذابة مادة صلبة في مذيب سائل مثل معامل الهيدروجين (PH) ودرجة الحرارة. فمن خلال التعريف العام ل (lyoluminscence) والتي تعني انبعاث موجات ضوئية من للمادة والتي تم

</div>

---

*Email: ammar.physicist@yahoo.com

تعريضها الى اشعاعات مؤينه ;فعند تعرض مادة الفسفور الى اشعة كاما فان ذلك يسبب تهيج الكتروني مما يجعل الطاقة الاضافية سوف تنبعث بشكل موجات ضوئية ذات طول موجي 420 –500 نانومتر . وبذلك فقد تم التوصل الى ان شدة (LL) تزداد بازدياد مقدار ال PH ووجد ان الازدياد الامثل في الشدة عند معامل هيدروجين (8.5–9) ولكن تتناقص عند ما يصل معامل الهيدروجين الى اكثر من12كما تم التوصل الى الشدة الضوئية الأمثل للمحلول عند درجة حرارة (45–48) درجة سيليزية. ان التالق الكلي سيزداد مع ارتفاع درجة الحرارة ولكن هذه الزيادة بسب زيادة التوهج الذاتي لصبغة اللوسجنين وهذا يتم على حساب نقصان شدة التالق بسب تحلل التركيب الكيمياوي لمادة التالق (الفسفور)بالإضافة الى إمكانية الحصول على شدة ضوئية اعلا عند درجة حراره 70 درجة سيليزية ولكن ذلك يسبب توهج ذاتي للمقنن الاشعاعي.

Introduction

From historical point review, lyoluminscence (LL) of organic solids can be considered as a special case of chemiluminscence [1]. Many years after wiedemann initial observations, Ahnstrom and Ehrestein and later Westermark and Grapengieser, have reported LL in organic solids [2]. Lyoluminescencce yield depends on many parameters such as gamma dose, particle size of the sample, amount of the solute, amount of the solvent, pH value of the solvent, temperature of the surroundings, etc.[3].

It is well-known that the phenomenon of luminescence shows the intensity depends on radiations. The intensity of LL signal is a measure of absorbed dose in the material. Repeatedly, LL has been reported from gamma irradiated and electrolytic dyed alkali halide with water containing luminal as solvent; excess color centers lead to increase LL intensity [4]

The present interest in LL and its applications stems from the work initiated in Birmingham by Ettinger. The Birmingham group investigated the effect of LL in both organic and inorganic materials in more detail and first proposed the use of it for the purpose of radiation dosimetry [5]. LL has been observed in the following categories of organic compounds: mono-, poly- and oligosaccharides[6], aminoacids [7], proteins [8], as well as in some complex dry biological materials such as milk [9].

The mechanisms of LL were discussed by the aid of its spectra [10]. Strong evidence is given in favor of the involvement of peroxy radicals, formed by oxidation of radiation produced radicals in the solid [11].

While a kind of defects formed in irradiated inorganic salts, like NaCl, known as color centers, named F-centers and V-centers [12] which release energy of the ionizing radiation in the form of light when dissolved in suitable solvents. Many studies were done in order to enhance LL signal, Eriksson showed that LL signal about ten times brighter in water saturated with N_2 than with O_2 [13]. C.Bhawna *etal.* Study the effect of pH on LL signal by using the color centers formed in NaCl [14].

In this study , the LL of L-proline incorporated with luciginine were developed, such phosphors raises hopes that the practical range of radiation doses extends well below and its dependence on pH and the temperature of solution.

The experiment

Different concentrations of luciginine (10^{-3}M up to 10^{-5}M) were added to a fixed weight of L-proline (10mg), the solution left to dry at ambient temperature. Then the powder having different grain sizes were separated by using sieves of particular dimensions which represented in (Table-1). Then powder was colored for 30 seconds by exposing them to *Caesium-137* (Cs^{137}) gamma source of dose rate 0.35 Gy/min. Figure-1 shows the experimental set up that is done locally in order to be used for LL measurements, solvent(water of different pH) was dropped on the powder using syringe. The intensity of LL produced was detected by an electronic integrator scalar.

Table 1-The experimental data of the concentrations of lucigenin correspond to LL intensity peak

L-prolin mass(mg)	Luciginine concentration(M)	LL intensity (normalized unit)
10	10^{-5}	0.83
10	5×10^{-5}	1
10	10^{-4}	0.78
10	5×10^{-4}	0.59
10	10^{-3}	0.31
10	5×10^{-3}	0.18
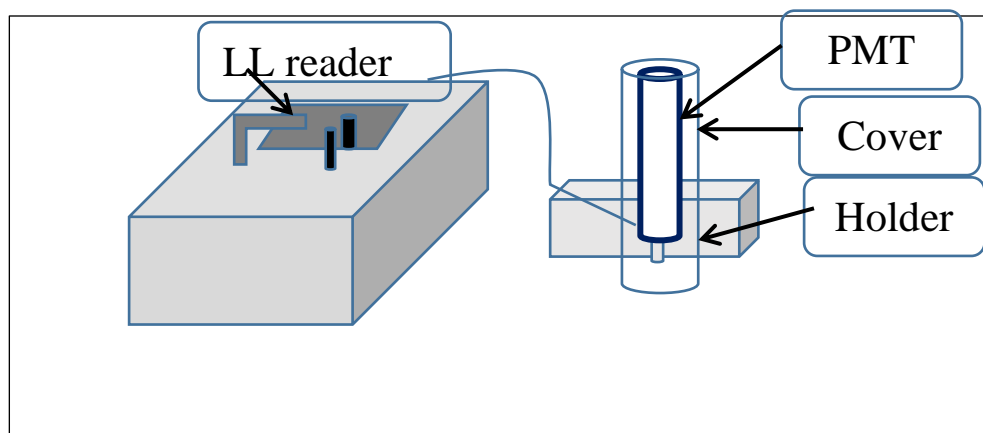
Figure 1-Schematic view to LL apparatus that is set up locally.

Results

Figure-2 shows the time dependence of the LL intensity of γ-irradiated L-prolin incorporated with luciginin for different grain sizes (millimeters). It is seen that when irradiated grains are dissolved in an affixed volume of distilled water (5ml), then it decreases and finally disappears. The Highest intensity of LL was determined at grain size of 0.1 mm.
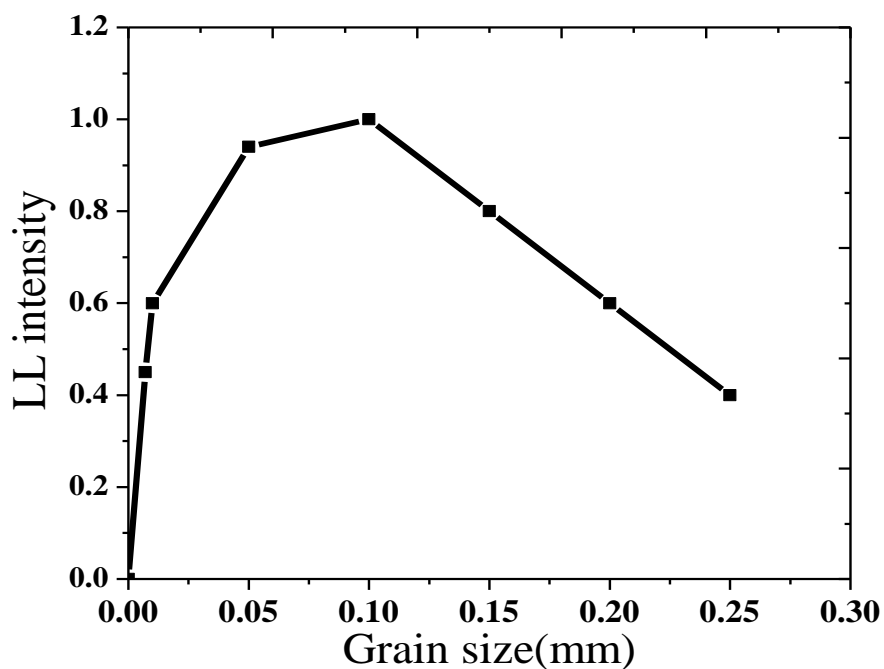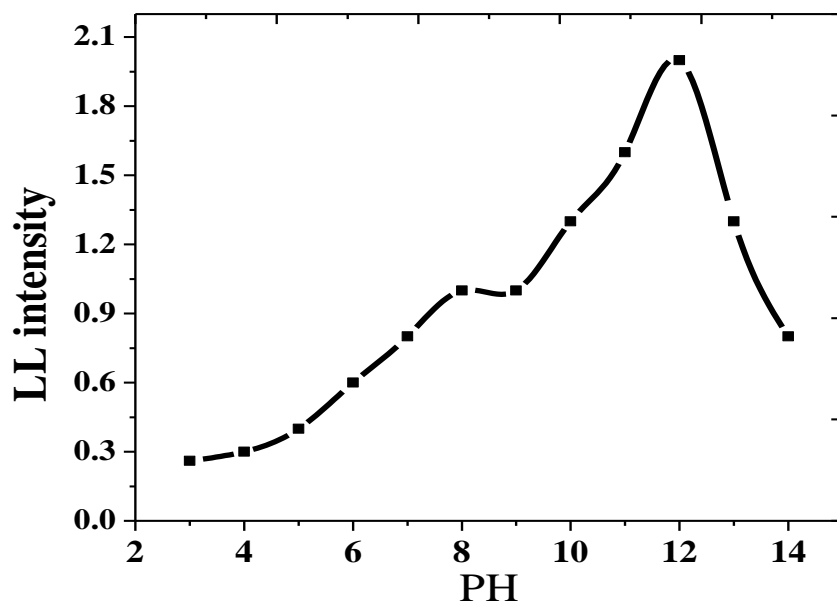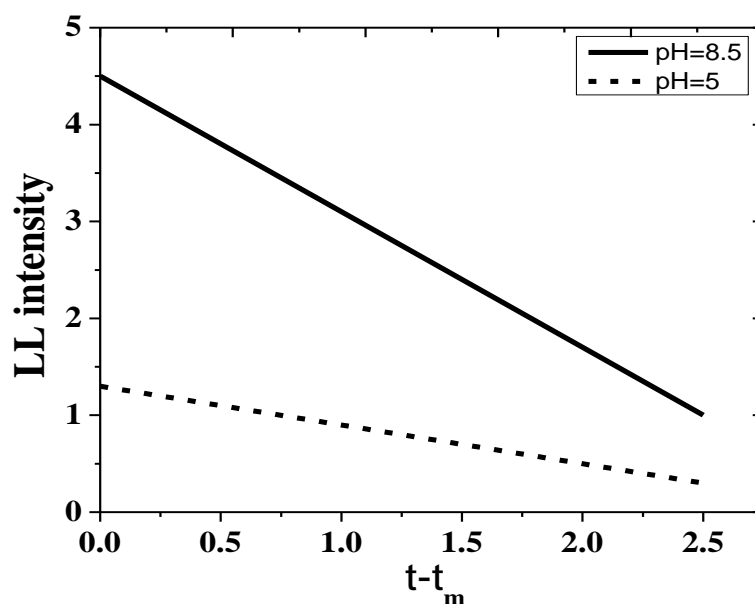

Figure 2- the dependence of LL intensity with grain sizes of the phosphorus.

Figure-3 shows the time dependence of the LL intensity for different pH of the solution for L-prolin incorporated of lucigenin. It had seen that LL intensity increases with an increasing pH value of the solvent and then it was decreased with increasing the pH value of the solvent for pH>12; so when grain size 0.1 mm, The best value for pH is 8.5.

Figure 3-The dependence of LL intensity on pH of the solvent.

Figure-4 shows the exponential decay of LL versus $(t-t_m)$, it is a straight line with a negative slope. This fact shows $(t-t_m)$ plot depends on the pH of the solvent and its maximum for a particular pH of the solution for which the LL value is optimum. The LL signal for pH=8.5 decay slower than that of pH=5.

Figure 4-The relation between LL intensity and $t-t_m$. Decay curve of LL signal.

Figure-5 shows the dependence of LL signal, the total lumin. separated from self-glow where the self-glow is a lumen without radiate, on different solvent temperature. From the figure, it has seen LL intensity increases with increasing of solvent temperature, but after 45-48 ^oC self-glow of lucigenin become large, which makes a large uncertainty in measurements. Solvent temperature degrees more than 70 ^0C cause dissociate the structure of the phosphor which causes decreasing LL signal as temperature increase.
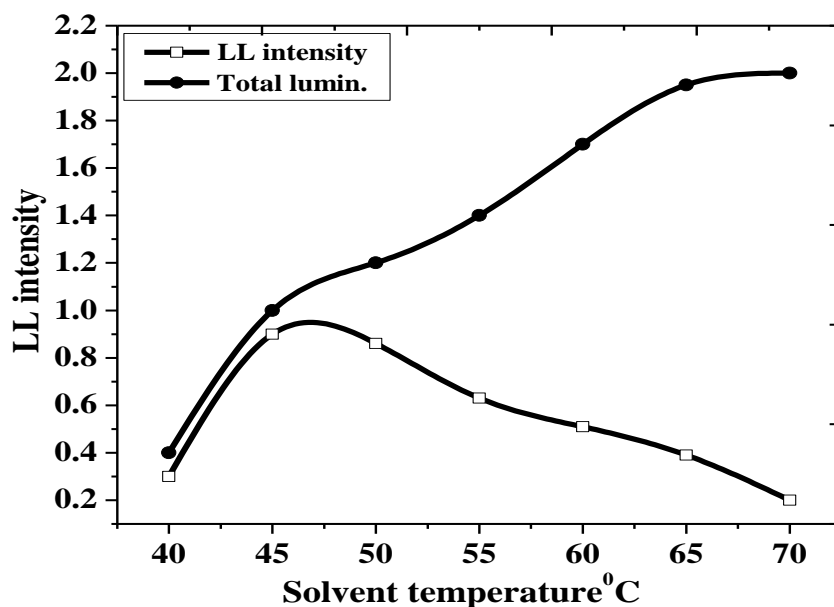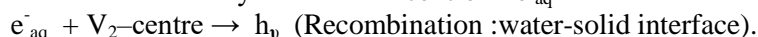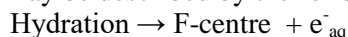

Figure 5-The linear dependence of LL intensity on solvent temperature.

Discussion

When irradiated organic solids are dissolved in water, then the free radicals (reactive oxygen species), that trapped within the solid matrix, releases from F-centres and the formation of hydrate electrons (e^-_{aq}) take place. The subsequent recombination of hydrated electrons with its counterpart (V-centers) at water solid interface gives rise to luminescence.

Schematically the mechanism of LL may be described by the following equations:

$$Hydration \rightarrow F\text{-centre} + e^-_{aq}$$

$$e^-_{aq} + V_2\text{--centre} \rightarrow h_\upsilon \text{ (Recombination :water-solid interface).}$$

Chandra *et al*. [12] have shown that the LL intensity (I) exponentially depends on different parameters and it can be expressed as:

$$I \alpha \{exp(-\alpha t)\text{-}exp(-\beta t)\} \quad \text{.......................................} \quad (1)$$

Where: β is the rate constant for the recombination of free radicals, α, rate of dissolution of a solute in the solvent, t is time dissolution. The above equation shows that when water will be dropped into the solute, initially the LL intensity should increase linearly with time, attain maximum value and then it should decrease exponentially with time. This fact is supported by the result illustrated in Figure-4. It is evident from Figure-2 that I_{max} initially increases and then decreases with increasing grain size of the crystals.

Equation.1 indicates I decrease with increasing grain size of the phosphorus, firstly due to the formation of less density of free radicals in larger grain as compared to that in the phosphorus of smaller grains, and secondly due to the decreases of (α) rate of dissolution with increasing grain size of the phosphorus. For smaller grain size, I may decrease with decreasing grain size because of the less stability of the free radicals in the phosphorus of smaller dimensions, where the significant bleaching of the free radicals which agree with [13].

Figure-3 shows the dependence of LL intensity on the pH of the solution. It is seen that LL intensity is optimum for the particular pH of the solvent. It has been shown that the maximum intensity in LL is observed the pH range in which the stability of the hydrated electron is optimum

which agree with [10-11]. Equation (1) shows that the LL intensity depends on different parameters. These factors β, N_o (relation constant of equation 1)   t and α are independent of the pH value of the solution.

It's known that pH is the negative logarithm of hydrogen ion concentration: pH = -log [H$^+$], pure water is essentially a covalent compound. It ionizes very slightly and the following equilibrium is established.

$$H_2O \rightarrow H^+ + OH^-$$

Where H$^+$ is a hydrogen ion and OH$^-$ is a hydroxyl ion. The removal of one orbital electron from a hydrogen atom yields the positive hydrogen ion or hydrogen cation, which is, in fact, a bare proton. The bare protons have no separate existence in solution and own its stability to salvation by a water molecule to give a hydronium ion (H$_2$O$^+$). The ionization equilibrium of water is thus represented more accurately as:

$$2H_2O \rightarrow H_3O^+ + OH^-$$
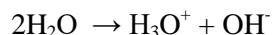
The pH of a neutral solution is 7. In acidic solution [H$^+$] > 10^{-7} or [H$^+$] > [OH$^-$] or [H$_3$O$^+$] > [OH$^-$] . In basic solution [OH$^-$] > 10^{-7} or [OH$^-$] >[H$^+$] or [OH$^-$] > [H$_3$O$^+$]. In water [H$^+$] = [OH$^-$] = 10^{-7} $^.$
It has been found for the low value of pH, the LL intensity decreases with decreasing pH of the solution. The decreasing pH means the increase in the hydrogen ion concentration or [H$_3$O$^+$] concentration. For lower pH the existence of more hydrogen ions may cause decreases in the number of hydrogen ions. Because the electron of the hydrated electron may combine with the hydrogen ions. Thus the probability of non-radioactive recombination of the hydrated electron may combine with hydrogen ions. Thus the probability of non-radiative combination of hydrate electron may decrease with decreasing pH of the solution and consequently the LL intensity may decrease with decreasing pH of the solution and consequently the LL intensity may decrease with decreasing pH of the solution.
 It has been found that for higher pH, the LL intensity decreases with increasing pH of the solution. As the pH increasing means the increasing concentration of [OH$^-$] ions. Consequently, the number of holes responsible for luminescence may decrease with increasing pH of the solution. As a matter of the fact, for higher pH value, the LL intensity may decrease with increasing pH of the solution. In this way, the LL intensity should be optimum for a particular pH of solution.

Conclusion

It was concluded that amino acid (L-prolin) incorporated with chemiluminscence reagent (luciginine)is the best dosimeter for LL technique. It was proven that LL intensity is related to the construction of free radicals that are generated by the radiation. In our procture it was dealing with omino acid which is the smallest building unite of protein that is the main component of human muscles, therefore, the mentioned Phosphor can be used as a tissue equivalent for dosimetry purposes in case of invitro studies. The optimum conditions of LL signal were obtained at considered phosphorus of size 0.1 mm, pH= (8.5-9) and solvent temperature 45-48°C. These conditions was the best approach of the LL signal.

References
1. Lind, J., Merenyi, G. and Ericksen,T.E. **1983.** "chemiluminscence mechanism of cyclic hydrazids such as luminol in aqueous solution". *JACS*, **105**: 7655-7661.
2. Lissi, E. Pascaul, C. and Del Castillo M.D. **1992.** "Luminol luminescence by 2-2-azo-bis(2-amidinopropane) thermolysis". *Free radical Reaserch communications*, **17**(5): 299-311.
3. Mishra, G. C. Dhoble, S. J. Srivastava, Ashok Dwiwedi, Surendra Kher **2018.** R. S. "Study of lyoluminescence of gamma-irradiated GdCa4O(BO3)3:Ce phosphors: Mass of solute and pH of solvent as a key factor" *Optik*, **158**: 826-830
4. Bhujbal, P.M. and Dhoble, S.J. **2013.** "Lyoluminescence properties of g-irradiated and Dy 3þ activated (K0.5 Na0.5) Cl phosphors for accidental radiation dosimetry" *Journal of Luminescence*, **136**: 90-94
5. MacDonald, A. and Nieman., T. A. **1985.** "low injection and liquid chromatography detector for amino acids based on a post colum reaction with luminal". *Analytical Chemistry*, **57**: 936-940.
6. Arora, A. and Strasburg. G. M. **1997.** "Development and validation of fluorescence spectroscopic assays to evaluate antioxidant efficacy. Application to metal qulators". *JAOCS*, **74**(9): 1031-1041.
7. Yasaei. P.M. , Yang, G.C. and Warner, C.R. **1998**. "Singlet oxygen oxidation of lipid resulting from photochemical sensitizers in precence of antioxidants". *JAOCS*, **73**(9): 1177-1181.

8. Lugaci, A. Dworschak, E. and Balzovics, A. **1998**. "Antioxidant and free scavenging properties of squeezed juice from black radish". *Phototherapy research*, **12**: 502-506.
9. Nabi,A., Rashid, A. and Yaqoob, M.**1996.** "Chemiluminescent determination of cholesterol by flow injection analysis". *Analytical Letters*. **29**(13): 2281-2288.
10. Majros, R. E., Barth, H.G. and Lochmuller,C.H. **1984.** "Column liquid chromography". *Analytical Chemistry*, **36**: 300R-349R.
11. Parejo, I., Petrakis, C. and Kefalas, P. **2000.** "A transition metal enhanced luminol chemiluminscence in the presence of a chelator". *J. of Pharmacological and Toxicological methods*, **34**: 183-190.
12. Yalids, G., Demiryrck, A.T., Sahin-Erdmli,I. and Kansik.I **1998.** "Comparisonof antioxidant activities of aminoguanidine, methylguaidine by luminol enhanced chemiluminscence". *British journal of pharmacology*, **124**: 905-910.
13. Speroni, E., Guerra, M.C., Minghetti, A. and Roda, A.**1998.** "Oleuropein evaluated in *vitro* and *in vivo* as an antioxidant". *Phototherapy Reaserch*, **12**: S98-S100.
14. Araujio, F.P. and Barbosa,D.S. 1995. "Evaluation of oxidant stress in patient with hyper-lipidemia". *Atherosclenosis*, **117**: 61-71.