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Short Communication

Photostability determination of arbutin, a vegetable whitening agent

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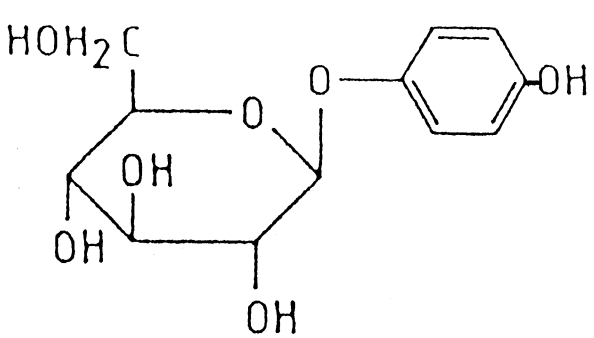
Abstract

The target of this research was to evaluate the photostability at various pH values of 1.20×10^{-4} M aqueous solution of arbutin ($\lambda_{max} = 267$ nm; $\varepsilon = 7500$ M^{-1}. cm^{-1}). This photodegradation appeared to follow first-order kinetics whatever the pH. The degradation rate constant was calculated to be 5.5×10^{-4}, 7.0×10^{-4} and 24.1×10^{-4} min^{-1}, respectively at pH 5, 7 and 9.

Keywords: Arbutin; Photodegradation; Aqueous solutions; pH effect

1. Introduction

Whitening preparations are of major importance because acute exposures to UV radiation allows negative effective like skin blemishes and brown spots. A lot of whitening molecules are commonly used to formulate topic preparations in order to eliminate the ineasthetic marks: ascorbic acid [1], β-caroten, α-tocopherol, hydroquinone [2–4], kojic acid [5–10] and arbutin [11–16]. Arbutin is a glycosylated hydroquinone found at high concentration in certain plants capable of surviving extreme and sustained dehydration conditions [13] and especially in bearberry (*Arctostaphylos uva-ursi*, Ericaceae), vanilla slice (*Achillea millefolium*, Asteraceae), or silver birch (*Betula alba*, Betulaceae). Arbutin is not an irritant for skin and eyes. Its properties are skin whitening by inhibiting melanin synthesis, sunscreen agent and antioxidant. In a previous study, we have determined arbutin thermostability. The analysis revealed a $t_{90\%}$ (time necessary to obtain a decrease of 10% of the initial concentration) of 15.4 days at 20°C. So, it appears that this whitening agent is very thermolabile [16]. In order to complete the knowledge of arbutin stability and to know the optimal storage conditions, we have realized a photostability study.



arbutin or glycosylated hydroquinone

$C_{12}H_{16}O_7$ $\varepsilon = 7500\ M^{-1}\ cm^{-1}$

Molecular weight : 272.25 U.V. (water) $\lambda_{max} = 267$ nm

Fig. 1. Chemical structure of arbutin, wavelength of maximum absorbance (λ_{max}) and value of molar absorptivity (ε).

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Table 1
Added buffer salt composition and pH solutions

Name of added buffer	Concentration used (M)	pH obtained
None		5
$Na_2B_4O_7$	7.75×10^{-5}	7
$Na_2B_4O_7$	0.020	9

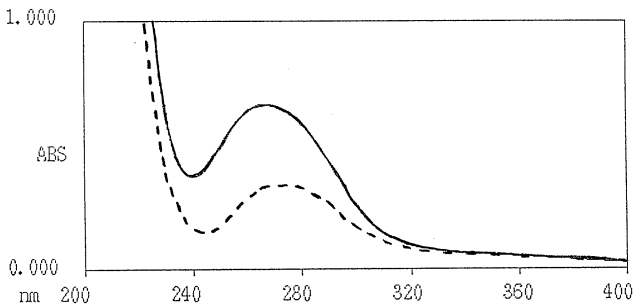

Fig. 2. Set of spectra obtained with the 1.20×10^{-4} M arbutin aqueous solution between 200 and 400 nm, at pH 5, before (—) and after a 21 h irradiation (- - -).

2. Experimental

2.1. Chemistry

Arbutin (trade name CIT Arbutin, batch number 96007-CAS no 497-76-7) was obtained from Cosmetic Innovations and Technologies (Dreux, France). Arbutin is a dry extract of bearberry plant, in crystal form containing 70% of arbutin, which is a 4-hydroxyphenyl-β-D-glucopyranoside (Fig. 1). Arbutin is a yellow powder soluble in water and alcohols. All chemicals were of analytical quality. Distilled water was obtained from an Autostill 4000X (Jencons) apparatus. Demineralized, deionized water was obtained from a Milli-Q system (Millipore). HPLC grade methanol and acetic acid were from Merck.

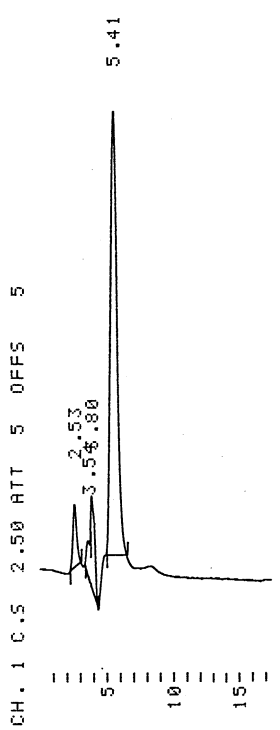

Fig. 3. HPLC chromatogram obtained from 1.20×10^{-4} M irradiated arbutin.

2.2. Photodegradation study

Solutions of arbutin (1.20×10^{-4} M) at various pH were enclosed in quartz spectrophotometric tubes and exposed to the light source in the light-stability cabinet (Original Hanau, no. 7011, Original Hanau Quartzlampen GmbH). The intensity of UV-A and UV-B was measured with an Osram apparatus (Centra-UV-Mebgerät). This intensity was maintained at 6.45 and 1.47 mW cm^{-2} for UV-A and UV-B, respectively. All tubes containing arbutin solutions were covered with aluminum foil before exposure, in order to eliminate the influence of heat generated by the light within the cabinet. The pH of these solutions was adjusted to the desired values with $Na_2B_4O_7$ 7.75×10^{-4} and 0.02 M. The pH of these solutions were determined using a Metrohm Herisau pH-meter, model E300B, equipped with a Refill Ingold I 3556 (pH 0–14, $T = 0$–80°C)

Table 2
Photodegradation of aqueous solution of arbutin

Times (min)	C/C_0		
	pH 5	pH 7	pH 9
0	1.000	1.000	1.000
60	0.966	0.959	0.867
120	0.935	0.919	0.750
180	0.904	0.881	0.649
240	0.875	0.845	0.561
300	0.847	0.810	0.486
360	0.819	0.777	
420	0.793	0.744	
480	0.767	0.714	
540	0.742	0.684	
600	0.718	0.656	
660	0.695	0.629	
720	0.672	0.603	
780	0.651	0.578	
840	0.630	0.554	
900	0.609	0.531	
960	0.589	0.509	
1020	0.570		
1080	0.552		
1140	0.534		
1200	0.517		
1260	0.500		

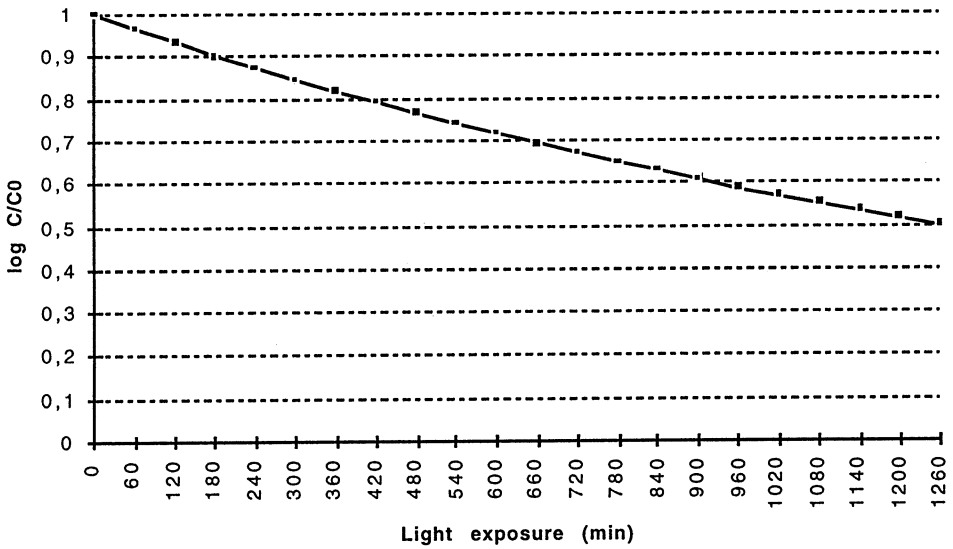

Fig. 4. Kinetic diagram for the photodegradation during irradiation of the arbutin aqueous solution (1.20×10^{-4} M) at pH 5. Data is the average of three determinations.

electrode and standardized with Panreac solutions, respectively at pH 4 and 10. These measures were carried out at 20°C.

2.3. Analytical procedure

The absorbance spectrum of arbutin was analyzed between 200 and 400 nm using a Hitachi UV–vis, double beam spectrophotometer, model U-2000. Slit width was fixed at 2 nm. Solutions were recorded in 1 cm quartz cells over a 200–400 range ($\Delta\lambda = 2.3$ nm). The scan speed was 400 nm min^{-1}. The arbutin concentrations initially and at time t, after irradiation, were determined using high performance liquid chromatography. The liquid chromatograph consisted of a Waters Model 6000 A pump, a Waters Lambda Max model 481 LC variable wavelength detector and a D-2500 Merck integrator. A 20 μl sample of the various arbutin solutions was injected onto a reversed-phase column (Nucleosil 5C18, 70×4.6 mm I.D., Macherey–Nagel, Düren) and eluted at a flow rate of 1.0 ml. The eluant was the following: methanol–water–acetic acid (60/35/5). The solvents were filtered separately through a 0.45 μm filter (Millipore) and mixed in the desired proportions. The detector was set to the wavelength of the maximum absorbance. Each analysis was carried out on triplicate samples and the difference between the triplicates was less than 1%.

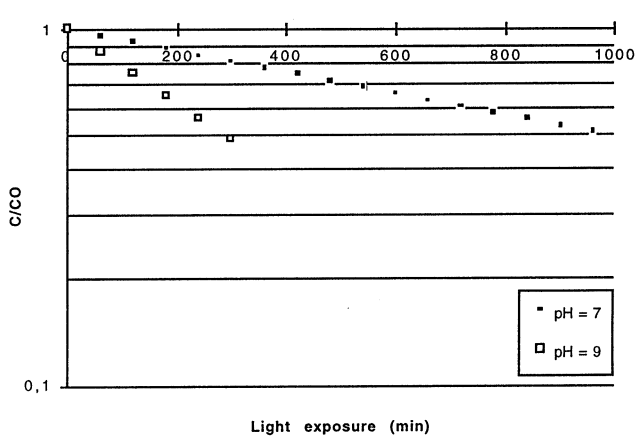

Fig. 5. Kinetic diagram for the photodegradation of arbutin (1.20×10^{-4} M) at various pH during irradiation. Data is the average of three determinations.

3. Results and discussion

3.1. Kinetics of arbutin photodegradation

The pH of different solutions is set out in Table 1. The absorbance spectrum of arbutin showed a minimum at 240 nm and maximum at 267 nm (see Fig. 2). Then the detector was set to this wavelength.

The HPLC analysis demonstrates the gradual decrease during photolysis. The photodegradation of arbutin was expressed as the rate of change of the area of its peak (Fig. 3). The degradation rate constant was calculated from the slope of the line of the area of the peak versus time. The percentage of substance remaining was calculated (Table 2). The photodegradation of arbutin in diluted aqueous solution (see Fig. 4) follows apparent first-order kinetics and is described by the following equation:

$$C/C_0 = e^{-k_a t} \quad (1)$$

where C and C_0 are the concentrations of arbutin at time t after irradiation and initial time and k_a is the

Table 3
Degradation rate constants of 1.20×10^{-4} M arbutin solutions at various pH

pH	Degradation rate constants k (min^{-1}) ± SEM [a]
5	$5.49 \times 10^{4} \pm 0.22 \times 10^{-4}$ [b]
7	$7.03 \times 10^{-4} \pm 0.56 \times 10^{-4}$ [b]
9	$24.1 \times 10^{-4} \pm 1.50 \times 10^{-4}$ [b]

[a] SEM, standard error of means of three determinations.
[b] Values are significantly different ($P < 0.05$) relative to pH.

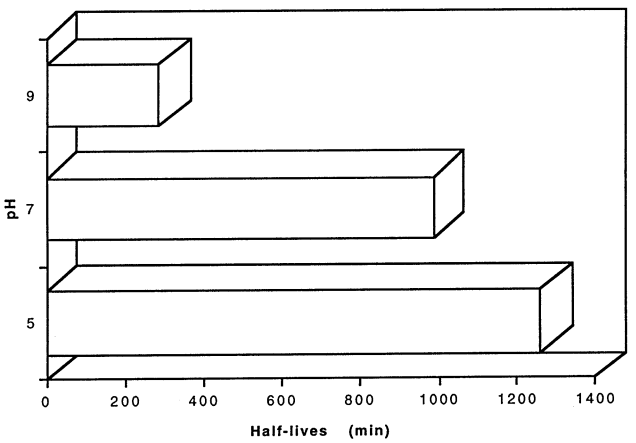

Fig. 6. Half lives (min) of 1.20×10^{-4} M arbutin solution at various pH (bars are significantly different from each other at $P < 0.05$).

apparent first-order degradation rate constant. Eq. (1) gives us the value of the degradation rate constant, which is equal to 5.5×10^{-4} min^{-1}.

3.2. Effect of pH

The photodegradation of arbutin (1.20×10^{-4} M) in buffer solution at pH 7 and 9 was studied. The degradation rate was calculated from the slope of the line of area of the peak versus time. The percentage of arbutin remaining was calculated (Table 2). Whatever pH, the photodegradation of arbutin in diluted buffer solution follows apparent first-order kinetics (Fig. 5) and is described by the following equation:

$$C/C_0 = e^{-k_b t} \quad (2)$$

where C and C_0 are the concentrations of arbutin at time t and initial time and k_b is the apparent first-order degradation rate constant. At pH 7 and 9, we have noted a variation of the values of rate constant k_b (see Table 3). The pH of the solution has an influence on the photostability of arbutin (Fig. 6). This conclusion has already been reached for many organic molecules [17]. The effect of pH on the 90% shelf life (defined as the time by which the arbutin concentration had decreased by 10% from the initial concentration) of arbutin is significant at pH values of 5, 7 and 9. The percentage decrease in the stability of arbutin by the addition of buffer was found to be 21 and 77% between pH 5 and 7 and pH 5 and 9, respectively.

So, we can concluded that arbutin is a photostable but a thermodegradable substance [16] which can be incorporated in various formula at room temperature.

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