Enhanced electrodetection of ascorbic acid in *Adansonia digitata* fruit by use of surface modified electrodes

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Received 2 August 2000; accepted 23 November 2000

Surface modified electrodes have been used to study the seed of *A. digitata*. The results show the ascorbic acid redox peak is greatly enhanced and the oxidation/reduction peaks coincide with those of the corresponding chemical standard. It is also shown that ascorbic acid adsorbs onto the clay-modified electrode.

KEY WORDS: ascorbic acid; *Adansonia digitata* seed; cyclic voltammetric responce

1. Introduction

Traditionally natural products chemistry has focussed on identification of the chemical components of a given plant material. The identification procedure has been revolved primarily on extractions carried out in different solvent media followed by separation and identification via columns/media such as TLC or NMR.

On the same token surface modified electrodes, also christened derivatized electrodes, have also been used to study adsorbed chemical species as first studied by Hubbard and Lane [1,2], conducting polymers such as polyaniline, polythiophene, polypyrrole, etc. [3–10]. This has entailed deliberate modification of an electrode surface so as to exhibit the redox properties of the chemical species attached on the electrode surface. Surface modified electrodes have not been used to study natural products and especially raw plant material prior to any extraction procedures. In this paper the objective was to establish whether electrochemical analysis is possible on a raw natural product and whether the electrochemical signal obtained from the analysis can be enhanced via derivation of the electrode surface and standard electrocatalytic procedures. The natural product of choice was the *Adansonia digitata* fruit. The fruit has an outer hairy greenish part (Ad_1), a corky woody (fibrous on the inside) covering (Ad_2), a pulpy powdery interior (Ad_3) and the seed (Ad_4). The botanical aspects of the plant and its ethnomedical recipe are detailed in [11–17].

2. Experimental

Chemical reagents such as hydrochloric acid (Kobian Kenya Ltd.), sulphuric acid (Gower), ascorbic acid (Howse & McGeorge), and sodium chloride (BDH) were used as received. The clay montmorillonite bentonite (Athi River Mining Company) was also used as received. The aniline (Aldrich) was triply distilled until a colourless liquid was obtained prior to use. All these solutions were prepared using triply distilled water. The *Adansonia digitata* fruit was collected from the eastern province region of Kenya and stored at room temperature.

The electrochemical instrument used in the analysis consisted of a three-electrode assembly comprising of carbon graphite working electrode, a platinum auxiliary electrode and saturated calomel (as reference electrode). The electrochemical cell was an undivided 50 ml beaker. The cyclic voltammograms were generated from a PAR model 173 potentiostat/galvanostat used in conjunction with a PAR model 175 universal programmer. The output signal was fed into a PAR RE0089 X-Y recorder.

The FTIR analyses were conducted on a Shimadzu Fourier transform infrared spectrophotometer model 8101 equipped with a Michelson interferometer and a beam splitter of germanium coated on KBr plate, a black coated heated wire as a source and a highly sensitive pyroelectric detector ($LiTaO_3$). For data sampling the He–Ne laser was used. The preparation of the bentonite electrode was as discussed in [3,17].

3. Results and discussion

Prior to the commencement of electrochemical analysis of the ascorbic acid in the *Adansonia digitata* fruit seed the latter was subjected to FTIR analysis to verify the presence of functional groups associated with ascorbic acid. The resultant spectrum is shown in figure 1. The data confirms the existence of ascorbic acid functional groups.

The electrochemical analyses were carried out by dissolving 0.45 g of crushed seed material in varying solutions containing 1 M hydrochloric acid and sulphuric acid. In all the solutions the potential of the working electrode was cycled from -0.2 to 0.98 V (in the case of HCl) and

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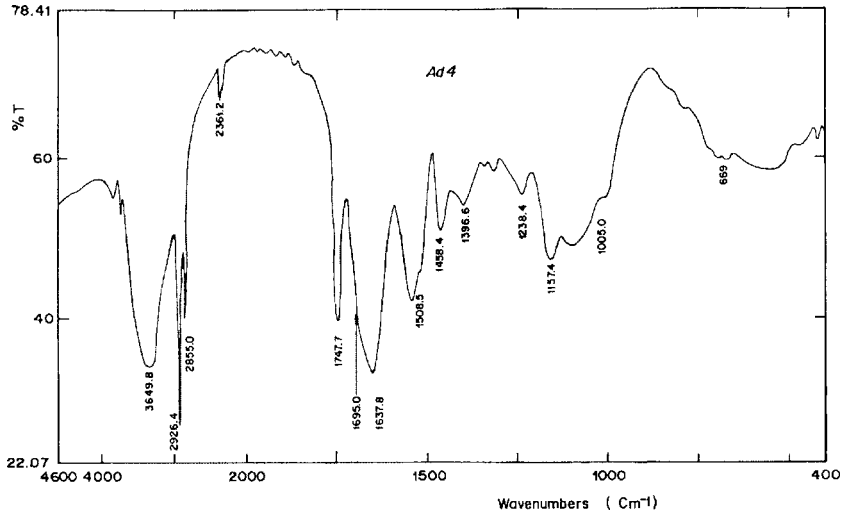

Figure 1. FTIR spectrum of the seed of *Adansonia digitata.*

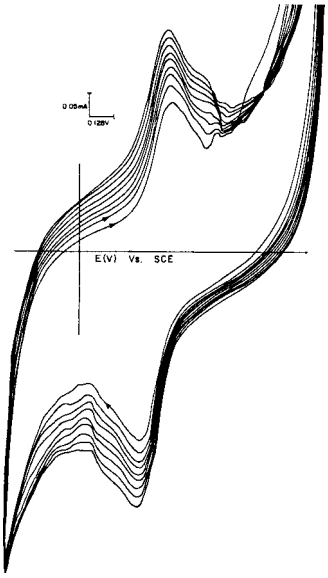

Figure 2. Cyclic voltammetric response when a bare carbon working electrode is cycled from −0.4 to 1.4 V in a solution containing 0.45 g of crushed seed in 2 M H_2SO_4 at 50 mV/s.

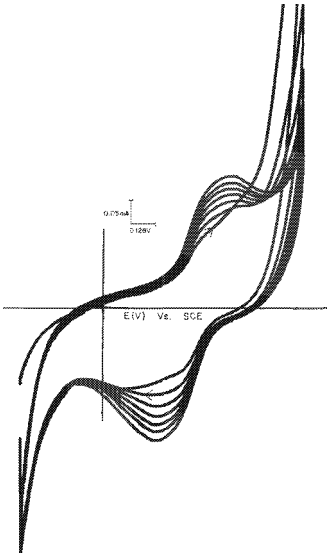

Figure 3. Cyclic voltammetric response when a bare carbon working electrode is cycled from −0.2 to 0.98 V in a solution containing 0.4155 g of crushed seed in 1 M HCl at a scan rate of 50 mV/s.

from −0.4 to 1.4 V (in the case of H_2SO_4) at a scan rate of 50 mV/s. The cyclic voltammetric response in HCl yielded oxidation/reduction peaks at 0.55 V/0.30 V, whilst that in H_2SO_4 had oxidation/reduction peaks at 0.52 V/0.35 V (see figures 2 and 3).

This closely matched the oxidation peak potentials obtained when the working electrode was cycled within the same potential window in solutions containing 0.01 M ascorbic acid chemical standard in 1 M HCl and 1 M H_2SO_4, i.e., 0.55 and 0.52 V for HCl and H_2SO_4, respectively. These observations are an electrochemical confirmation of the presence of ascorbic acid in the seed of *Adansonia digitata*.

The next step was to attempt to improve the electrochemical response of the ascorbic acid in the *Adansonia digitata* seed by surface modification/derivatization of the working electrode. This was considered based on the previous observations of electrocatalysis resulting from the modification of the electrode surface [3]. The two modification agents used were conducting polymer, polyaniline and bentonite, a clay montmorillonite. The working electrode surface was modified with polyaniline by cycling its potential from −0.2 to 0.75 V in a solution containing 0.1 M aniline at a scan rate of 20 mV/s, while the montmorillonite host matrix was mounted on the working electrode surface as discussed in [3,17]. The resultant cyclic voltammograms are as shown in figures 4 and 5. The oxidation/reduction potentials were 0.48 V/0.37 V and 0.44 V/0.42 V for the H_2SO_4 and HCl cases, respectively, on the polyaniline-modified electrode. This represents a shift in the oxidation potential corresponding to 36 and 112 mV as compared to the bare carbon case. In the case of bentonite-modified electrodes the oxidation/reduction peaks appeared at 0.46 V/0.36 V in H_2SO_4 representing a shift of approximately 50 mV. The HCl case

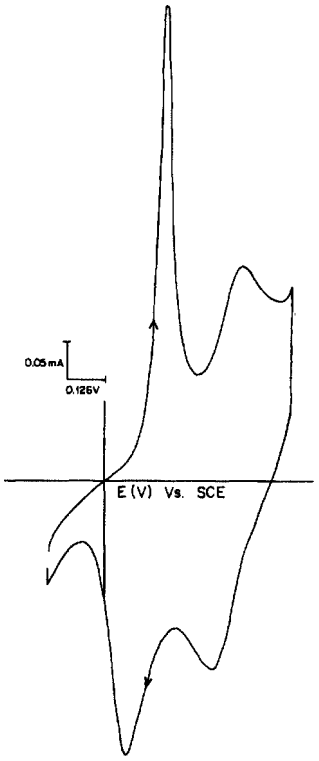

Figure 4. CV response for polyaniline-modified electrode cycled from −0.2 to 0.65 V in a solution containing crushed *A. digitata* seed in 2 M H_2SO_4. Scan rate 20 mV/s.

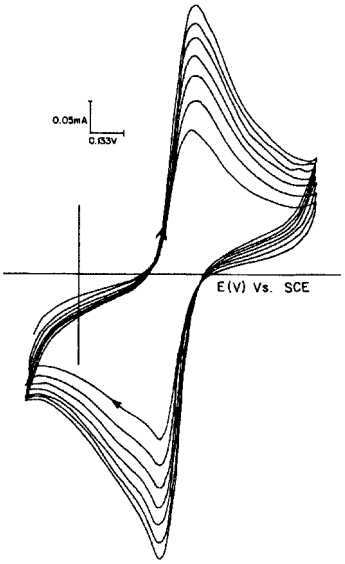

Figure 5. CV response for bentonite-modified electrode cycled from −0.2 to 1.0 V in a solution containing crushed *A. digitata* seed in 2 M H_2SO_4. Scan rate 20 mV/s.

has the oxidation/reduction peak appearing at 0.48 V/0.39 V, respectively, representing a shift of 67 mV in the oxidation potential.

The H_2SO_4 experiment was repeated but this time the bentonite-modified electrode was dipped into the electrolyte solution with no potential cycling for 2 h. This electrode was then removed and left to dry for about 12 h after which

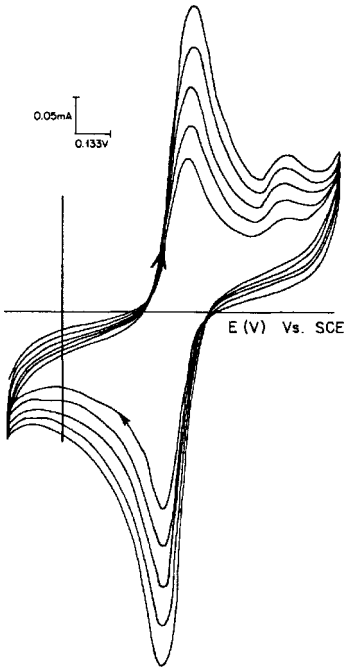

Figure 6. CV response for bentonite-modified electrode initially dipped into the solution of Ad_4 in 2 M H_2SO_4 for some time (with no potential cycling), air-dried and then cycled within the potential from −0.2 to 1.0 V at 20 mV/s in the same solution.

it was cycled in the same potential window as before. The cyclic voltammetric response showed two oxidation peaks and one reduction peak. The first peak occurred at the same potentials as the one observed earlier, i.e., 0.46 V/0.36 V and a second peak without any reduction peak appeared at 0.785 V (see figure 6).

In all the cases mentioned so far the scan rate dependence studies yielded linear plots for anodic peak current versus square root of scan rate suggesting a diffusion-limited process. This was not the case with the peak observed at 0.785 V, which yielded linear plots for peak current versus scan rate and square root of scan rate. This duality in behaviour suggests process that is both diffusion limited and where there are surface attached species, a pointer to the adsorption of ascorbic acid. Its significant to mention that the electrochemical signal of the *A. digitata* seed was well defined despite the low concentration of ascorbic acid in the plant material. To verify the latter assertion a fresh bentonite electrode was dipped into the electrolyte media containing the 0.01 M ascorbic acid in 1 M H_2SO_4 and allowed to stay for 2 h prior to any electrochemical analysis. The potential of the electrode was cycled from −0.2 to 1.0 V in the same solution containing 0.01 M ascorbic acid in 1 M H_2SO_4. The resultant cyclic voltammogram had an oxidation/reduction peak at 0.43 V/0.36 V and an irreversible peak at 0.754 V, i.e., the adsorption peak (see figure 7).

The voltammetric pattern obtained is an indicator of a strong product adsorption. The oxidation/reduction peak at 0.45 V/0.37 V corresponds to the reaction of solution species whilst the peak at 0.79 V corresponds to the reaction of the adsorbed species. Since both the adsorbed and

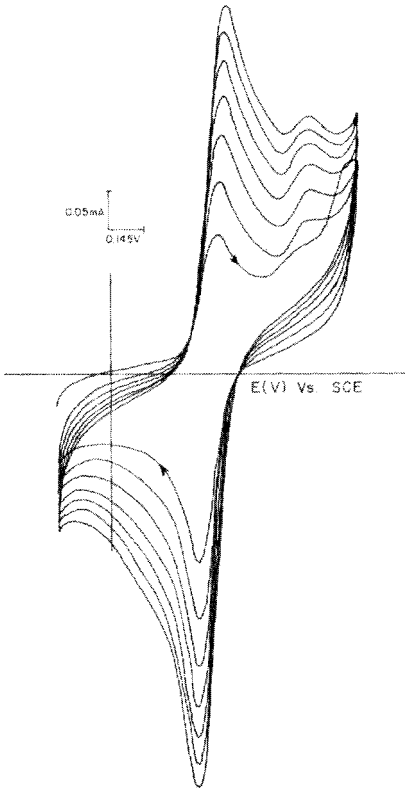

Figure 7. CV response for a bentonite-modified electrode allowed to first stay for 2 h (with no potential cycling) in a solution of 0.01 M ascorbic acid in 1 M H_2SO_4 and then cycled in the potential range from -0.2 to 1.0 V at a scan rate of 20 mV/s.

solution species are electroactive, the redox process can be represented, as follows [16]:

$$O_{Soln} \rightleftharpoons O_{ads.}$$
$$O + ne^- \rightleftharpoons R$$

The fact that the potential of the peak associated with the adsorption is approximately 340 mV more positive than the corresponding solution peak suggests that the adsorbed product is stabilised and reacts less readily with respect to the electrode reaction. Such a strong product adsorption has been observed in the reduction of proton on a platinum electrode even though in this case the peaks were reversible. The duality obtained from the scan rate dependence studies can be apportioned with the linear variation with scan rate being due to adsorption and that with square root of scan rate being attributed to the solution species. The significant separation, i.e., 340 mV, between the solution and adsorption peaks is a pointer to the relative strength of the adsorption [16]:

4. Conclusion

The observation that the electrochemical signal attributed to ascorbic acid in the *A. digitata* seed is significant (i.e., large peak current and well defined peaks) on the bentonite-modified electrode, despite the fact that it is estimated that the concentration of the ascorbic acid in the seed is not more than 250 mg/100 g. This points to the preconcentration effect and/or electrocatalytic role of the bentonite host matrix. The product adsorption fingerprints ascorbic acid detection on the bentonite-modified electrode.

Acknowledgement

We acknowledge with thanks the African Academy of Sciences (AAS) for giving the grant that enabled this work to be done.

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