POLAROGRAPHIC EXAMINATION OF ACTIVE COMPONENTS OF *ARTEMISIA MARITIMA*

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ABSTRACT

The polarograms, the current-pH, $E_{\frac{1}{2}}$-pH, current $vs \sqrt{h}$, current-concentration plots and slopes of log i vs. log h (uncorrected) plots of active components of *Artemisia maritima* leaf- and flower-extracts in 1% $HClO_4$ solution prove the irreversible diffusion-controlled nature of limiting currents, similar to those of santonin. Milli-coulometry proves a two-electron process at pH values of 4.5 and 9.3. Calibration curve (limiting current vs concentration) of santonin at pH 5.3 shows that the air-dried leaves and flowers of the plant contain 0.96% and 0.98% of santonin respectively.

INTRODUCTION

POLAROGRAPHY together with routine chromatography offers the most rapid and sensitive analytical technique for identification, estimation and establishment of the course of electrode processes of organic compounds present as active ingredients in the medicinal plants[1]. Organic compounds present in different plants exhibit different behaviours at dropping mercury electrode depending upon their chemical nature and hence the polarographic technique may be used for identification and estimation of drugs present in the plants.

The plant, *Artemisia maritima* under investigation, contains an α,β-unsaturated ketone, santonin, which is well reputed for its considerable therapeutic value as a vermifuge[2,3]. The present work has been aimed at establishing a routine polarographic method for the estimation of santonin in various parts of the plant.

EXPERIMENTAL

Polarograms have been recorded (298 K) with a Radiometer pen-recording polarograph (Polariter PO4 g). The dropping mercury electrode (DME) used at a height of 60 cm, has the following characteristics: $m = 0.952$ mg sec^{-1} and $t = 4.3$ sec at zero applied potential (sce) in 0.5 mol dm^{-3} solution. The pH-values of the solutions have been measured before and after recording each polarogram using a pH meter (ELICO model LI-10) with an accuracy of ± 0.1 pH.

All the reagents used are of A.R. grade. The leaves and flowers of the plant, *A. maritima* have been collected in May–June, separately dried in air, crushed and 40 g of each have been kept immersed in 1% $HClO_4$ (400 ml) at room temperature for a week and the cold extracts filtered before use. Each extract has

been diluted 2000 times with conductivity water after adding tetramethyl ammonium acetate-borate buffer (0.075 mol dm^{-3}; final strength) and tetramethyl-ammonium bromide (0.1 mol dm^{-3}; final concentration) and ethanol in appropriate quantities for obtaining test solutions in 30% ethanol medium. The number of electrons involved in the electrode process has been determined by millicoulometry with mercury pool cathode.

RESULTS AND DISCUSSION

The polarograms of Artemisia leaf-extract at different pH-values are shown in figure 1. They are single waves for pH's 2.6 and 3.7, two waves in the pH-range 4.5 to 7.2 and single wave again at higher pH-values. The height of first wave decreases with increasing pH-values (pH-range, 4.5–7.2), the total height remaining constant. For pH 2.6, the limiting current is smaller, while at pH's greater than 7.2, it exhibits a small but gradual increase with pH. The plots of the fractional currents (ratios of currents of each of the two waves to the total current) against pH (in the range, 4.5–7.2) have the form of dissociation curves (figure 2). The half-wave potentials become more negative with increasing pH-values (figure 3) with slopes, 60, 110 and 25, 10 (mV) at two ranges of pH, indicating two types of electrode processes. Limiting current shows proportional increase with concentration in terms of dilution of the extract from 500 to 29.4 times while the half-wave potentials become increasingly more negative, indicating complex nature of the polarographic waves. Linear dependence of limiting currents on the square-root of height of mercury reservoir (figure 4) at pH 5.3 confirms the diffusion-controlled nature of the polarographic waves, which has further been verified by the
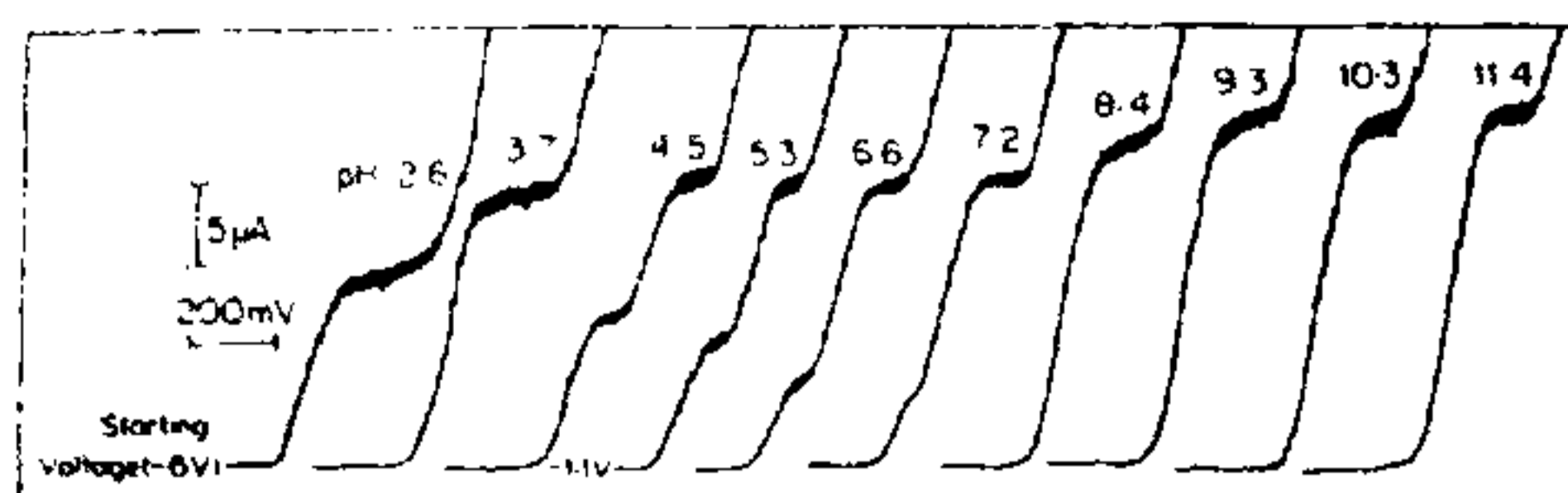
Figure 1. pH-dependence of polarograms of Artemisia leaf-extract (0.02 ml of 1 % HClO₄ solution made up to 10 ml of test solution).
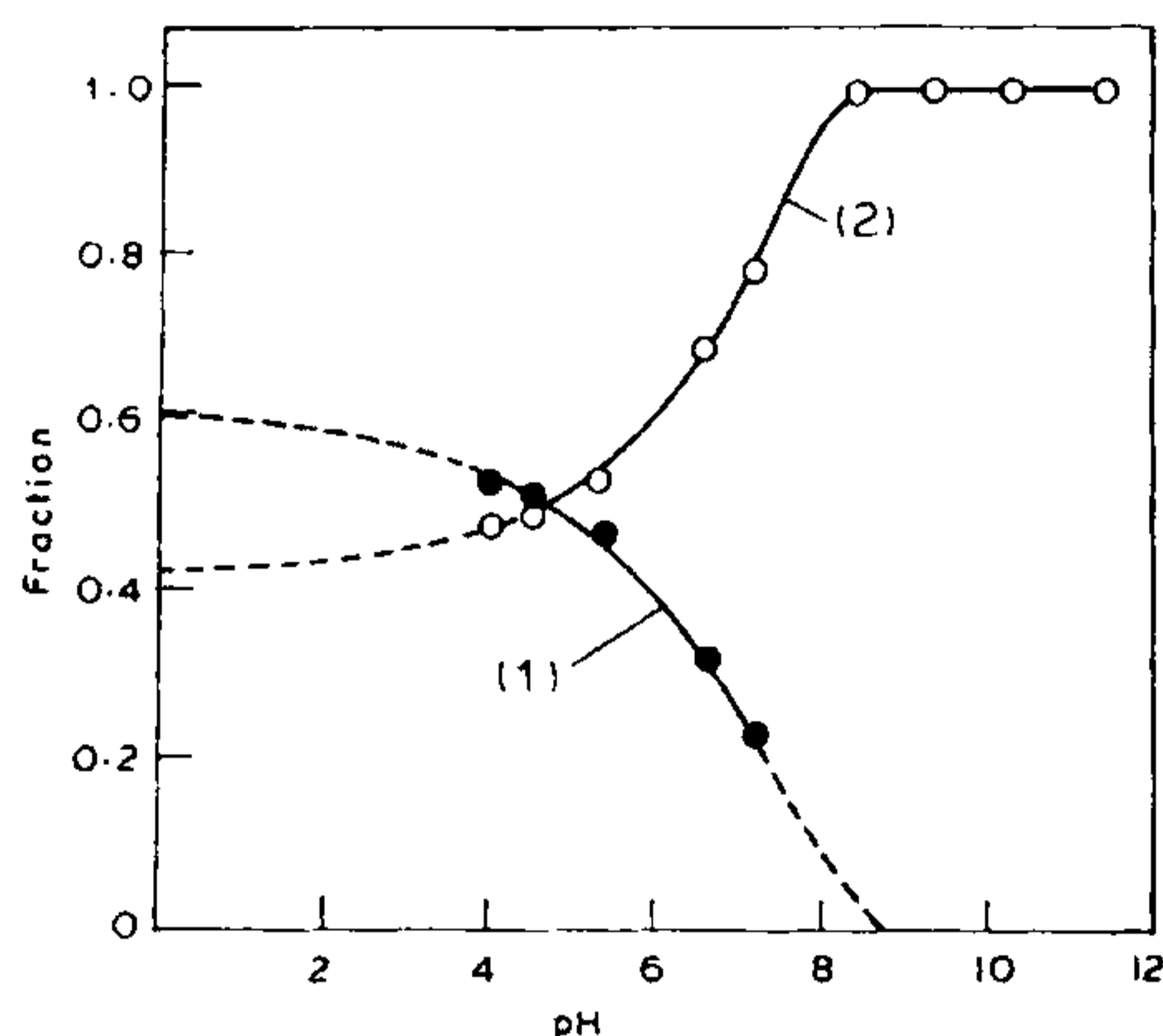

Figure 2. Plot of ratio of currents vs. pH 1. $\bar{i}_1/(\bar{i}_1 + \bar{i}_2)$; 2. $\bar{i}_2/(\bar{i}_1 + \bar{i}_2)$.
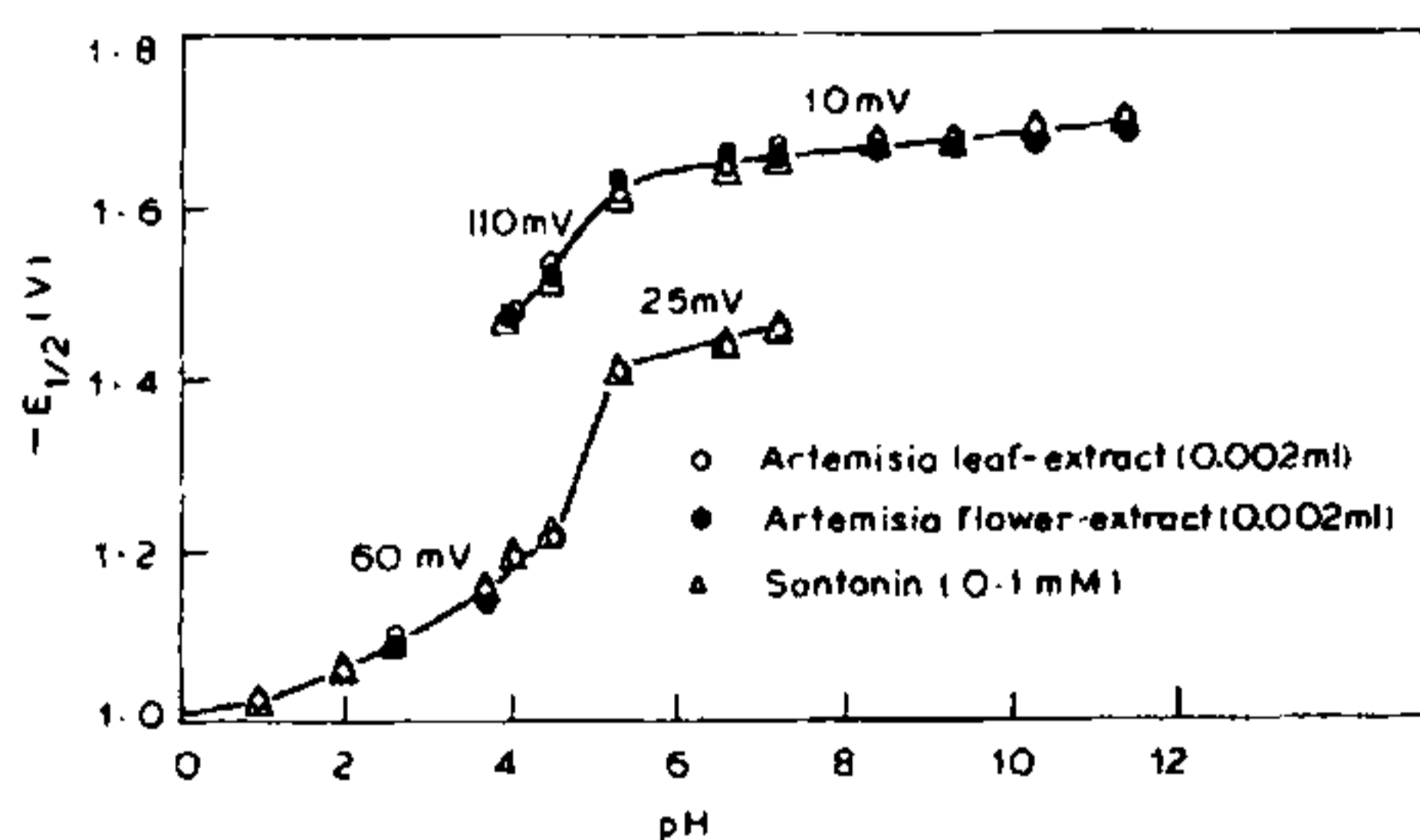

Figure 3. pH-dependence of half-wave potentials.

slopes of log $\bar{i}$ vs log h (uncorrected) plots over the whole wave at pH's 2.6, 5.3 and 10.3. Slopes range from 0.25 to 0.47 at the limiting plateau for pH 2.6; the
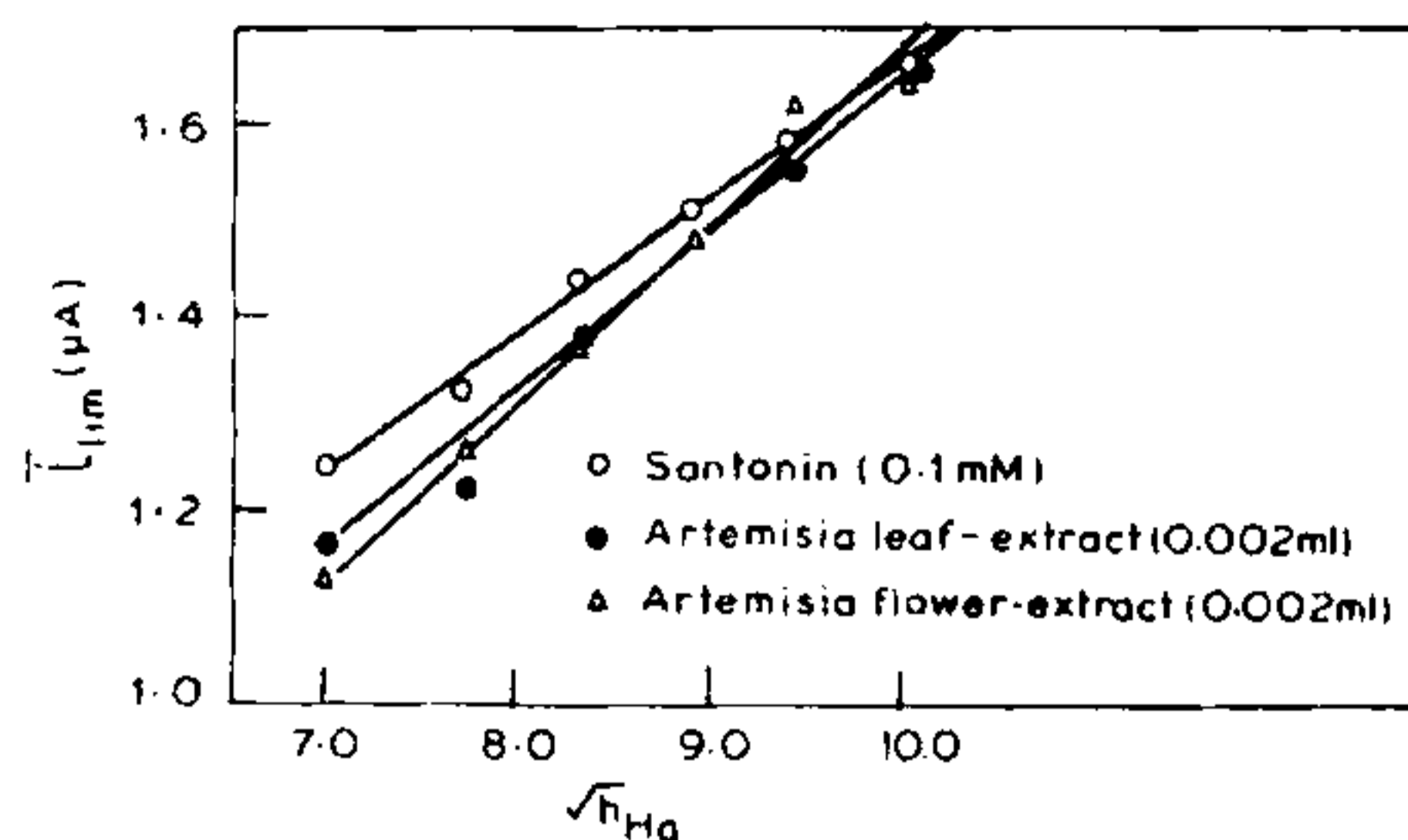

Figure 4. Dependence of limiting currents on square-root of height of mercury reservoir at pH 5.3.

corresponding slopes for the first wave at pH 5.3 range from 0.08 to 0.44 while those for the second wave range from 0.06 to 0.45, slopes of the waves at pH 10.3 range from 0.19 to 0.42.

The polarograms of cold and diluted extracts of Artemisia flowers at different pH-values under identical conditions as employed above are similar to figure 1. The fractional current vs pH, $E_{\frac{1}{2}}$-pH, current vs $\sqrt{h}$ plots are similar to those of Artemisia leaf-extract indicating a similar nature of the active component of the leaves and flowers. The log $\bar{i}$ vs. log h_{uncorr} plots for the waves of flower-extract have similar slopes ranging from 0.25 to 0.47 (pH 2.6), from 0.08 to 0.44 (I wave) and 0.06 to 0.45 (II wave) (pH 5.3) and from 0.19 to 0.43 (pH 10.3) respectively.

The polarograms of santonin (0.1 mol m⁻³) at different pH-values under the conditions employed for the extracts show striking resemblance with those in figure 1. The plots of fractional current vs. pH (figure 2), $E_{\frac{1}{2}}$-pH (figure 3), current-$\sqrt{h}$ (figure 4), current-concentration and slopes of log $\bar{i}$ vs. log h_{uncorr} plots for the waves at pH's 2.6, 5.3 and 10.3 [0.23–0.48; 0.08–0.45 (I wave), 0.06–0.46 (II wave); 0.18–0.43 respectively] confirm the irreversible nature of the polarographic waves and identity of the active component of the Artemisia leaves and flowers with santonin. The mixed polarogram of santonin and each extract (1:1 v/v) at pH 8.4 shows single wave with enhanced current, confirming the above conclusion.

The number of electrons involved in the electrode process, determined by millicoulometry of 0.6 ml of santonin (0.1 mol m⁻³) at pH's 4.5 and 9.3 has been found to be two at both the pH-values. The mechanism of the electrode process can thus be explained in the following manner:[4]
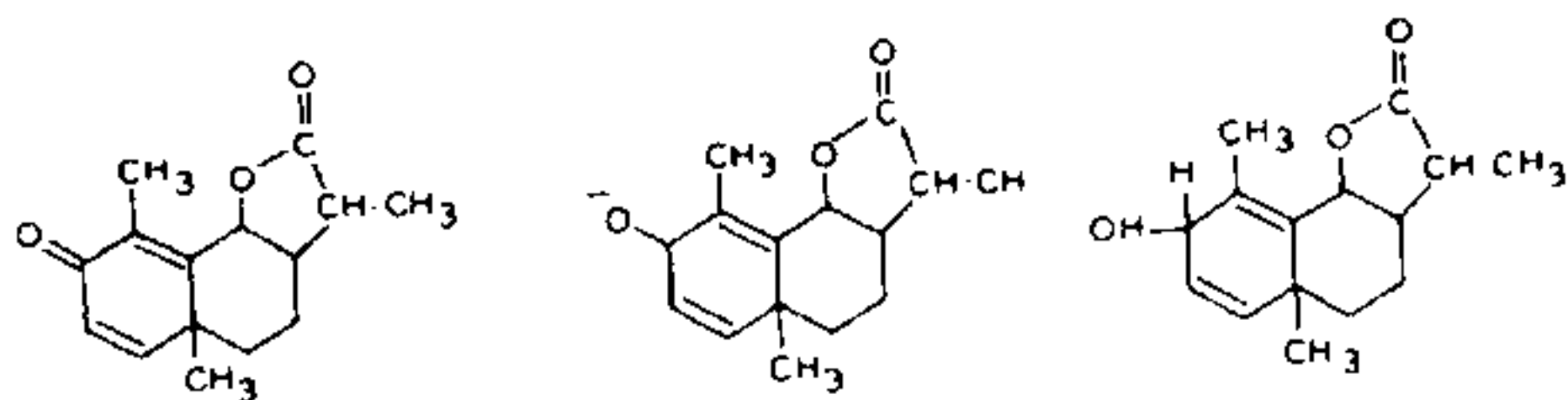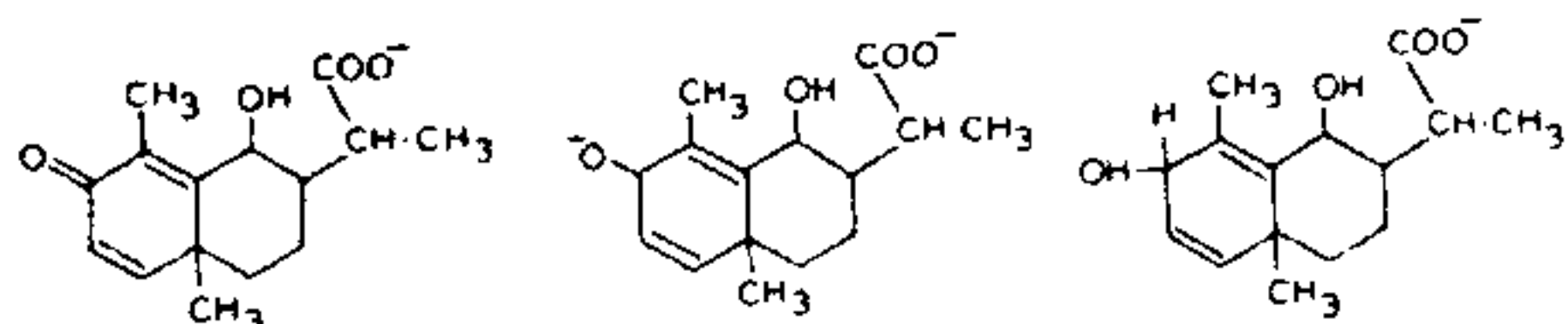
Mechanism (a)
Below pH 4.0
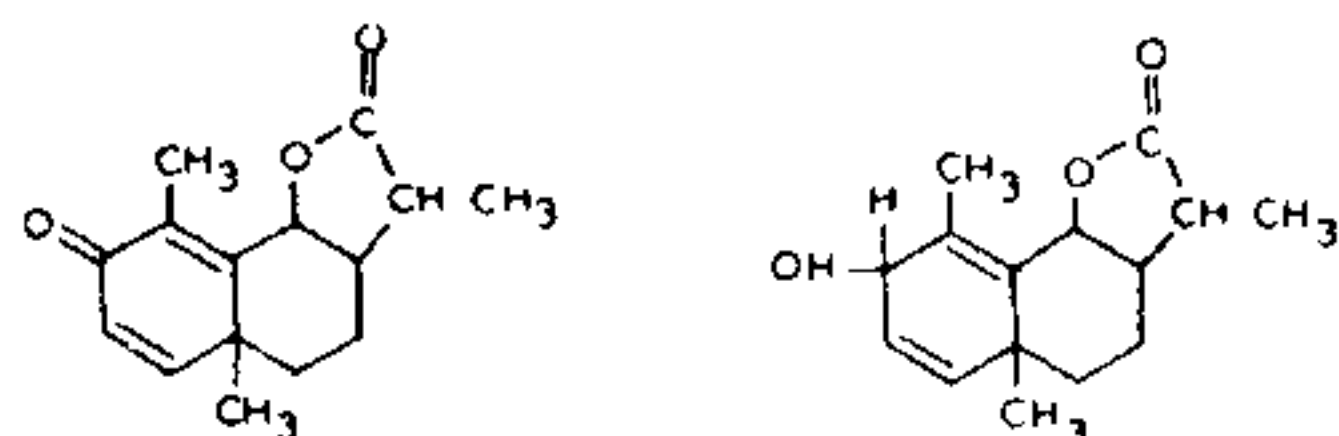
Mechanism (b) Between pH 4.0 and 5.3
First wave: Mechanism (a)
Second wave: Mechanism (b)
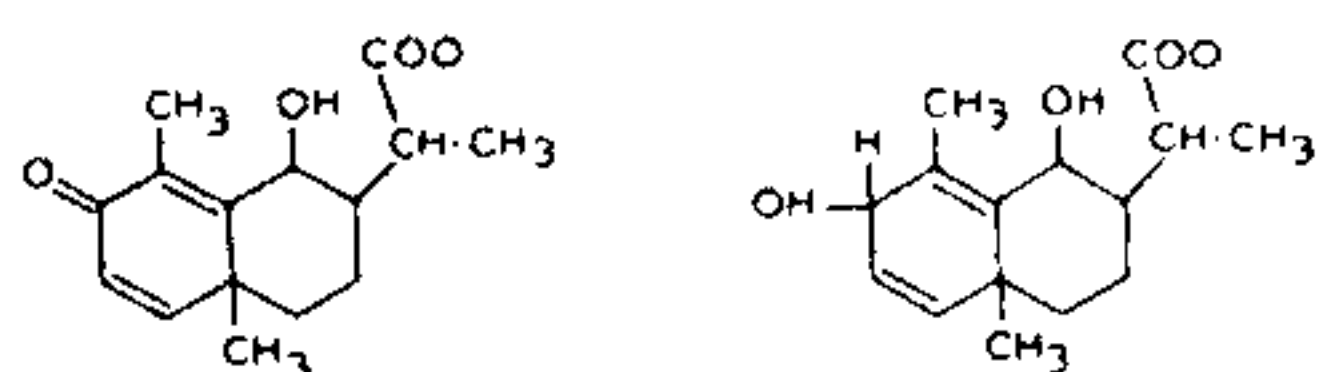
Between pH 5.3 and 7.2
First wave:

Second wave:

Above pH 7.2: Mechanism same as for second wave between pH 5.3 and 7.2.

The rate constants, (k_f) have been calculated for polarographic waves of santonin at both pH-values which are 8.77×10^{-22} at -1.22 V (first wave), 3.25×10^{-28} at -1.53 V (second wave) at pH 4.5 and 6.54×10^{-21} at -1.68 V at pH 9.3.

To estimate the concentration of santonin in different parts of Artemisia plant, polarograms for different concentrations (0.04 to 1.3 mol m^{-3}) of santonin (pH 5.3) have been recorded. The calibration curve ($\bar{i}_{lim}$ vs. concentration plot) gives the diffusion-current constant value of 18.15 μAmmol^{-1} and the concentration of santonin in air-dried leaves and flowers of *A. maritima* have, thus, been estimated to be 0.96% and 0.975% respectively.

ACKNOWLEDGEMENT

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