547.7

A STUDY OF ELECTROCHEMICAL TRANSFORMATIONS

OF SOME CONSTITUENTS

OF SRI LANKAN ESSENTIAL OILS

Ъч

POLPITI ARACHCHIGE SRIYANI HEMALATHA DHARMASENA B.Sc. (Hons.), University of Peradeniya, Sri Lanka

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF PHILOSOPHY

of

UNIVERSITY OF PERADENIYA

July, 1983

Department of Chemistry
University of Peradeniya
Sri Lanka

- 367048

- ii -



ABSTRACT

Electrochemical transformations of eugenol, citral. citronellal and citronellol were investigated.

The oxidation of eugenol on stationary platinum wire electrode in 0.5 M sodium perchlorate/acetonitrile was investigated by using linear scan voltammetry, cyclic voltammetry and chronoamperometry. Bench-scale electrolysis of eugenol in this system was carried out using both controlled potential and constant current methods and 4-allyl catechol (the demethylated product of eugenol) was isolated as the major product. The mechanism of this conversion was deduced using linear scan voltammetry, cyclic voltammetry and chronoamperometry and was found to involve a reversible charge transfer followed by an irreversible chemical reaction. The rate constant of the chemical

reaction was determined by using double potential step chronoamperometry to be $2.5 \times 10^{-2} \text{s}^{-1}$.

The constant current oxidation of eugenol on a platinum electrode in 0.1 M lithium perchlorate/ methanol, resulted in 2-methoxy,5-allyl benzoquinone as the major product.

Linear scan voltammograms obtained for eugenol in aqueous sodium hydroxide on a carbon paste electrode indicated the occurrence of two reactions.

The electrochemical oxidation of citral was attempted in various supporting electrolyte/solvent systems on different electrodes. None of these systems produced a reproducible wave in linear scan voltammetry. Bench-scale oxidation using both controlled potential and constant current modes were carried out. Both electrolyses produced mixtures of compounds as the products.

The behaviour of dilute solutions of citronellal in a number of supporting electrolyte/solvent systems was studied polarographically. A bench-scale constant current reduction of citronellal was carried out in 0.5 M sodium acetate/0.5 M acetic acid in 50% aqueous methylated spirit. The major product was found to be citronellol.

Electrochemical oxidation of citronellol was also attempted with the view to producing citronellal, in a number of supporting electrolyte/solvent systems. But none of the systems produced a voltammetric wave and the bench-scale constant current electrolysis also failed to result in a significant conversion of the starting material to products.

Machan

Sheatast Reserves

2.2.2.7 Linear Soun Maringa .

Rethod

2-2. Disphostic Criteria.....