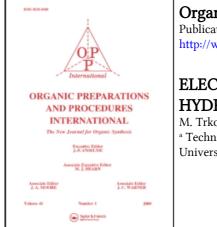
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ELECTROCHEMICAL SYNTHESIS OF 3-AMINO-4-

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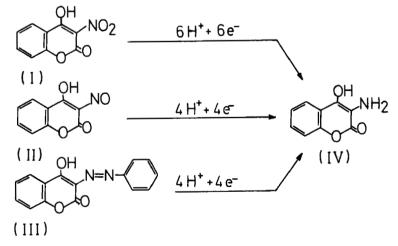
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ELECTROCHEMICAL SYNTHESIS OF 3-AMINO-4-HYDROXYCOUMARIN

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3-Amino-4-hydroxycoumarin(IV)-which is a constituent part of the antibiotic novobiocin¹ has been found to possess antibacterial and fungicidal properties of its own.^{2,3} The published syntheses of IV are based in most cases, on the reduction of 3-nitro(I), 4 3-nitroso(II), 5 or 3-phenylazo-4hydroxycoumarin(III)⁶ by conventional methods.^{4,7-9} These methods either give low yields, involve complex procedures or require the use of expensive catalysts. These disadvantages severely diminish the value of chemical reduction as a method of preparation of substantial amounts of IV .

Electrochemical reduction which has recently been



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TRKOVNIK, LACAN, STUNIC AND NAHMIJAZ

competing successfully with classical chemical methods even on an industrial,¹⁰ offers important advantages. We now describe the novel electrochemical reduction of (I),(II) and (III) (see Scheme).

EXPERIMENTAL

Mps were determined on a Kofler block and are uncorrected.

<u>Electrolytic cell</u>.¹¹ A magnetic stirrer bar was placed on the bottom of a 1000 ml beaker and covered with a pool of mercury to serve as the cathode. An unglazed cylindrical porcelain diaphragm was used to separate a compartment containing the platinum-wire anode. During electrolyses the beaker was immersed in a water bath kept at the temperatures specified and the mercury cathode was stired. Cathode potentials were measured with a vacuum-tube voltmeter against a S.C.E.

> Catholytes: (A) 100ml glac. $CH_3COOH + 50$ ml 20 %HCl (B) 100 ml 96 % $C_2H_5OH + 50$ ml 20% HCl. Anolyte: 20% HCl in all experiments.

<u>Fixed potentials</u> for controlled-potential reductions were selected on the basis of preliminary data obtained by electrolyses at constant current densities.¹²

<u>Numbers of electrons</u> transferred in electrochemical reductions were determined coulometrically at controlled potentials.

<u>3-Amino-4-hydroxycoumarin</u>.-Compounds I, II, or III in amounts ranging from 1 to 10 g, dissolved in catholyte, were placed into the cathode compartment of the cell and electrochemically reduced at either constant current density or at

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3-AMINO-4-HYDROXYCOUMARIN

controlled potential under conditions specified on Tables I and II, respectively. When electrolysis was complete, the catholyte was removed and its volume brought to about 30 ml under reduced pressure. After having been adjusted to pH 5 with saturated Na_2CO_3 solution the light-green residue was placed in a refrigerator for several hours. The separated solid was collected by filtration and dried over $CaCl_2$ for 24 hrs before weighing. Identification of products was carried out after several recrystallizations from 70% ethanol. The purified compound, mp. 222-224^O(unchanged after admixture with authentic (IV) gave correct elemental analyses: its ir spectrum was identical with that of (IV) and it yielded the same azomethine derivative with benzaldehyde¹³ as did authentic (IV).

TABLE I.	- ELECTROLYS	ES AT CONSTANT	CURRENT DENSITI	ES
Compound	<u>Catholyte</u>	Temp.	i (A/dm ²)	Yield (%)
I II III	B B A	80 ⁰ 20 ⁰ 20 ⁰	1.580 1.620 1.428	74.6 68.5 96.5
TABLE II.	- ELECTROLY	SES AT CONTROLL	ED POTENTIALS	
Compound	Catholyte	E (V vs. S.C.E	.) Temp. n ^a	Yield (%)
I II III	A B B A	-0.130 -0.400 -0.130 -0.090	50° 5.27 80° 5.21 40° 3.40 40° 3.72	60.8 85.5 52.5 98.2
^a Number of electrons transferred determined coulometrically				

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TRKOVNIK, LACAN, STUNIC AND NAHMIJAZ

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