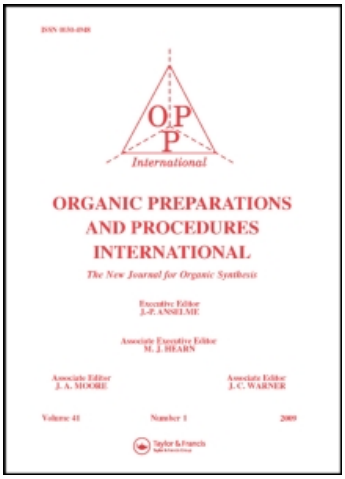


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

ELECTROCHEMICAL SYNTHESIS OF 3-AMINO-4-HYDROXYCOUMARIN

M. Trkovnik[a]; M. Laćan[b]; Z. Stunić[a]; D. Nahmijaz[a]
[a] Technical Faculty, University of Sarajevo, Banja Luka, YUGOSLAVIA [b] Technological Faculty, University of Zagreb,

To cite this Article Trkovnik, M. , Laćan, M. , Stunić, Z. and Nahmijaz, D.(1975) 'ELECTROCHEMICAL SYNTHESIS OF 3-AMINO-4-HYDROXYCOUMARIN', Organic Preparations and Procedures International, 7: 1, 47 — 50
To link to this Article: DOI: 10.1080/00304947509356815
URL: http://dx.doi.org/10.1080/00304947509356815

ORGANIC PREPARATIONS AND PROCEDURES INT. 7(1), 47-50 (1975)

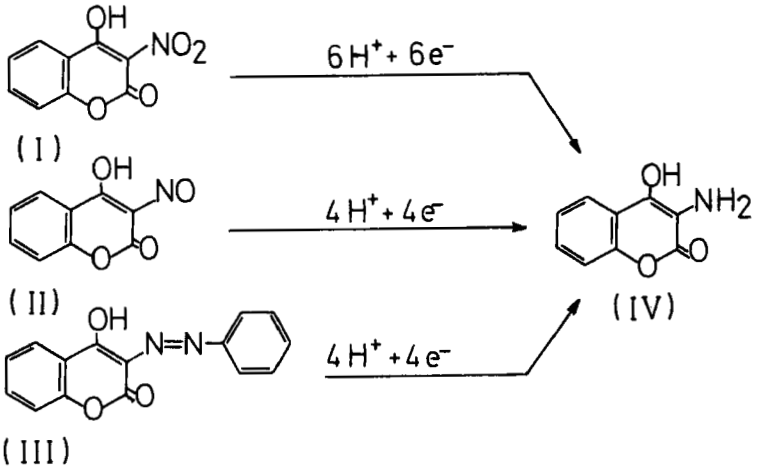
ELECTROCHEMICAL SYNTHESIS OF 3-AMINO-4-HYDROXYCOUMARIN

M. Trkovnik,* M. Lačan,† Z. Stunić and D. Nahmijaz

Technical Faculty, University of Sarajevo (Branch Dept.)
78000 Banja Luka, YUGOSLAVIA

3-Amino-4-hydroxycoumarin(IV)-which is a constituent part of the antibiotic novobiocin[1] 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-4-hydroxycoumarin(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



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.

Electrolytic cell.[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.

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

Numbers of electrons transferred in electrochemical reductions were determined coulometrically at controlled potentials.

3-Amino-4-hydroxycoumarin.-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

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°(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 benzaldehyde[13] as did authentic (IV).

TABLE I. - ELECTROLYSES AT CONSTANT CURRENT DENSITIES

Compound	Catholyte	Temp.	i (A/dm^2)	Yield (%)
I	B	80°	1.580	74.6
II	B	20°	1.620	68.5
III	A	20°	1.428	96.5

TABLE II. - ELECTROLYSES AT CONTROLLED POTENTIALS

Compound	Catholyte	E (V vs. S.C.E.)	Temp.	n[a]	Yield (%)
I	A	-0.130	50°	5.27	60.8
	B	-0.400	80°	5.21	85.5
II	B	-0.130	40°	3.40	52.5
III	A	-0.090	40°	3.72	98.2

[a]Number of electrons transferred determined coulometrically

Acknowledgment. - This investigation was supported financially by a Grant-in-aid from the Republic's Association for Scientific Work of Bosnia and Hercegovina.

REFERENCES

*To whom inquiries should be directed.

†Technological Faculty, University of Zagreb.

1. C. F. Spencer, I. O. Rodin, E. W. Walton, S. W. Folley and K. Folkers, J. Am. Chem. Soc., 80,140 (1958).
2. K. Okumura, K. Ashino and T. Okuda, Yakugaku Zasshi, 81, 1482 (1961); CA,56,7938d (1962).
3. A. Del Campo and P. L. Fazzi, Riv. ist. sieroterap. ital., 33, 389 (1958); CA, 52, 10447b (1958).
4. F. Arndt, L. Loewe, R. Un and E. Ayca, Chem. Ber., 84, 319 (1951).
5. R. Anschütz, Ann.,367, 169 (1909).
6. C. F. Hübner and K. P. Link, J. Am. Chem. Soc., 67,99 (1954).
7. J. Klosa, Pharmazie, 8,221 (1953); CA, 48, 7602g (1954).
8. L. Reppel and W. Schmollak, Arch. Phram., 296, 365 (1963).
9. Th. Kappe, K. Burdeska and E. Ziegler, Monatsh. Chem.,97, 77 (1966).
10. H. Nohe, Chem. Ing. Techn.,46, 594 (1947).
11. M. Laćan, I. Tabaković, J. Hranilović, N. Bujas and Z. Stunić, Croat. Chem, Acta, 43,229 (1971).
12. M. J. Allen, Can. J. Chem., 37,257 (1959).
13. M. Deželić, M. Trkovnik, J. Grujić-Vasić and R. Ivanović Glas.Hem. Tehnol. B. i H., 12,117 (1963); CA, 63, 18009f (1965).

(Received August 12, 1974; in revised form December 12, 1974)