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On the Electrochemical Behaviour of 5(1*H*)-Pyrromethenones and 3,4-Dihydro-5(1*H*)-pyrromethenones

Short Communication

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Cyclic voltammetry and polarography measurements in anhydrous dimethylformamide indicate that 1,3,4,5-tetrahydro-3-methoxycarbonylmethyl-3′,4,4,4′-tetramethyl-5-oxo-2,2′-pyrromethen-5′-carboxylic acid *tert*-butylester [a 3,4-dihydro-5(1*H*)-pyrromethenone] is both easier to reduce and to oxidize than structurally related 5(1*H*)-pyrromethenones.

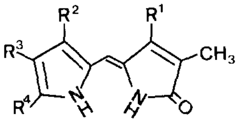
(Keywords: Bile pigments; Cyclic voltammetry; Polarography; Pyrromethenones)

Notiz über das elektrochemische Verhalten von 5(1H)-Pyrromethenonen und 3,4-Dihydro-5(1H)-pyrromethenonen (Kurze Mitteilung)

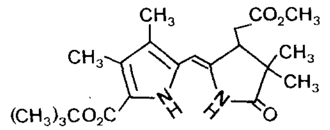
Cyclische Voltammetrie und Polarographie in wasserfreiem Dimethylformamid haben gezeigt, daß 1,3,4,5-Tetrahydro-3-methoxycarbonylmethyl-3′,4,4,4′-tetramethyl-5-oxo-2,2′-pyrromethen-5′-carbonsäure-*tert*-butylester sowohl leichter zu reduzieren als auch zu oxidieren ist als 5(1*H*)-Pyrromethenone mit ähnlicher Struktur.

The electrochemical behaviour of bile pigments and their partial models [e.g. 5(1*H*)-pyrromethenones and 2,2′-pyrromethenes] has not been as extensively studied[1,2] as the electrochemistry of the cyclic tetrapyrrole pigments. Here we report electrochemical data, to compare the redox behaviour of a 3,4-dihydro-5(1*H*)-pyrromethenone (**5**) with that of a series of structurally related 5(1*H*)-pyrromethenones (**1**–**4**). Table 1 summarizes the reduction potentials of these compounds, obtained by cyclic voltammetry.

All compounds measured (**1**–**5**) by cyclic voltammetry in anhydrous dimethylformamide (*DMF*), using $LiClO_4$ as supporting electrolyte (see the table for other experimental details), show two irreversible reduction peaks. However, the 3,4-dihydropyrromethenone **5** shows also a third reduction peak on the anodic sweep at a potential of —1.71 V, an intermediate value between those of the two reduction peaks of the cathodic sweep (—1.58 V and —1.81 V).



	R^1	R^2	R^3	R^4
1	CH_3	H	H	H
2	CH_3	CH_3	CH_3	H
3	C_2H_5	CH_3	C_2H_5	CH_3
4	CH_3	CH_3	CH_3	$C_2H_5O_2C$



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From the experimental data of the table, the following conclusions can be drawn. First, alkylation on the pyrrole ring determines higher reduction potentials, a result which agrees with the effect of such a substitution on 5(1*H*)-pyrromethenones giving lower oxidation potentials[2]; second, a 5′-alkoxycarbonyl substitution determines lower reduction potentials, owing to its electron-withdrawing effect (compare the first reduction potentials of **2**, and **4**); third, the 3,4-dihydro-5(1*H*)-pyrromethenone **5** shows a first reduction potential lower than the structurally related 5(1*H*)-pyrromethenone **4** does. This behaviour is also corroborated by the polarographic first half-wave potentials found for the same *DMF* solutions; —1.38 V for **5**, and —1.62 V for **4** (drop time 2 s: 0.95 mg $Hg \cdot s^{-1}$).

Falk et al. have studied[2] the anodic oxidation in acetonitrile (using a platinum rotating electrode) of a series of 5(1*H*)-pyrromethenones and 2,2′-pyrromethenes. However, no alkoxycarbonyl derivative was investigated. Consequently, in order to compare the 3,4-dihydro-5(1*H*)-pyrromethenone **5** with the 5(1*H*)-pyrromethenones **1**–**4**, we tested by cyclic voltammetry the oxidation behaviour of **5**, and that of **4** and **3** (**3**, and other compounds structurally very close to **1** and **2** were measured by *Falk* et al.[2]) using a platinum electrode, under the same experimental conditions as for our experiments summarized in Table 1. Our results show that the 3,4-dihydro structure is easier to oxidize than the unsaturated one: the first oxidation peak potentials for the compounds **3**, **4**, and **5** are + 0.57 V, + 0.94 V, and + 0.79 V respectively (Ref.[2], + 0.39 V for **3**). MINDO/3 calculations[3] agree with these results: the pyrromethenone **1** shows a higher first ionisation potential than its *trans*-3,4-dihydro derivative ($\Delta = 0.06$ eV).

Table 1. *Cyclic voltammetry reduction peaks of some* $5 \cdot 10^{-4}$ mol l^{-1} *solutions of* 5(1*H*)*-pyrromethenones in anhydrous dimethylformamide containing* 0.1 mol l^{-1} $LiClO_4$ *(*100 mV s^{-1}; Hg *electrode,* $2.22 \cdot 10^{-2}$ cm^2*)*

Compound	Reduction	Potentials (V)
1	—1.84	—1.98
2	—1.88	—2.03
3	—1.90	—[a]
4	—1.84	—2.02
5	—1.58[b]	—1.81

[a] Second peak overlaps with the supporting electrolyte discharge.
[b] See the text.

There is no reason not to extrapolate these results to other 3,4-dihydro and fully unsaturated 5(1*H*)-pyrromethenones. According to these results, 3,4-dihydro-5(1*H*)-pyrromethenones are easier to reduce and also to oxidize than the structurally related pyrromethenones. If this behaviour is maintained in the tetrapyrrole series, it may be of interest for the study of their biological role (e.g. in the case of phytochrome and phycocyanins).

All compounds studied are described in the literature: (*Z*)-3,4-dimethyl-5-(2-pyrrolylmethylene)-3-pyrrolin-2-one (**1**)[4], (*Z*)-3,4-dimethyl-5-[(3,4-dimethyl-2-pyrrolyl)methylene]-3-pyrrolin-2-one (**2**)[5], (*Z*)-4-ethyl-3-methyl-5-[(3,5-dimethyl-4-ethyl-2-pyrrolyl)methylene]-3-pyrrolin-2-one (**3**)[6], (*Z*)-3,4-dimethyl-5-[(3,4-dimethyl-5-oxo-3-pyrrolin-2-yliden)methyl]-1*H*-pyrrole-2-carboxylic acid ethyl ester (**4**)[7], and (*Z*)-3,4-dimethyl-5[4,4-dimethyl-3-methoxycarbonylmethyl-5-oxo-pyrrolydin-2-yliden)methyl]-1*H*-pyrrole-2-carboxylic acid *tert*-butyl ester (**5**)[8].

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