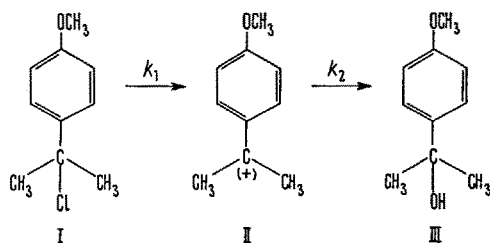


with an exponent $\sim 0.70^6$. (Criteria of a fully rate controlled volume reaction). It can be rigorously concluded that the reducible species responsible for this polarographic wave is indeed the carbonium ion II. Only the starting chloride I, the carbonium ion II and the product III participate in the SN1 displacement. The product III is nonreducible and can not be responsible for the wave. Moreover, its concentration is growing with time whereas the polarographic wave is diminishing. Since the wave is fully rate controlled, it can not be due to the starting chloride I but must be due to a species produced from I by a chemical reaction. The carbonium ion II is thus the only candidate.



In agreement with this conclusion one may directly observe a beautifully developed one electron reduction wave of the carbonium ion II if one dissolves the alcohol III in sulphuric acid-water or sulphuric acid-acetic acid mixtures of extreme acidity ($E_{1/2} = -0.49$ V vs S.C.E. at $H_0 = -2$; $E_{1/2} = -0.40$ V vs S.C.E. in 6% sulphuric acid in acetic acid. The small differences in half wave potential are understandable in view of the large differences in solvent, ionic strength, and the resulting uncorrected diffusion potentials).

Consequently, we have concluded that we are indeed dealing with a case as discussed above and we proceeded with the evaluation of k_2 in the manner indicated. The decrease of the wave gave an excellent straight line fit in a first order plot from which k_{exp} was evaluated. The value of k_{exp} was independent of mercury pressure, surfactants and the concentration of I. The straight line plots also gave the values of \bar{i}_{k_0} for the individual concentrations of I. The value of \bar{i}_d was determined from the known waves of acetophenone in the same medium. To insure sufficient conductivity around time zero (before more hydrochloric acid is formed) an initial concentration of hydrochloric acid 0.05 M was used. It was also ascertained experimentally that the changing concentration of hydrochloric acid had no influence on the magnitude of the limiting current of the wave which was measured and specifically that hydrochloric acid did not influence the current at the potential (-0.45 V vs S.C.E.) at which the readings of $\bar{i}_{k(t)}$ were made. In this manner the data assembled in the Table were obtained.

A Defense Alkaloid in a Carnivorous Beetle

The common European ladybug *Coccinella septempunctata* L. (Coleoptera, Coccinellidae) has long been known to possess the chemical defenses that are expected to be associated with its aposematic coloration¹. The insect, when molested, releases droplets of orange haemolymph at its articulations. This 'reflex bleeding' of

Values of k_1 and k_2 derived for the SN1 reaction of *p*-methoxy 2-phenyl propyl chloride

| % H ₂ O (v/v) | $k_{exp} = k_1 s^{-1}$ * | \bar{i}_{k_0}/\bar{i}_d * | $k_2 s^{-1}$ |
|--------------------------|--------------------------|-----------------------------|-------------------|
| 5 | 9.2×10^{-3} | 3.2×10^{-4} | 2.0×10^3 |
| 7.5 | 10.5×10^{-3} | 2.7×10^{-4} | 3.9×10^3 |
| 8.7 | 12.4×10^{-3} | 2.1×10^{-4} | 8.6×10^3 |

*Data obtained at -0.45 V vs S.C.E., drop time = 2.50 s, 25°C.

The value of k_1 derived experimentally in this study is about six times smaller than that previously obtained by extrapolation from results at low temperatures and different water concentrations⁵. The increase of k_1 with increasing water concentration is only about half of that previously extrapolated⁵. In view of the higher concentrations of I (5% v/v) in our case and the fact that the previous study obtained the results by extrapolation, the two values of the overall rate constants can be considered compatible. As would be expected the value of k_2 increases more rapidly than k_1 with increasing water concentration. There is a difference of almost six orders of magnitude between the rate of the first and second step.

This example is the first case in which the rate of the second step of an SN1 displacement has been directly determined. Polarography is uniquely suitable for such a study, since relaxation techniques are only capable of studying equilibrium systems.

Zusammenfassung. Die Zeitabhängigkeit des polarographischen Stromes, welche man bei der gemäss SN1 verlaufenden Hydrolyse von *p*-Methoxy-2-phenylpropylchlorid beobachtet, ermöglicht die Bestimmung der Geschwindigkeitskonstanten k_1 der Gesamtreaktion sowie auch der Geschwindigkeitskonstanten k_2 des zweiten raschen Schrittes, welcher nach pseudo-erster Ordnung verläuft. Für k_2 ergibt sich in Aceton, das 5% Wasser enthält, bei 25°C $k_2 = 2,0 \times 10^3$ sec⁻¹.

D. BARNES and K. WIESNER⁷

Natural Products Research Center,
The University of New Brunswick,
Fredericton (N.B., Canada), 19 July 1971.

⁶ K. WIESNER, Colln Czech. chem. Commun. 12, 64 (1947).

⁷ We would like to thank the N.R.C. for provision of a grant to purchase the Electrochemical System and the University of New Brunswick for a Fellowship for one of us (D.B.).

Coccinellidae insures a relative immunity towards predators, especially ants².

In a preliminary study, 1600 *C. septempunctata* (collected in Brussels in December 1970) were blended at room temperature in methanol. The supernatant was separated by centrifugation and partitioned between methanol and

n-pentane. Subsequent fractionation of the methanolic phase was monitored by tasting the fractions in order to locate the exceedingly bitter taste of the beetles³ and by testing their efficiency as repellent against the ant *Myrmica rubra*.

Repeated column chromatography on alumina, followed by several recrystallizations afforded 135 mg of a compound $C_{13}H_{23}NO$ as white needles charring at 235° without melting and for which the name coccinellin was coined. The empirical formula was established by high-resolution mass spectrometry: a molecular ion was measured at *m/e* 209.1777 (calculated for $C_{13}H_{23}NO$: 209.1779), with fragmentation peaks at *m/e* 193 and 192. Coccinellin shows only end-absorption in UV and its NMR-spectrum shows the absence of vinyl protons. The compound is soluble both in water and in methylene chloride. Coccinellin forms a hydrochloride that gives the same mass spectrum as the original product and displays prominent IR-bands at 2550 (broad) and 1530 cm^{-1} ⁴.

Our fractionation procedure also afforded 10 mg of another, less polar, amorphous compound $C_{13}H_{23}N$ (by mass spectrometry), precoccinellin. Our data strongly suggested that coccinellin is the N-oxide of precoccinellin and that relationship was confirmed by reduction of the N-oxide with ferrous sulphate.

Coccinellin is responsible for the bitter taste of *C. septempunctata* but not for its peculiar smell. Its efficiency as a defensive compound could be demonstrated by its activity towards ants. Water containing 0.5% coccinellin was almost completely refused by thirsty *Myrmica rubra* and even a concentration of 0.1% markedly prevented drinking. These concentrations are much smaller than that of the compound in the haemolymph of the beetle. Coccinellin can repel ants without direct contact with their mouthparts: evaporation of 2 mg from methylene

chloride on a filter paper around their food prevented hungry ants from reaching it.

Coccinellin could be detected directly in the haemolymph of *C. septempunctata* by TLC on alumina plates. Neither coccinellin nor precoccinellin could be found in the aphids that constitute the prey of the beetle. Both compounds were detected in *C. undecimpunctata* L. but not in *Adalia bipunctata* L. nor in *Propylaea quatuordecimpunctata* L. Other coccinellid chemical defenses and the chemical structure of coccinellin are currently being investigated in our laboratories.

Résumé. Le composé utilisé pour la défense chimique de *Coccinella septempunctata* (Coleoptera, Coccinellidae) a été isolé. Il s'agit de la coccinelline $C_{13}H_{23}NO$, qui est un N-oxyde de l'alkaloïde précoccinelline $C_{13}H_{23}N$, également présent dans l'hémolymph de l'insecte.

B. TURSCH, D. DALOZE, MARIANNE DUPONT, J.M. PASTEELS and MARIE-CLAIRE TRICOT

Chimie des Substances Animales et Biologie des Insectes Sociaux, Département de Biologie Animale, Faculté des Sciences de l'Université Libre de Bruxelles, Bruxelles 5 (Belgique), 19 May 1971.

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The Isolation and Structure of Trichosiderin B¹

The trichosiderins² are a group of phaeomelanin pigments occurring in human and mammalian red hair and in the feathers of many species of birds.

In previous reports³⁻⁵ we have shown that a suitable source for the extraction of these pigments are the feathers of the New Hampshire chicken, from which 3 homogenous

trichosiderins (C, E and F) have been isolated and characterized as 1²,2'-bi(2H-1,4-benzothiazine) derivatives (I, II, III)⁶. From the same source we have now isolated an isomer of trichosiderin C which has been called trichosiderin B (IV), since it corresponds to the fraction designated B2 in earlier chromatographic work⁷.

