In the paper on directional hearing in cod[1], it was therefore concluded that the direction of the sound sources is decisive for the discrimination and not the timbre or intensity differences between the sound sources.

Zusammenfassung. Der «Likelihood»-Quotiententest wird auf einer 3×2-Kontigenztafel mit unbekannten Wahrscheinlichkeiten p_{ij} $(i = 1, 2, 3; j = 1, 2)$ angewandt, um die Hypothese $H_0: p_{i1} = p_{i2}$ $(i = 1, 2, 3)$ gegen die alternative Hypothese $H_1: p_{11} > p_{12}, p_{31} < p_{32}$ zu prüfen, und zwar wenn kleine Stichproben vorhanden sind. Ausserdem wird die Kombination solcher Tests behandelt. Als Beispiel wird diese Testtheorie beim Wahlverhalten des Kabeljaus im Dressurversuch über akustische Lokalisation in zwei Stimulussituationen verwendet.

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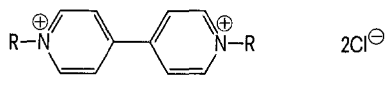
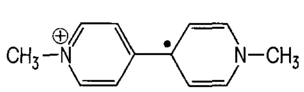
The 2,2'-Dicyano-1,1'-Dimethyl-4,4'-Bipyridylium Di-cation: A Viologen Indicator with a High Redox Potential

Diquaternary salts of 4,4'-bipyridyl, especially methyl viologen (I; R = CH_3) and benzyl viologen (I; R = $CH_2.Ph$)[1] have been used considerably as redox indicators and electron carriers in biological systems[2] and in chemical reactions[3]. These salts are reduced in aqueous solution by a one electron transfer which is reversible to give highly coloured stable radical cations (e.g. II). The salts originally studied[1] had redox potentials (E_o) between −0.36 and −0.45 volts. With the discovery of the phytotoxic properties of (I; R = CH_3)[4] and its development as the herbicide paraquat interest in salts of this type has increased. Several diquaternary salts of 2,2'-bipyridyl, for example, the herbicide diquat (III)[4], behave similarly as redox systems and they too have found applications as electron carriers and indicators in biological[5-9] and chemical[10] systems. Reversible redox indicators based on diquaternary salts of 2,2'- and 4,4'-bipyridyls have thus been extended over a range from about −0.15 to −0.70 volts[4,7-9,11-17]. We now report the preparation of a viologen indicator with a much higher redox potential.

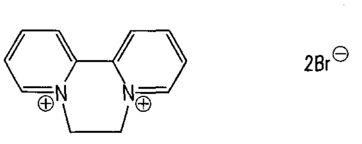
4,4'-Bipyridyl-1,1'-dioxide[18] (1.0 g) and dimethyl sulphate (5 ml) were heated at 150 °C for 30 min. The cooled solution was added to ethyl acetate (100 ml) and the resultant white precipitate of 1,1'-dimethoxy-4,4'-bipyridylium dimethosulphate was collected (cf. ref.[18]). Without purification the salt was dissolved in water (20 ml) and the pH adjusted to 10.0 with sodium carbonate solution. Potassium cyanide (2 g) in water (15 ml) was added and a white precipitate of 2,2'-dicyano-4,4'-bipyridyl (IV) formed immediately (cf. ref.[19]).



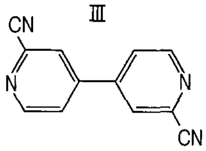
I



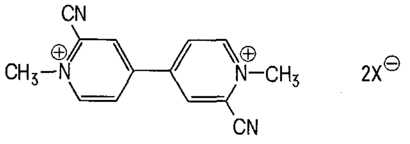
II



III



IV



V

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(Yield 90%). It crystallized from ethanol as a white powder, m.p. 248°. (Found: C, 69.9; H, 3.2; N, 27.5; $C_{12}H_6N_4$ requires C, 69.9; H, 2.9; N, 27.2). The NMR-spectrum in CF_3CO_2D consisted of a multiplet in the range $\delta = 8.45$–8.69 assigned to the 3, 5, 3′, 5′ protons and a doublet at $\delta = 9.22$–9.31 ppm due to the 6, 6′ protons. The UV-spectrum in ethanol showed maxima at λ 243 slog ε 4.12), 282 (3.94) and 311 sh nm (3.80). The IR-(pectrum showed a band at 2240 cm^{-1} (CN).

Compound (IV) (3 g) was heated in dimethyl sulphate (15 ml) at 120 °C for 15 min. The cooled mixture was added to ethyl acetate (200 ml) and the white precipitate of 2, 2′-dicyano-1. 1′-dimethyl-4, 4′-bipyridylium dimethosulphate (V; X = CH_3SO_4) collected. It crystallized from aqueous ethanol, m.p. 253° (dec.). (Yield 3.9 g) . (Found: C, 41.6; H, 4.0; N, 12.3; $C_{16}H_{18}N_4S_2O_8$ requires C, 41.9; H, 3.9; N, 12.2). The UV-spectrum in water (pH 6.1) showed maxima at λ 220 (log ε 4.45) and 274 nm (4.30). It was converted to the dibromide (V; X = Br) by crystallization from a mixture of alcohol and conc. hydrobromic acid, m.p. 265° (dec.). (Found: C, 42.7; H, 3.1; N, 13.9; $C_{14}H_{12}Br_2N_4$ requires C, 42.4; H, 3.0; N, 14.1). The NMR-spectrum in D_2O consisted of a singlet at $\delta = 4.40$ (methyl protons), a quartet at 8.85–9.0 (5, 5′ protons), a doublet at 9.24–9.26 (3, 3′ protons) and a doublet at 9.42–9.52 ppm (6, 6′ protons).

The salt (V; X = CH_3SO_4) is stable in aqueous solution up to a pH of about 7.5 but it is decomposed by stronger alkali. An aqueous solution of (V; X = CH_3SO_4) on treatment with zinc dust developed immediately an intense violet colouration due to the radical cation analogous to (II). When the reducing agent was removed and the solution was shaken in air the deep colour discharged. The NMR-spectrum obtained then was identical with that of the original salt indicating that the one electron transfer is essentially completely reversible. On polarographic examination in the pH range 1.9–7.0 the salt gave a typical symmetrical one-electron reduction wave with a half-wave potential (E_o) of +0.09 volts independent of pH. A second reduction wave was also present at lower potential but it was not always distinct. The high reduction potential of (V; X = CH_3SO_4) compared with methyl viologen, E_o −0.45 volts, is clearly due to the presence of the electron attracting cyano groups. The salt (V; X = CH_3SO_4) thus provides a considerable extension to the range of viologen indicators whose redox potentials now extend from +0.09 to −0.70 volts.

The salt (V; X = CH_3SO_4) was inactive as a herbicide when tested at 8 lbs./acre, a result in keeping with its high reduction potential (cf. refs.[16,17]).

Zusammenfassung. Herstellung eines neuen Viologen-Indikators mit hohem Redox-Potential.

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19-Deoxydideacetylfusicoccin, a Minor Metabolite of *Fusicoccum amygdali* Del.

The plant pathogenic fungus *Fusicoccum amygdali* Del. produces a number of phytotoxic substances[1], among which fusicoccin (I)[2,3] predominates both in quantity and activity. Studies aimed at establishing the structure of minor metabolites chemically related to fusicoccin have shown the occurrence in the culture filtrates of *F. amygdali* of two types of compounds, namely those which only differ from the major toxin for the number and/or the position of *O*-acetyl groups (II-VIII)[4-7], and those which have a lower oxygen content in the aglycone moiety (IX–X)[6]. The structure assigned by us to IX has been recently confirmed by British workers[8], who have, interestingly, demonstrated that it can act as a biogenetic precursor of fusicoccin.

In this paper we report the determination of the structure XI of a new minor metabolite of *F. amygdali*, and its synthesis from dideacetylfusicoccin (VIII).

Methods. UV-spectra were recorded for solutions in ethanol with a Beckman DK-2 spectrophotometer. IR-spectra were recorded for solutions in chloroform on a Beckman IR-9 spectrophotometer. NMR-spectra were recorded on a Varian HA-100 apparatus with TMS as an internal reference. Rotations were measured for solutions in chloroform with a Perkin-Elmer 141 polarimeter. Mass spectra were recorded on a A.E.I. MS-902 spectrometer operated at 70 eV. Melting points are uncorrected.

Results and discussion. Thin layer chromatography of a group of fractions eluted from silica gel columns between pure isofusicoccin (II) and 3′-monodeacetylfusicoccin (IV) (indicated as F-III and F-IV respectively in a previous paper[6]) indicated the presence of a third substance, unaffected by an alkaline treatment (0.1 *N* NaOH, 30 min at room temperature) which converted the accompanying compounds to dideacetylfusicoccin (VIII). The hydrolyzed mixture was extracted with butan-1-ol and chromatographed on a silica gel column. Elution with chloroform-methanol (8:2, v/v) yielded compound XI, $C_{32}H_{52}O_9$, m.p. 91° (from ethylacetate-light petroleum 30–50°), $[\alpha]_D^{25}$ + 21 (c = 0.3), $\lambda_{max} < 220$, ν_{max} 3500 cm^{-1} (OH), 1630 (olefinic) and 920 cm^{-1} (vinyl). The NMR-spectrum is very similar to that of dideacetylfusicoccin (VIII), but shows signals for 3 secondary C-Me groups, 2 of them being part of an isopropyl group whose CH resonates at 3.22 δ in $CDCl_3$-d_5-pyridine solution. The mass spectrum shows the molecular ion at *m/e* 580 and prominent peaks at *m/e* 512 ($M^+ - 68$), 350 (aglycone), 69($C_5H_9^+$). On acid

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