(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 δ = 8.45–8.69 assigned to the 3, 5, 3′, 5′ protons and a doublet at δ = 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 δ = 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.

R. FIELDEN and L. A. SUMMERS

Department of Chemistry, University of Newcastle, New South Wales (Australia), 18 March 1974.

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), λ_{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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[6] A. BALLIO, C. G. CASINOVI, M. FRAMONDINO, G. GRANDOLINI, G. RANDAZZO and C. ROSSI, Experientia *28*, 1150 (1972).
[7] Two further derivatives containing 3 acetyl groups have been recently identified as 12-*O*-acetylfusicoccin and 12-*O*-acetylisofusicoccin (paper in preparation).
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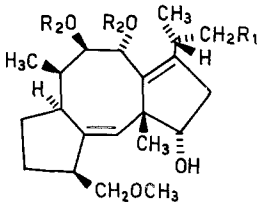
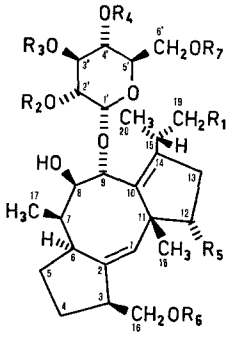
hydrolysis, compound XI yields one mole of D-glucose (assayed by glucose oxidase).

Tetra-acetyl-XI, $C_{40}H_{60}O_{13}$, prepared by room-temperature acetylation of XI with Ac_2O in dry pyridine, was obtained as an oil; $[\alpha]_D^{25}$ + 26 (c = 0.9), ν_{max} 3450 cm^{-1} (OH). The NMR-spectrum shows 4 acetyl resonances. The mass spectrum shows the molecular peak at *m/e* 748, a peak at *m/e* 392 (monoacetylaglycone), and very strong peaks at *m/e* 289 (triacetylglycosyl), 229 (289–60), 169 (229–60), 109 (169–60), 69($C_5H_9^+$). The occurrence of only 3 acetyl groups in the glucosyl moiety indicates that one OH group is not available for acetylation; this must correspond to OH–6′ carrying a C_5H_9 group, as in fusicoccin, because periodate oxidation of XI affords a compound $C_{31}H_{48}O_8$ (M^+ 548) that has lost 32 mass units but still contains all peaks derived from the fragmentation of the aglycone[9].

The aglycone (XII), $C_{21}H_{34}O_4$ (M^+ 350), prepared by treatment with alkali of the periodate reaction product of XI, was obtained after column chromatography on silica gel (chloroform-propan-2-ol 95:5 v/v) as an amorphous solid with $[\alpha]_D^{25}$ − 14 (c = 0.8) which gave an amorphous acetonide (XIII), $C_{24}H_{38}O_4$ (M^+ 390), $[\alpha]_D^{25}$ + 4.0 (c = 1.0). The spectral properties of the aglycone (XII) and its derivative (XIII) were fully consistent with those expected on the assumption that XI was 19-deoxydideacetylfusicoccin. A compound identical in all its properties (Rf on silica gel plates with 3 solvent systems, optical rotation, IR-, NMR- and mass-spectra) to the acetonide (XIII) was obtained after lithium aluminium hydride reduction (4 h under reflux in tetrahydrofurane) of the monotosylate (XIV) prepared by reaction of fusicoccin deacetylaglycone acetonide[2] (XV) with 1.5 equivalents of toluene-*p*-sulphonyl chloride in dry pyridine (24 h at room temperature). Chromatography on a silica gel column, eluted with benzene containing increasing quantities of ethylacetate, resolved the monotosylate (XIV) (m.p. 174° from ethylacetate) from some ditosylate (m.p. 142–3° from ethylacetate-light petroleum 30–50°); both compounds had properties in close agreement with those reported by Barrow et al.[8]. Having thus established the structure, absolute configuration included, of the aglycone (XII) and on the assumption that the glucose unit was linked in compound XI as in fusicoccin (I), we attempted a direct correlation with dideacetylfusicoccin (VIII). This was treated with one equivalent of toluene-*p*-sulphonyl chloride in dry pyridine (20 h at room temperature) to give a mixture that was fractionated by column chromatography on silica gel (chloroform-propan-2-ol, 95:5 v/v) to yield a monotosylate and small amounts of a ditosylate. The monotosylate (XVI), $C_{39}H_{58}O_{12}S$ (M^+ 750) m.p. 86° (from ethyl ether-light petroleum 40–70°, $[\alpha]_D^{25}$ + 40 (c = 0.78) furnished on reduction with lithium aluminium hydride (16 h at room temperature in dry ether) a substance identical in all its properties (Rf on silica gel plates with 3 solvent systems, optical rotation, IR-, NMR-, and mass spectra, mixed m.p.) to compound XI. This established conclusively that compound XI is 19-deoxydideacetylfusicoccin[10].



XII R_1, R_2 = H
XIII R_1 = H; R_2, R_2 = $C(CH_3)_2$
XIV R_1 = O-Ts; R_2, R_2 = $C(CH_3)_2$
XV R_1 = OH; R_2, R_2 = $C(CH_3)_2$



	R_1	R_2	R_3	R_4	R_5	R_6	R_7
I	OAc	H	Ac	H	OH	CH_3	$C(CH_3)_2CH{:}CH_2$
II	OAc	H	H	Ac	OH	CH_3	$C(CH_3)_2CH{:}CH_2$
III	OAc	Ac	H	H	OH	CH_3	$C(CH_3)_2CH{:}CH_2$
IV	OAc	H	H	H	OH	CH_3	$C(CH_3)_2CH{:}CH_2$
V	OH	Ac	H	H	OH	CH_3	$C(CH_3)_2CH{:}CH_2$
VI	OH	H	H	Ac	OH	CH_3	$C(CH_3)_2CH{:}CH_2$
VII	OH	H	H	H	OAc	CH_3	$C(CH_3)_2CH{:}CH_2$
VIII	OH	H	H	H	OH	CH_3	$C(CH_3)_2CH{:}CH_2$
IX	H	H	H	H	H	H	H
X	H	H	H	H	OH	H	$C(CH_3)_2CH{:}CH_2$
				(stereochemistry not yet demonstrated)			
XI	H	H	H	H	OH	CH_3	$C(CH_3)_2CH{:}CH_2$
XVI	OTs	H	H	H	OH	CH_3	$C(CH_3)_2CH{:}CH_2$

Riassunto. Un metabolita secondario di *Fusicoccum amygdali* Del., presente in piccola quantità nelle acque madri di cristallizzazione della fusicoccina, corrisponde alla 19-deossidideacetilfusicoccina. Il nuovo composto è stato anche ottenuto per sintesi a partire dalla dideacetilfusicoccina.

A. Ballio, C.G. Casinovi, V. d'Alessio, G. Grandolini[11], G. Randazzo and C. Rossi[12]

Istituto di Chimica Organica dell'Università, Via Mezzocannone 16, I–80134 Napoli; and Laboratori di Chimica Biologica, Istituto Superiore di Sanità, Roma (Italy), 12 February 1974.

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[11] On leave from the Istituto di Chimica Farmaceutica e Tossicologica, University of Perugia.

[12] On leave from the Istituti di Tecnica e Legislazione Farmaceutica, University of Perugia.