could be impurified by a minor component of very similar structure.

On GLC a sample previously purified by preparative TLC showed a certain amount of another component, with a slightly higher retention time on a SE-30%-Chromosorb-W-AW column than the major one. The same mixture, but with substantially lesser amounts of the minor component, was formed during permanganate oxidation of ocoteine (I) in acetone at room temperature[11] (26% yield, m.p. 201–202°), thus confirming structure III for the major component, which was accordingly named dehydroocoteine.

The heterogeneous character of the isolated product was confirmed by mass spectrometry, where 2 series of peaks appear, with relative intensities depending on the operating temperature. Spectra run at normal temperatures show peaks corresponding to II (m/e 367 (M^+), 352 (M-15), 337, 322, 183.5 (M^{++})), together with peaks due to a lower molecular weight component (M^+ 365). Runs made at higher temperature, and when most of the sample had volatilized, exhibit only the peaks corresponding to the minor component (m/e 365 (M^+), 350 (M-15), 335, 320, 182.5 (M^{++})). The similarity of both fragmentation patterns, although – as in the aporphine field[12–14] – of no diagnostic value, indicates a close structural similarity. Taking into account the NMR data of the isolated material, which favors a similar substituent orientation, formula IV can be advanced for the second component. Didehydroocoteine (IV) is a representative of a new kind of aporphine-type alkaloids.

Zusammenfassung. Zwei neue Alkaloide des Aporphintypus, Dehydroocotein (III) und Didehydroocotein (IV), wurden aus *Ocotea puberula* (Nees et Mart.) Nees isoliert, und ihre Strukturen aufgeklärt.

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The Structure of Mesobilirhodin

Mesobilirhodin was recorded as a minor product during the synthesis of mesobiliviolin[1]. SEIDEL and MÖLLER[2] proposed a biladiene b, c structure isomeric with mesobiliviolin (biladiene a, b) and containing the same side chain substituents. Mesobiliviolin and mesobilirhodin have recently been prepared[3] from mesobilirubinogen. A structure was proposed[3] for mesobilirhodin but certain alternate possibilities were not eliminated. The structure proposed is different to that[4,5] for mesobilirhodin prepared by alkaline isomerization of i-Urobilin.

We have prepared a rhodinoid pigment from mesobilirubinogen[6,7] which is presumably the same as mesobilirhodin prepared by STOLL and GRAY[3]. Analysis of the mass spectrum and NMR-spectrum supports the proposed structure I. This establishes that the two preparative methods yield identical products, and not different as is currently indicated.

Crude mesobilirubinogen was prepared by the sodium amalgam reduction[7] of two 300 mg lots of bilirubin (Nutritional Biochemicals). The crude mesobilirubinogen was dissolved in methanol and heated for 7 min with 1/10 volume of 20% $FeCl_3$ in HCl[6]. The products were phased into $CHCl_3$ and washed free of acid. Complete esterification was assured by the addition of diazomethane. Mesobilirhodin ester was purified to chromatographic homogeneity by preparative thin layer chromatography[8,9] on silica gel with CCl_4:CH_3COOCH_3 (1:2 v/v). Analytical chromatography of the red presumptive mesobilirhodin dimethyl ester on 2 additional systems[9] revealed only 1 pigment zone. The electronic absorption spectra of mesobilirhodin dimethyl ester showed absorption maxima at 557 and 306 nm in 5% HCl-CH_3OH w/v; 578,541 and 316 nm in ethanol saturated with zinc acetate.

The mass spectrum of the pure precipitated dimethyl ester was recorded in an AEI-MS 9 instrument. Direct inlet probe was employed, with a source temperature about 220° at 70 eV.

Principal fragment ions from mesobilirhodin dimethyl ester with their intensities in parentheses. 494 *m/e* (100) is taken as the base peak, and only peaks with intensity greater than 5% are given. Below 300 *m/e* only peaks with intensity greater than 10% are given. Peaks below 170 *m/e* are not given.

618 (5) M+	333 (5)	303 (10)	211 (12)
494 (100)	334 (5)	302 (11)	208 (12)
480 (3)	319 (5)	301 (9)	194 (27)
420 (5)	318 (12)	300 (5)	185 (18)
417 (8)	317 (15)	299 (10)	183 (19)
373 (8)	316 (31)	287 (11)	182 (10)
372 (18)	315 (13)	244 (11)	181 (31)
371 (27)	314 (5)	243 (26)	180 (78)
348 (7)	305 (7)	229 (17)	170 (18)
346 (6)	304 (19)	213 (11)	

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The proposed structure and fragmentation pattern are presented in Figure 1. The fragmentation pattern follows that for phycoerythrobilin dimethyl ester[8] and mesobiliviolin[3]. The identity of the fragment ions at 371 *m/e*; 194 *m/e*; is not known. It is possible that they are derived from an impurity, or Urobilin admixture in the sample.

Dimethyl esters of:	Max in nm in ethanol saturated with zinc acetate		Number of double bonds conjugated
Mesobiliverdin	685		10
Phycocyanobilin	664		9
Mesobiliviolin	626	576	8
Phycoerythrobilin	603	557	7
Mesobilirhodin	578	541	6

The probable assignment of the proton resonances from the NMR-spectrum is given in the Table. Assignment is based on earlier work with biladienes[8,9,12], and bilatrienes[9,10,11] and stercobilin[13].

Possible structures, in which the methylene bridge and pyrrolidone ring are adjacent[8] would be expected to show a similar biladiene fragmentation pattern. The fragmentation peaks, however, would be expected to occur at 492 and 478 *m/e* (tripyrrole); 318 and 302 *m/e* (dipyrrole).

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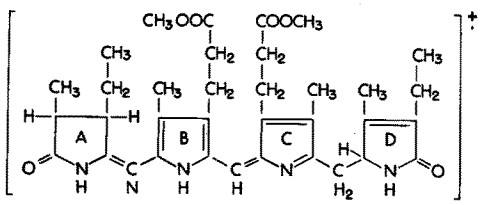
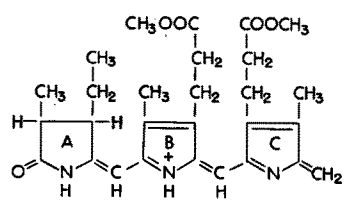
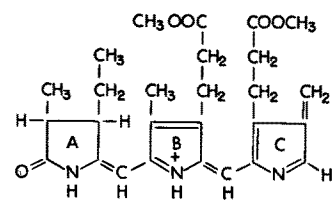
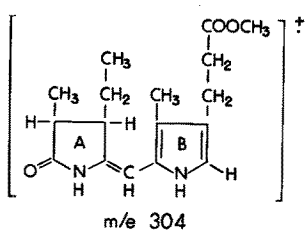
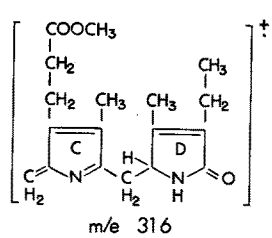


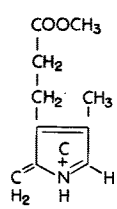








$-CH_2COOCH_3 \rightarrow$ m/e 243
$-CH_2CH_2COOCH_3 \rightarrow$ m/e 229



Chemical shifts	Relative intensity	Assignment	
6.59 Singlet	1	–CH=	Methine Bridge proton
5.43 Singlet	1	–CH=	Methine Bridge proton
4.24 Unresolved	2	$-CH_2=$	Methylene Bridge proton
3.62 Singlets	3	$-OCH_3$	Methyl ester protons
3.60 Singlets	3	$-OCH_3$	Methyl ester protons
3.24 Unresolved	1	H×	C-7' Proton
3.04 Unresolved	1	H+	C-1 Proton
2.87 Triplet	4	$-CH_2-$	β-Methylene of propionic ester
2.46 Triplet	4	$-CH_2-$	α-Methylene of propionic ester
2.10 Multiplet	2	$-CH_2-$	Methylene of A ring ethyl
1.97 Singlets	3	$\geqslant CH_3$	β-Methyls (B or C ring)
1.95 Singlets	3	$\geqslant CH_3$	β-Methyls (B or C ring)
1.85 Quartet	2	$-CH_2-$	Methylene of D ring ethyl
1.69 Singlet	3	$\geqslant CH_3$	β-Methyl (D-ring)
1.32 Doublet	3	$+CH_3$	C-1 Methyl
1.05 Triplets	3	$-CH_3$	Methyl of A or D ring ethyl
1.03 Triplets	3	$-CH_3$	Methyl of A or D ring ethyl

C-2 proton not definitely identified. Chemical shifts in ppm (δ) from internal TMS HA-100 Varian NMR-Spectrometer.

The mass spectrum does not allow a distinction between the proposed structure and one in which rings A and D are interchanged and in which the methylene bridge is at the α position. Our proposed structure (I) possesses 6 conjugated double bonds in the conjugated chain. This alternate structure would have a conjugated bond chain of only 5 bonds and would be expected (see below) to have absorption maxima at shorter wavelengths. We have, therefore, assigned biladiene a, b isomer structure (I) to mesobilirhodin dimethyl ester.

The structure proposed here is identical to that proposed for mesobilirhodin prepared from i-Urobilin[4,5]. This establishes that mesobilirhodin prepared by alkaline isomerization of i-Urobilin and $FeCl_3$ oxidation of mesobilirubinogen are identical[14].

Zusammenfassung. Für das Pigment Mesobilirhodin wird aufgrund von massenspektrometrischen Daten und der NMR-Spektren eine neue Struktur abgeleitet.

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7 February 1972.

[14] Part of this work was performed at the Brookhaven National Laboratory under the auspices of the United States Atomic Energy Commission, and part (H. B.) at the Technische Hochschule Braunschweig, West Germany.

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Isolation of Maridomycins and Structure of Maridomycin II

Maridomycins, a new group of macrolide antibiotics, were obtained from *Streptomyces hygroscopicus*[1], and named as maridomycin I, II, III, IV, V and VI, respectively, and characterized as follows:

All of these antibiotics show nothing but ultraviolet end absorption in methanol. They are classified as macrolide antibiotics from their physico-chemical, chemical and microbiological properties. The structure of maridomycin II was elucidated as shown in the chart.

Maridomycin II (II) was obtained as colorless prisms, pKa′ 6.9, IR[2]: 1740 (–O–CO–), 1235 (–OAc), 2730 (–CHO), NMR[3]: 1.01 (9H, *d*, –CH–$(CH_3)_2$, –CH–CH_3), 2.25 (3H, *s*, –O*Ac*), 2.54 (6H, *s*, –N$(CH_3)_2$), 3.56 (3H, *s*, –OCH_3), 5.66 (1H, *dd*, >C=C<), 6.10 (1H, *dd*, >C=C<), 9.65 (1H, *s*, –*CH*O); (in d_6-Me_2CO), 3.96 (1H, *q*, HO–C–*H*, J = 9, 2.5 Hz), 6.04 (1H, *dd*, >C=C<, *J* = 16, 9 Hz), 5.49 (1H, *dd*, >C=C<, *J* = 16, 9 Hz), 3.10 (1H, *dd*?, –O–*H*). NMR inspection and spin decoupling experiments of II showed that the compound contains HO–C(H)–C(H)=C–C(O)–C– group.

When II was acetylated with one mole of acetic anhydride, the 2′-monoacetate (VIII), $C_{44}H_{71}NO_{17}$, pKa′ 4.7, MS: *m/e* 885 (M^+), NMR: 2.06 (3H, *s*, –OAc), 4.02 (1H, *q*, HO–C–*H*) was obtained. An alternative acetylation of II with one mole of acetyl chloride gave the 9-monoacetate (IX), pKa′ 6.6, MS: *m/e* 885 (M^+).

Acetylation of VIII and IX led to the same diacetate $C_{46}H_{73}NO_{18}$ (VII), $[\alpha]_D^{29}$ –81.4° (c = 0.5 in EtOH), pKa′ 4.7, MS: *m/e* 927 (M^+), IR ($CHCl_3$): 3480 (–C–OH), 1240 (–OAc), NMR: 2.02, 2.04 (each 3H, *s*, –OAc).

On catalytic hydrogenation II gave tetrahydro II (X), $C_{42}H_{73}NO_{16}$, NMR: disappearance of olefinic protons of II at 5.5–6.3 ppm, and on acetylation X afforded the triacetate (XI), $C_{48}H_{79}NO_{19}$, IR ($CHCl_3$): 3500 (–C–OH), 1240 (–OAc), NMR: 2.00, 2.02, 2.06 (each 3H, *s*, –OAc).

Name		m.p. (decomp.)	$[\alpha]_D^{23}$ (c = 1.0 in EtOH)	MW[2] (VPO in EtOAc)	MS[2] *m/e* M^+	Mol. Formula	MIC[2] (mcg/ml)
Maridomycin I	(I)	129–132°	–72.3°	910	857	$C_{43}H_{71}NO_{16}$	0.5
Maridomycin II	(II)	134–136°	–71.9°	881	843	$C_{42}H_{69}NO_{16}$	0.5
Maridomycin III	(III)	135–138°	–76.0°	911	829	$C_{41}H_{67}NO_{16}$	1.0
Maridomycin IV	(IV)	143–146°	–76.2°	896	815	$C_{40}H_{65}NO_{16}$	2.0
Maridomycin V	(V)	144–149°	–73.6°	882	815	$C_{40}H_{65}NO_{16}$	5.0
Maridomycin VI	(VI)	149–154°	–77.7°	864	801	$C_{39}H_{63}NO_{16}$	5.0