$C_{12}H_{14}N_6$[8], respectively, and displayed absorption maxima (Table) consistent with a tetrazacyclopentazulene chromophore. Unfortunately, due to the very small quantities available, they were not further investigated.

To correlate the structures of the new pigments isolated from *P. axinellae* with that of zoanthoxanthin, a sample of the latter was subjected to *N*-demethylation with boiling 40% hydrobromic acid. Fractionation of the butanolic extract of the reaction mixture on silica gel gave, as major product, 3-norzoanthoxanthin, identical with natural parazoanthoxanthin D, along with the dinor-derivative (VI) and fully *N*-demethylated zoanthoxanthin[9]. While the latter was found to correspond in all respects (TLC, UV and MS) to parazoanthoxanthin A, (VI) had chromatographic and spectral properties different from those of the isomeric parazoanthoxanthin B which, consequently, may be either 1- or 3- methylparazoanthoxanthin A.

The simple structural relationship existing among the pigments isolated from *P. axinellae* suggests that the various related fluorescent pigments occurring in zoanthids differ only in the number and position of methyl group linked to the diaminotetrazacyclopentazulene chromophore. The basic skeleton of this new group of marine nitrogen metabolites, for which we propose the generic name zoanthoxanthins, probably arises biogenetically from two C_5N_3 units derived from arginine.

Riassunto. Ulteriori studi degli estratti etanolici di *Parazoanthus axinellae* hanno condotto all'isolamento di altri quattro pigmenti fluorescenti, denominati parazoantoxantina A, B, C e D, che differiscono dalla zoantoxantina (I) unicamente per il numero di gruppi metilici legati al cromoforo diamminotetrazaciclopentazulenico.

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[9] Notably, the hydrolysis of zoanthoxanthin afforded also small amounts of the 2-desaminohydroxyderivative of (I), (II) and (III).

Two New Anthraquinones from the Seeds of *Cassia occidentalis* Linn

An anthraquinone glycoside from *Cassia occidentalis* seeds has been isolated[1]. We now report here the presence of 2 new anthraquinones in the seeds of this plant.

Materials and methods. The chloroform extract of the de-fatted seeds (7.5 kg) was fractionated with petroleum ether (b.p. 40–60°) and benzene. The benzene fraction (1.8 g) was chromatographed on silica gel column and eluted with petroleum ether, benzene, ethyl acetate and also with their mixtures. Petroleum ether eluate yielded physcion (510 mg) as has also been reported by KING[2]. Petroleum ether: benzene (1:1) eluate yielded a yellow compound (106 mg). The compound was designated as 'compound A'. The benzene: ethyl acetate (1:1) eluate was concentrated and separated by preparative thin layer chromatography using benzene: ethyl acetate (1:1) as developer. Two bands, yellow and dark red, were obtained. Yellow band yielded emodin (120 mg) as is also quoted by CHOPRA[3]. Dark red band was extracted with hot chloroform. It yielded a dark red compound (120 mg). The compound was designated as 'compound B'.

Results and discussion. Compound A, m.p. 307–09°, $C_{15}H_{10}O_4$, was soluble in benzene, chloroform, pyridine, ethanol and glacial acetic acid; sparingly soluble in petroleum ether, acetone, ethyl acetate and methanol. Colour reactions were characteristic for an anthraquinone compound. An orange colour with 0.5% methanolic magnesium acetate[4] was obtained. Insolubility of the compound in 5% aqueous sodium carbonate indicate[5] the absence of free hydroxyl group in β-position.

Acetylation gave a diacetyl derivative: from methanol yellow green needles, m.p. 145–47°. The compound gave no characteristic colour reaction with cerric ammonium nitrate indicating that both the hydroxyl groups are phenolic in nature. The compound did not contain any methoxyl group as determined by the semi-micro method of BELCHER[6]. On zinc dust distillation, compound A gave 2-methyl anthracene.

The UV-spectrum of the compound showed λ_{max} at 432 nm indicating the presence of two α-hydroxyl groups[7,8]. The two α-hydroxyl groups might be expected to be at positions 1,4, 1,5 or 1,8. However, the possibility of 1,4 hydroxyls have been excluded due to the absence of fluorescence in glacial acetic acid[9], likewise 1,4 as also 1,5 possibilities were excluded[10] due to the presence of 2 peaks at 1675 and 1620 cm^{-1} in the IR-spectra. Thus, the only possibility left is 1,8 position for the 2 hydroxyl groups. The specific colour reaction with 0.5% methanolic magnesium acetate is in conformity with this possibility.

On the basis of all these observations, compound A can be represented either as 1,8-dihydroxy-2-methyl-anthraquinone or as 1,8-dihydroxy-3-methyl-anthraquinone. The latter is known as chrysophanol. Therefore, compound A possesses the structure of 1, 8-dihydroxy-2-methyl-anthraquinone.

Compound B, m.p. 285–87°, $C_{16}H_{12}O_6$, was soluble in benzene, acetone, chloroform, carbon tetrachloride, pyridine, dioxan and glacial acetic acid; sparingly soluble in petroleum ether, ethyl acetate, methanol and ethanol. Colour reactions were characteristic for an anthraquinone compound. Purple colour with 0.5% methanolic magnesium acetate[4] was obtained. It was insoluble in 5% aqueous sodium carbonate, thereby showing[5] the absence

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of free β-hydroxyl group. Zirconium nitrate test[11] indicated that no hydroxyl groups are present at *ortho* position to each other.

Acetylation yielded a triacetyl derivative: from methanol organge red needles, m.p. 255–57°. All hydroxyl groups are phenolic in nature as shown by negative test with cerric ammonium nitrate. Compound B was found to contain 1 methoxyl group as determined by semi-micro method of BELCHER[6]. Thus, all the 6 oxygen atoms are accounted for, 3 as phenolic hydroxyl groups, 1 as methoxyl group and the remaining 2 as part of the anthraquinone nucleus. On zinc dust distillation, 2-methyl anthracene was obtained.

The compound could not be demethylated by 80% sulfuric acid, indicating the absence of methoxyl group at α-position. On demethylation by glacial acetic acid and hydrobromic acid, a demethylated compound was obtained which was recrystallized from hot methanol into brown crystals, decomposed above 300°. It was soluble in 5% aqueous sodium carbonate solution, showing the presence of methoxyl group at β-position in compound B. Zirconium nitrate test showed that no hydroxyl groups were present at *ortho* to each other in the demethylated product; therefore the methoxyl group cannot occupy a position at *ortho* to α-hydroxyl groups.

BLOOM et al.[12] have shown that if an anthraquinone contains 3 α-hydroxyl groups, there appears a single peak in the carbonyl streching frequency region in the IR-spectrum for the chelated carbonyl groups only, which lies between 1616 and 1592 cm^{-1}. The observed peak in the IR-spectrum of the compound is at 1610 cm^{-1}, thereby indicating the presence of 3 hydroxyl groups at 1,4,5-positions in the compound.

Thus for compound A the structures of 1,4,5-trihydroxy-7-methoxy-2-methyl-anthraquinone (I) or 1,4,5-trihydroxy-7-methoxy-3-methyl-anthraquinone (II) or 1,4,5-trihydroxy-7-methoxy-6-methyl-anthraquinone (III) are possible. Structure I corresponds to erythroglaucin[13], m.p. 205–06°. Demethylation of III should lead to 1,4,5,7-tetrahydroxy-6-methyl-anthraquinone[13]. The demethylated product of compound B was found to be different from the latter product. Hence the structure of 1,4,5-trihydroxy-7-methoxy-3-methyl-anthraquinone is assigned tentatively to compound B.

Résumé. Deux nouvelles anthraquinones, 1,8-dihydroxy-2-méthyl anthraquinone et 1,4,5-trihydroxy-3-méthyl-7-méthoxy anthraquinone ont été isolées des graines de *Cassia occidentalis*.

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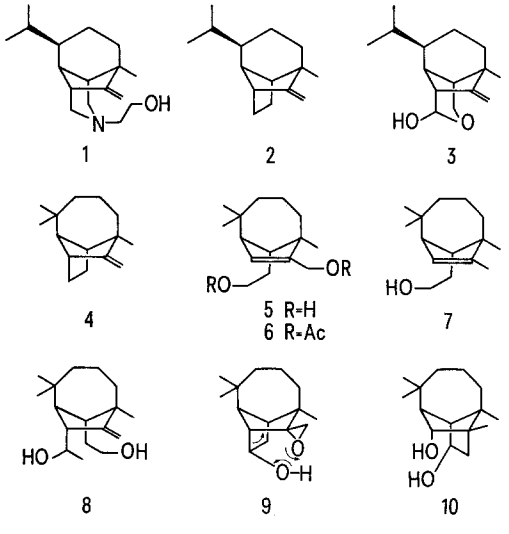
Ein bicyclischer Abkömmling von (−)- Longifolen aus *Helminthosporium sativum* und *H. victoriae*

Die Struktur von Victoxinin, **1**,[1] einem Phytotoxin aus *Helminthosporium sativum* und *H. victoriae*, macht es wahrscheinlich, dass die Verbindung biogenetisch durch oxidative Ringspaltung und nachträgliches Einschieben einer Aethanolamineinheit aus dem Kohlenwasserstoff (−)-Sativen, **2**,[2] entsteht. Sativen und Secoderivate vom Typ des Praehelminthosporols, **3**, sind bereits früher aus *H. sativum* isoliert worden[3], und wir haben inzwischen gefunden, dass die Kulturen beider Pilze eine reiche Palette neuer Verbindungen mit Sativan- bzw. Secosativangerüst enthalten[4]. Nachfolgend wird gezeigt, dass beide *Helminthosporium*-Arten auch Verbindungen mit intaktem bzw. modifiziertem Longifolangerüst zu produzieren vermögen.



Die Sesquiterpenkohlenwasserstoff-Fraktion, die aus dem Myzelextrakt der zwei Pilze gewonnen worden war, bestand zu über 95% aus (−)-Sativen, **2**. Eine weitere Komponente (ca. 3%) liess sich durch wiederholte Chromatographie an argentiertem Silicagel sauber abtrennen. Sie wurde aufgrund ihrer Drehung, $[\alpha]_D^{25} = -49°$ ($CHCl_3$), und durch spektroskopischen und chromatographischen Vergleich mit dem (+)-Isomeren als (−)-Longifolen, **4**, identifiziert.

Eine neue Verbindung mit modifiziertem Longifolangerüst, Smp. 117°, $[\alpha]_D^{25} = +3°$, konnte aus dem Kulturfiltrat der Pilze durch Extraktion mit Aether und anschliessende Chromatographie an Silicagel in Mengen von ca. 1 mg/l isoliert werden. Massenspektrum und Verbrennungsanalyse führten auf die Bruttoformel $C_{15}H_{26}O_2$ (ber: C 75,58, H 11,00%; gef: C 75,52, H 11,09%).

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