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THREE NEW CHLORINE CONTAINING BISANTHRONYLS
FROM A LICHEN, ANAPTYCHIA OBSCURATA VAIN

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In the previous communication1), we reported the isolation of six new coloring substances from a lichen, Anaptychia obscurata Vain and elucidated the structures of two of them designated tentatively AO-1 and AO-2 as I and II respectively. We wish to describe here the further investigation on the rest of the pigments named flavoobscurin A, B_1, and B_2 leading the structures III, IV and V, which possess hitherto undescribed chlorine containing 10,10'-bisanthronyl skeletons.

On silicic acid column chromatography, the $NaHCO_3$ soluble portion fractionated from the ether extract of the lichen afforded a yellow pigment mixture (ca. 0.1% from the air dried lichen), whose composition was revealed on TLC ($CHCl_3$: MeOH=2:1) as mostly flavoobscurins A, B_1, and B_2 (from top to bottom, and B_2 is major). These three pigments (yellow spots on TLC) were noticed fairly sensitive to light and their further separation was only effected by preparative TLC in the dark.

Flavoobscurin A (III) (most labile and its yellow spot on TLC gradually turns to greenish on exposure to light), $C_{30}H_{19}O_8Cl_3$*1, $[\alpha]_D$ +30° (c=0.1, acetone) was crystallized from AcOH as greenish yellow needles, mp.> 360° (darkening from 195°). It exhibited positive Beilstein test and negative $Mg(OAc)_2$ coloration2), the latter suggests that flavoobscurin A does not possess hydroxy-anthraquinone moiety in its structure. The following spectral properties: IR (KBr, cm^{-1}): 3470, 3400 (OH), 1626 (chelated and conjugated CO); λ_{max}^{EtOH} ($m\mu$, $\log\varepsilon$): 233 (infl., 4.59), 281 (4.27), 370 (4.33), are quite indicative of assuming flavoobscurin A to be a bisanthronyl derivative, especially on comparison with 1,3,8-trihydroxy-2-chloro-6-methyl-anthrone (=AO-1-anthrone)(VI)*2 (λ_{max}^{EtOH} : 226 (4.44), 273 (4.01), 360 (4.16)3)) whose constitution was clarified by Yamamoto et al. recently3). On CrO_3-AcOH oxidation at room temperature, flavoobscurin A furnished AO-1 (I) and AO-2 (II) in good

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*1 Satisfactory analytical values were obtained in all compounds given in chemical formulae.
*2 Generous gift by Prof. Y.Yamamoto, Kanazawa University, to whom the authors are very grateful.

Table I (in τ values, 100Mc.)

	flavoobscurin A (III)(in d_6-acetone)	flavoobscurin B_2 (V)(in d_6-DMSO*)	
C_4-H	2.81 (1H,s.)	——	
C_5,$C_{5'}$-H	4.62 (1H,br.s.), 4.70 (1H,br.s.)	4.58 (2H,br.s.)	
C_7,$C_{7'}$-H	3.49 (2H,br.s.)	3.40 (2H,br.s.)	
C_{10},$C_{10'}$-H	5.40 (1H,d., J=3 cps.)	5.07 (2H,s.)	
	5.66 (1H,d., J=3 cps.)		
others	OH**	OH**	CH_3
	-1.21 (1H,s.), -2.63 (1H,s.)	-1.05 (2H,br.s.)	8.04 (6H,s.)
	-1.42 (1H,s.), -2.85 (1H,s.)	-2.46 (2H,s.)	

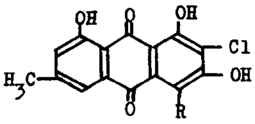
*The spectrum was taken immediately after the preparation of the solution without heating.
**Only the signals due to four hydroxyls among six were observed.

yields respectively[*3]. The evidence is nicely reminiscent of the investigations on sennidins A,B[4] (VII), and C[5] (VIII), among which the former gave rhein (IX) while the latter yielded rhein and aloe-emodin (X) on either CrO_3 or $FeCl_3$ oxidation, thus suggesting the structure III for flavoobscurin A most probable. Although the molecular ion of flavoobscurin A was not given upon electron impact, the observed peak intensities (m/e): $C_{15}H_{10}O_4{}^{37}Cl_2$ (328, highest mass; 5.8% to the base peak), $C_{15}H_{10}O_4{}^{37}Cl^{35}Cl$ (326; 30.3%), $C_{15}H_{10}O_4{}^{35}Cl_2$ (324; 48.3%), ascribable to AO-2-anthrone ion and $C_{15}H_{11}O_4{}^{37}Cl$ (292; 36.7%), $C_{15}H_{11}O_4{}^{35}Cl$ (290; base peak), due to AO-1-anthrone ion, support the above formulation of two anthronyl moieties of AO-1 and AO-2 linking at C_{10} and $C_{10'}$. For comparison, the mass spectrum of sennidin A (VII) prepared from the authentic sennoside A[*4] was measured and it was found that the highest and most abundant peak above m/e 100 is m/e 270 due to rhein-anthrone ion as expected.

Furthermore, the NMR inspection of flavoobscurin A (Table I) discloses that (i) in acetone solution it exists in such a conformation that the dihedral angle of C_{10}-H and $C_{10'}$-H satisfies the coupling constant (J=3 cps.) which is either ca. 60° or 120° based on the Karplus equation[7], and in addition (ii) the signals attributable to C_5-H and $C_{5'}$-H are appearing in considerably shielded region (τ 4.70, 4.62) on account of the anisotropy caused by aromatic ring of the other half, as could be depicted by (XI) as one of the several possible conformations. Accordingly, flavoobscurin A is now formulated as 1,3,8,1',3',8'-hexahydroxy-2,2',4'-trichloro-6,6'-dimethyl-bisanthronyl (10, 10') (III).

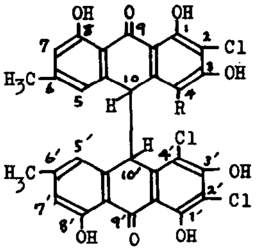
[*3] The yield of II varied rather unexplicably depending upon the reaction condition. For instance, in one experiment, the oxidation was performed in a suspension whereupon the almost equal amount of I and II formation was observed, although in another run the respective yields of I and II were 68 and 27% (based on the theoretical yields).

[*4] Kindly provided by Dr. M.Miyamoto[6] of Takeda Chem. Ind., to whom the authors deepest thanks are due.



I R=H : AO-1

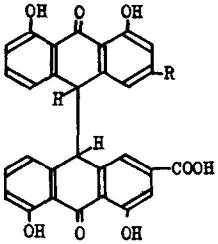
II R=Cl : AO-2



III R=H : flavoobscurin A

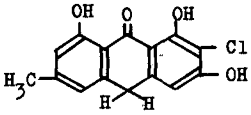
IV and V : R=Cl

flavoobscurins B_1 and B_2

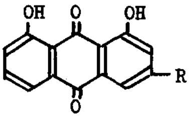


VII R=COOH : sennidins A and B

VIII R=CH_2OH : sennidin C

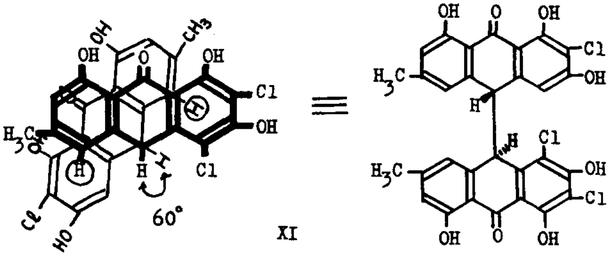


VI



IX R=COOH : rhein

X R=CH_2OH : aloe-emodin



XI

Flavoobscurins B_1 and B_2 are two isomers. Either B_1 or B_2 isolated in a pure form by preparative TLC*5, furnished an identical equilibrium mixture of B_1 and B_2 upon refluxing in acetone for some time. When the refluxing was started with B_1, one minute was enough to reach the equilibrium while five minutes refluxing was needed with B_2*6. Therefore, the chemical properties were surveyed on B_1, B_2, and the B_1+B_2 mixture.

Flavoobscurin B_1 (IV), mp.> 360° (darkening from 210°), $[\alpha]_D$+35° (c=0.1, acetone), IR (KBr): 3425 (OH), 1628 (chelated and conjugated CO), λ_{max}^{EtOH} : 233 (infl., 4.60), 286 (4.26), 377 (4.35), was fairly troublesome to isolate in a pure form because of easy transformation to the B_1+B_2 mixture as mentioned above. On CrO_3-AcOH oxidation, B_1 afforded AO-2 only. Due to the shortage of the pure material further examination was not performed.

Flavoobscurin B_2 (V), $C_{30}H_{18}O_8Cl_4$, mp.> 360° (darkening from 215°), $[\alpha]_D$+7° (c=0.1, acetone), λ_{max}^{EtOH} : 232 (infl., 4.61), 276 (4.27), 383 (4.32), IR (KBr): 3465, 3385 (OH), 1631 (chelated and conjugated CO), could be obtained in a pure state by recrystallization of the B_1+B_2 mixture with acetone due to its less solubility comparing to B_1. The NMR spectrum of B_2 (Table I) reveals the pretty resemblance of the proton signals with those of A (III), except that the signals attributable

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*5 Heating was avoided throughout the procedure and the purities of B_1 and B_2 thus obtained were confirmed by TLC.

*6 On checking the ether immersion (without heating) of the lichen, we found that both of B_1 and B_2 originally exist in the plant.

to C_5, $C_{5'}$-H and C_{10}, $C_{10'}$-H appearing as 2H singlets (τ 4.58, 5.07) respectively. This gives account of the identical two anthrone constituents in B_2.

The B_1+B_2 mixture (IV+V) (obtained as yellow needles by recrystallization with acetone-$CHCl_3$), $C_{30}H_{18}O_8Cl_4$, mp. > 360° (darkening from 245°), $[\alpha]_D$+19° (c=0.1, acetone), IR (KBr): 3435, 3400, 1632 λ_{max}^{EtOH} : 232 (infl., 4.57), 278 (4.23), 380 (4.31), showed positive Beilstein and negative $Mg(OAc)_2$ color tests. The mass spectrum of the mixture gave m/e 324 ($C_{15}H_{10}O_4{}^{35}Cl_2$) (most abundant peak above m/e 100) accompanied by m/e 326 ($C_{15}H_{10}O_4{}^{35}Cl^{37}Cl$) (69.4% to m/e 224 peak) and m/e 328 ($C_{15}H_{10}O_4{}^{37}Cl_2$) (12.7%) (highest mass), which are ascribable to AO-2-anthrone ion and whose peak intensities are in good accord with the natural isotope abundance of chlorine. The oxidation of the mixture with CrO_3-AcOH furnished AO-2 in high yield (72%) analogously as sennidin A (VII)[4].

All the evidence mentioned above lead us to formulate the plane structures of flavoobscurins B_1 and B_2 as 1,3,8,1',3',8'-hexahydroxy-2,4,2',4'-tetrachloro-6,6'-dimethyl-bisanthronyl (10,10') (IV and V, isomeric at C_{10} or $C_{10'}$[*7]). Flavoobscurins A, B_1, and B_2 presented in this paper are the first occasion as chloro-bisanthronyls appearing in nature, and also they are first appearance as bisanthronyls in the lichen family.

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[*7] Although the further study is needed to reach the conclusion, B_1 and B_2 would be assumed to be two rotational isomers (due to the restricted rotation at C_{10}-$C_{10'}$ bond) considering the isolation procedure (used alkali) and the isomerization experiments (described above) rather than in the isomeric relationship derived by anthrone-anthranol tautomerism which is pointed out by a referee.

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