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TWO NEW CHLORINE CONTAINING ANTHRAQUINONES
FROM A LICHEN, ANAPTYCHIA OBSCURATA (NYL.) VAIN

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During the course of the investigation on the lichen triterpenoids, we have been able to isolate from a lichen, Anaptychia obscurata (NYL.) VAIN (syn. A. heterochroa), two new chlorine containing anthraquinone derivatives, tentatively designated AO-1 (I) and AO-2 (II), in addition to emodin (III) (yield: 0.002%) and four other hitherto unidentified yellow pigments. In this communication, we wish to outline the structural study leading the structures I and II for AO-1 and AO-2 respectively.

AO-1 (I) (orange needles from MeOH, yield: 0.06%), $C_{15}H_9O_5Cl$, mp. 286-7°*, IR (KBr, cm^{-1}): 3333, 1663, 1611; λmax (EtOH, mμ) (log ε): 273 (4.35), 282 (4.35), 307 (4.18), 431 (4.05), 460 (3.96), 521 (3.42), showed the following positive color tests (c. H_2SO_4: red, $Mg(OAc)_2$: pink-red1), Beilstein test), indicative itself being a halogeno-anthraquinone derivative. The molecular ion peak in the mass spectrum of AO-1 appearing at m/e 304 ($C_{15}H_9O_5{}^{35}Cl$, base peak) accompanied with a satellite peak at m/e 306 ($C_{15}H_9O_5{}^{37}Cl$, 34.5% intensity) supports to formulate AO-1 possessing one chlorine atom in its molecule. On $Na_2S_2O_4$ reduction in aqueous NaOH at room temperature followed by the aerial oxidation, AO-1 afforded smoothly emodin (III) in high yield (83.5%). Further, the reduction of AO-1 with zinc and AcOH also yielded emodin. These facts along with the quite resemblance of UV and visible light absorption spectra between AO-1 and emodin2) enabled us to assume the former to be monochloroemodin where the chlorine atom probably be linked directly to the aromatic ring. The existence of three hydroxyl functions was verified by preparing a trimethylether (IV)**, $C_{18}H_{15}O_5Cl$, mp. 217-8°, IR (KBr): no hydroxyl, 1661, 1669 cm^{-1}, with $(CH_3)_2SO_4$-K_2CO_3-acetone.

The NMR spectra provided the most definite evidence to assign AO-1 by I. Thus, as shown in Table 1., the signal pattern (a pair of broad singlets) due to two ring protons of AO-1 appearing at τ 2.51, 2.95 (ascribable to C_5-H, C_7-H) resembles nicely to the corresponding signals (τ 2.46 for

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* The melting point was taken with the Yanagimoto micro-melting point apparatus (a hot-stage type) and recorded uncorrected.

** The trimethylether seems to be identical with fragilin-dimethylether (mp. 208-9°)3) although the direct comparison has not been performed.

Table 1 (in τ values)

	AO-1 (I)	IV	AO-2 (II)	parietin (V)	VI
solvent	dioxane*	$CDCl_3$	dioxane*	dioxane*	$CDCl_3$
C_2-$\underline{H}$	—	—	—	3.30 (d.)	3.28 (d.)
C_4-$\underline{H}$	2.80 (s.)	2.48 (s.)	—	2.75 (d.)	2.72 (d.)
C_5-$\underline{H}$	2.51 (br.s.)	2.39 (br.s.)	2.47 (br.s.)	2.46 (br.s.)	2.38 (br.s.)
C_7-$\underline{H}$	2.95 (br.s.)	2.92 (br.s.)	2.92 (br.s.)	2.95 (br.s.)	2.93 (br.s.)
others	$O\underline{H} \times 3$	$C\underline{H}_3$ (at C_6)	$O\underline{H} \times 3$	$O\underline{H} \times 2$	$C\underline{H}_3$ (at C_6)
	-0.76	7.52	-0.74	-1.95	7.56
	-1.84	$C\underline{H}_3O \times 3$	-1.64	-2.15	$C\underline{H}_3O \times 3$
	-2.71	6.02 (3H)	-3.43		6.06 (3H)
		5.97 (6H)			6.04 (6H)

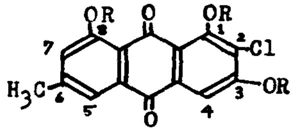
* The signals in the high field (above τ 4.0) could not be obtained.

C_5-H, 2.95 for C_7-H) of parietin (V), whereas a pair of doublets (τ 3.30 for C_2-H, 2.75 for C_4-H) of parietin disappears in AO-1 and a sharp singlet (one proton) at τ 2.80 arises instead. The similar spectral tendency is noticed in the trimethylether (IV) of AO-1 and emodin-trimethylether (VI). Here again, a sharp singlet at τ 2.48 (one proton) is observed in the former in place of a pair of doublets at τ 3.28 and 2.72 in the latter. These findings suggest to locate the chlorine atom of AO-1 at C_2 or C_4 rather than at C_5 or C_7. Finally, the position C_2 is preferred based on the empirical rule proposed by Ballantine and Pillinger.$^{4)**}$ The calculated τ value for C_4-proton in I or IV (having Cl at C_2) is 2.60. On the other hand, provided that the chlorine atom of AO-1 located at C_4 rather than C_2, the calculated τ value for C_2-proton results 3.25. Accordingly, the structure of AO-1 can now be formulated by 1,3,8-trihydroxy-2-chloro-6-methyl-anthraquinone (I).

Checking the literature, we noticed that recently Y.Yamamoto et al. have proposed$^{5)}$ the structure I for their compound B which they obtained from a Penicillium sp. (unidentified strain). Making a direct comparison (mixed mp., IR, TLC) we found that their compound B and AO-1 are identical.

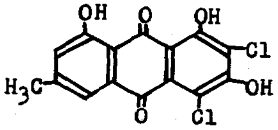
AO-2 (II) (orange needles from benzene, yield: 0.009%), $C_{15}H_8O_5Cl_2$, mp. 267-9°, IR (KBr, cm^{-1}): 3317, 1666, 1623, exhibited the similar positive color tests as for AO-1. The mass spectrum of AO-2 clearly indicates the existence of two chlorine atoms in its molecule by the following three peaks, i.e. m/e 338 ($C_{15}H_8O_5{}^{35}Cl_2$, base peak), 340 ($C_{15}H_8O_5{}^{35}Cl{}^{37}Cl$, 65.5%), and 342 ($C_{15}H_8O_5{}^{37}Cl_2$, 12.5%)

** Although the empirical rule was established using the data measured in $CDCl_3$, the data obtained in dioxane have also been found to be treated similarly as far as the compound handled here.

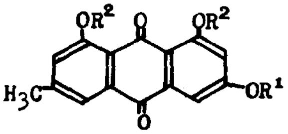


I R=H : AO-1

IV R=CH_3



II AO-2



III $R^1=R^2=H$ emodin

V $R^1=CH_3$, $R^2=H$ parietin

VI $R^1=R^2=CH_3$

(the theoretical relative peak intensity should approximately be 9:6:1). On the reduction of AO-2 with $Na_2S_2O_4$-NaOH at room temperature followed by the aerial oxidation, AO-1 (I) and emodin (III) were obtained, thus proving that AO-2 corresponds to a monochloro-derivative of AO-1. The NMR spectrum of AO-2 (Table 1), showing the existence of a characteristic pair of broad singlets assignable to two ring protons at C_5 and C_7, corroborates to locate the additional chlorine atom at C_4 of AO-1. Consequently, AO-2 can be expressed by 1,3,8-trihydroxy-2,4-dichloro-6-methyl-anthraquinone (II).

In 1965, T.Bruun et al. reported$^{3)}$ the structure of fragilin as 1,8-dihydroxy-2-chloro-3-methoxy-6-methyl-anthraquinone, which was isolated from two lichens, Sphaerophorus fragilis (L) ACH. and S. globulus VAIN. Therefore the two compounds described in this paper are the second instances of chlorine containing anthraquinone derivatives found in the lichen family. The other four colorling substances found in the lichen are currently under study in this laboratory.

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