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PAPULOSIN, A NOVEL CHLORINATED ANTHRAQUINONE FROM LASALLIA PAPULOSA (ACH.) LLANO†

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Thin-layer chromatography of extracts of several species of the lichen genus Lasallia has revealed the presence of quinoid pigments. Since there is some taxonomic significance in the presence or absence of these compounds, a species was selected (L. papulosa) and the major quinoid compounds were identified.

Air-dried lichen thallus (350 g) was coarsely ground under liquid nitrogen in a mortar. The resulting powder was extracted in a Soxhlet apparatus with benzene for 18 hr. On evaporation of the benzene a rust-coloured mixture of quinones (3.1 g) was found. The crude extract was sublimed at 130-140° (0.5 mm Hg) and the sublimate was recrystallized several times from acetone followed by recrystallization from acetic acid. Alternatively, the crude extract was recrystallized from acetone or tetrahydrofuran to yield orange-coloured plates that were subsequently purified by repeated crystallization from acetic acid. Preparative thin-layer chromatography on silica gel was suitable for only one of the two major pigmented components (I) because the second compound (II) formed a deep-purple pigment that could not be eluted from the gel.

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Compound I was obtained by preparative thin-layer chromatography of the mother liquors from the recrystallization of the crude extract. This material ran as a yellow spot (benzene-methanol-acetic acid, 85:10:5, R_f 68-72) and was determined by high resolution mass spectrometry to be $C_{15}H_9O_5Cl$ (calculated mass 304.0141,35 Cl). Comparison with a known sample of 1,3,8-trihydroxy-2-chloro-6-methyl-anthraquinone (1) (AO-1, Compound B) generously provided by Prof. Yosioka showed the two substances to be identical (mixed MP, IR, UV and mass spec.).

The second compound, designated papulosin (II), was obtained as brown needles from acetic acid or methanol and as reddish-brown plates from methyl-ethyl ketone (MP 268-269 subl.). Infrared spectra showed evidence of two chelated carbonyl groups (peaks at 1590 cm^{-1}, no peak above 1600 cm^{-1}) and at least one β hydroxyl group (peak at 3480 cm^{-1}) (2). High resolution mass spectra gave a molecular formula of $C_{15}H_9O_6Cl$ (calculated mass 320.0086). The UV spectrum (methanol) with maxima at 239, 264, 307, 351, 465, 491, 520 and 572 nm is consistent with a tetrahydroxy anthraquinone with at least two hydroxyls in the para position. Treatment of the compound with potassium carbonate and dimethyl sulfate in refluxing acetone for two days yielded a small amount of a tetramethyl ether (MP 173-74) proved by mass spectra.

The NMR spectrum of the tetra-trimethylsilyl ether (3) of papulosin shows unequivocally that the two aromatic protons are on carbons 5 and 7. Firstly, these protons have chemical shifts almost identical with those of the protons on C5 and C7 in the trimethylsilyl ethers of emodin (III) and parietin (IV) (Table I). Secondly, the spin coupling of the protons in papulosin tetra-trimethylsilyl indicates that two aromatic protons are on the same ring as a methyl group. These protons appear as very broad singlets (width at half height = 4 Hz) which are changed to sharp doublets (J = 1.5 Hz meta coupling) upon decoupling from the methyl group. Decoupling the aromatic protons from one another produced relatively sharp singlets (width at half height = 2 Hz). The decoupling verifies the assignments based on the chemical shifts thus firmly establishing the substitution pattern of the A ring.

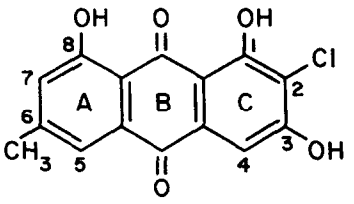
Since the IR and UV dictate that a hydroxyl is on either carbon 4 or

5, the position of the hydroxyl is established to be on carbon 4. Thus the structure of papulosin is indicated to be (II).

TABLE I

(τ values, CCl_4 solution)

	H_2	H_4	H_5	H_7	CH_3
Papulosin			2.52 br.s.	3.21 br.s.	7.60
Emodin	3.55d J = 2.5	2.81d J = 2.5	2.45 br.s.	3.20 br.s.	7.60
Parietin	3.53d J = 2.5	2.79d J = 2.5	2.49 br.s.	3.20 br.s.	7.61



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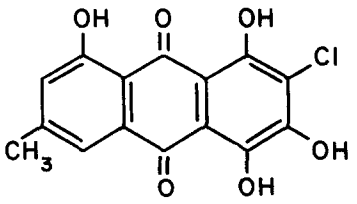
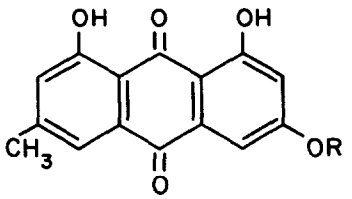


II



III R = H
IV R = CH_3

The occurrence of two chlorinated compounds in the same plant possibly represents a biogenetic sequence in which the parahydroxy quinone is formed after or at the same time that the chlorine is attached to the ring. The chemotaxonomic significance and the distribution of these compounds will be discussed at a later date.

We are indebted to Prof. I. Yosioka of Osaka University for a generous sample of his compound AO-1.

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