Altersolanol A, a Novel Tetrahydroanthraquinone

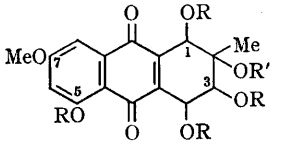
By A. STOESSL

(*Research Institute, Canada Department of Agriculture, London, Ontario*)

CULTURE filtrates of *Alternaria solani* yield substantial amounts of a pigment, altersolanol A (I), m.p. 218° dec., $[\alpha]_D^{23}$ −290° (*c* 0·25 in pyridine), and constitution $C_{16}H_{16}O_8$ (elemental analysis in conjunction with evidence below). The u.v. spectrum [λ_{max}(EtOH) 422, 285 (inf), 268, 240, 219 mμ (log ε 3·65, 3·84, 4·15, 3·96, 4·57)] is very similar to that reported[1] for the "quinone A monomethyl ether" from protoaphin fb. The i.r. spectrum has ν_{max}(KBr) 1671 (m, free quinone CO), 1635 (hydrogen-bonded quinone CO), 1603, and 1595 (hydrogen-bonded CO and C=C) cm.$^{-1}$. The n.m.r. spectrum (Table) reveals the presence of an aromatic methyl ether, two *meta*-coupled aromatic protons, a moderately deshielded *C*-methyl group not coupled to

hydrogen, and the similarly isolated systems ·CH(O–)·CH(O–)· and ·CH(O–)·. Other protons, subject to deuterium exchange and not shown in the Table, absorb at τ −2·17 (s, sharp, 1H), *ca* 4·33 (d, broad, 1H), and 4·9—5·8 (m, 3H, superimposed on the other signals) and are due to a chelated phenol and four alcoholic hydroxyls respectively. The assignments were confirmed as follows. Altersolanol A in pyridine–acetic anhydride forms a tetra-acetate [(II) m.p. 188—192° with prior charring] which retains an alcoholic hydroxyl [ν_{max} (CCl_4) 3,600 (w, sharp), 3,500 (s, broad) cm.$^{-1}$, τ 7·1 (broad, 1H, exchangeable)]. In contrast, a penta-acetate [(III) m.p. 169—173°, molecular weight found (osmometer): 534, required by $C_{26}H_{26}O_{13}$: 546·5], obtained from (I) or (II) with acetic anhydride–perchloric acid, lacks hydroxylic absorption. The two acetates have virtually identical u.v. spectra [λ_{max} (EtOH) 383, 266, 210 mμ (log ϵ 3·34, 4·31, 4·48)] while the n.m.r. signals due to acetoxyl (Table) are clearly grouped as phenolic (one each) and saturated (three and four respectively). Further, the n.m.r. spectra show downfield shifts, relative to (I), for only three protons and the *C*-methyl group has remained nonaromatic. The additional acetoxyl group of the penta-acetate must therefore be tertiary. The formation of the penta-acetate cannot involve a rearrangement because, on treatment with 0·05N-aqueous sodium hydroxide at room temperature, it yields (I) as a major product, together with aromatization products of (I).

On sublimation *in vacuo* at 120—150°, altersolanol A affords, as principal product, an orange compound $C_{16}H_{12}O_6$, m.p. 265—267°, which was defined as 3,4,5-trihydroxy-7-methoxy-2-methylanthraquinone (IV) by its u.v. [λ_{max} (EtOH) 425, 312, 280, 258, 229 mμ (log ϵ 4·03, 4·00, 4·43, 4·16, 4·36)] and n.m.r. spectra [very broad absorption (3H) at τ −2·5 to −0·8, consistent with the system ·C(OH):C(OH)·CO·C(OH)·; other signals in Table]. Methylation (Me_2SO_4–K_2CO_3) of (IV) gives (V) which has the m.p. and u.v. spectrum reported[2] for 3,4,5,7-tetramethoxy-2-methylanthraquinone.



(I) R=R'=H
(II) R=Ac; R'=H
(III) R=R'=Ac

TABLE

τ-Values of nonexchangeable protons[a]

	Area	Mult.	J_{AB}	(I)[b]	(II)[c]	(III)[c]	(IV)[b]
H^1	1	s	—	5·62	3·81	2·83	2·77
H^3	1	d	7·5	6·13	4·65	4·47	—
H^4	1	d	7·5	5·46	3·71	3·70	—
H^6	1	d	2·75	3·28	3·19	3·12	3·47
H^8	1	d	2·75	3·07	2·61	2·47	3·15
OMe	3	s	—	6·32	6·12	6·03	6·17
CMe	3	s	—	8·69	8·72	8·41	7·85
$MeCO_2Ar$ ..	3	s	—	—	7·65	7·62	—
$MeCO_2R$ ..	3	s	—	—	7·87	7·81	—
	3	s	—	—	7·91	7·87	—
	3	s	—	—	7·97	7·94	—
	3	s	—	—	—	8·02	—

[a] To tetramethylsilane as internal reference.
[b] In $(CD_3)_2SO$.
[c] In $CDCl_3$.

These facts require that altersolanol A be represented by (I). A discussion of its stereochemistry is reserved for the full Paper which will also report on several co-metabolites. One of these has the properties described[3] for macrosporin (3,5-dihydroxy-7-methoxy-2-methylanthraquinone); another, altersolanol B, is closely related to altersolanol A.

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[1] D. W. Cameron, R. I. T. Cromartie, D. G. I. Kingston, and Lord Todd, *J. Chem. Soc.*, 1964, 51.
[2] L. H. Briggs, F. E. Jacombs, and G. A. Nicholls, *J. Chem. Soc.*, 1953, 3069.
[3] R. Suemitsu, M. Nakajima, and M. Hiura, *Agric. and Biol. Chem.* (*Japan*), 1961, **25**, 100, and references cited.