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RHODOQUINONE-9 FROM ASCARIS LUMBRICOIDES VAR. SUIS

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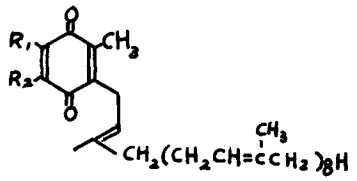
In the previous communication[1] the isolation of an aminoquinone, m.p. 66.5-67°, $C_{53}H_{81}NO_3$ (M^+ 779.618 m/e), λ_{max}^{EtOH} 285, 515 mμ (log ε 4.037, 3.086), ν_{max}^{KBr} 3470, 3330, 3050-2850, 1643, 1600 cm^{-1}, from the muscle of Ascaris lumbricoides var. suis (5 mg from 1600 g of the muscle) and the identity with the synthetic mixture of rhodoquinone-9 (I) and isorhodoquinone-9 (II) prepared from ubiquinone-9 (III) by ammonolysis[2,3] were reported. Now the quinone has been proved to be I and further correlated with 5-demethoxyubiquinone (IV) isolated from Pseudomonas ovalis.[4]



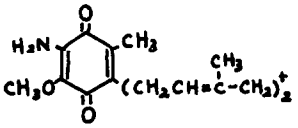
(I)	R_1 : NH_2	R_2 :	OCH_3
(II)	OCH_3		NH_2
(III)	OCH_3		OCH_3
(IV)	H		OCH_3

Preparative thin-layer chromatography on Silica-gel G plates using the multiple developing technique[5] was applied for the separation of the mixture of I and II employing chloroform as the solvent and two bands were obtained; the upper band gave a quinone, m.p. 50-52°,*1 while the lower, a quinone, m.p. 42-52°.*1 Although the both quinones showed almost superimposable UV, IR, and NMR spectra, some noticiable difference was found in the finger-print regions of IR spectra. The most remarkable difference was observed in the separation

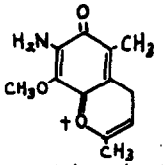
*1 The ratio of the two is ca. 1:6. Due to the scarcity of the samples further purification to obtain the specimens of higher m.p. was impossible. It has been suggested that the ubiquinone analogs prepared by nuclear prenylation are generally contaminated with cis-isomers in the nearest double bond to the ring and show lower m.ps.[6] Our starting material might be the case.

of ring methyl and ring methylene resonances by solvent shifts.[6] Since the two signals in the upper quinone are separated by 1.41(benzene) and 1.67 ppm (pyridine) as compared with the separation of 1.17(benzene) and 1.45 ppm(pyridine) for the lower quinone, they are respectively assigned as I and II. IR and t.l.c. comparisons of the natural quinone with I and II revealed that it must be I, the homolog of rhodoquinone-10 from Rhodospirum rubrum.[2] I or II was isolated from Euglena gracilis[3] but the distinction between the two remained uncertain.*2

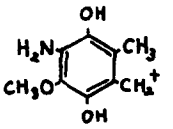
Mass spectrum of I shows the following fragments: m/e 764(M^+ - 15), 710 (M^+ - 69), 642(710 - 68), 574(642 - 68), 506(642 - 68), 438(506 - 68), 370(430 - 68), 302.178(a), 234(a - 68), 220.097(b), 182.080(c), and they are respectively assigned as follows:



(a) (calcd. 302.176)



(b) (calcd. 220.097)



(c) (calcd. 182.082)

5-Demethoxyubiquinone-9(IV) isolated from Pseudomonas ovalis[4] was differentiated from the 6-demethoxy isomer by the difference of UV spectra and chromenol formation of the model compounds. 1,4-Addition of ammonia to IV in methanol-ether[5] gave an aminoquinone, which was proved to be identical with I by t.l.c. and IR. Thus the relative positions have been further confirmed and I, III, and IV are directly correlated as in the case of the higher homologs.[2,5] Biological significance of the occurrence of I in the worm has been discussed.[1]

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*2 By the courtesy of Dr. Hemming, University of Liverpool, we have received the sample of the quinone and the copies of the spectral data. The direct comparison was impossible due to the small amount of the sample and decomposition in storage but the comparison of IR spectra suggested that the quinone was identical with I.