The conversion of ubiquinone to ubichromenol

MORTON[1] has recently elucidated the structure of a substance, first described in 1953[2] as a constituent of the unsaponifiable matter of the livers of rats deficient in vitamin A, and has given it the name ubichromenol, because it is a hydroxychromene isomeric with ubiquinone. Ubichromenol has been reported to accompany ubiquinone in the kidneys and liver of many species[3].

The purpose of this note is to draw attention to the fact that adsorption of ubiquinone on alumina, a procedure used in the isolation from natural products of ubichromenol together with ubiquinone, brings about the partial conversion of ubiquinone to a product which appears to be identical with ubichromenol.

When a solution of pure ubiquinone(50)* in 0.5 ml petroleum ether (b.p. 60°–80°) was poured on to a column of alumina (Brockmann quality, purchased from Brocades, Stheeman & Pharmacia), 0.9 cm dia, the colour changed within 1 min from yellow orange to brown. After 24 h the pigment (now yellow brown) was extracted with acetone–10 % aq. HCl (9:1, v/v) and the absorption spectrum measured in ethanol. This showed maxima at 225 mμ, 275 mμ (with a shoulder at 282 mμ) and 329 mμ (*cf.* maxima at 233 mμ, 275 mμ, 283 mμ and 332 mμ in cyclohexane reported by MORTON[1]). The spectrum was not changed by addition of KBH_4. The compound was, however, oxidizable with $HAuCl_4$, which caused an increase in the absorption at 275 mμ.

The rate of conversion of ubiquinone into ubichromenol was decreased by pretreatment of the alumina with HCl, or by the addition of water (*e.g.* 4 %) and increased by lowering the concentration of ubiquinone adsorbed on the alumina (by partial elution with petroleum ether containing 4 % ether).

These findings must raise doubts as to the existence of ubichromenol in tissues. Solanachromene[7], also a chromenol, may also be a cyclic isomer of a natural quinone (KOFLER's quinone[8]) formed from the latter during isolation. (If this is the case the structure of solanachromene should be revised so that it has 8 instead of 9 isoprenoid units in the long side chain.)

A possible mechanism of the conversion of these quinones to hydroxychromenes is given in reactions (a) and (b) of Fig. 1. Attention should be given to the possibility that DIMTER's "hepene"[9] (which may be identical with MORTON's unsaturated hydrocarbon[10]) was also derived by the degradation of ubiquinone during isolation (reaction (c)).

Ubichromenol, which is formed by isomerization of ubiquinone, should not be confused with the acid-reduction product of ubiquinone (λ_{max}, 292 mμ (ethanol)), which we have suggested[4] is a chroman. A suitable name for this compound, which probably has the structure 3,4-dihydroubichromenol[11], is ubichromanol.

* The preparation of ubiquinone used, like that previously described[4], was isolated from horse heart by a method essentially the same as that used by MORTON's group in their early work[5], except that pyrogallol was added during the extraction. A redetermination of the extinction coefficients of our first sample gave the following values: $E^{1\%}_{1\,cm}$ (ethanol) at 275 mμ, 165; after addition of KBH_4, $E^{1\%}_{1\,cm}$ (ethanol) at 290 mμ, 46.5. The m.p. of 48° previously reported[4] has been confirmed. The infrared spectrum, previously determined by Dr. P. J. VAN DER HAAK, showed none of the typical bands of the monoethoxy homologue at 10.10 μ and 11.18 μ, or of the diethoxy homologue at 8.51 μ, 10.20 μ and 11.05 μ. These measurements do not support the suggestion[6] that MORTON's isolation procedure yields ethoxy artifacts as the main product. The 8.30 μ, 8.67 μ and 10.55 μ bands ascribed to coenzyme Q_{10} by FOLKERS[6] were present in the spectrum of our product.

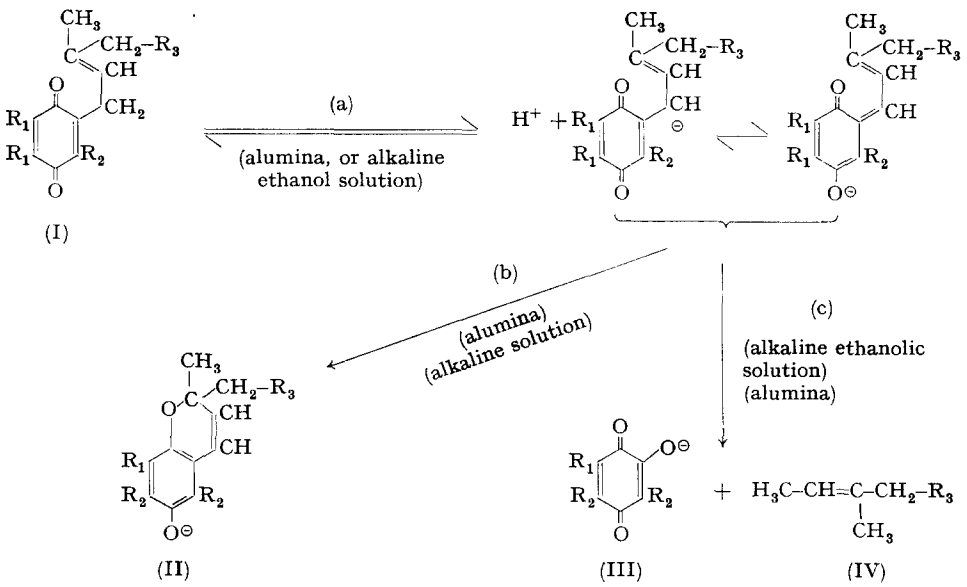

Fig. 1. Possible mechanism of conversion of substituted allylbenzoquinones into 6-hydroxychromenes and "hepene" homologues.

I	II	IV	R_1	R_2	R_3
Ubiquinone(50)	Ubichromenol	Hepene	$-OCH_3$	$-CH_3$	$-(CH_2-CH=C(CH_3)-CH_2)_9-H$
Kofler's quinone	Solanachromene	$C_{45}H_{74}$	$-CH_3$	$-H$	$-(CH_2-CH=C(CH_3)-CH_2)_8-H$

Experiments are in progress to test whether other substituted allylbenzoquinones, *e.g.* trimethylphytylbenzoquinone, vitamins K_1 and K_2 are also converted to 6-hydroxychromenes by adsorption on alumina.

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