THE CONVERSION OF UBIQUINONE TO UBICHROMENOL

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Received March 28, 1960

Links (1960) has recently described the preparation of a substance having ultraviolet absorption maxima similar to those of ubichromenol 50 (a cyclic isomer of ubiquinone 50, isolated from human kidney by Laidman, Morton, Paterson and Pennock, 1960) by the adsorption of ubiquinone 50 on alumina, followed by elution with an acetone-hydrochloric acid mixture. He has suggested that ubichromenol itself might be an artefact formed during the isolation of ubiquinone and, further, that solanochromene (Rowland, 1958) might be an artefact of plastoquinone (Shunk, Erickson, Wong and Folkers, 1959). The choice of eluting agent in Links' experiments was unfortunate in that substances having absorption maxima in the same region as ubichromenol are produced by the action of HCl on acetone; moreover, the mechanism proposed for the cyclisation reaction would appear to demand a stage of proton catalysis that could not have occurred during the isolation procedure described by Laidman et al., (1960). It therefore seemed advisable to repeat the reaction described by Links.

Ubiquinone 50 (10 mg.) was adsorbed from light petroleum onto alumina (Peter Spence, Type O, 3 g.). After 24 hours, during which the colour changes described by Links were observed, the column was eluted with solvent mixtures known to elute ubichromenol. No reducing substance could be eluted, even with the most polar solvents tried (ethanol, acetone, etc.). Subsequent elution with either acetone-hydrochloric acid (9:1) or a 10% solution of HCl gas in dry methanol removed some yellow pigments and a

strongly reducing fraction ($FeCl_3$-dipyridyl). Separation by means of 2-dimensional paper chromatography, as described elsewhere (Diplock, Green, Edwin and Bunyan, in the press), gave, in about 30% yield, a substance that, from its ultraviolet and infrared spectra and its chromatographic behaviour in comparison with an authentic sample, appeared to be identical with ubichromenol 50. It remains possible, though, that some slight modification of the side-chain could have occurred, which might not have been detected on the small amount of compound used.

In further experiments, ubiquinone could not be converted to ubichromenol by the action of ethanolic alkali for varying lengths of time (as suggested by Links), either with or without subsequent acid treatment, although the quinone was rapidly destroyed by the alkali treatment. If ubiquinone is treated with alkali in the presence of pyrogallol, it can, under certain circumstances, be recovered quantitatively; in any case, no ubichromenol is formed. Cunningham and Morton (1959) examined several kinds of animal tissue after preliminary saponification in the presence of pyrogallol and, whilst they found ubichromenol in some tissues, demonstrated that it was absent from others that contained ubiquinone. We have independently confirmed this to be so. A particular example is beef liver, which is a rich source of ubiquinone but contains no ubichromenol. Diplock *et al.* have described the analysis of tissues for ubiquinones and ubichromenols (several isoprenologues of the latter have now been isolated in this laboratory) by methods that do not involve the use of alumina columns.

The cyclisation of ubiquinone under the conditions described by Links is thus acid-catalysed during the second stage and, in fact, bears obvious resemblances to similar isomerisations undergone by hydroxy-quinones such as flavoglaucin and lapachol. It seems unlikely that either sclanochromene or "hepene" (Dimter, 1941, 1942) are artefacts of chromatography.

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