Photochemical Synthesis:† Stipitotanic Acid

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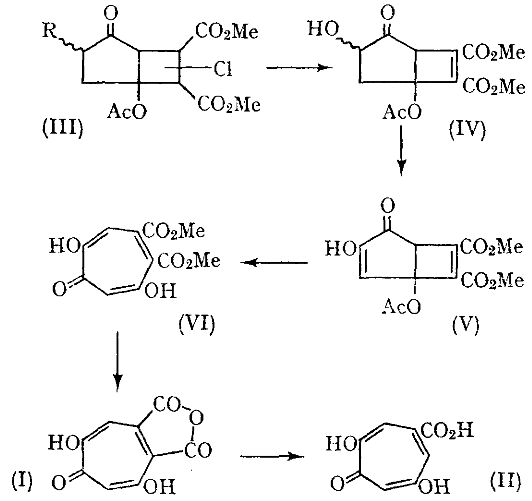
THE mould metabolite stipitatonic acid was first examined by Segal[1] and, later, by Doi and Kitahara[2] and by Segal,[3] the structure (I) being arrived at. We report here a simple synthesis of this compound. In view of its ready decarboxylation[1] to stipitatic acid (II) this synthesis affords an alternative route[4] to the latter also.

Irradiation of a solution of 3-acetoxycyclopenten-2-one and dimethyl chloromaleate in dioxan gave the adduct (III; R = H) in high yield. Bromination of (III) (pyridinium bromide perbromide) gave (III; R = Br) as a mixture of isomers converted by silver oxide in aqueous dioxan into (IV), also a mixture of epimers. Oxidation with bismuth oxide in acetic acid gave the dione (V) which was treated directly with 1N-hydrochloric acid in methanol to give the crystalline dimethyl stipitatonate (VI); saponification then gave (I) identical in all respects with the natural product.‡ The overall yield, based on ketone consumed was near 4%.



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† Previous Paper: P. de Mayo and J. J. Ryan, *Tetrahedron Letters*, 1967, 827.

‡ We thank Professor R. Bentley, University of Pittsburgh for a sample of stipitatonic acid. Both the synthetic and natural products exhibited the same striking change with time, in visible and ultraviolet spectrum, on dissolution in water.

[1] W. Segal, *Chem. and Ind.*, 1957, 1040.
[2] K. Doi and Y. Kitahara, *Bull. Chem. Soc. Japan*, 1958, **31**, 794.
[3] W. Segal, *Chem. and Ind.*, 1958, 1726; *J. Chem. Soc.*, 1959, 2847.
[4] J. R. Bartels-Keith, A. W. Johnson, and W. I. Taylor, *J. Chem. Soc.*, 1951, 2352.