Tetrahedron Letters No.11, pp. 1395-1396, 1968. Pergamon Press. Printed in Great Britain.

# MEVALONIC ACID A PRECURSOR OF THE SUBSTITUTED BENZENOID RING OF RUBIACEAE-ANTHRAQUINONES

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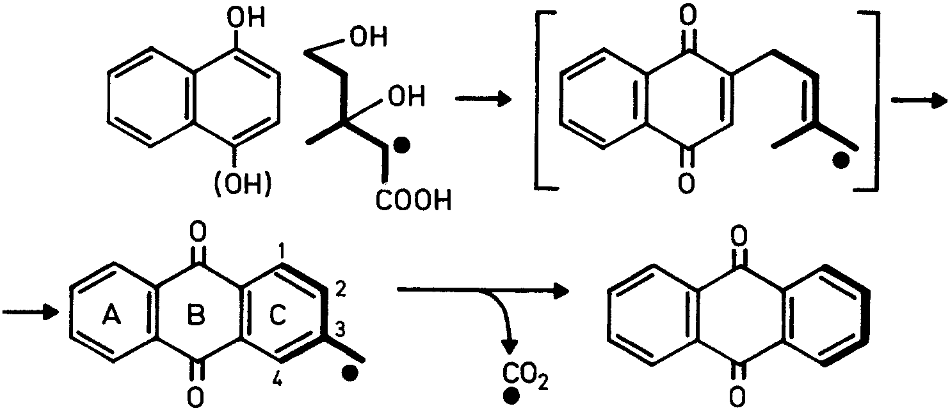
(Received in UK 14 November 1967)

Shikimic acid and 1,4-naphthoquinone have been established as precursors of 1,2-dihydroxyanthraquinone (alizarin) and purpurin-3-carboxylic acid[1]. However the origin of the carbon atoms 1,2,3 and 4 of the *Rubiaceae*-anthraquinones had not been established. Sandermann and co-workers[2] have proposed a biosynthetic sequence for the formation of methylanthraquinones in teak wood involving the condensation of dimethylallylpyrophosphate with α-naphthol, p-hydroxylation and oxidation of this product to prenylnaphthoquinone and ring closure of this intermediate to yield methylanthraquinones. Thus ring C of the methylanthraquinones should be partially formed from mevalonic acid. In order to determine the origin of carbon atoms 1,2,3 and 4 of ring C of *Rubiaceae* anthraquinones and to test the hypothesis of Sandermann and co-workers[2], DL-mevalonic acid 2-$^{14}$C was supplied to the root system of 1 1/2 year old *Rubia tinctorum* (madder) plants as already decribed[1]. The *trans*-methyl group of dimethylallylpyrophosphate, which arrives from the labelled carbon atom of mevalonic acid 2-$^{14}$C, could be incorporated either into carbon atom 4 of the substituted benzenoid ring or in to the attached carbon atom, e.g. the carboxyl group of purpurin-3-carboxylic acid. Therefore purpurin-3-carboxylic acid was chosen for degradation. This acid was obtained after hydrolysis of purified purpurin-3-carboxylic acid-glucoside of constant specific activity, and diluted with unlabelled carrier material.

Purpurin-3-carboxylic acid was quantitatively decarboxylated by heating with quinoline at 150-170°C. The specific activity of the $CO_2$ as well as of the resulting purpurin was determined. Mevalonic acid-2-$^{14}$C was incorporated into purpurin-3-carboxylic acid glucoside to 0,043 % and into galiosin (purpurin-3-carboxylic acid-primverosid) to o,o62 %. The isolated purpurin carboxylic acid had a specific activity of 2o8 dpm/µMole and after dilution with unlabelled purpurin-carboxylic acid the product had a specific activity of 11,8 dpm/µMole. Decarboxylation of this acid and isolation of the carboxyl group as $BaCO_3$ showed that the $CO_2$ was radioactive and had a specific activity of lo,1 dpm/µMole (= 85 %), while the specific activity of purpurin dropped to 1,7 dpm/µMole.

These results indicate that the hypothesis of Sandermann[2] is correct and show clearly that in the anthraquinones of *Rubiaceae* and mos probably *Verbenaceae* and *Bignoniaceae*, the substituted benzenoid ring (ring C) is isoprenoid in origin and that the carbon atom adjacent to the anthraquinone ring C is derived from the *trans*-methyl group of dimethylallylpyrophosphate, i.e. the $C_{(2)}$-atom of mevalonate, according to the following scheme:



(o Denotes majority of label from mevalonate $2-^{14}C$ ).

Our sincere thanks are due to Miss M.Knobloch for her enduring excellent assistance, to Prof.R.Hill, Cambridge for a generous gift of purpurin-3-carboxylic acid and its glucoside and to the "Deutsche Forschungsgemeinschaft" for financial support.

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