

## Biogenesis of Anthraquinones in Rubiaceae

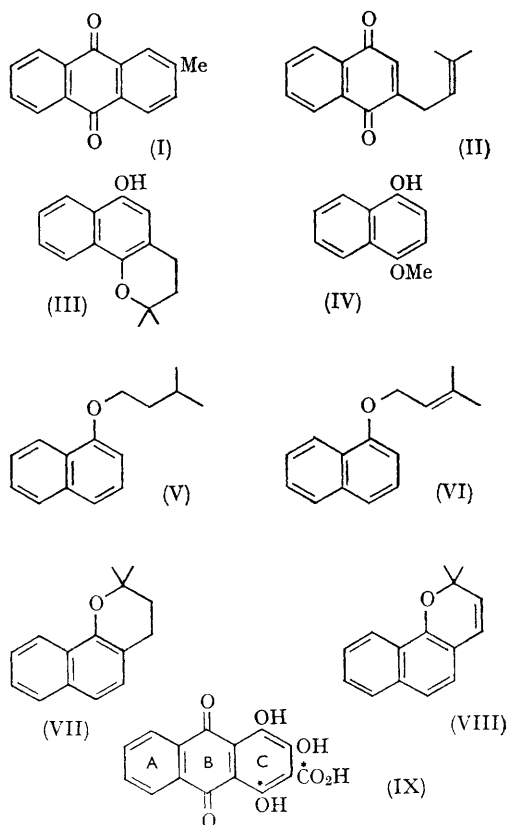
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THE coexistence of  $C_{15}$  anthraquinones, naphthaquinones, and naphthapyrans [e.g. (I) (II), and (III)] in teak (Verbenaceae)<sup>1</sup> and in certain Bignoniaceae,<sup>2</sup> and the *in vitro* conversion (II)  $\rightarrow$  (I),<sup>2</sup> provide strong circumstantial evidence that the anthraquinones in these woods are derived from naphthalenic precursors, most probably *via* (II), and that one benzenoid ring originates from mevalonic acid. These anthraquinones include the 1-hydroxy-2-methyl and 3-hydroxy-2-methyl derivatives which also occur in the Rubiaceae, as does (I),<sup>3</sup> suggesting that the numerous Rubiaceae quinones are biosynthesised in a similar manner.<sup>4</sup> We have obtained evidence for this in two ways.

(1) By extraction of the roots of seven species of *Galium* (Rubiaceae), we have isolated and identified† from four to thirteen anthraquinones in each species, together with at least one of the naphthalenic compounds (IV)—(VIII), while in the closely related genus *Rubia*, we obtained (III) from *R. tinctorum* (madder). Young madder plants yielded four, and mature plants, nineteen anthraquinones of the usual type. This demonstrates that *Galium* and *Rubia* can elaborate a naphthalene nucleus oxygenated at C-1, or C-1 and C-4, to which an isopentyl unit may be attached either on oxygen or on carbon. In the latter case, cyclisation onto oxygen will lead to pyran derivatives whereas cyclisation onto carbon provides a pathway to the anthraquinones.

† By comparison with authentic specimens in all cases.



(2) One year old plants of *R. tinctorum* were fed with sodium [ $2\text{-}^{14}\text{C}$ ]mevalonate. After 15 days, the four pigments were isolated from the roots and purified, without dilution, to constant activity (see Table). The pseudopurpurin (IX) was decarboxylated by heating, to give radioactive carbon dioxide ( $5.56 \times 10^3$  d.p.m./mmole) and purpurin ( $5.57 \times 10^3$  d.p.m./mmole), and the latter was degraded with alkaline hydrogen peroxide to inactive phthalic anhydride. The other three radioactive pigments also gave inactive phthalic anhydride on oxidation. These results establish that mevalonic acid is incorporated into ring c in these anthraquinones; carbon-2 provides the side-chain carbon atom in pseudopurpurin (and

rubiadin) and also the ring carbon at C-4. Leistner and Zenk<sup>5</sup> have shown that *R. tinctorum* utilises

Pigment	Specific activity (d.p.m./mmole)	Incorporation (%)
Alizarin	$5.56 \times 10^3$	0.02
Purpurin	$5.57 \times 10^3$	0.02
Pseudopurpurin	$1.13 \times 10^7$	0.05
Rubiadin	$1.13 \times 10^7$	0.06

shikimic acid to form ring A of alizarin and one of the carbonyl carbon atoms, and evidently the observed incorporation of labelled acetate into ring c (0.0069%)<sup>5</sup> proceeded *via* mevalonate.

(Received, September 6th, 1967; Com. 978.)

<sup>1</sup> W. Sandermann and M. H. Simatupang, *Holz als Roh- und Werkstoff*, 1966, **24**, 190.

<sup>2</sup> A. R. Burnett and R. H. Thomson, *J. Chem. Soc. (C)*, 1967, 2100, and in preparation.

<sup>3</sup> W. H. Hui and C. W. Yee, *Phytochemistry*, 1967, **6**, 441.

<sup>4</sup> R. H. Thomson in "Comparative Biochemistry", Vol. IIIA, Academic Press, New York, 1962, p. 712.

<sup>5</sup> E. Leistner and M. H. Zenk, *Tetrahedron Letters*, 1967, 475.