Tetrahedron Letters No.7, pp. 861-863, 1968. Pergamon Press. Printed in Great Britain.

INCORPORATION OF 1,4-NAPHTHOQUINONE INTO 1,2-DIHYDROXYANTHRAQUINONE (ALIZARIN) IN RUBIA TINCTORUM L.

E.Leistner and M.H.Zenk

Botanisches Institut der Universität München (Germany)

(Received in UK 3 October 1967)

It has been demonstrated in this laboratory[1], that shikimic acid is specifically incorporated into the Rubiaceae-anthraquinone aglyca alizarin and purpurin-3-carboxylic acid. Thus the existence of a biosynthetic pathway for the formation of anthraquinones entirely different from the polyacetate route is established. The mode of incorporation of shikimic acid into the anthraquinone nucleus, with the retainment of the carboxyl group of this acid is highly reminiscent of the formation of naphthoquinones in bacteria[2] and higher plants[3,4]. We therefore investigated the possibility of 1,4-naphthoquinone being a biosynthetic precursor of anthraquinones. The suggestion, that naphthalene derivatives may serve as precursors of anthraquinones has already been put forward for the formation of methylanthraquinones by Sandermann and co-workers[5] on comparative phytochemical grounds during their study of teakwood constituents.

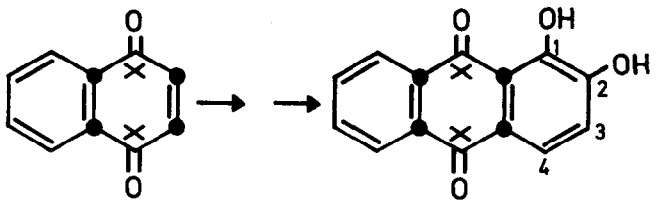
1,4-Naphthoquinone (1,4-^{14}C and 2,3,9,10-^{14}C) was synthetized[4] and supplied to the root system of 1 1/2 year old Rubia tinctorum (madder) plants as already described[1,4]. Alizarin was obtained after hydrolysis of purified ruberythric acid[1] and the diacetate of alizarin, which was diluted with unlabelled carrier material, was subsequently prepared. The diacetate did not change its specific activity after recrystallization. This derivative was subjected to permanganate oxidation and the phthalic acid formed was decarboxylated[1].

Precursor	Incorporation into alizarin (%)	Spec. activity DAA (dpm/mMole)	Phthalic acid		CO_2	$2CO_2$
			(dpm/mMole)	% of DAA	(dpm/mMole	% of DAA
NQ (2,3,9,1o-^{14}C)	o,25	11 ooo	5 3oo	48,2	o	o
NQ (1,4-^{14}C)	o,63	44 7oo	44 8oo	1oo,2	21 1oo	94,3

NQ = 1,4-naphthoquinone; DAA = diacetylalizarin.

TABLE I: Incorporation of differently labelled 1,4-naphthoquinone into alizarin and degradation of this anthraquinone.

Table I shows, that 1,4-naphthoquinone is incorporated into alizarin. Degradation of the alizarin which was formed after supplying either naphthoquinone 1,4-^{14}C or 2,3,9,1o-^{14}C to the madder plant demonstrates the specific incorporation of this compound into the anthraquinone according to the following scheme:



● = NQ (2,3,9,1o-^{14}C); × = NQ (1,4-^{14}C)

The origin of the carbon atoms 1,2,3 and 4 of the alizarin molecule remains to be determined, however they seem to stem from the acetate metabolism as already shown[1].

Our thanks are due to Miss M. Knobloch for her excellent assistance and

to the "Deutsche Forschungsgemeinschaft" for financial support.

REFERENCES

1 E.Leistner and M.H.Zenk, Tetrahedron Letters No 5, 475 (1967); Z.Naturforschg. 22b, 865 (1967).

2 I.M.Campbell, C.J.Coscia, M.Kalsey and R.Bentley, Biochem.Biophys.Res. Commun. 28, 25 (1967); E. Leistner, J.H.Schmitt and M.H.Zenk, Biochem. Biophys.Res.Commun. in press.

3 M.H.Zenk and E.Leistner, Z.Naturforschg. 22b, 46o (1967).

4 E.Leistner and M.H.Zenk, Z.Naturforschg. in press.

5 W.Sandermann and H.H.Dietrichs, Holzforschung 13, 137 (1959).
W.Sandermann and M.H.Simatupang, Holz als Roh- und Werkstoff, 24, 19o