69. THE CONSTITUTION OF CARVIOLIN: A COLOURING MATTER OF *PENICILLIUM* *CARMINO-VIOACEUM* BIORGE

By H. G. HIND

University College, Nottingham, and the Lister Institute, London

(Received 15 February 1940)

It has recently been shown [Hind, 1940] that *P. carmino-violaceum* Biorge produces two pigments, which were named carviolin ($C_{16}H_{12}O_6$) and carviolacin ($C_{20}H_{16}O_7$). These compounds are polyhydroxyanthraquinones and each contains a methyl ether group.

From a study of the properties of carviolin, and from analogy with other mould anthraquinones [Raistrick, 1938] this compound appeared to be a methyl ether of a tetrahydroxy- β -methylantraquinone. Further examination of the chemical properties of the pigment has in fact, revealed that it is a methyl ether of ω -hydroxyemodin. This conclusion was arrived at from a consideration of the following properties of carviolin.

(1) It is well known that oxidation of α -hydroxyanthraquinones with Pb_3O_4 or MnO_2 in conc. H_2SO_4 , followed by reduction of the product in aqueous solution with SO_2 , introduces a hydroxyl group in the p -position to the α -hydroxyl group already in the molecule. Treatment of carviolin after this manner gave a compound having the absorption bands of a 1:4:5:8-tetrahydroxyanthraquinone. This result could only be expected from a compound having α -hydroxyl groups in both benzene nuclei. In view of the fact that all mould anthraquinones so far identified have been derivatives of 1:8-dihydroxyanthraquinone, it was thought probable that this might also apply to carviolin.

(2) Treatment with HBr in boiling glacial acetic acid solution gave a monobromo derivative of the demethylated pigment. The bromine atom was removed from the molecule by boiling for a short time with aqueous silver acetate, indicating the presence of a $-CH_2OH$ or a $-CH_2OMe$ grouping in the carviolin molecule. It is a necessary corollary of (1) that this grouping must be in the β -position.

(3) Since carviolin is soluble in cold carbonate solution it has probably a free β -hydroxyl group. Dyeing tests with demethylated carviolin showed that this was not a derivative of alizarin and the methoxyl was not therefore adjacent to one of the α -hydroxyl groups.

(4) The absorption curves for carviolin in alcoholic acid and alkali were similar to those of *Frangula*-emodin in the same solvents.

These properties indicated that the demethylated pigment might be identical with ω -hydroxyemodin.

Through the kindness of Prof. Raistrick it has been possible to make a direct comparison of ω -hydroxyemodin and carviolin. These compounds yield identical

fully methylated methyl ethers. Allowing for the free β -hydroxyl group, carviolin must have one of the following three structures.

EXPERIMENTAL

Demethylation of carviolin

Demethylation of carviolin by heating with conc. H_2SO_4 was unsatisfactory; much resinification occurred at 150° . The demethylation was successfully carried out by refluxing with HBr and glacial acetic acid; this method was found to be satisfactory for demethylation of methoxyanthraquinones by Graves & Adams [1923].

Carviolin (100 mg.) was refluxed with HBr (constant-boiling, 15 ml.) and glacial acetic acid (10 ml.) for 5 hr. The cooled solution was filtered, water (50 ml.) was added and the yellow precipitate which separated was collected (yield 0.1 g. approx.).

This was recrystallized five times from 40% acetic acid and was obtained as golden brown rods (M.P. 248°). Found (dried at 140° *in vacuo*) C, 52.0; H, 2.9; MeO, 0.0%. $\text{C}_{15}\text{H}_9\text{O}_5\text{Br}$ requires C, 51.6; H, 2.6; MeO, 0.0%. A bromine estimation on a minute quantity of the compound indicated the presence of one Br atom.

20 mg. of the bromo-derivative were boiled in solution with 200 mg. of silver acetate in 50 ml. water and 10 ml. acetic acid. Some silver bromide was formed which was filtered from the hot solution. On cooling demethylated carviolin separated. It was recrystallized from 75% acetic acid from which it separated in golden yellow rods. The amount was too small to recrystallize to constant melting point. M.P. $278\text{--}280^\circ$. Found (dried at 110° *in vacuo*) C, 63.5, H, 3.7%. $\text{C}_{15}\text{H}_{10}\text{O}_6$ requires C, 63.0; H, 3.5%

Oxidation of carviolin

Carviolin (100 mg.) was dissolved in conc. H_2SO_4 (20 ml.) and Pb_3O_4 (250 mg.) was added a few mg. at a time over 20 min., with constant shaking. The blood-red colour gradually changed to blue. The solution was poured on to ice, and the deep bluish purple solution thus obtained was reduced with SO_2 . The colour changed to eosin pink and a reddish precipitate separated. This precipitate, when dissolved in alcohol and ether, showed strong absorption bands at wave-lengths

of 565, 548, 525 and 508 m μ . Bands at approximately the same wave-lengths were observed for 1:4:5:8-tetrahydroxyanthraquinone and cynodontin in the same solvents.

Comparison of carviolin and ω -hydroxyemodin

ω -Hydroxyemodin (kindly presented by Prof. Raistrick) was methylated in the usual way with dimethyl sulphate and alkali. The product had the same M.P. as carviolin trimethyl ether (186°) and no depression of M.P. was observed when the two compounds were mixed.

SUMMARY

Carviolin, a pigment of *P. carmino-violaceum* Biourge, has been shown to be a monomethyl ether of ω -hydroxyemodin. The compound has probably a free β -hydroxyl group.

I am indebted to Prof. J. M. Gulland and Prof. H. Raistrick for much helpful advice, and to Prof. Raistrick for samples of cynodontin and ω -hydroxyemodin.

REFERENCES

- Graves & Adams (1923). *J. Amer. chem. Soc.* **45**, 2439.
Hind (1940). *Biochem. J.* **34**, 67.
Raistrick (1938). *Ergebn. Enzymforsch.* **7**, 333.