**611.   *Chemistry of the* Coprosma *Genus.   Part VII.**   *A Revised Constitution for Lucidin.***

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By consideration of the infra-red spectrum and reconsideration of known properties the constitution of lucidin has been revised to 1 : 3-dihydroxy-2-hydroxymethylanthraquinone.

In Part IV (*J.*, 1949, 1241) structure (I) was suggested for lucidin. The compound afforded a triacetate and a tribenzoate, indicating three hydroxyl groups. An alleged " trimethyl ether," formed by the action of methyl sulphate and potassium carbonate, further showed that all the hydroxyl groups were phenolic. A positive *C*-methyl determination (Found : 4·7; theory, 10·0%) indicated the presence of one such group, placed in the β-position after the isolation of 2-methylanthracene on distillation of lucidin with zinc. Further evidence was given for the position of the three hydroxyl groups, one significant fact being that the ultra-violet absorption maxima of lucidin and rubiadin (II), in alcohol and in concentrated sulphuric acid solution, were at exactly the same wave-lengths and differed only slightly in the degree of absorption.
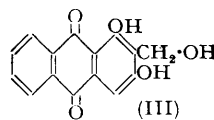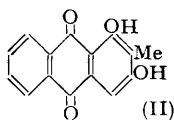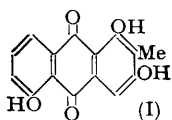
In Part VI (*loc. cit.*) consideration of the ultra-violet absorption spectra of a number of related anthraquinone compounds showed that the main carbonyl band was greatly affected by the presence of α-hydroxyl groups, β-hydroxyl groups having little effect. Compounds with one α-hydroxyl group had a carbonyl band at *ca.* 410 mμ, while those with two α-hydroxyl groups exhibited a band at *ca.* 430 mμ. In further agreement with this, rubiadin, with one α-hydroxyl group, has a maximum at 415 mμ.

Lucidin, however, exhibits maxima identical in wave-length with those of rubiadin and, on this basis, should possess only one α-hydroxyl group and not two as suggested.

In order to reconcile these facts, the *C*-methyl determinations were repeated, with negative results. Since a methyl group, therefore, does not occur in lucidin but appears after distillation with zinc, this leads to the formulation of lucidin as (III), which fits all the known facts.

The formations of the triacetate, tribenzoate, and the monomethyl ether (lucidin 3-methyl ether) obtained as a by-product on methylation, and the great similarity between the

absorption spectra of lucidin and rubiadin are now fully explained on this formula. The alleged " trimethyl ether," m. p. 173°, is, however, the *dimethyl ether* (*lucidin* 1 : 3-*dimethyl ether*), the alcoholic group remaining free (Found : C, 68·2; H, 5·05; OMe, 22·1, 22·5. New results : C, 68·4; H, 4·8. $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7; 2OMe, 20·8%).

The infra-red absorption spectra of lucidin and its ethers confirm the new formula. Lucidin, above the 1600-cm.$^{-1}$ region, exhibits maxima at 3448, 3367, 1667, and 1621 cm.$^{-1}$. The first two bands are assigned to the alcoholic and β-hydroxyl groups but it is not possible to distinguish between them. The band at 1667 cm.$^{-1}$ is assigned to the unassociated carbonyl group while the band at 1621 cm.$^{-1}$ is assigned to the carbonyl group co-ordinated with the α-hydroxyl group (cf. Flett, *J.*, 1948, 1441, and forthcoming communication). Lucidin 3-methyl ether in the same region exhibits maxima at 3521, 1658, and 1629 cm.$^{-1}$. The first band is assigned to the alcoholic group, the second to the unassociated carbonyl group and the third to the co-ordinated carbonyl group. Lucidin 1 : 3-dimethyl ether in the same region exhibits maxima only at 3279 and 1669 cm.$^{-1}$, assigned to the alcoholic group and an unassociated carbonyl group respectively.