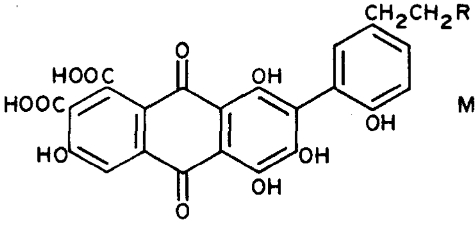
Tetrahedron Letters No.26, pp. 2437-2440, 1967. Pergamon Press Ltd. Printed in Great Britain.

THE CONSTITUTION OF LACCAIC ACID B*

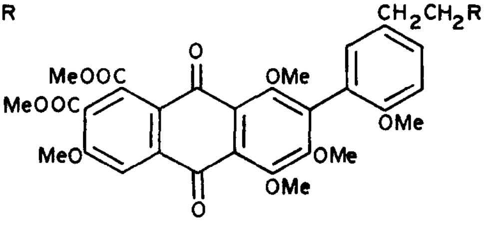
E.D. Pandhare, A.V. Rama Rao, I.N. Shaikh and
K. Venkataraman
National Chemical Laboratory, Poona, India.

(Received 17 April 1967)

By chromatography of a butanolic hydrochloric acid solution on polycaprolactam powder, the water-soluble pigments of stick lac have been separated into two major fractions, laccaic acid A and B. Structure I (R = $NHCOCH_3$) was assigned to laccaic acid A, and it was suggested that laccaic acid B is an intermolecular or intramolecular carbonate of the analogous alcohol (I; R = OH), because an ether-ester (methylated laccaic acid; MLA V), obtained by methylation of laccaic acid B or by chromatography of the ether-esters of crude laccaic acid,[1] was shown to be constituted as II (R = OCOOMe).[2]



I



II

---

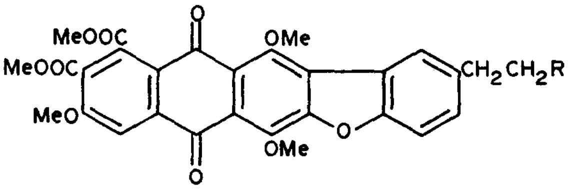
* NCL Communication No. 1073

Further work has shown that laccaic acid B, which has now been obtained as a pure homogeneous compound after separation from a minor fraction (laccaic acid C), is merely the alcohol (I; R = OH) and that the carbonate group in MLA V (II; R = OCOOMe) is formed by the action of dimethyl sulphate and potassium carbonate via dimethyl carbonate. β-Phenylethanol yielded β-phenylethyl methyl carbonate by (a) refluxing with dimethyl sulphate and potassium carbonate in acetone for 36 hours (yield 45%) or (b) heating with dimethyl carbonate at 100° for 48 hr (yield 90%).

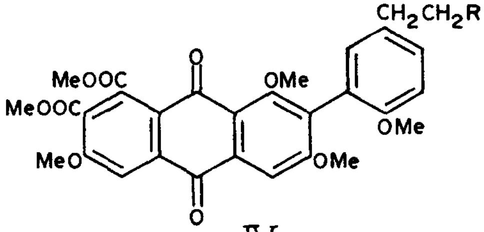
The absence of a carbonate group in laccaic acid B was confirmed by (a) the IR spectrum in nujol (ν_{max} 1712; 1695; 1618 cm^{-1}; cf. laccaic acid A: 1715; 1692; 1667; 1626 cm^{-1}); and (b) the negligible amount of CO_2 produced by shaking the acid with aqueous barium hydroxide and treating the precipitated barium salt with phosphoric acid. Similar observations on crude lac dye,[1] isolated from stick lac by procedures not involving butanolic hydrochloric acid and chromatography on polycaprolactam, excluded the possibility of a laccaic acid being present as a carbonate and undergoing hydrolysis to the alcohol (I; R = OH).

Seven ether-esters (MLA I-VII) of laccaic acid have so far been isolated. Based mainly on NMR data which will be discussed in greater detail elsewhere, structures (III; R = OCOOMe and $NHCOCH_3$ respectively) were assigned to MLA I and MLA III.[2] Alkaline hydrolysis of MLA I, followed by methylation with methyl iodide and silver oxide in dimethylformamide has now yielded III (R = OMe), m.p. 222° (*M* 562, mass spectrum), identical with the product of similar methylation of MLA II. MLA II (*M* 548; mass spectrum), m.p. 227°, thus has the structure III (R = OH), supported by the close similarity of the NMR spectra of MLA I and II, except that MLA II has one methoxyl group less and the triplet for the methylene group (CH_2R) occurs at 5.6τ in MLA I and at 6.13τ in MLA II in agreement with the change of R from OCOOMe to OH. MLA II (III; R = OH) has been converted to MLA I (III; R = OCOOMe) by treatment with methyl chloroformate and pyridine in chloroform.

MLA VI, m.p. 188-189°, has the molecular formula $C_{31}H_{30}O_{12}$ (elemental analysis and mass spectral $\underline{M}$). The NMR spectrum supports structure II (R = OH), confirmed by its conversion to MLA V (II; R = OCOOMe) by (a) treatment with methyl chloroformate and pyridine in chloroform and (b) refluxing with dimethyl sulphate and potassium carbonate in acetone.



III



IV

By preparative layer chromatography on silica gel and multiple development with benzene-acetone, the ether-ester MLA VII (II; R = $NHCOCH_3$), m.p. 115-116°, corresponding to laccaic acid A and not involving cyclisation to a furan, has now been isolated from the product of methylation (dimethyl sulphate-potassium carbonate) of both crude lac dye and pure laccaic acid A.

As stated earlier,[1,2] the laccaic acids undergo the purpurin → xanthopurpurin reduction; methylation of the mixed xantholaccaic acids by methyl iodide and silver oxide in dimethylformamide, followed by chromatography on silica gel, yielded three crystalline ether-esters (methylated xantholaccaic acids), MXLA I, II and III, m.p. 139°, 223-224°[d], and 169° respectively. On the basis of mass spectral and NMR data, structures IV (R = OMe and $NHCOCH_3$) were assigned to MXLA I and III respectively. MXLA II has now been found to be the alcohol (IV; R = OH), confirmed by methylation (silver oxide method) to MXLA I (IV; R = OMe). When the xantholaccaic acid obtained from pure laccaic acid B was methylated by dimethyl sulphate and potassium carbonate in acetone, a new methylated xantholaccaic acid (MXLA IV), m.p. 153°, was isolated; its NMR spectrum showed that it is the carbonate (IV; R = OCOOMe).

Finally, the conversion of laccaic acids A & B to common derivatives has been achieved. Treatment of MLA III in acetic acid-acetic anhydride with nitrous fumes yielded the *N*-nitroso derivative, which on heating with absolute methanol[3] was converted to III (R = OMe), m.p. 222°, identical with the product of methylation of MLA II (III; R = OH) by methyl iodide and silver oxide. Similarly, *N*-nitrosation followed by treatment with absolute methanol converted MXLA III (IV; R = $NHCOCH_3$) to MXLA I (IV; R = OMe).

Experimental details and a full discussion of the chemical and spectral data will be shortly communicated to the Indian Journal of Chemistry.

We are grateful to Prof. K. Schofield for sending us a copy of the paper communicated by him to the Journal of the Chemical Society in which he and his collaborators have also arrived at the structures assigned by us to laccaic acid A and MLA III; and to the Indian Lac Cess Committee and the Director, Indian Lac Research Institute, Ranchi, for sponsoring this project.

References:

1. N.S. Bhide, B.S. Joshi, A.V. Patwardhan, R. Srinivasan and K. Venkataraman, *Bull.Nat.Inst.Sci., India*, No.28,114(1965).
2. E.D. Pandhare, A.V. Rama Rao, R. Srinivasan and K. Venkataraman, *Tetrahedron*, Suppl. 8, Part I, 229 (1966).
3. R. Huisgen and H. Reimlinger, *Ann*, *599*, 183 (1956).