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THE STRUCTURE OF THELEPHORIC ACID

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IN the course of our investigation of Indian lichens, a species of Lobaria obtained from Darjeeling yielded a dark purple and sparingly soluble compound agreeing closely with the description[1,2] of thelephoric acid in properties, colour reactions, its elemental composition and that of its derivatives. It did not melt below 360° and had the composition of $C_{20}H_{12}O_9$. The triacetate ($C_{26}H_{18}O_{12}$) crystallized from nitrobenzene as orange-red needles, m.p. 330° (decomp.). The leuco penta-acetate ($C_{30}H_{24}O_{14}$), obtained as colourless needles from nitrobenzene, did not melt below 360°. Through the kindness of Prof. S. Shibata, a sample of thelephoric acid[2] which had been isolated from the lichen Lobaria retigera and which had also been compared with thelephoric acid isolated from the fungus Thelephora palmata, was made available for comparison and there was full agreement

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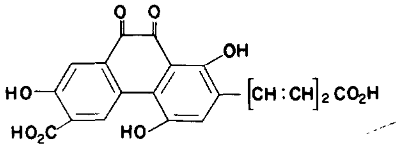
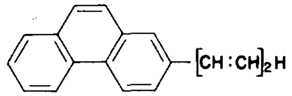
[1] F. Kögl, H. Erxleben and L. Jänecki, Ann. **482**, 110 (1930).
[2] Y. Asahina and S. Shibata, Ber. **72**, 1531 (1939).

between this sample and ours. Comparison was effected using infra-red and ultra-violet spectra and X-ray diffraction pattern also.



I



II

Kögl *et al.*[1] made a detailed investigation of the structure of thelephoric acid and formulated it as a derivative of phenanthrenequinone (I). By the zinc dust distillation of its triacetate they obtained a hydrocarbon $C_{18}H_{14}$ (m.p. 125°), for which they assigned the structure 1-2'-phenanthrylbuta-1:3-diene (II). Millward and Whiting[3] recently synthesized trans-1-2'-phenanthrylbuta-1:3-diene and found it to have a different melting point (107-109°). Since the original sample of Kogl was not available for comparison, the question of identity could not be settled. We have, therefore, carried out the zinc dust distillation of the triacetate of thelephoric acid. Our product was different from the one reported by Kögl *et al.*[1] It had m.p. 202-205° and its ultra-violet spectrum had a single maximum at 2795 Å ($E^{1\%}_{1cm}$ 1253 in $CHCl_3$); it was identified as terphenyl. A synthetic sample, prepared for comparison,[4]

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[3] B. B. Millward and M. C. Whiting, *J. Chem. Soc.* 903 (1958).

[4] H. France, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.* 1370 (1938).

exhibited a single maximum in the ultra-violet region[5] at 2790 Å ($E_{1cm}^{1\%}$ 1258 in $CHCl_3$), melted at 207-209° and the mixed m.p. with the zinc dust distillation product was 205-207°. As terphenyl (m.p. 202-205°) had been obtained by the zinc dust distillation of polyporic acid,[6] muscarufin[7] and other terphenylquinones,[8] it seemed quite likely that thelephoric acid also is a derivative of terphenylquinone.

In order to test for the butadiene side chain which had been postulated to be present in thelephoric acid,[1] the <u>leuco</u> penta-acetate was subjected to condensation with maleic anhydride by refluxing the reactants for 3 hr in nitrobenzene medium (compare <u>leuco</u> acetate of muscarufin[7]). The Diels-Alder reaction did not take place.

Catalytic reduction of thelephoric acid followed by permethylation with excess of diazomethane yielded two products as reported by Kögl <u>et al.</u>, one sparingly soluble, m.p. 254-256° (earlier reported m.p. 246°) and another more soluble in alcohol. The first fraction was obtained after a number of crystallizations from chloroform and ether, and its analysis agreed with the requirements of a heptamethyl ether. Thus while thelephoric acid formed only a <u>leuco</u> penta-acetate, it yielded a heptamethyl ether after reduction and permethylation. Kögl <u>et al.</u>[1] explained

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[5] A. E. Gillam and D. H. Hey, <u>J. Chem. Soc.</u> 1171 (1939).

[6] F. Kögl, <u>Ann.</u> **447**, 78 (1926); J. Murray, <u>J. Chem. Soc.</u> 1345 (1952).

[7] F. Kögl and H. Erxleben, <u>Ann.</u> **479**, 11 (1930).

[8] M. Akagi, <u>J. Pharm. Soc. Japan</u> **62**, 129 (1942).

this by assuming the presence of two carboxyl groups in thelephoric acid. When we examined the infra-red spectrum of the heptamethyl ether we found no absorption which could be attributed to ester groupings. It had only one strong band in the double bond and carbonyl region at 6.12 μ and this could not be attributed to any ester group. This conclusion was further confirmed by the fact that the heptamethyl ether did not undergo any reduction with lithium aluminium hydride in dioxane solution.

The above findings necessitate a revision of the formula for thelephoric acid. Of the twenty carbon atoms in the molecule, eighteen are accounted for by the terphenyl system, and of the nine oxygen atoms, two can be placed in the benzoquinone system and three in the three hydroxyl groups. Then two carbon atoms and four oxygen atoms are left. Since there are no carboxyl groups, a possibility that suggests itself is the presence of two methylenedioxy groups in the molecule. The test performed according to the method of Feigl[9] showed them to be present in thelephoric acid and its derivatives. The heptamethyl ether gave positive evidence for the presence of methylenedioxy group when the test was carried out following the modified method of Schmid et al.[10]

Oxidation of thelephoric acid with alkaline hydrogen peroxide was next attempted employing Kögl's procedure.[1] We could obtain only a trace of acidic products which showed positive tests for the methylenedioxy groups

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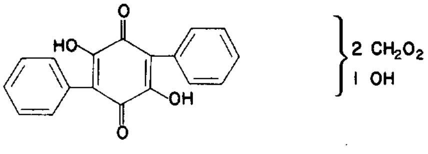
[9] F. Feigl, Spot Tests in Organic Analysis p. 190. Elsevier, Amsterdam (1956).

[10] J. Eisenbeiss and H. Schmid, Helv. Chim. Acta **42**, 61 (1959).

according to the method of Schmid *et al.*,[10] but we have not so far been able to isolate any crystalline substance in this reaction. Due to shortage of material, we could not pursue this observation further immediately and hope to do so shortly. The results so far obtained indicate that thelephoric acid is a derivative of polyporic acid having the partial structure (III).



III

The increase in methoxyl groups after reduction and permethylation may be due to the reason that one of the methylenedioxy groups might have undergone cleavage under the reducing conditions. Although such a reaction does not appear to have been reported before, the above mentioned observation suggests this possibility.

We convey our thanks to Mr. M. V. R. Rao of our department for the X-ray analysis, and to Professor S. Shibata of Tokyo for the sample of thelephoric acid.