

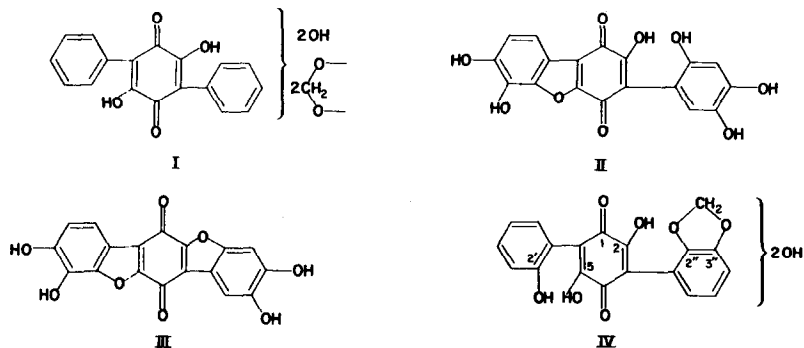
THE STRUCTURE OF THELEPHORIC ACID

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AFTER our first communication¹ on the structure of thelephoric acid (I) made last year, two papers have appeared on this subject, one proposing the formula (II) and/or a closely related isomer by Read and Vining², and the other advocating the formula (III) by Gripenberg³ based mainly on spectroscopic



evidences. We present below some more results of our experiments and our conclusions based on them which lead to a small revision of our original structure as in (IV).

(i) Heterogeneity of thelephoric acid samples:

Read and Vining² suggested that the thelephoric acid samples may be

¹ K. Aghoramurthy, K.G. Sarma and T.R. Seshadri, Tetrahedron Letters No. 8, 20 (1959).

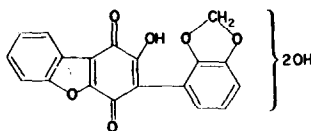
² G. Read and L.C. Vining, Canad. J. Chem. 37, 1442 (1959).

³ J. Gripenberg, Suomen Kemistilehti, 33B, 72 (1960).

heterogeneous though they advanced no direct evidence. We have examined the I.R. and X-ray spectra of the following samples of thelephoric acid:

(A) sample obtained by us from the lichen Lobaria isidiosa Wain.; (B) sample obtained by Asahina and Shibata from the lichen Lobaria retigera;⁴ (C) sample of Gripenberg isolated from the fungus Hydnum aurantiacum Batsch⁵ and (D) our sample after being heated at 200° in high vacuum for 7 hr.

The I.R. spectra of all natural samples (A, B & C) taken in potassium bromide agree in general though there are some minor differences, but the absorption peaks are not very well defined. In the case of (D), absorption peaks tend to become sharper and well defined and there are some definite differences as compared with others. Thus heating seems to produce a marked effect. This effect is also shown in the X-ray patterns. It could be reasonably concluded that the natural samples contain a predominantly major entity (formula IV) and a minor entity (formula V), and heating at 200° in vacuo produces more of the latter. This is also supported by analytical values given in Table 1.



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(ii) Leucothelephoric acid methyl ethers:

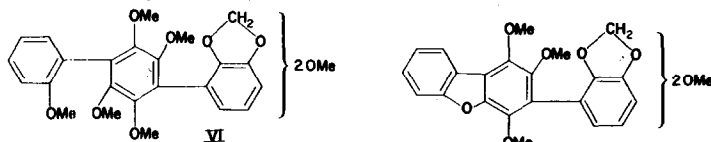
The formation of two methyl ethers (after catalytic hydrogenation followed by methylation with diazomethane) in Kögl et al.⁶ as well as in our experiments¹ could now be explained on the above basis. The major product m.p. 254-256° obtained is the heptamethyl ether of leucothelephoric

⁴ Y. Asahina and S. Shibata, Ber. 72, 1531 (1939).

⁵ J. Gripenberg, Acta Chem. Scand. 12, 1411 (1958).

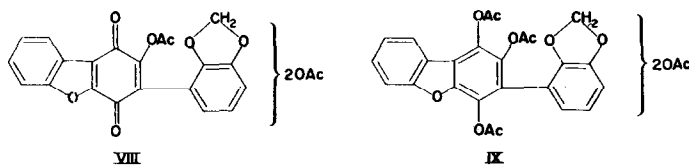
⁶ F. Kögl, H. Erxleben and L. Jänecke, Ann. 482, 105 (1930).

acid (VI) and the minor product may be its pentamethyl ether (VII) corresponding to the dehydrated form. The latter could not be studied by us because of paucity of material; it would appear that for the same reason K \ddot{O} gl *et al.*⁶ also did not examine it in detail. We have now carried out the reduction and methylation of telephoric acid in aqueous medium using alkaline sodium hydrosulphite and dimethyl sulphate and obtained only the heptamethyl ether (VI), m.p. 254-256 $^{\circ}$ and none of the second product (VII). It seems to be possible that the minor entity might have undergone ring opening under the alkaline reaction conditions generating the major compound thus leading to the formation of only one methyl ether. The ring fission could be visualized as taking place in the quinone stage in which the oxygen link will have ester characteristics.



(iii) Acetate and leucoacetate of telephoric acid: VI VII

The formation of a heptamethyl ether indicates the existence of seven hydroxyl groups in the molecule of leucothelephoric acid. But telephoric acid forms only a triacetate (VIII) and a leucopentaacetate (IX) instead of a pentaacetate and a leucoheptaacetate. This shows that during acetylation and leucoacetate formation, dehydration also takes place involving 5- and 2'-hydroxyl groups, leading to the formation of a furan ring (cf. Read and Vining²).



As already mentioned, similar ring closure may also take place when telephoric acid (IV) is heated in high vacuum yielding the furan (V). This change also will be facilitated by boiling with acidic reagents like hydriodic acid (cf. Erdtman *et al.*⁷)

(iv) Methylenedioxy groups in telephoric acid:

Since the above ideas explain satisfactorily the formation of a leucoheptamethyl ether and a leucopentaacetate, our original suggestion¹ that telephoric acid contains two methylenedioxy groups (formula I) is no more necessary. It seems to contain only one methylenedioxy group and the analytical results (Table 1) also agree with the requirements of the new formulation.

We would like to mention that the test for methylenedioxy group^{8,9} is given by telephoric acid and its derivatives, and that it is markedly prominent in its hydrogen peroxide oxidation products. Apart from the colour reactions, I.R. spectra of telephoric acid and its derivatives contain bands attributable to the presence of such groups¹⁰ in the regions 1478 - 1465, 1369 - 1328, 1265 - 1263, and 1041 - 1014 cm^{-1} .

Our earlier attempts to demethylenate telephoric acid with hydriodic acid and acetic anhydride met with difficulties because of the readiness with which the leucocompound separated out. However by prolonged refluxing of telephoric acid with aqueous hydriodic acid we could finally succeed in

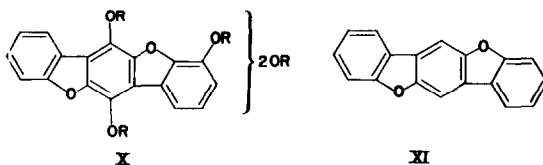
⁷ H. Erdtman and N.E. Stjernstrom, Acta Chem. Scand. 13, 653 (1959).

⁸ F. Feigl, Spot Tests in Organic Analysis p. 190. Elsevier, Amsterdam (1956).

⁹ J. Eisenbeiss and H. Schmid, Helv. Chim. Acta 42, 61 (1959).

¹⁰ L.H. Briggs, L.D. Colebrook, H.M. Fales and W.C. Wildman, Analyt. Chem. 29, 904 (1957).

demethylenating it and obtaining the nor-leucothelephoric acid. In this reaction, closure of one furan ring should necessarily have taken place for the reasons mentioned already. Hence the product should give, a heptaacetyl derivative (due to regeneration of 2 hydroxyl groups from the methylenedioxy group) and a heptamethyl ether. But actually it gave only a pentaacetyl derivative and a pentamethyl ether. This showed that demethylenation is also accompanied by a further dehydration resulting probably in a second furan ring closure giving a dioxidoterphenyl of the formula (X, R = H). The I.R. spectrum of the acetate of this compound is different from that of the leucoacetate of telephoric acid, and also it showed the disappearance of bands due to methylenedioxy group, particularly in the regions 1348 and 1014 cm^{-1} , which were found in the I.R. spectrum of the leucoacetate of telephoric acid. The U.V. spectrum of the acetate of this compound (X, R = Ac) [λ_{max} and $E_{1\text{cm}}^{1\%}$ 2640 (210), 3080 (shoulder) (517), 3200 (960) and 3350 (1065)] seems to resemble that of the dioxidoterphenyl (XI) reported by Gripenberg.³ The analytical values (Table 1) are also in agreement with this structure. This reaction, besides proving the presence of methylenedioxy group in the molecule, has also enabled us to locate its position as (2":3") in the molecule.



(v) Attempted fission of telephoric acid:

There has been considerable difficulty in carrying out potash fusion and oxidative degradations and these have not yielded any fruitful results so far. Alkaline hydrogen peroxide oxidation gave only a trace of acidic

TABLE 1
Analytical Values

S. No.	Name of the compound	Found Values			Formula	Calc. Values		
		C%	H%	OAc/OMe%		C%	H%	OAc/OMe%
1.	Telephoric acid*	60.5	3.0	-	IV, C ₁₉ H ₁₂ O ₉	59.4	3.2	-
	" after heating	61.5	3.3	-	V, C ₁₉ H ₁₀ O ₈	62.3	2.4	-
2.	Triacetate	60.5	3.8	29.4	VIII, C ₂₅ H ₁₆ O ₁₁	61.0	3.3	3 OAc, 26.2
3.	Leucoentaacetate	59.4	3.7	36.7	IX, C ₂₉ H ₂₂ O ₁₃	60.0	3.2	5 OAc, 37.2
4.	Methyl ether (obtained by catalytic reduct.) major component	64.8	5.8	38.8**	VI, C ₂₆ H ₂₈ O ₉	64.5	5.8	7 OMe, 44.8
5.	Methyl ether (obtained by hydrosulphite method)	65.0	5.8	42.8				
6.	nor-leucothelephoric acid methyl ether	67.2	4.8	33.0**	X, R = Me C ₂₃ H ₂₀ O ₇	67.6	4.9	5 OMe, 38.0
7.	nor-leucothelephoric acid acetate.	61.5	3.5	43.9	X, R = Ac C ₂₈ H ₂₀ O ₁₂	61.3	3.7	5 OAc, 39.2

* Found values lie in between those required for formulae IV and V.

** The methoxyl estimations of this and similar compounds sometimes give low values (cf. K^ogl et al. Ann. 465, 211 (1928)).

components which gave quite vivid colour in the tests for methylenedioxy group. Paper chromatography revealed the presence of at least two acids, but none of them corresponded with piperonylic acid or orthopiperonylic acid.¹¹ Oxidation of telephoric acid with lead tetraacetate to convert it into pulvinic acid derivative^o (cf. atromentin¹² and polyporic acid¹³) were unsuccessful probably because under the acidic conditions used, dehydration is enhanced resulting in the formation of the furan ring which stabilizes the molecule. Further work to locate the position of the other two hydroxyl groups will be undertaken when more material is available and fuller details will be published elsewhere.

We convey our thanks to Professor Jarl Gripenberg of Finland for a specimen of telephoric acid, and to Mr. M. V. R. Rao of our department for the X-ray spectra.

¹¹ W.H. Perkins, Jr. and V.M. Trikojees, J. Chem. Soc. 2929 (1926).

¹² O.P. Mittal and T.R. Seshadri, Curr. Sci. 26, 4 (1957).

¹³ R.L. Frank, G.R. Clark and J.N. Coker, J. Amer. Chem. Soc. 72, 1824 (1950).