# Constitution of Triphloretide, a Novel Macrocyclic Triester

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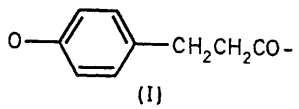
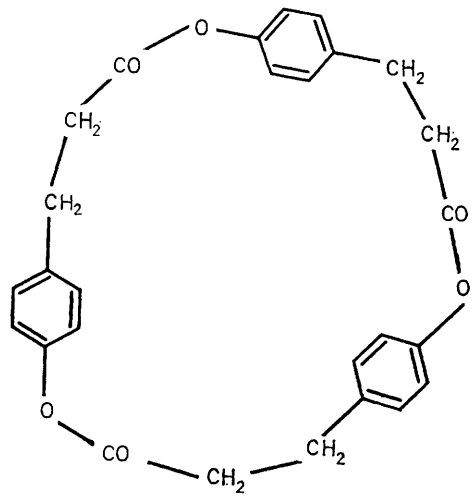
*Summary* Reaction of phloretic acid with $POCl_3$ yields the symmetrical macrocyclic ester (II).

TRIPHLORETIDE, prepared by reaction of phloretic acid with phosphorus oxychloride, was reported by Schiff[1] to be a trimeric anhydride of formula $C_{27}H_{26}O_7$.




(I)




(II)

We have re-examined the material prepared by Schiff's procedure and found the product analysed for $C_{27}H_{30}O_9$, m.p. 257° (from AcOH). The n.m.r. spectrum ($CF_3CO_2H$) showed a singlet at $\delta$ 3·12 and an aromatic AA'BB' pattern at $\delta$ 6·82—7·55, both of equal integral. A single band was present in the carbonyl region of the i.r. spectrum at 1759 $cm^{-1}$. This evidence is consistent with a symmetrical constitution based on a dehydrated phloretic acid unit (I).

The 70 eV mass spectrum of the material gave a molecular ion at *m/e* 444·1556, which corresponds to three of the basic units (I), *i.e.* $C_{27}H_{24}O_6$ required 444·1572. The authenticity of this ion as the molecular ion was substantiated by the significant increase in ion intensity at low eV. An intense ion at *m/e* 148, corresponding to (I), was also observed in the mass spectrum along with resultant characteristic ions at *m/e* 120, 107 (base peak), 94, and 91.†

The evidence presented above indicates that triphloretide is the trihydrate of the symmetrical triester (II). Although symmetrical cyclic esters of *o*-[2] and *m*-[3] hydroxy-benzoic acids are known, triphloretide appears to be of a new constitutional type.

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† A low intensity ion (<0·1% rel. int.) at *m/e* 592 was also observed in the mass spectrum. This may be attributed to the analogous tetrameric compound which by low eV work, is apparently present as a trace impurity.

[1] H. Schiff, *Annalen*, 1874, **172**, 356; *Gazetta*, 1874, **4**, 187.
[2] W. Baker, J. B. Harborne, A. J. Price, and A. Ruth, *J. Chem. Soc.*, 1954, 2042 and preceding papers.
[3] M. Nierenstein, *Ber.*, 1908, **41**, 3015.