The Constitution of Sordidone and its Relation to Thiophanic Acid

By M. ARSHAD, J. P. DEVLIN, and W. D. OLLIS*
(*Department of Chemistry, The University, Sheffield S3 7HF*)
and R. E. WHEELER
(*Department of Chemistry, The University, Bristol*)

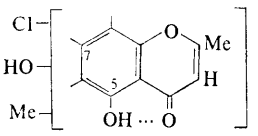
THIOPHANIC ACID (m.p. 242°; suggested formula $C_{12}H_6O_{12}$) was first isolated by Hesse[1] from *Lecanora sordida* (Pers.) Th.Fr., var. *Swartzii* (Ach.) and it has since been regarded[2] as a rather unusual lichen metabolite in that it did not obviously belong to one of the various structural types characteristic of lichen products.[2] Subsequently Nolan *et al.*[3] examined an Irish specimen of *Lecanora sordida* and they isolated another compound, m.p. 258—260°, formulated as $C_{24}H_{20}O_9Cl_2$, which they considered to be identical with Hesse's "thiophanic acid". In an attempt to resolve this situation we have examined a sample of *Lecanora sordida* collected in North Wales.† This yielded a compound which was obviously different from the yellow thiophanic acid described by Hesse,[1] but it is clearly identical with the cream-coloured substance described by Nolan *et al.*[3] We suggest that the latter compound should be named sordidone and we now report upon its constitution and synthesis.

Sordidone, m.p. 260—262°, was shown (mass spectrum) to have the molecular formula $C_{11}H_9O_4Cl$ and its n.m.r. spectrum (C_5D_5N solution) showed singlet signals which could be assigned to two C-Me groups (τ 7·79 and τ 7·58), one hydrogen (τ 3·87), and two hydroxyl groups (broad singlets, τ 0·05 and τ −3·60). This evidence was thus compatible with the partial structure, $C_9O_2(CH_3)_2(OH)_2(H)(Cl)$, which was supported by the formation of sordidone dimethyl ether, m.p. 145°. The nature of the undefined C_9O_2-residue was indicated by the i.r. spectrum of sordidone [ν_{max} (Nujol) 1660, 1624, and 1586 cm.$^{-1}$] and its u.v. spectrum [λ_{max} (ϵ_{max}) in EtOH: 263 mμ (16,000), 296 mμ (5750), and 332 mμ (3650)]. This suggested that sordidone was a chromone derivative (I), in which the chelated hydroxyl group (τ −3·60) was placed in position 5. On biogenetic grounds, the 7-position was favoured for the second hydroxyl group (τ 0·05) so on the basis of spectroscopic evidence two structures (II or III) could be considered for sordidone.

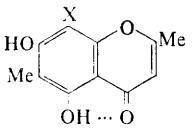
The decision between the structural possibilities (II or III) for sordidone was settled by synthesis. The constitutions of eugenitol (IV) and isoeugenitol (V) are firmly established[4] and both isomers are available by synthesis.[4,5] Chlorination of eugenitol (IV) with sulphuryl chloride in tetrahydrofuran gave sordidone (II), and isoeugenitol (V) similarly yielded isosordidone (III; m.p. 280—282°). Any possibility of a

† We thank Mr. N. Woodhead of the Department of Botany, University College of North Wales, Bangor, for his advice regarding the location of this lichen in Dyffryn Ardudwy, Merionethshire, and for his identification of the lichen.

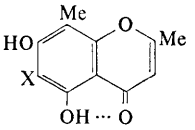
Wessely–Moser rearrangement[6] during these reactions was firmly excluded by the following transformations. Alkaline hydrolysis of sordidone dimethyl ether gave 3-chloro-2-hydroxy-4,6-dimethoxy-5-methylacetophenone, m.p. 94°, which was clearly different from the monochloro-derivative, m.p. 108°, (5-chloro-2-hydroxy-4,6-dimethoxy-3-methylacetophenone), obtained either by a similar alkaline hydrolysis of isosordidone dimethyl ether or by chlorination of 2-hydroxy-3-methyl-4,6-dimethoxyacetophenone.



(I)



(II) X=Cl
(IV) X=H



(III) X=Cl
(V) X=H

Recently Huneck[7] has examined *Lecanora rupicola* (L.) Zahlbr. (syn. *L. sordida* Th.Fr.) and isolated a compound clearly identical with Hesse's thiophanic acid; it was shown to be 2,4,5,7-tetrachloro-1,3,6-trihydroxy-8-methylxanthone. Thus sordidone (II) and thiophanic acid[1,7] belong to the increasing number of known halogen-containing fungal metabolites, but as far as we are aware sordidone is the first example of a naturally occurring chloro-substituted chromone.

(*Received, December 5th*, 1967; *Com.* 1296.)

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[7] S. Huneck, *Tetrahedron Letters*, 1966, 3547.