

In the case of compound I the crystal, on heating, melts directly to the (normal) nematic phase. In the other two cases, it melts to the smectic A phase, which then goes over to the nematic phase at a higher temperature. On cooling, the normal nematic phase transforms first to the smectic A phase, which on supercooling gives the re-entrant nematic phase, metastable with respect to the crystalline phase (see Table I). The re-entrant nematic phase was identified by the typical schlieren textures, mobility of the phase when the cover slip is displaced, and by its miscibility with other nematic compounds.

In compound I, the re-entrant phase occurs just before solidification (at  $\sim 32.5^\circ\text{C}$ ) on cooling the smectic A phase very rapidly. In fact in ref. 7, the phase was reported to be a smectic phase exhibiting a schlieren texture, but we have now confirmed by miscibility studies that it is indeed the re-entrant nematic phase. In compounds II and III, the re-entrant nematic phase is formed more readily and the crystallisation occurs well below the smectic A-re-entrant nematic transition point (see Table I), even when the sample is cooled relatively slowly. The transition points could be determined on a Mettler hot stage (Model FP 52), as well as from thermograms taken on a differential scanning calorimeter (Perkin-Elmer, Model DSC-II). It is interesting to note that

heat is liberated at both the nematic-smectic A and smectic A-re-entrant nematic phase transitions. Comparing the data on the compounds II and III (Table I) it is seen that both these transitions are somewhat stronger, involving larger heats of transition, for the higher homologue, viz., compound III. Further details about the phase transitions in these compounds and some mixtures will be discussed elsewhere.

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## CONSTITUTION OF LAXANTHONE-III SYNTHETIC STUDIES

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### ABSTRACT

Constitutions assigned to laxanthone-III (I) isolated from *Lawsonia inermis*, and the monoethyl ether (IV) of its deacetylation product (IX) have been confirmed by the characterisation of this ethyl ether by comparing with three isomeric 1-hydroxy-3,6,7-dimethoxymonoethoxyxanthenes (II, III and IV) now obtained synthetically.

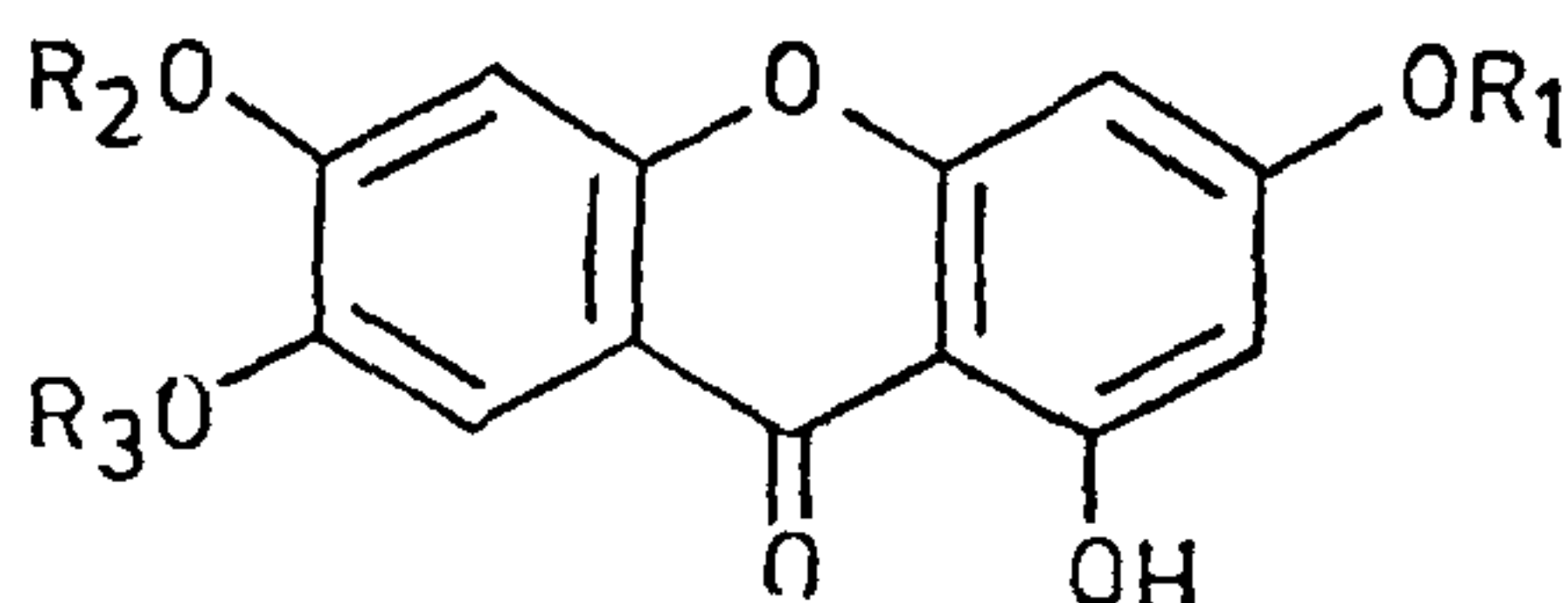
**L**AXANTHONE-III ( $\text{C}_{17}\text{H}_{14}\text{O}_7$ ), a new 1,3,6,7-tetraoxygenated xanthone isolated from *Lawsonia inermis*, its deacetylation product ( $\text{C}_{15}\text{H}_{12}\text{O}_6$ ) and the monoethyl ether ( $\text{C}_{17}\text{H}_{16}\text{O}_6$ ) of the latter were given their constitutions as 1-hydroxy-3,7-dimethoxy-6-acetoxyxanthone (I), 1,6-dihydroxy-3,7-dimethoxyxanthone (IX) and 1-hydroxy-3,7-dimethoxy-6-ethoxyxanthone (IV). However, these structural assignments had not been substantiated by direct synthetic evidences. This paper reports the characterisation of the ethyl ether as 1-hydroxy-3,7-dimethoxy-6-ethoxyxanthone (IV) by its comparison with various synthetic isomeric 1-hydroxy-3,6,7-dimethoxymonoethoxyxanthenes (II, III and IV), and thus confirms the proposed structures

for laxanthone-III and its derivatives. In this connection the three isomeric xanthenes: 1-hydroxy-3-ethoxy-6,7-dimethoxyxanthone (II), 1-hydroxy-3,6-dimethoxy-7-ethoxyxanthone (III) and 1-hydroxy-3,7-dimethoxy-6-ethoxyxanthone (IV) have been synthesised as described in this communication.

1-hydroxy-3-ethoxy-6,7-dimethoxyxanthone (II) was obtained by the monoethylation of 1,3-dihydroxy-6,7-dimethoxyxanthone<sup>2</sup> (V). 1-Hydroxy-3,6-dimethoxy-7-ethoxyxanthone (III) was prepared by the monomethylation of 1,3-dihydroxy-6-methoxy-7-ethoxyxanthone<sup>3</sup> (VI) as well as by the monoethylation of 1,7-dihydroxy-3,6-dimethoxyxanthone<sup>1</sup> (VII). On the other hand, 1-hydroxy-3,7-dimethoxy-6-ethoxyxan-

thone (IV) was made by the monomethylation of 1,3-dihydroxy-6-ethoxy-7-methoxyxanthone<sup>3</sup> (VIII) and also by the monoethylation of 1,6-dihydroxy-3,7-dimethoxyxanthone<sup>4</sup> (IX).

The identity of the monoethyl ether of the deacetylated laxanthone-III with 1-hydroxy-3,7-dimethoxy-6-ethoxyxanthone (IV) but not with other isomeric 1-hydroxy-3,6,7-dimethoxymonoethoxyxanthones (II and III) confirmed the placements of the free hydroxyl at C<sub>1</sub> and two methoxyl functions at C<sub>3</sub> and C<sub>7</sub> positions respectively thereby supporting the placement of the acetoxy function at C<sub>6</sub>. This confirmed the constitution of laxanthone-III as 1-hydroxy-3,7-dimethoxy-6-acetoxyxanthone (I).



- I. R<sub>1</sub> = R<sub>3</sub> = CH<sub>3</sub>; R<sub>2</sub> = COCH<sub>3</sub>
- II. R<sub>1</sub> = C<sub>2</sub>H<sub>5</sub>; R<sub>2</sub> = R<sub>3</sub> = CH<sub>3</sub>
- III. R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>; R<sub>3</sub> = C<sub>2</sub>H<sub>5</sub>
- IV. R<sub>1</sub> = R<sub>3</sub> = CH<sub>3</sub>; R<sub>2</sub> = C<sub>2</sub>H<sub>5</sub>
- V. R<sub>1</sub> = H; R<sub>2</sub> = R<sub>3</sub> = CH<sub>3</sub>
- VI. R<sub>1</sub> = H; R<sub>2</sub> = CH<sub>3</sub>; R<sub>3</sub> = C<sub>2</sub>H<sub>5</sub>
- VII. R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>; R<sub>3</sub> = H
- VIII. R<sub>1</sub> = H; R<sub>2</sub> = C<sub>2</sub>H<sub>5</sub>; R<sub>3</sub> = CH<sub>3</sub>
- IX. R<sub>1</sub> = R<sub>3</sub> = CH<sub>3</sub>; R<sub>2</sub> = H

#### EXPERIMENTAL

##### 1-Hydroxy-3-ethoxy-6,7-dimethoxyxanthone (II)

A solution of 1,3-dihydroxy-6,7-dimethoxyxanthone<sup>2</sup> (V) (0.4 g) in acetone (35 ml) was treated with diethyl sulphate (0.2 ml) and ignited potassium carbonate (2 g) and then heated under reflux for 6 h. The inorganic salts were filtered, washed with hot acetone and the solvent was removed from the combined filtrate. The reaction product thus obtained was treated with water, filtered, washed and dried. It crystallised from methanol as pale yellow needles (0.3 g), m.p. 179-80° (Found: C, 64.2; H, 5.5. C<sub>17</sub>H<sub>16</sub>O<sub>6</sub> requires C, 64.55; H, 5.10%). It gave green colouration with alcoholic ferric chloride.

##### 1-Hydroxy-3,6-diethoxy-7-ethoxyxanthone (III)

(a) A solution of 1,3-dihydroxy-6-methoxy-7-ethoxyxanthone<sup>3</sup> (VI) (0.5 g) in acetone (50 ml) was treated

with dimethyl sulphate (0.2 ml) and ignited potassium carbonate (2 g) and then heated under reflux for 6 h. The inorganic salts were filtered, washed with hot acetone and the solvent was removed from the combined filtrate. The methylation product (III) crystallised from methanol as pale yellow needles (0.4 g), m.p. 216° (Found: C, 64.3; H, 5.4. C<sub>17</sub>H<sub>16</sub>O<sub>6</sub> requires C, 64.55; H, 5.10%). It gave positive ferric reaction.

(b) A solution of 1,7-dihydroxy-3,6-dimethoxyxanthone<sup>1</sup> (VII) (0.2 g) in acetone (30 ml) was treated with diethyl sulphate (0.12 ml) and ignited potassium carbonate (1 g) and then heated under reflux for 5 h. The ethylation product was worked up as usual. It crystallised from methanol as pale yellow needles (0.1 g), m.p. 216°. This compound was found to be identical with the sample obtained earlier (m.p., m.m.p. and Co-TLC).

##### 1-Hydroxy-3,7-dimethoxy-6-ethoxyxanthone (IV)

(a) A solution of 1,3-dihydroxy-6-ethoxy-7-methoxyxanthone<sup>3</sup> (VIII) (0.4 g) in acetone (50 ml) was treated with dimethyl sulphate (0.15 ml) and ignited potassium carbonate (2 g) and then heated under reflux for 8 h. The methylation product was worked up as usual. It crystallised from methanol as pale yellow needles (0.3 g), m.p. 221-22° (Found: C, 64.5; H, 5.3. C<sub>17</sub>H<sub>16</sub>O<sub>6</sub> requires C, 64.55; H, 5.10%). It gave positive ferric reaction.

(b) A solution of 1,6-dihydroxy-3,7-dimethoxyxanthone<sup>4</sup> (IX) (0.15 g) in acetone (30 ml) was treated with diethyl sulphate (0.08 ml) and ignited potassium carbonate (1 g) and then heated under reflux for 6 h. The ethylation product was worked up as usual. It crystallised from methanol as pale yellow needles (0.1 g), m.p. 221-22°; identical with the sample obtained earlier (m.p., m.m.p. and Co-TLC).

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