

## STUDIES IN THE BIOCHEMISTRY OF MICROORGANISMS

Part XXVI. Structure of Shahenxanthone and Najamxanthone, Metabolic Products of *Aspergillus Stellatus Curzi*

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**Abstract.** The structure of Shahenxanthone,  $C_{25}H_{28}O_7$  and Najamxanthone,  $C_{26}H_{28}O_8$ ; metabolic products of *Aspergillus stellatus* have been established as 3,4-dihydro-2,7-dihydroxy-3-(1-hydroxy-2-isopropylallyl)-5-(hydroxymethyl)-2,8-dimethyl-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one (I) and 3,4-trihydro-2,5,7-trihydroxy-3-(1-hydroxy-2-isopropylallyl)-2,8-dimethyl-2*H*,6*H*-pyrano[3,2-*b*]xanthen-6-one 5-acetate\*(II) respectively, through physical methods.

In the previous three communications<sup>1,2,3</sup> the isolation of tajixanthone, shamixanthone and ajamxanthone have been described and their structures established. In the present communication the structures of shahenxanthone, and najamxanthone, which could only be isolated in very small yields, have been established.

*Shahenxanthone*

*Shahenxanthone.* M.p. 163-164°C;  $C_{25}H_{28}O_7$  (m/e 440<sup>+</sup>)  $[\alpha]_{20}^D -19.2$  (in  $CHCl_3$ ) gave light green colour with ferric chloride indicating the presence of a hydrogen-bonded phenolic hydroxyl group. It gave positive test for  $\gamma$ -pyrone with acetic acid and sulphuric acid. Its IR spectrum bands appeared at  $3470\text{ cm}^{-1}$  and  $3420\text{ cm}^{-1}$  for phenolic and free hydroxyl groups. The carbonyl group of the  $\gamma$ -pyrone system showed a strong band at  $1650\text{ cm}^{-1}$ . The stretching vibrations for benzene ring showed up at  $1610\text{ cm}^{-1}$  and  $1575\text{ cm}^{-1}$ . These were analogous to the bands recorded for tajixanthone.<sup>2</sup>

The visible and UV absorption spectra (Fig. 1a, 1b) showed up at  $\lambda_{max}$  389 nm ( $\epsilon$  6926), 292 nm ( $\epsilon$  99490), 271 nm ( $\epsilon$  36440), 263 nm (s) ( $\epsilon$  33770) and 238 nm ( $\epsilon$  28410) and were identical to those of tajixanthone, shamixanthone and ajamxanthone (Table I). With the addition of a drop of base the bands appeared at  $\lambda_{max}$  409, 272 and 238 nm. Addition of a drop of acid to the above solution restored the bands to show up at  $\lambda_{max}$  389, 292, 271, 263 (s) and 235 nm. Addition of a crystal of aluminium chloride resulted in bathochromic shift of the bands which showed up at  $\lambda_{max}$  420, 310, 283, 271(s), 262(s) and 235 nm.

\*This nomenclature is based on the fundamental ring system

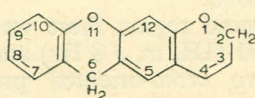
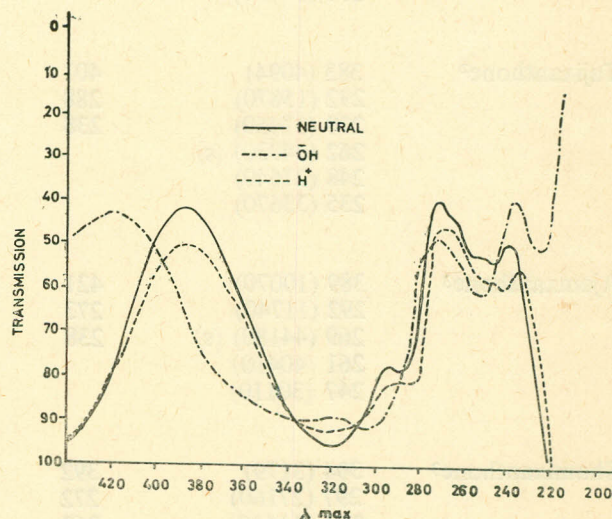
2*H*, 6*H*-Pyrano [3,2-*b*] xanthenone

Fig. 1(a). Visible and UV absorption spectrum of shahenxanthone in methanol.

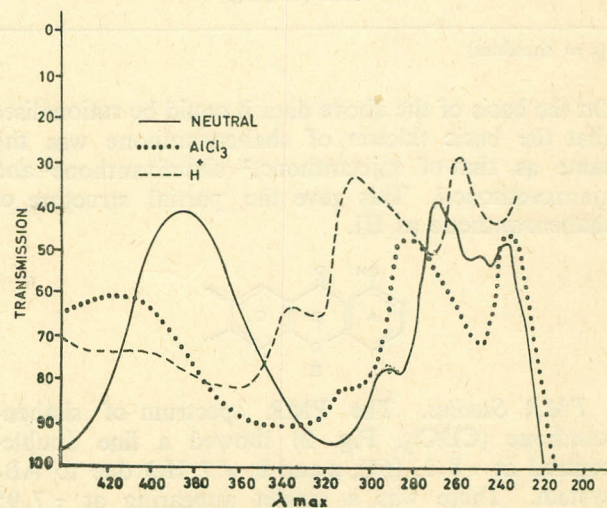


Fig. 1(b). Visible and UV absorption spectrum of shahenxanthone in methanol.

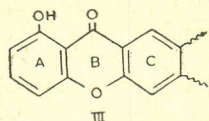


TABLE I. VISIBLE AND UV ABSORPTION SPECTRA OF SHAHENXANTHONE AND OTHER RELATED XANTHONES.

Compound	$\lambda_{\max}$ in MeOH nm ( $\epsilon$ ) (A)	$\lambda_{\max}$ on addition of NaOH to A nm (B)	$\lambda_{\max}$ on addition of HCl to B nm (C)	$\lambda_{\max}$ on addition of AlCl <sub>3</sub> to A nm (D)	$\lambda_{\max}$ on addition of HCl to D nm (E)
Shahenxanthone (I)	389 (6926) 292 (99490) 271 (36440) 263 (33770) (s) 238 (28410)	409 272 238	389 292 271 263 (s) 235	420 310 283 271 (s) 262 (s) 235	389 292 271 (s) 263 (s) 235
Najamxanthone (II)	388 (3979) 294 (14460) 272 (44690) 264 (40290) (s) 238 (39290)	400 274 238	388 294 271 262 (s) 238	410 315 384 270 238	399 287 272 264 (s) 238
Tajixanthone <sup>2</sup>	383 (4094) 292 (15870) 270 (37450) 262 (34930) (s) 248 (27640) 235 (33670)	401 288 238	383 292 270 262 (s) 248 235	388 314 272 261 (s) 235	383 292 270 262 248 235
Ajamxanthone <sup>3</sup>	389 (10070) 292 (11740) 269 (44180) (s) 261 (40410) 247 (30110)	421 273 238	319 294 271 262 (s) 249 238	410 311 284	394 284 273 (s) 261 (s) 247
Shamixanthone <sup>3</sup>	394 (3179) 297 (27160) 272 (11610) 262 (10390) (s) 238 (10160)	392 272 262 238	398 295 272 264 238	429 285 269 262 (s) 238	384 284 270 269 238

(s = shoulder)

On the basis of the above data it could be rationalised that the basic skeleton of shahenxanthone was the same as that of tajixanthone,<sup>2</sup> shamixanthone<sup>2</sup> and ajamxanthone.<sup>3</sup> This gave the partial structure of shahenxanthone as III.



**PMR Studies.** The PMR spectrum of shahenxanthone (CDCl<sub>3</sub>, Fig. 2) showed a fine double-centred at  $\tau$  8.1. (6H, a and b,  $J$  7 Hz) due to AB<sub>3</sub> system. There was a singlet appearing at  $\tau$  7.95 (3H, c) for a methyl group substituted on the benzene

ring. Another singlet appearing at  $\tau$  7.5 (3H, d) was due to the angular methyl group. Three multiplets centred at  $\tau$  7.12 (1H, f),  $\tau$  6.82 (1H, e) and  $\tau$  6.5 (1H, d) could be assigned to an angular methine proton and two hydroxyl protons respectively, there is another multiplet, centered at  $\tau$  5.65 (1Ha',  $J$  7.5 Hz) There were three doublets and a quartet centred at  $\tau$  6.2, (2H, e,  $J$  8 Hz),  $\tau$  5.2 (2H, h and g,  $J$  4 Hz),  $\tau$  4.52 (1H, k) and  $\tau$  4.45 (1H, l,  $J$  4 Hz) corresponding to methylene and one hydroxyl group. There were two sharp singlets centred at  $\tau$  4.92 (1H, j) and  $\tau$  4.78 (1H, i) for two geminal-methine protons adjacent to a double bond.

In the benzenoid region there were two doublets centred at  $\tau$  2.81 (1H, m,  $J$  8 Hz) and  $\tau$  1.92 (1H, n,  $J$  8 Hz) for two ortho-oriented protons. Another singlet appearing at  $\tau$  2.1, o) for one isolated ben-



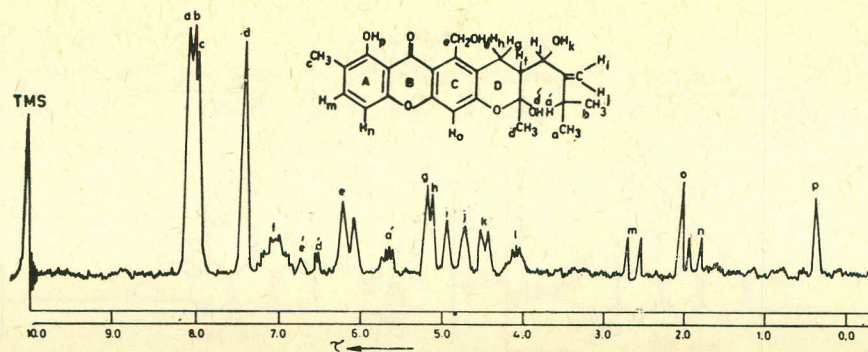


Fig. 2. PMR spectrum of shahenxanthone.

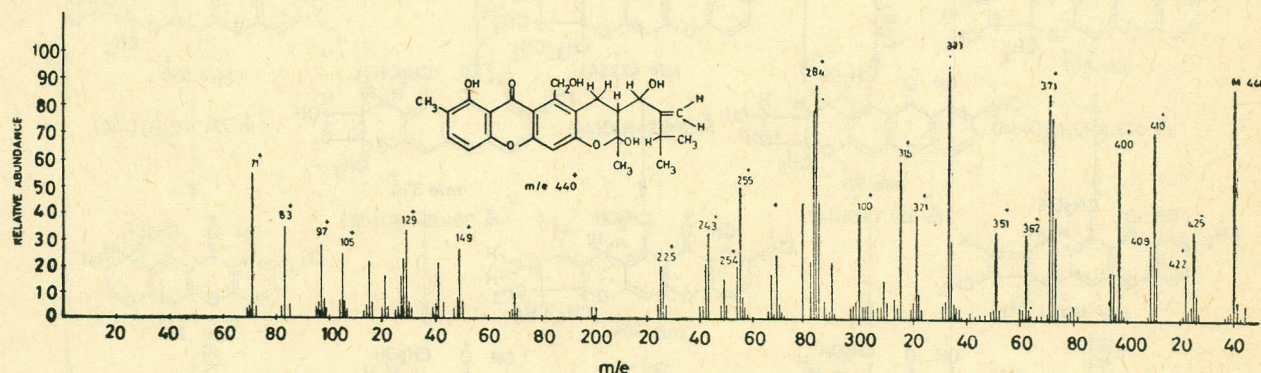
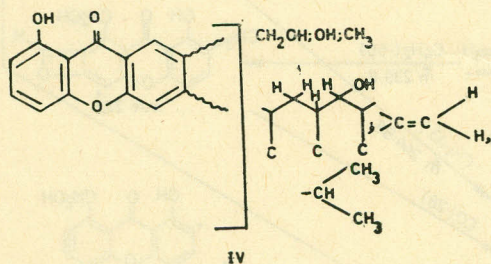


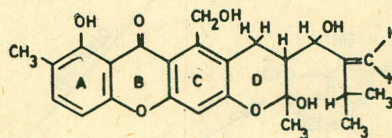
Fig. 3. Mass spectrum of shahenxanthone.

zenoid proton of ring C. Finally, the proton of the phenolic hydroxyl which appeared as a singlet at  $\tau$  0.36 (1H, p) accounted for the 28 protons in the molecule. With the nature of distribution of the protons now known the next step was to arrange the various groups present on the rings A and C shown in IV.



The molecular weight of shahenxanthone ( $C_{25}H_{28}O_7$ ;  $M^+$  440) being 18 mass units higher than tajixanthone ( $C_{28}H_{26}O_6$ ;  $M^+$  422), one could safely assume the presence of one oxygen and two hydrogen atoms over and above the molecule of tajixanthone. Ring D in tajixanthone may be assumed to be present in shahenxanthone as well. The absorption bands for the visible and UV regions were more or less identical to tajixanthone. The values (Table 2) for *gem*-dimethyls, *C*-methyl, angular *C*-methyl, methylene and methine protons were in agreement with those obtained from tajixanthone. The presence of a doublet for

*gem*-dimethyl groups and a quartet for a methine proton clearly indicated that the ring E present in tajixanthone was open in the case of shahenxanthone. Further, the methyl group substituted on benzene ring C of tajixanthone could be, in this case, considered to be oxidised to the primary alcoholic group. The presence of  $C > C = CH_2$  group in the side-chain of the ring D was confirmed by the ozonolysis of shahenxanthone followed by reduction and steam distillation which gave hydrazone of formaldehyde. All this evidence pointed to the structure for shahenxanthone as I.



I

*Mass Fragmentation Studies of Shahenxanthone.*—The above proposed structure was further supported by the detailed study of its mass spectral fragmentation pattern (Fig. 3) which showed intense molecular ionic peak at  $m/e$  440<sup>+</sup>. The presence of secondary alcoholic group C.C. HC(OH) and the tertiary-alcoholic group C.C(OH)CH<sub>3</sub> on ring D in the molecule could easily be established due to the losses of molecule of water (4) and formaldehyde (3) from the molecular ionic species (1). Most of the charged species formed were due to similar losses as were



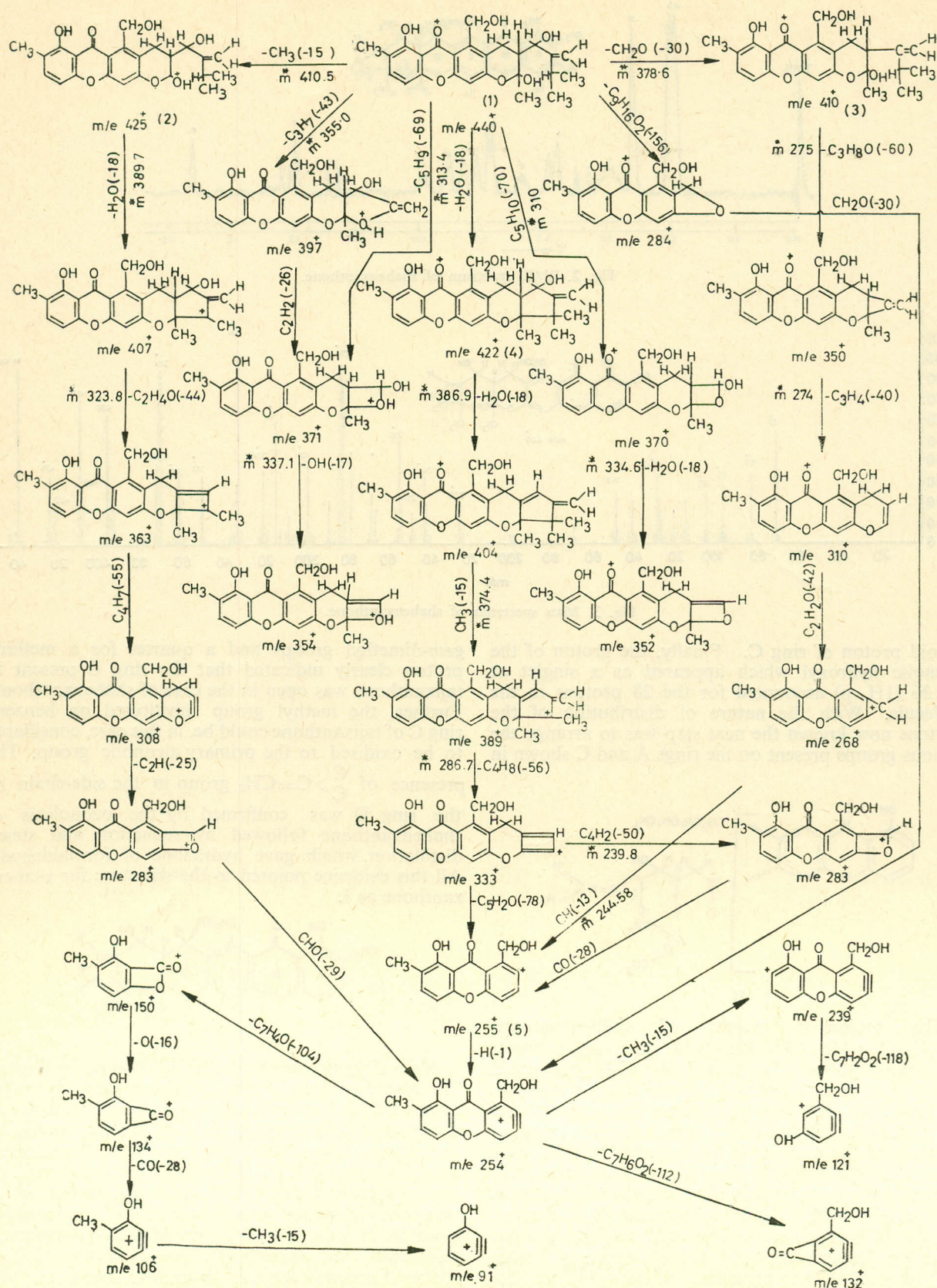


Chart 1. Mass fragmentation pattern of shahenxanthone.



observed for the previous three compounds: tajixanthone,<sup>2</sup> shamixanthone and ajamxanthone.<sup>3</sup> All these charged species were also followed by their appropriate metastable peaks. The most intense peaks appeared at  $m/e$  425<sup>+</sup>, 410<sup>+</sup>, 407<sup>+</sup>, 404<sup>+</sup>, 397<sup>+</sup>, 389<sup>+</sup>, 371<sup>+</sup>, 370<sup>+</sup>, 363<sup>+</sup>, 354<sup>+</sup>, 352<sup>+</sup>, 350<sup>+</sup>, 333<sup>+</sup>, 310<sup>+</sup>, 308<sup>+</sup>, 284<sup>+</sup>, 283<sup>+</sup>, 268<sup>+</sup>, 255<sup>+</sup>, 254<sup>+</sup>, 239<sup>+</sup>, 150<sup>+</sup>, 134<sup>+</sup>, 132<sup>+</sup>, 121<sup>+</sup>, 106<sup>+</sup> and 91<sup>+</sup>, corresponding to the ionic species as shown in Chart 1.

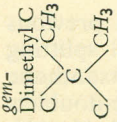
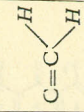
### Najamxanthone

Najamxanthone (II) m.p. 181–182°C;  $[\alpha]_D^{20} - 61.2$  (CHCl<sub>3</sub>) gave a molecular formula of C<sub>26</sub>H<sub>28</sub>O<sub>8</sub> (mol wt 468), which is 28 units higher than that of shahenxanthone. It gave a light green colour with ferric chloride indicating the presence of a hydrogen-bonded phenolic group. Like shahenxanthone it gave positive test for  $\gamma$ -pyrone with acetic acid and sulphuric acid. It also gave a positive iodoform test indicating the presence of a C-acetyl or possibly *O*-acetyl group. Its IR spectrum (in KBr) showed the presence of two hydroxyl group, one at 3494 cm<sup>-1</sup> (free OH) and the second at 3900 cm<sup>-1</sup> (hydrogen-bonded OH). The carbonyl group of  $\gamma$ -pyrone systems showed a strong band at 1648 cm<sup>-1</sup>. There was another small band at 1750 cm<sup>-1</sup> due to the carbonyl of an acetyl group. The stretching vibration bands for benzene appeared at 1608 and 1582 cm<sup>-1</sup>.

The visible and the UV spectra (Fig. 4) showed bands at  $\lambda_{max}$  388 nm ( $\epsilon$  3979), 294 nm ( $\epsilon$  14460) 272 nm ( $\epsilon$  44690), 264 nm (s) ( $\epsilon$  40290), 238 nm ( $\epsilon$  39290), i.e. the same as found for tajixanthone and the other xanthenes reported by us.<sup>2</sup> Addition of a drop of base resulted in bathochromic shift with bands appearing at  $\lambda_{max}$  400, 274 and 238 nm. With the addition of a drop of acid to the above solution the bands were regained to appear at  $\lambda_{max}$  388, 294, 271, 262(s) 248(s) and 238 nm. The red shift was observed with a crystal of aluminium chloride with bands showing up at  $\lambda_{max}$  410, 315, 384, 270 and 238 nm. On addition of a drop of acid to the above solution the original bands were restored to appear at  $\lambda_{max}$  399, 287, 272, 264 (s) and 238 nm. The above data pointed to the basic similarity of the structure of najamxanthone with that of shahenxanthone and the other xanthenes reported earlier (Table 1).

**PMR Studies of Najamxanthone.** Its PMR (in CDCl<sub>3</sub> Fig. 5) studies showed a fine doublet at  $\tau$  8.76, (6H, a and b,  $J$  7.5 Hz) due to two *gem*-dimethyl groups substituted at the end of a side-chain. There was a singlet appearing at  $\tau$  8.18 (3H, c) for a *C*-methyl group substituted on benzene ring A. The angular *C*-methyl group and the CH<sub>3</sub> of the acetyl group appeared as two sharp singlets at  $\tau$  7.75 (CH, d) and  $\tau$  7.51 (CH, e) respectively. In the lower region there was a multiplet centred at  $\tau$  7.32 (1H, f) for an angular methine proton, and a doublet and a quartet centred at  $\tau$  7.53 (1H, d') and  $\tau$  6.98 (1H, a';  $J$  7.5 Hz) for a *OH* and a methine proton. There was a doublet centred at  $\tau$  5.62 (2H, g and h,  $J$  4 Hz)

TABLE 2.

Name of compound	<i>gem</i> -Dimethyl C 	<i>C</i> -Methyl CH <sub>3</sub> ring A	Angular C—CH <sub>3</sub>	C—CH <sub>3</sub> ring C	CH <sub>2</sub> —OH	CH <sub>2</sub>		—CH	Geminal methine protons —CH	Alcoholic OH	Phenolic OH	Benzenoid H	CH <sub>3</sub> CO.O
Shahenxanthone (I)	$\tau$ 8.1(a,b) $J$ 7 Hz	$\tau$ 7.95 (c)	$\tau$ 7.50 (d)	—	$\tau$ 6.2(e) $J$ 8 Hz	$\tau$ 5.20 (g,h) $J$ 4 Hz	$\tau$ 4.92 (i) 4.78 (j)	$\tau$ 4.45 (l) $J$ 4 Hz $\tau$ 5.65 (a') 2 Hz $J$ 7.5 Hz	$\tau$ 7.12 (f)	$\tau$ 6.82 (e) $\tau$ 6.50 (d') $\tau$ 4.52 (k) $J$ 3.5 Hz	$\tau$ 0.36 (p)	$\tau$ 2.81(m) $J$ 8 Hz $\tau$ 1.92(n) $J$ 8 Hz $\tau$ 2.1(o)	—
Najamxanthone (II)	$\tau$ 8.76(a,b) $J$ 7.5 Hz	$\tau$ 8.18 (c)	$\tau$ 7.75 (d)	—	—	$\tau$ 5.62 (g,h) $J$ 4 Hz	$\tau$ 5.4 (i) $\tau$ 5.2 (j)	$\tau$ 4.55 (l) $J$ 4 Hz $\tau$ 6.98 (a') $J$ 7.5 Hz	$\tau$ 7.32 (f) 2 Hz	$\tau$ 5.01 (k) $J$ 4 Hz $\tau$ 7.53 (d')	$\tau$ 0.12 (p)	$\tau$ 3.25(m) $J$ 10 Hz 2.45(n) $J$ 10 Hz $\tau$ 2.75(o)	$\tau$ 7.51
Tajixanthone*	$\tau$ 8.70(a) $\tau$ 8.55(b)	$\tau$ 8.20 (c)	$\tau$ 7.70 (d)	$\tau$ 6.98 (e)	—	$\tau$ 5.57 (g,h) $J$ 2.5 Hz	5.38 (i) $\tau$ 5.17 (j)	$\tau$ 4.58 (l) $J$ 2 Hz	$\tau$ 7.28 (f) $J$ 2 Hz	$\tau$ 5.02 (k) $J$ 4 Hz	$\tau$ 0.76 (p)	$\tau$ 3.24(m) $J$ 10 Hz $\tau$ 2.48(n) $J$ 10 Hz $\tau$ 2.69 (o)	

\* The assignments of the various proton signals may please be seen in the earlier paper.<sup>2</sup>



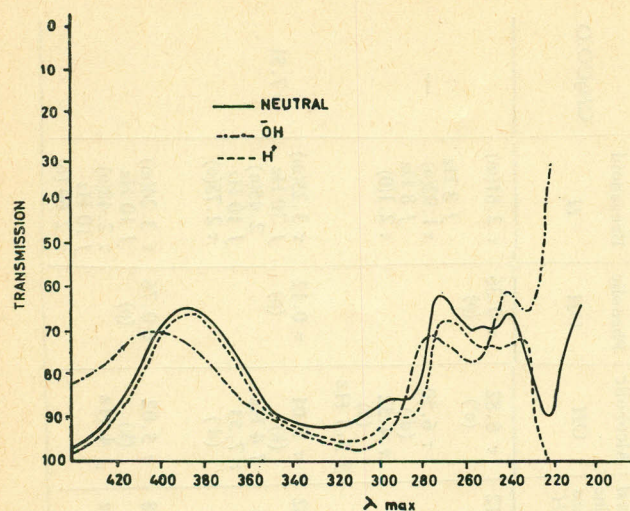


Fig. 4a. Visible and UV absorption spectrum of najamxanthone in methanol.

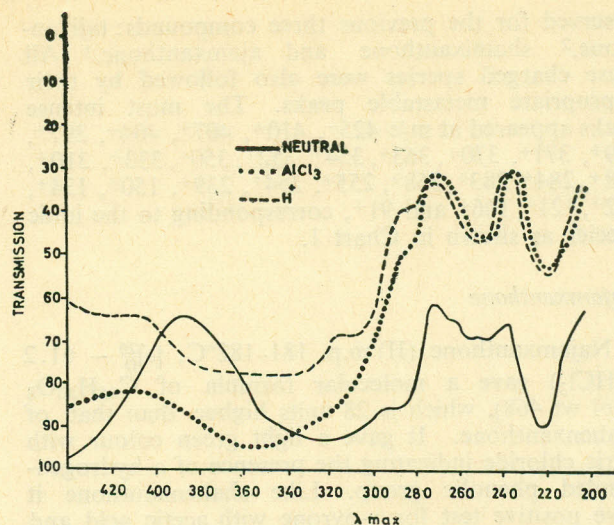


Fig. 4b. Visible and UV absorption spectrum of najamxanthone in methanol.

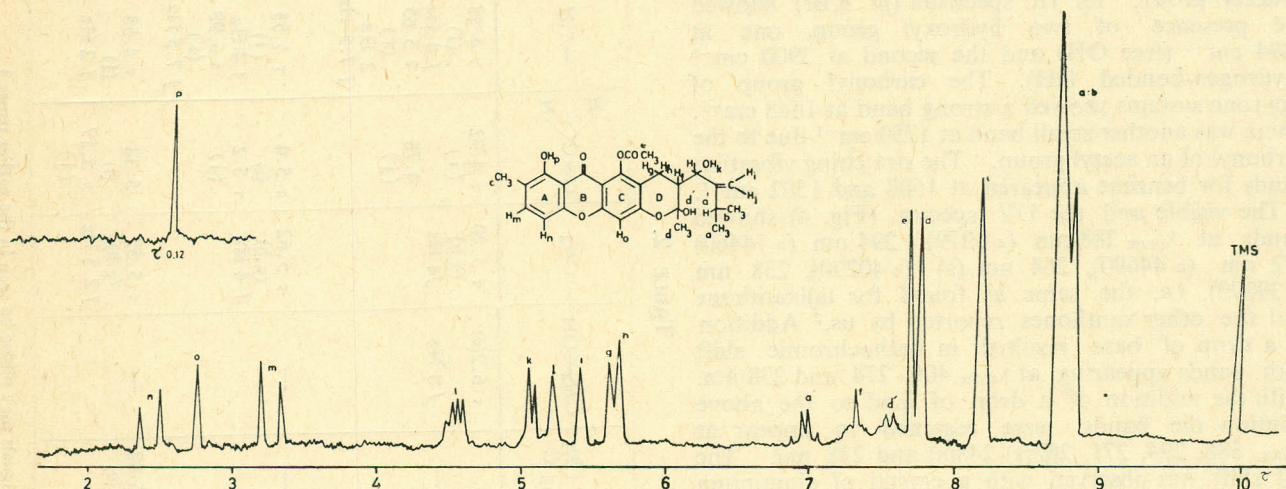
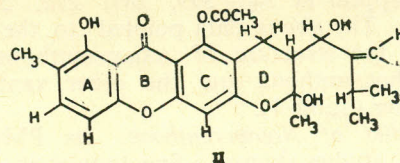


Fig. 5. PMR spectrum of najamxanthone.

for two methylene protons. The presence of two broad singlets appearing at  $\tau$  5.4 (1H, i) and  $\tau$  5.2 (1H; j) indicated two vinyledene protons. There was a doublet and a quartet centred at  $\tau$  5.01 (1H, k,  $J$  4 Hz) and  $\tau$  4.55 (1H, l,  $J$  4 Hz) confirming the presence of the same  $-\text{CH}_2-\text{CH}-\text{CHOH}$  group arrangement in this molecule as present in previous cases.<sup>2,3</sup> In the benzenoid region identical splitting pattern was observed as in the cases of shahenxanthone and tajixanthone. There were two double-doublets centred at  $\tau$  3.25 (1H, m,  $J$  10 Hz) and  $\tau$  2.45 (1H, n,  $J$  10 Hz) indicating the *ortho*-oriented protons in ring A. A sharp singlet at  $\tau$  2.75 (1H, o) stood for one benzenoid proton in ring C. The last (28th) proton of the hydroxyl group appeared as a singlet at  $\tau$  0.12 (1H, p).

On the basis of the above data najamxanthone could be assigned the structure II.



It will be noted that the group  $\text{CO}-\text{CH}_3$  as *O*-acetyl is being allocated position 5 in ring C in preference to three other possible sites. This has been done because of biogenetic reasons. Further, since in a number of cases of xanthenes reported earlier<sup>2</sup> it is only on ring C that *O*-methylation has been observed and not of the phenolic OH on the benzene ring A, we assume that *O*-acetylation should also take place in the same position.

The other possibility that either one or the other of the two alcoholic OH, one directly attached to ring D and the other substituted on the



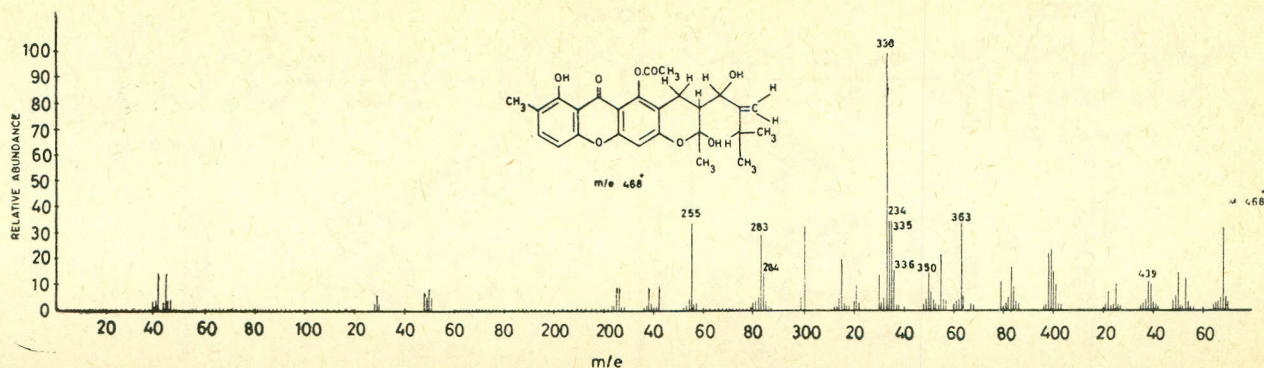
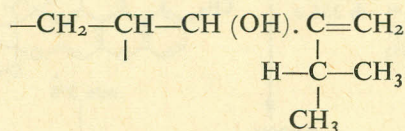


Fig. 6. Mass spectrum of najamxanthone.



side-chain on the same ring is acetylated, is ruled out as this possibility was not supported by the high-resolution mass spectral studies.

**Mass Spectral Studies.** The confirmation of the structure of najamxanthone as II came through its high resolution mass spectral fragmentation studies which showed an intense molecular ion peak at  $m/e$  468<sup>+</sup> corresponding to the molecular formula  $C_{26}H_{28}O_8$ . This ion underwent more or less identical losses as were observed in the cases of four previously reported xanthenes.\* The molecular ion (1) underwent successive losses of 30 ( $CH_2O$ ), 18( $H_2O$ ), 18( $H_2O$ ) mass units giving rise to peaks at  $m/e$  438<sup>+</sup>, 450<sup>+</sup>, 432<sup>+</sup> and forming ionic species (3), (4) and (5). The losses of two molecules of water directly from ionic species (1) suggested that the  $CH_3COO$ —indicated to be present by both IR and PMR spectral studies, was located on the benzene ring C.

The most intense peaks corresponding to the major losses appeared at 453<sup>+</sup>, 452<sup>+</sup>, 450<sup>+</sup>, 438<sup>+</sup>, 435<sup>+</sup>, 432<sup>+</sup>, 399<sup>+</sup>, 397<sup>+</sup>, 391<sup>+</sup>, 382<sup>+</sup>, 378<sup>+</sup>, 364<sup>+</sup>, 361<sup>+</sup>, 355<sup>+</sup>, 338<sup>+</sup>, 337<sup>+</sup>, 312<sup>+</sup>, 296<sup>+</sup>, 267<sup>+</sup>, 160<sup>+</sup>, 149<sup>+</sup> corresponding to the ionic species as outlined in Chart 2. Most of the fragment ions were followed by their appropriate metastable peaks.

The presence of the *O*-acetyl group was confirmed by alkaline hydrolysis under nitrogen. The hydrolysis yielded acetic acid which was confirmed as its *p*-bromophenacyl ester derivative. The presence of the vinylidene group was established by ozonolysis followed by reduction and steam-distillation. The hydrazone of formaldehyde so obtained confirmed the presence of a vinylidene side-chain.

Work on the absolute configuration of both shahenxanthone and najamxanthone is in progress.

### Experimental

Melting points were determined on a Kofler block. UV and visible spectra were recorded with a Beckman

\*Tajixanthone, shamixanthone, ajamxanthone and shahenxanthone.

D.B. spectrophotometer and the IR spectra were recorded with Perkin Elmer 137 in KBr disc. The PMR spectra were obtained with a Varian A-60, and DSP-60 (in  $CDCl_3$ ) containing TMS as internal reference. Mass spectra were determined on an AEI MS9 at 90 eV. Petroleum ether used had b.p. 65–85°C. Microanalyses were by Dr. A. Bernhardt, Mulheim, West Germany.

**Isolation of Shahenxanthone and Najamxanthone.** Shahenxanthone and najamxanthone were isolated and purified as already described in a previous communication.<sup>1</sup> Shahenxanthone crystallized from ether, was obtained as yellow plates, m.p. 163–164°C.  $[\alpha]_D^{20}$  —19.2 in  $CHCl_3$  (0.027% solution). It was soluble in ether, ethyl acetate, chloroform, acetone; sparingly soluble in ethanol and methanol and insoluble in carbon tetrachloride and water. It gave a positive test for  $\gamma$  pyrone with the formation of an orange ring with acetic and sulphuric acids.

Najamxanthone was purified through several crystallization from methanol, yellow needles, m.p. 181–182°C;  $[\alpha]_D^{20}$  —61.2 (0.78% solution in  $CHCl_3$ ).

**Ozonolysis of Shahenxanthone.** Shahenxanthone (10 mg) was dissolved in acetic acid (5 ml) and ozonised oxygen bubbled through the solution. One or two drops of water was added, and the reaction product was reduced with Zn dust (10 mg) and steam-distilled into 2,4-dinitrophenyl hydrazine solution. DNP of formaldehyde was isolated and crystallized from methanol, m.p. 187°C.

**Alkaline Hydrolysis of Najamxanthone.** Najamxanthone (50 mg) was heated with aqueous potassium hydroxide (5 ml; 10%) for 2 hr. The reaction mixture was acidified and the acetic acid liberated from its potassium salt was steam-distilled into NaOH solution (2 ml, 1N). About 50 ml distillate was collected and concentrated to 1 ml. It was again acidified with dil HCl and a 5% solution of *p*-bromophenacyl bromide (2 ml) added. *p*-Bromophenacyl ester derivative of acetic acid was obtained which melted at 86°C, undepressed on admixture with an authentic sample of the material (m.p. 86–87°C).

**Iodoform Test for Najamxanthone.** Najamxanthone (10 mg) in dioxane (2 ml) was treated with aqueous NaOH (10%, 0.2 ml). A solution prepared from KI (20 mg) and  $I_2$  (10 mg) in water (50 ml) was added till absorption of iodine was complete. The mixture



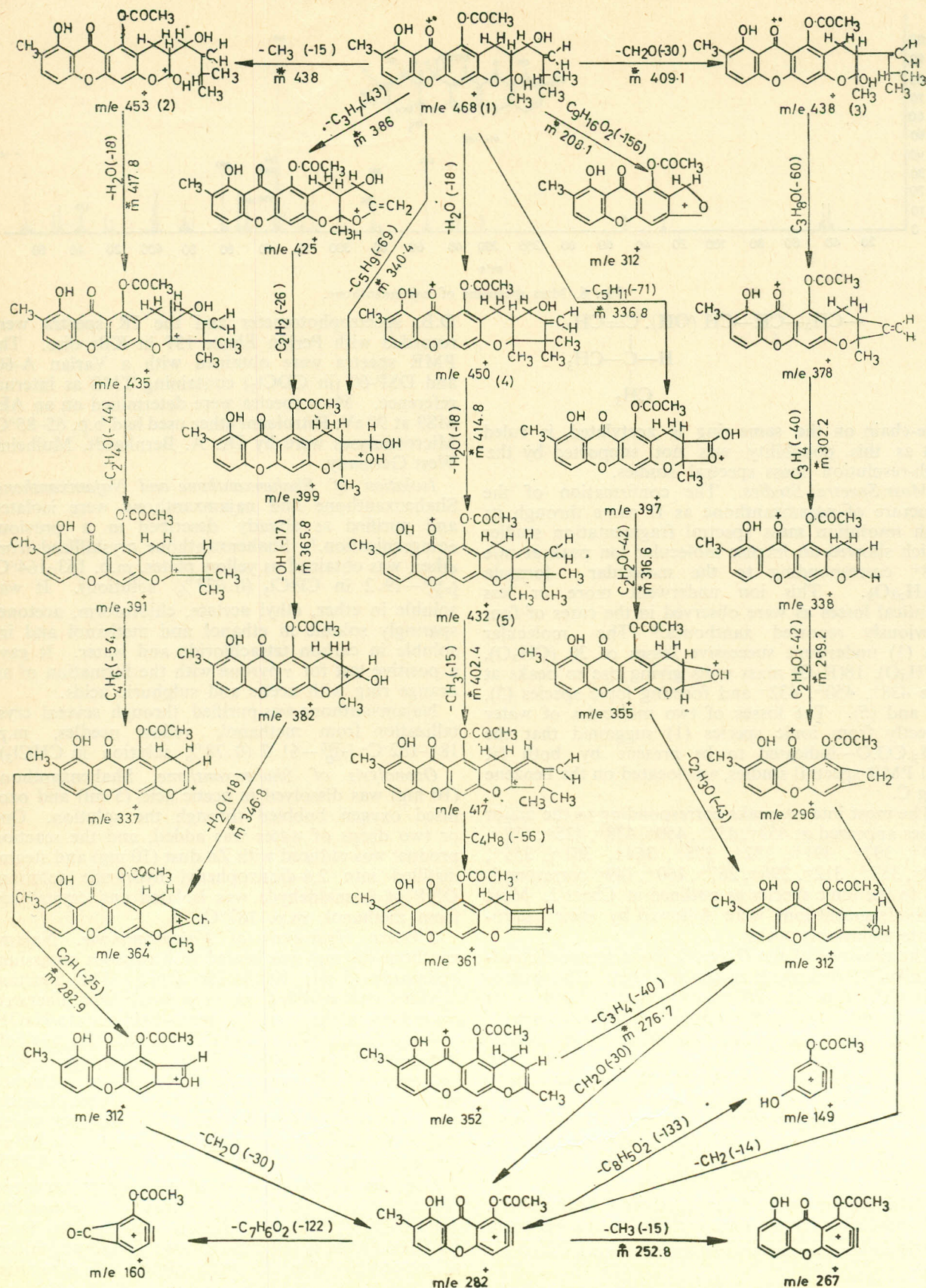


Chart 2. Mass fragmentation pattern of najamxanthone.



was heated on water-bath for 5-10 min. A distinct smell of iodoform was detectable. The filtrate was acidified with 2N HCl, extracted with ether, dried and the solvent removed. Iodoform obtained had m.p. 119°C which was undepressed with an authentic sample.

*Ozonolysis of Najamxanthone.* Through a solution of najamxanthone (50 mg dissolved in acetic acid 10 ml), ozonised oxygen was bubbled (3 hr). On steam distillation into 2, 4-dinitrophenyl hydrazine solution DNP of formaldehyde was isolated and was crystallized from methanol, m.p. 186-187°C, undepressed on admixture with an authentic sample of the material (m.p. 187°C).

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