

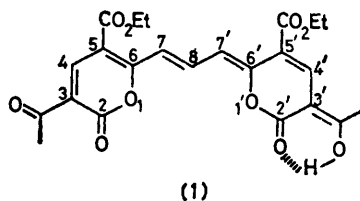
## Investigation of Crystal and Solution Structures of Glaucyrones by X-Ray, Nuclear Magnetic Resonance, and Ultraviolet Methods

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A single-crystal X-ray study of the black 3,3'-diacetyl-5,5'-bisethoxycarbonylglaucyrene (diethylglaucophanic enol) confirms the enolic structure (1). Abnormally short intermolecular contacts indicate the conjugated molecules to be connected by self charge-transfer interactions above and below the molecular plane, forming a linear but 'zig-zag' arrangement through the crystal.  $^1\text{H}$  N.m.r. data for the glaucyrones are solvent dependent, the AMX system of bridge protons (and other signals) in dry  $\text{CDCl}_3$  readily passing into the slow exchange region if moisture is present: addition of base gives a symmetrical anion (AMA' bridge protons) and this type of spectrum is observed in  $[\text{}^2\text{H}_6]\text{DMSO}$ . 3'-Acetyl-3,5,5'-trismethoxycarbonylglaucyrene shows related  $^1\text{H}$  n.m.r. behaviour, but 3,3',5,5'-tetrakisethoxycarbonylglaucyrene exists as a 7'-H form (7) in  $\text{CDCl}_3$  and as a symmetrical form in  $[\text{}^2\text{H}_6]\text{DMSO}$ . Electronic spectra in a variety of solvents show the glaucyrones to be highly ionised in polar solvents (blue) and unionised in non-polar solvents (red) with gradations in certain solvent systems.  $^{13}\text{C}$  N.m.r. assignments for glaucyrones and xanthyrone are based on model pyrones.

APART from interesting chemical behaviour, glaucyrones<sup>1,2</sup> show unusual features in the solid state and in solution. Diethylglaucophanic enol (3,3'-diacetyl-5,5'-bisethoxycarbonylglaucyrene) (1) forms glittering black crystals from benzene. Its solution in benzene or chloroform is red but in ethanol or dimethyl sulphoxide blue: the colour in some solvents such as acetone is red, becoming blue on the addition of small amounts of water. In this paper we report an X-ray study of the black crystals which confirms our original proposal (1):  $^1\text{H}$ -n.m.r. and u.v. spectroscopy is used to clarify aspects of the solution behaviour.

A single-crystal X-ray study was undertaken using direct-phasing procedures and atomic parameters were refined using least-squares and difference-Fourier methods, converging to  $R$  5.1% over 2 157 independent



observed reflections. The resulting molecule (Figure 1) shows an essentially planar glaucyrene core (no torsion angles  $>5^\circ$  away from 0 or  $180^\circ$  as appropriate), with bond lengths (Figure 3) and angles (Figure 4) not differing appreciably from values expected: Figure 2 shows crystallographic numbering. One pyrone ring (A) is unenolised, the other (B) enolised: the hydrogen-bonded hydrogen of the latter was located  $0.94 \text{ \AA}$  from the enol oxygen and  $1.69 \text{ \AA}$  from the carbonyl oxygen of the pyrone, the  $\text{O-H}\cdots\text{O}$  angle being  $149^\circ$ .† By contrast, the acetyl carbonyl at the ketonic enol (A) of the molecule is turned completely away from the lactonic

† The hydrogen was clearly located in a difference map. Other bonding to hydrogen is not mentioned, but all C-H bonds occur in the range  $0.85\text{--}1.10 \text{ \AA}$  ( $\sigma$  0.06) with bond angles involving hydrogen satisfactory.

carbonyl, minimising carbonyl-carbonyl interactions. The acetyl is also twisted  $16^\circ$  out of the plane of the pyrone ring, thereby reducing interactions between the acetyl methyl and the pyrone carbonyl (carbon to

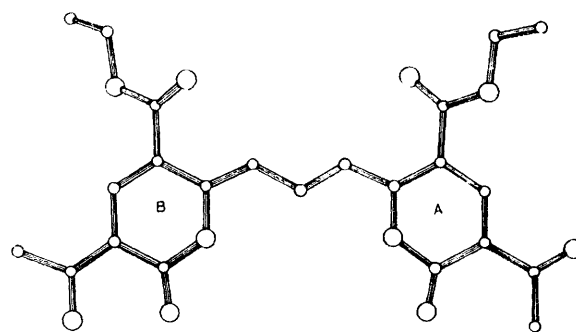


FIGURE 1 X-Ray structure of diethylglaucophanic enol

oxygen  $2.90 \text{ \AA}$ ). The ester addenda to the glaucyrene core lie out of plane by  $20^\circ$  at the ketonic end and  $30^\circ$  at the enolic end.

The arrangement of the molecules within the unit cell is shown in Figure 5, projected perpendicular to the  $b$ -

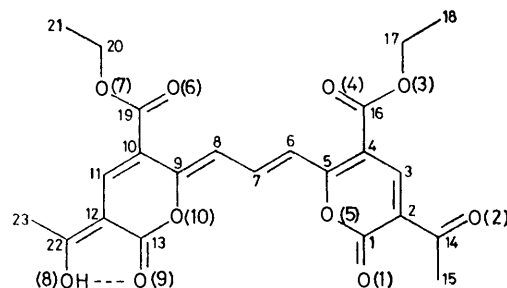


FIGURE 2 Diethylglaucophanic enol. Crystallographic numbering

axis. This is approximately parallel to the molecular plane and displays the overall flat nature of the glaucyrene framework, the twisting of the two esters, and the out of plane acetyl. Two different types of planar

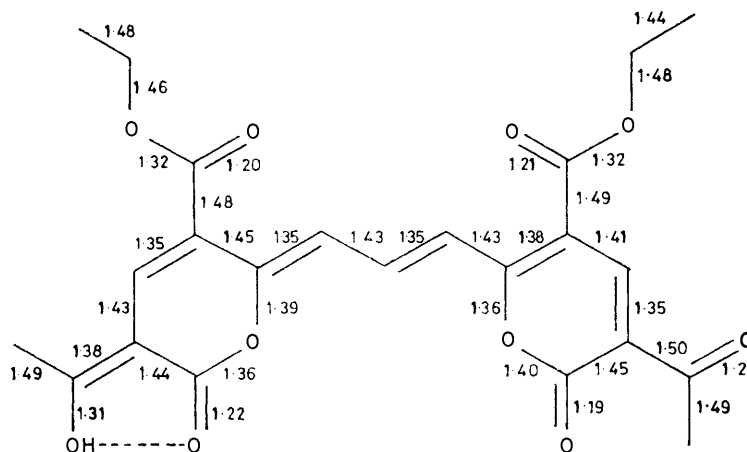


FIGURE 3 Diethylglaucophanic enol. Bond lengths (Å). Largest standard deviation 0.006 Å

overlap are shown in Figure 6. The first (Figure 6a) is an overlap between the untransformed (white) molecule

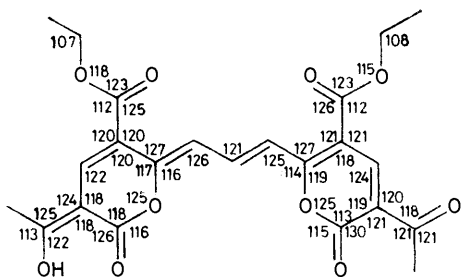


FIGURE 4 Diethylglaucophanic enol. Bond angles (°). All standard deviations 0.3°

and the upper (black) molecule transformed by  $1 + x$ ,  $y$ ,  $z$ . A number of close approach distances between these two molecules are listed in Table I: the carbon-

carbon separation between C(12) and C(1<sup>I</sup>) for example is 3.27 Å. This distance is considerably shorter than the sum of the van der Waals radii and is characteristic of a charge-transfer interaction (below 3.40 Å).<sup>3</sup> It will be noted that the sense of twisting of the ethyl ester side-chains is the same for this overlap and does not impede close approach of the planes. Figure 6b shows a side-on view.

Figure 6c shows the overlap on the other side of the plane between the untransformed (white) molecule and the lower (black) molecule transformed by  $1 + x$ ,  $\frac{1}{2} - y$ ,  $\frac{1}{2} + z$ . Here close planar approach is impeded by twisting of the ethyl ester side-chain in which there is an interatomic contact O(7) ··· O(5<sup>II</sup>) of 3.15 Å. The closest planar approach is exemplified by a carbon-carbon separation of 3.40 Å for C(11) ··· C(5<sup>II</sup>) which, while short, is only marginal for a charge-transfer interaction.

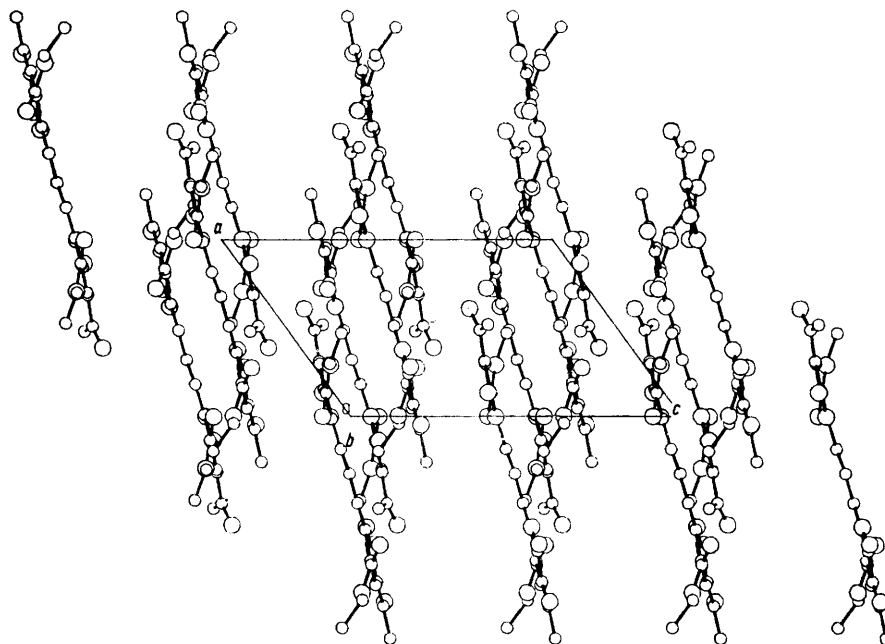


FIGURE 5 Diethylglaucophanic enol. Projection perpendicular to the  $b$  axis

TABLE I  
Diethylglaucophanic enol  
intramolecular separations (<3.50 Å)

C(12) ... C(1 <sup>I</sup> )	3.27	O(7) ... O(5 <sup>III</sup> )	3.15
C(22) ... O(1 <sup>I</sup> )	3.29	O(7) ... C(1 <sup>III</sup> )	3.36
O(8) ... O(1 <sup>I</sup> )	3.29	O(7) ... O(1 <sup>III</sup> )	3.38
O(6) ... C(16 <sup>I</sup> )	3.34	O(9) ... O(3 <sup>III</sup> )	3.38
O(6) ... O(3 <sup>I</sup> )	3.35	C(11) ... C(5 <sup>III</sup> )	3.40
O(10) ... C(14 <sup>I</sup> )	3.35	C(13) ... O(3 <sup>III</sup> )	3.41
O(10) ... O(2 <sup>I</sup> )	3.35	C(6) ... O(2 <sup>III</sup> )	3.44
C(10) ... C(3 <sup>I</sup> )	3.39	C(9) ... C(3 <sup>III</sup> )	3.49
C(12) ... O(1 <sup>I</sup> )	3.41	C(8) ... C(14 <sup>III</sup> )	3.49
C(22) ... C(1 <sup>I</sup> )	3.49	C(23) ... O(2 <sup>III</sup> )	3.30
C(13) ... C(2 <sup>I</sup> )	3.49	O(8) ... C(17 <sup>IV</sup> )	3.42
C(13) ... C(1 <sup>I</sup> )	3.50	O(8) ... C(20 <sup>V</sup> )	3.44
C(13) ... O(1 <sup>I</sup> )	3.50	O(6) ... C(18 <sup>VI</sup> )	3.42

Roman numerical superscripts refer to the following transformations of atomic co-ordinates:

I	$1 + x, y, z$	IV	$1 - x, y - \frac{1}{2}, 1\frac{1}{2} - z$
II	$1 + x, \frac{1}{2} - y, \frac{1}{2} + z$	V	$2 - x, y - \frac{1}{2}, 1\frac{1}{2} - z$
III	$2 + x, \frac{1}{2} - y, \frac{1}{2} + z$	IV	$-x, 1 - y, 1 - z$

Thus in the crystal as a whole any one molecule is engaged in charge-transfer interactions at one end with a molecule above it, at the other with a molecule below it, leading to linear, but zig-zag, continuous arrangements

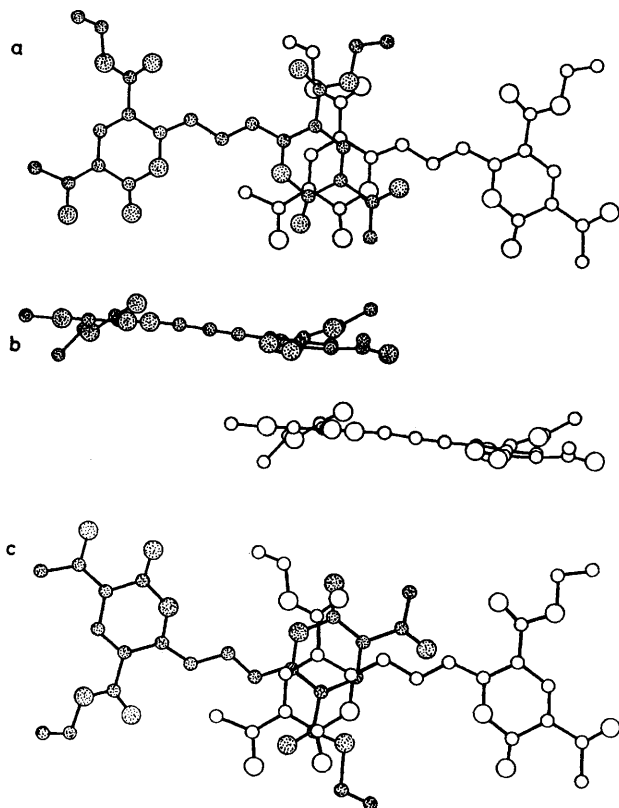


FIGURE 6 Arrangements of neighbouring molecules of diethylglaucophanic enol: a, pairs of molecules in close approach; b, pairs of molecules in close approach (side on view); c, pairs of molecules in more distant approach

(Figure 7). This type of arrangement, well shown in the projection of Figure 8, suggests possibilities for linear electrical conductance within single crystals. Only a

\* From this point onwards chemical numbering is employed in the discussion.

preliminary compaction measurement has as yet been made, giving a value at room temperature of  $5.2 \times 10^{-9}$  S cm<sup>-1</sup> which is rather high for a pure organic solid (usually <10<sup>-12</sup> S cm<sup>-1</sup>).

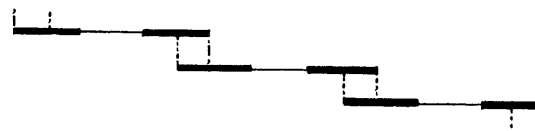


FIGURE 7 Short contact overlaps in diethylglaucophanic enol crystal

The black colour of 3,3'-diacetyl-5,5'-bisethoxycarbonylglaucyrone (1)\* (a reflectance spectrum of the solid shows absorption across the visible range,  $\lambda_{\text{max}}$ .

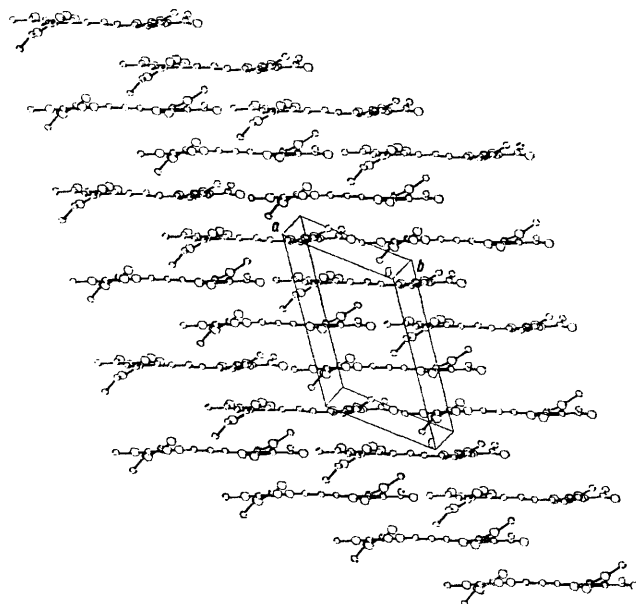
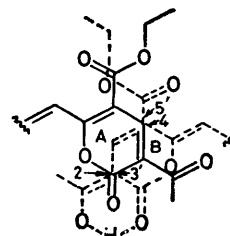


FIGURE 8 Diethylglaucophanic enol. Projection showing 'staircase' arrangement of molecules

670, 589infl, 423, 385, and 334infl nm)† appears understandable in terms of the solid being a self-charge-transfer complex. Whilst whole electronic



(2)

systems are obviously involved, crude analysis (2) suggests that enolic ring B acts as a donor, positions of excess electron density being developed at 3' and 5'

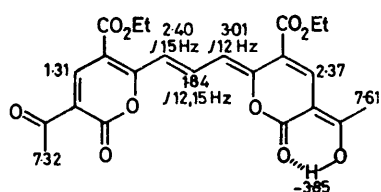
† The reflectance spectrum of the black sodium salt showed  $\lambda_{\text{max}}$ . 762, 672, 523, 422, 390, 332, and 262 nm; the solid tetramethyl-ester glaucyrone (7) had  $\lambda_{\text{max}}$ . 719infl, 661, 568infl, 383, and 261 nm.

as the enolic hydrogen is associated with the carbonyl oxygen. Carbons 2 and 4 of ring A are positions of electron deficiency due to electron withdrawal by the carbonyl oxygen, and this ring is thought to act as an acceptor.

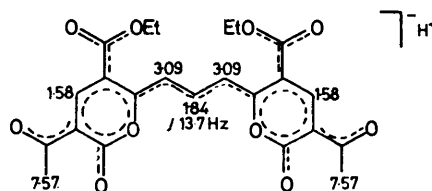
$^1\text{H}$  N.m.r. assignments for 3,3'-diacetyl-5,5'-bis-ethoxycarbonylglaucyrene in pure dry  $\text{CDCl}_3$  (3) are in accord with the X-ray structure and played a part, along with chemical work, in our original structure determination.<sup>1</sup> The molecule is clearly unsymmetrical, with two types of pyrone ring and a central AMX system (Figure 9). Addition of a drop of trifluoroacetic acid or measurement in ordinary (damp)  $\text{CDCl}_3$ , gives a slow

7'-H are differentiated as are 4- and 4'-H. The mobile proton cannot be located and a delocalised representation is given.

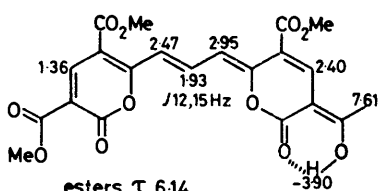
In pure dry  $\text{CDCl}_3$  the  $^1\text{H}$  n.m.r. spectrum of 3,3',5,5'-tetrakisethoxycarbonylglaucyrene<sup>2</sup> contrasts with those of (3) and (5). There is no enolised carbonyl or AMX type olefinic system: an AB system is present ( $J$  15.2 Hz) with the B proton coupled to an  $X_2$  system at  $\tau$  5.84 ( $J$  6.4 Hz) and this system persists on adding trifluoroacetic acid. In this solvent the molecule is present in the 7'-H form (7). Addition of a drop of cyclohexylamine causes formation of an AMA' system with a one-proton triplet at  $\tau$  1.89 ( $J$  13.8 Hz) and a two-



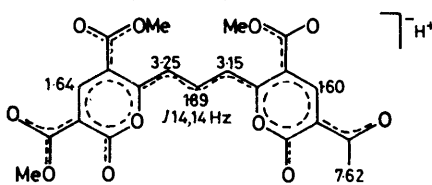
esters  $\tau$  5.65, 8.61,  $J$  7 Hz  
(3) ( $\text{CDCl}_3$ )



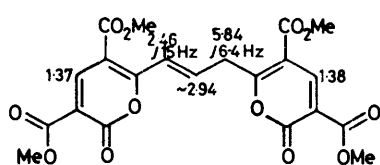
esters  $\tau$  5.79, 8.72,  $J$  7 Hz  
(4) (DMSO)



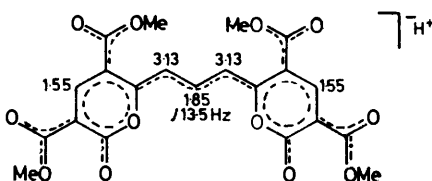
esters  $\tau$  6.14  
(5) ( $\text{CDCl}_3$ )



esters  $\tau$  6.28(2), 6.33(1)  
(6) (DMSO)



esters  $\tau$  6.15, 6.16, 6.17, 6.18  
(7) ( $\text{CDCl}_3$ )



esters  $\tau$  6.26(2), 6.30(2)  
(8) (DMSO)

exchange spectrum with the pyrone 4-H and 4'-H signals, the acetyl methyls and 7- and 7'-H becoming broad and ill defined: only the central 8'-H now remains sharp,  $\tau$  1.79 (t,  $J$  13.5 Hz), along with the ester ethyls. Addition of cyclohexylamine causes ionisation; the pyrone 4- and 4'-H signals appearing as a sharp (2 H) line at  $\tau$  1.47, the acetyls forming a sharp singlet,  $\tau$  7.57, and the bridge proton system appearing as an AMA' with a triplet at  $\tau$  1.80 (1 H,  $J$  13.8 Hz) and a doublet at  $\tau$  3.10 (2 H,  $J$  13.8 Hz). The spectrum in  $[\text{DMSO}]_6$  is similar in type to the latter as indicated in (4).

A related situation is found in the  $^1\text{H}$  n.m.r. spectra of 3'-acetyl-3,5,5'-trismethoxycarbonylglaucyrene (5).<sup>2</sup> In  $\text{CDCl}_3$  this resembles (3) having one acetyl in enolic form and a bridge AMX system. The spectrum in damp  $[\text{DMSO}]_6$ , however, resembles that of (4) but the species is now not inherently symmetrical and 7- and

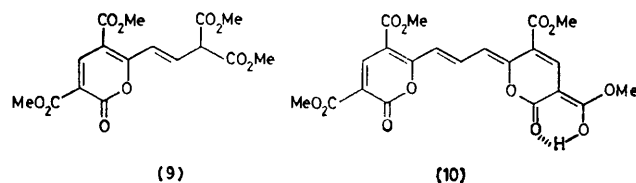
proton doublet at  $\tau$  6.76 ( $J$  13.8 Hz): this is clearly the spectrum of the ionised form. In damp  $[\text{DMSO}]_6$  the bridge protons are also in AMA' form with the two pyrone protons resonating at the same field, and representation (8) is used. The inability of the tetraester glaucyrene (7) to take up a fully conjugated enolised form in  $\text{CDCl}_3$  is paralleled in the xanthyrone series where members lacking an acetyl exist in similar incompletely conjugated form in this solvent:<sup>4</sup> ionisation in a polar solvent is also paralleled.

Both the tri- (5) and tetra- (7) ester glaucyrenes<sup>2</sup> crystallise from benzene in black form, but (5) also forms red needles from chloroform and ether. The two forms have different i.r. spectra and  $^1\text{H}$  n.m.r. examination in  $\text{CDCl}_3$  shows that the red form contains ca. 1 mol  $\text{CHCl}_3$  of solvation. It seems likely that the black forms have charge-transfer interactions in the crystal whilst the

chloroform solvated lattice is of a kind not permitting these. An interesting effect, noted when (3) was being crystallised from benzene, is that the red solution freezes to a blue solid, the process being reversed on thawing.

Electronic solution spectra for 3,3'-diacetyl-5,5'-bisethoxycarbonylglaucryne (3)—(4) in a number of solvents are presented in Table 2. There are two extreme classes of spectra. One class (benzene or

(3)—(4) and its sodium salt, measured under the same conditions in ethanol at pH 7 (Table 3), shows that the strong absorption at 670—680 nm is that of the anion



and this very extensive ionisation in neutral polar solvent and this very extensive ionisation in neutral polar solvents is in agreement with  $^1\text{H}$  n.m.r. data and is comparable with the situation in the xanthyrones.<sup>5</sup>

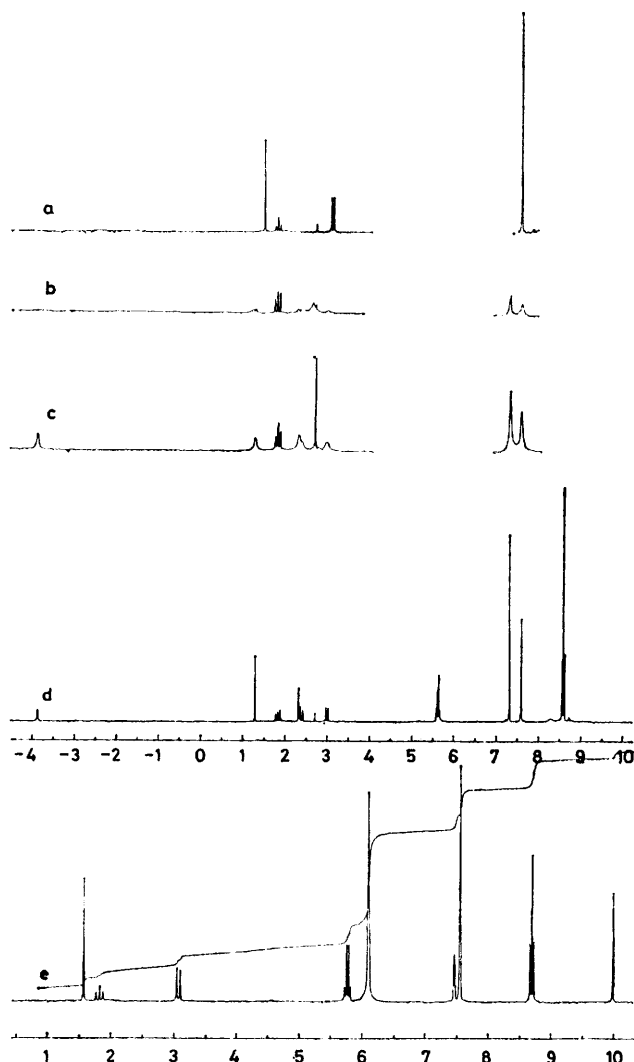
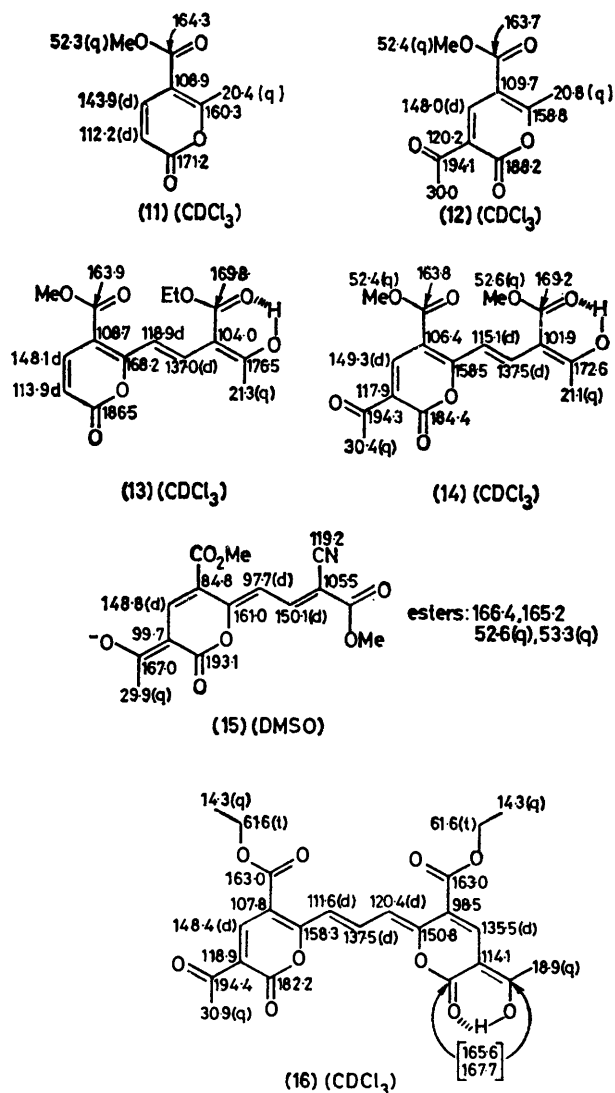


FIGURE 9  $^1\text{H}$  N.m.r. spectra (250 MHz) for 3,3'-diacetyl-5,5'-bisethoxycarbonylglaucryne in: a, pure  $\text{CDCl}_3$  + a drop of cyclohexylamine; b, pure  $\text{CDCl}_3$  + a drop of trifluoroacetic acid; c, 'ordinary grade' (damp)  $\text{CDCl}_3$ ; d, pure dry  $\text{CDCl}_3$ ; e,  $[\text{D}_6]\text{DMSO}$  (damp)

chloroform, red solutions) has a strong absorption at  $\lambda_{\text{max}}$  ca. 500 nm. The other, involving the most polar solvents (blue solution) has narrow intense absorption ( $\epsilon$   $1.25$ — $1.75 \times 10^5$ ) near 680 nm. Spectra are sensitive to the water content of the solvent and this is especially so in the case of solvents giving spectra of intermediate type such as acetone or acetonitrile (concentrated solutions red, becoming blue on adding a little water). Comparison of the spectrum of diethylglaucophanic enol



Both types of compound belong to the oxonol class and may be viewed as vinylogous carboxylic acids. In support of this, the spectrum of (3)—(4) in ethanol at pH 2 becomes similar to the chloroform type: this is

ascribed to unionised form and is in line with the  $^1\text{H}$  n.m.r. investigation described above.

U.v. data for the triester glaucyrene (5)—(6) and the tetraester glaucyrene (7)—(8) are given in Table 3. As

methoxycarbonyl enolate (10): this would be below the detection level of the n.m.r. work.

In order to facilitate further solution study of xanthyrone and glaucyrenes, a preliminary survey of  $^{13}\text{C}$  n.m.r.

TABLE 2

U.v. data for diethylglaucophanic enol (3)—(4) in various solvents [ $\lambda_{\text{max}}$ ( $10^{-3}\epsilon$ )/nm]							
EtOH	DMSO	DMF	PC <sup>a</sup>	MeCN	Me <sub>2</sub> CO	CHCl <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>
679 (126.0)	678 (124.8)	679 (156.0)	677 (173.0)	673 (42.0)	674 (38.3)		
		626infl (34.2)					
630infl (35.4)	641infl (35.9)	575 (23.4)	624infl (40.8)	620infl (13.0)			
				494 (22.8)	494 (29.1)	503 (43.4)	496 (33.0)
427 (9.0)	428 (11.7)	424 (10.6)	421 (11.0)	432 (12.7)			
387 <sup>b</sup> (14.0)	396 (17.5)	392 (17.1)	390 (17.6)				
370infl (11.8)	376infl (12.2)		370infl (12.9)	356 (11.8)		354 (11.4)	356 (11.1)
330 (8.9)	334 (7.0)	334 (13.4)	329 (12.9)	330 (13.9)		332 (12.7)	346 (11.5)
294 (8.6)	285 (8.8)	293 (12.8)	290 (14.6)	295 (10.3)		296 (6.6)	328 (14.1)
265 (14.0)	268 (17.2)		267 (20.4)	260 (11.8)			
245 (12.7)			243 (17.0)	235 (18.0)			

<sup>a</sup> PC = Propylene carbonate. <sup>b</sup> Also 396infl (13.0).

might be expected from the n.m.r. discussion above, spectra for compounds (3)—(4) and (5)—(6) compare well with each other in both neutral ethanol and chloroform. On the other hand the spectrum of glaucyrene (7)—(8) differs from those of the former compounds when determined in chloroform and reflects the 7'-H

assignments (25 MHz) has been made (all for CDCl<sub>3</sub> except where stated). Assignments were made first to 5-methoxycarbonyl-6-methyl-2-pyrone(11)<sup>4</sup> and 3-acetyl-5-methoxycarbonyl-6-methyl-2-pyrone(12),<sup>4</sup> using noise-decoupled and off-resonance spectra. With this as a basis assignments were then made to 3'-acetyl-3'-

TABLE 3

Sodium salt	U.v. data for diethylglaucophanic enol (3)—(4) and sodium salt [ $\lambda_{\text{max}}$ ( $10^{-3}\epsilon$ )/nm]							
	Glaucyrene (3)—(4)				Glaucyrene (5)—(6)		Glaucyrene (7)—(8)	
	EtOH pH 7	EtOH pH 2	CHCl <sub>3</sub>	EtOH pH 7	CHCl <sub>3</sub>	EtOH pH 7	CHCl <sub>3</sub>	
672 (111.2)	672 (127.5)			667 (137.4)		662 (136.9)		
	515 (8.4)	500 (32.8)	503 (43.4)	512 (5.7)	493 (66.9)		490 (0.75)	
425 (6.5)	425 (6.5)			426 (11.2)		417 (5.4)		
383 (10.4)	383 (7.4)	399 (10.2)	354 (11.4)	381 (15.1)	338 (22.3)	377 (7.7)	355 (19.2)	
330 (6.1)	330 (5.2)		332 (12.7)	327 (7.8)	321 (22.5)	312 (5.3)		
290 (6.3)	290 (6.9)							
	242 (7.9)					263 (11.1)	250 (22.2)	

structure revealed by  $^1\text{H}$  n.m.r. data in CDCl<sub>3</sub>. The chromophore of (7)—(8) in chloroform is reminiscent of that of the tetraester xanthyrone (9) which has a malonate terminus,<sup>4</sup> the main long wavelength absorption at 355 nm comparing with 349 nm for (9). The tetraester glaucyrene however, has a weak low-energy band at 490 nm ( $\epsilon 0.75 \times 10^3$ ) which is in a similar position to the low energy band of the enolised glaucyrenes (3)—(4) and (5)—(6) in this solvent. It may, therefore, signify that in chloroform there is a low concentration (*ca.* 1%) of the

ethoxycarbonyl-5-methoxycarbonylxanthyrone(13)<sup>4</sup> and 3,3'-diacetyl-3',5'-bismethoxycarbonylxanthyrone (14).<sup>4</sup> Mesomeric effects have pronounced influence on chemical shifts around the pyrone ring and on side-chain carbons. The enolisation of the 3'-acetyls is apparent, carbons attached to enolised oxygen appearing in the range 165—177 p.p.m. as opposed to *ca.* 194 p.p.m. for unenolised acetyls.

Assignments to the  $^{13}\text{C}$ -spectrum of 3,3'-diacetyl-5,5'-bisethoxycarbonylglaucyrene are given in (16). In this

spectrum (21 °C) there was marked line-broadening of all carbons except the central one (C-8) and the ethyl esters. It thus appears that degenerate proton exchange between the two ends is beginning to occur at a detectable speed, probably because of slight dampness in the CDCl<sub>3</sub> (see <sup>1</sup>H n.m.r. data above). At 48 °C further line broadening occurred to the point where some signals merged. Also included are provisional assignments for the cyanoxanthrone (15),<sup>4</sup> but unlike the other compounds this was measured in [<sup>2</sup>H<sub>6</sub>]DMSO and represents data for the delocalised anion.

#### EXPERIMENTAL

*Crystallographic Analysis of Diethylglauconic Enol.*— Suitable specimens were recrystallised from benzene. Oscillation and Weissenberg photographs were taken about the needle (*c*) axis to establish unit-cell dimensions and space group. For intensity measurement a crystal of dimensions *ca.* 0.7 × 0.2 × 0.2 mm<sup>3</sup> was mounted on a Hilger and Watts automatic, computer-controlled, four-circle diffractometer. Unit-cell dimensions were refined by a least-squares fit on the positions of 12 peaks found on the diffractometer. Intensity data were collected with Mo-*K*<sub>α</sub> radiation for 2θ ≤ 50° by use of an ω-2θ scan. A total of 3 844 independent reflections was measured of which 2 157 reflections with a net count greater than 3.0 standard deviations were considered observed and used in the subsequent structure refinement. No absorption corrections were made. Data reduction and subsequent crystallographic calculations were performed using the 'X-Ray '70' system of programs.<sup>6</sup> Atomic scattering factors were taken from ref. 7.

*Crystal Data.*—C<sub>23</sub>H<sub>22</sub>O<sub>10</sub>, *M* = 458.429. Monoclinic, *a* = 9.279(3), *b* = 20.823(6), *c* = 13.907(4) Å; β = 125.65(2)°, *U* = 2 183.51 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.39 g cm<sup>-3</sup>, *F*(000) = 960. Space group *P*2<sub>1</sub>/*c* uniquely from systematic absences; Mo-*K*<sub>α</sub> radiation, λ = 0.710 69 Å, μ(Mo-*K*<sub>α</sub>) = 1.19 cm<sup>-1</sup>.

The structure was solved by direct methods using the Multan program.<sup>8</sup> Several starting sets for the program were tried without success. Finally only those data for which 2θ ≤ 40° were used in the normalisation process. The 231 resulting reflections with *E* > 1.5 were then used in direct phase determination and the best set of phases produced had a figure of merit 1.010. A subsequent *E*-map based on these phases revealed the positions of 31 of the 33 carbon and oxygen atoms as the largest peaks on the map. Structure-factor calculations of these atomic positions showed an agreement factor *R* of 0.37 and a subsequent difference map revealed the positions of the two missing atoms, the outer carbons of the ethyl groups. Block-diagonal least-squares refinements of atomic positions and isotropic temperature factors were commenced and after six cycles the value of *R* was reduced to 0.139. The thermal parameters were then allowed to vary anisotropically and four further cycles lowered *R* to 0.089. A difference-Fourier synthesis was next calculated which revealed the positions of all 22 hydrogen atoms among the largest peaks in the map. The hydrogen atoms were then included in the refinement with isotropic temperature factors. Their inclusion lowered *R* to 0.057 after four more cycles. Analysis of the agreement between *F*<sub>o</sub> and *F*<sub>c</sub> suggested the adoption of a weighting scheme of the form: *w* = 1 for |*F*<sub>o</sub>| < 18.0 and *w* = (18.0/|*F*<sub>o</sub>|)<sup>2</sup> for |*F*<sub>o</sub>| > 18.0.

Three final cycles of full-matrix least-squares refinement converged when the largest parameter shifts were <1.0 σ reducing *R* to 0.051 after a total of 17 cycles. A final difference-map showed no peaks or depressions >0.2 e Å<sup>-3</sup>.

TABLE 4

Diethylglauconic enol. Atomic co-ordinates with standard deviations in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
C(1)	-0.152 9(4)	0.165 4(2)	0.520 8(3)
C(2)	-0.311 6(4)	0.203 7(1)	0.473 5(2)
C(3)	-0.297 8(4)	0.268 4(1)	0.477 0(3)
C(4)	-0.138 2(4)	0.301 4(1)	0.521 6(3)
C(5)	0.011 8(4)	0.265 5(1)	0.561 9(2)
C(6)	0.182 9(4)	0.288 7(2)	0.601 5(3)
C(7)	0.321 3(4)	0.251 3(2)	0.628 9(3)
C(8)	0.488 2(4)	0.279 3(2)	0.669 5(3)
C(9)	0.637 0(4)	0.246 9(1)	0.704 2(2)
C(10)	0.811 9(4)	0.273 8(1)	0.756 1(2)
C(11)	0.952 2(4)	0.234 4(1)	0.796 0(2)
C(12)	0.932 0(4)	0.166 4(1)	0.784 6(2)
C(13)	0.757 0(4)	0.139 8(1)	0.729 5(3)
C(14)	-0.489 0(4)	0.172 9(2)	0.418 9(3)
C(15)	-0.518 8(5)	0.104 3(2)	0.382 3(4)
C(16)	-0.132 1(4)	0.372 7(2)	0.523 1(3)
C(17)	-0.298 7(7)	0.468 8(2)	0.446 3(4)
C(18)	-0.471 0(8)	0.487 6(2)	0.345 2(5)
C(19)	0.835 3(4)	0.344 4(1)	0.763 0(3)
C(20)	1.037 6(5)	0.430 2(2)	0.869 2(4)
C(21)	1.194 9(6)	0.438 7(2)	0.992 2(4)
C(22)	1.070 0(4)	0.124 5(2)	0.818 9(3)
C(23)	1.255 5(5)	0.144 1(2)	0.870 5(4)
O(1)	-0.134 0(3)	0.108 6(1)	0.531 9(2)
O(2)	-0.609 7(3)	0.205 6(1)	0.402 6(2)
O(3)	-0.291 2(3)	0.397 8(1)	0.447 8(2)
O(4)	-0.000 7(3)	0.405 2(1)	0.584 7(3)
O(5)	0.001 5(3)	0.200 6(1)	0.562 3(2)
O(6)	0.724 1(3)	0.381 7(1)	0.693 7(3)
O(7)	0.994 6(3)	0.361 7(1)	0.853 6(2)
O(8)	1.046 4(3)	0.062 1(1)	0.805 9(2)
O(9)	0.719 1(3)	0.083 0(1)	0.710 8(2)
O(10)	0.621 3(4)	0.180 6(1)	0.695 1(2)
H(3)	-0.394(4)	0.290(1)	0.456(2)
H(6)	0.194(4)	0.336(1)	0.603(3)
H(7)	0.300(4)	0.206(2)	0.610(3)
H(8)	0.499(4)	0.323(1)	0.669(3)
H(11)	1.065(4)	0.251(1)	0.826(2)
H(15A)	-0.464(5)	0.094(2)	0.337(3)
H(15B)	-0.658(6)	0.092(2)	0.313(4)
H(15C)	-0.477(5)	0.079(2)	0.446(3)
H(17A)	-0.294(6)	0.474(2)	0.520(4)
H(17B)	-0.234(8)	0.490(3)	0.411(5)
H(18A)	-0.469(7)	0.538(2)	0.348(4)
H(18B)	-0.510(12)	0.479(4)	0.402(7)
H(18C)	-0.502(8)	0.472(3)	0.273(5)
H(20A)	0.936(4)	0.451(2)	0.854(3)
H(20B)	1.065(5)	0.440(2)	0.808(3)
H(21A)	1.300(5)	0.410(2)	1.011(4)
H(21B)	1.235(6)	0.481(2)	1.005(4)
H(21C)	1.162(6)	0.430(2)	1.041(4)
H(23A)	1.286(6)	0.183(2)	0.899(4)
H(23B)	1.329(7)	0.122(2)	0.933(4)
H(23C)	1.279(8)	0.129(3)	0.814(6)
H(O8)	0.925(6)	0.054(2)	0.770(4)

Final atomic co-ordinates are listed in Table 4; temperature factors and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22876 (12 pp.).\*

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\* For details of Supplementary Publications see Notice to Authors No. 7, in *J.C.S. Perkin I*, 1979, Index issue.

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