401. *Acylcyclopentanetriones: Comments on a Recent Synthesis,[1] and Observations from Proton Resonance on their Enolisation and on Isomerism in 5-Methoxyhept-4-en-3-one*

By J. A. Elvidge and R. Stevens

5-Methyl-3-propionylcyclopentane-1,2,4-trione (VIII), prepared by acylation of 3-methylcyclopentane-1,2,4-trione, differs from the product of a recent synthesis,[1] the spectral properties of which correspond to those of 6-ethyl-3-methyl-4-pyrone-2-carboxylic acid (XIII). Repetition of the synthesis [1] gave (VIII) as well as the by-product previously isolated, ethyl 6-ethyl-3-methyl-4-pyrone-2-carboxylate (XV). Ultraviolet, infrared, and proton magnetic resonance spectroscopy support these conclusions and show that the acylcyclopentane-1,2,4-triones are dienolic. The lower boiling, stable form of 5-methoxyhept-4-en-3-one is shown to have the *cis*-olefinic configuration.

Acylcyclopentanetriones, encountered as degradation products of hop constituents,[2] have recently been synthesised by two routes.[1,3] Leucht and Riedl [3] acylated 3-alkylcyclopentane-1,2,4-triones to give isohumulinic acid (I) (for many structural formulæ see Table 1), the known analogue (V),[2e] and two new analogues (VI and VII). Vandewalle *et al.*,[1] condensed ethyl oxalate with enol ethers of 1,3-diketones but only prepared new products so that the proof of the structures rested entirely upon spectroscopic evidence. Their data, however, differed significantly from both our own [2,4] and Riedl's [3] for 3-acylcyclopentane-1,2,4-triones. Thus Vandewalle's compounds showed maxima near 263 mμ in acid and 257 mμ in alkaline ethanol with ε *ca.* 8000 and 11,000, whereas the known compounds (I—VII) showed two maxima, near 255 and 280 mμ in acid, and at longer wavelengths near 275 and 300 mμ in alkaline solution, with more than twice the previous intensities (Table 1). In the infrared, Vandewalle's compounds showed bands near 1900 and at 1580—1565 cm.$^{-1}$ unlike the compounds (I—VII) (Table 2). The proton magnetic resonance (p.m.r.) spectra of Vandewalle's acylcyclopentanetriones indicated that they were monoenolic: in contrast, the compounds (I), (II), and (III) were dienolic.[4]

We concluded that Vandewalle's compounds were not the acylcyclopentanetriones claimed. Indeed, the spectroscopic data suggested that they were the isomeric 4-pyrone-2-carboxylic acids. Support for this came from the data for comanic acid (X), its esters (XI) and (XII), and ethyl chelidonate (XVI) (Tables 1, 2, 3). Confirmation came from preparative work.

We synthesised 5-methyl-3-propionylcyclopentane-1,2,4-trione (VIII), one of the products claimed by Vandewalle *et al.*,[1] by Leucht and Riedl's unambiguous route.[3] Acylation of 3-methylcyclopentane-1,2,4-trione [5] (XVII) with propionic anhydride and boron trifluoride afforded the yellow trione (VIII), m. p. 195°. This was dienolic from the p.m.r. spectrum (Table 3) and it showed ultraviolet and infrared absorption agreeing with that of previous compounds of the acylcyclopentanetrione series (see Tables 1 and 2) but differing from that reported by Vandewalle *et al.*,[1] for this compound.

From the base-induced condensation of ethyl oxalate with heptane-3,5-dione enol methyl ether (XIX), these workers had isolated [1] by countercurrent distribution (between ether and a buffer solution at pH 3·8, which could lead to hydrolysis) an acidic product

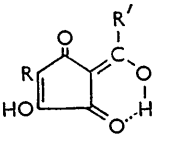
[1] Vandewalle, Dewaele, Alderweireldt, and Verzele, *J.*, 1964, 367; see also following Paper.
[2] (*a*) Wieland, *Ber.*, 1925, **58**, 102; (*b*) Harris, Howard, and Pollock, *J.*, 1952, 1906; (*c*) Howard and Tatchell, *J.*, 1954, 2400; (*d*) Howard and Slater, *J.*, 1957, 1924; (*e*) Brown and Howard, *J.*, 1960, 164; (*f*) Brown, Burton, and Stevens, *J.*, 1964, 4774.
[3] Leucht and Riedl, *Annalen*, 1963, **669**, 55.
[4] Forsén, Nilsson, Elvidge, Burton, and Stevens, *Acta Chem. Scand.*, 1964, **18**, 513.
[5] Orchin and Butz, *J. Amer. Chem. Soc.*, 1943, **65**, 2296.

$C_9H_{10}O_4$,* m. p. 187°, and the pyrone ethyl ester (XV). The former with diazomethane gave a " monomethyl enol ether," m. p. 79—83°. Repetition of the condensation afforded us a mixture from which a yellow product crystallised which was identical with the foregoing 5-methyl-3-propionylcyclopentane-1,2,4-trione (VIII). This was unchanged by methanolic hydrochloric acid, but the condensation mother-liquors on similar treatment afforded a colourless compound, $C_{10}H_{12}O_4$, m. p. 86—87°, soon identified as methyl 6-ethyl-3-methyl-4-pyrone-2-carboxylate (XIV). The compound showed ultraviolet and infrared

TABLE 1

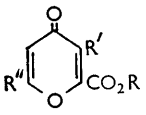
Ultraviolet light absorption data

Acylcyclopentane-1,2,4-triones



	R	R′	$\lambda_{max.}$ (ε) mμ in 0·1N-HCl–EtOH *	in 0·1N-NaOH–EtOH *	Ref.
(I)	$Me_2CH{\cdot}CH_2{\cdot}CH_2$	Bu^i	255 (25,000) 280 (22,000)	— —	2*b*, 3 ‡
(II)	$Me_2CH{\cdot}CH_2{\cdot}CH_2$	Pr^i	255 (23,100) 280 (17,550)	235 (12,300) 275 (30,400) 300 (27,600)	†
(III)	$Me_2C{:}CH{\cdot}CH_2$	Bu^i	255 (25,000) 280 (18,000)	275 (25,600) 303 (26,000)	2*d*
(IV)	$Me_2C{:}CH{\cdot}CH_2$	Pr^i	255 (16,300) 280 (12,100)	275 (26,600) 300 (24,400)	2*f*
(V)	Me	Me	253 (21,900) 273 (16,300)	275 (25,600) 303 (26,000)	2*e*, 3
(VI)	Me	Bu^i	255 (24,800) 278·5 (19,500) 340 (860)	237 (7,800) 273 (26,100) 300 (25,400) 433 (550)	3
(VII)	$Me_2CH{\cdot}CH_2{\cdot}CH_2$	Me	255 (26,400) 275 (18,600) 343 (1000)	235 (8300) 275 (27,700) 300 (24,500) 437 (570)	3
(VIII)	Me	Et	255 (24,100) 275sh (17,900)	235 (7500) 275 (27,200) 300 (24,500) 430 (537)	†
(IX)	Me	CO_2Et	255 (14,900) 275sh (13,100) 285 infl. (12,300)	240 (14,900) 275 (27,600) 302 (22,200)	† 5

4-Pyrone-2-carboxylic acids



	R	R′	R″			
(X)	H	H	H	260 (9860)	260 (5480) 350 (13,750)	† Cf. [10]
(XI)	Me	H	H	259 (7900)	260 (6400) 352 (16,400)	†
(XII)	Et	H	H	260 (7550)	260 (8050) 352 (16,100)	† Cf. [10]
(XIII)	H	Me	Et	266 (8760)	259 (15,600)	†
(XIV)	Me	Me	Et	267 (10,100)	260 (14,100)	†
(XV)	Et	Me	Et	265 (9000)	260 (12,800)	†
(XVI)	Et	H	CO_2Et	270 (10,000)	—	10

* Conditions used in this work. Other data, from references listed, refer to acidic ethanol (or ethanol) and basic ethanol. † This work. ‡ Leucht and Riedl [3] give complete spectrum.

* Given as $C_8H_{10}O_4$ in ref. 1, by typographical error.

absorption similar to that of ethyl comanate (XII) (Tables 1 and 2), and the p.m.r. characteristics (apart from the lines from the ester group) resembled those of Vandewalle's pyrone ethyl ester (XV). Moreover, hydrolysis of the product (XIV) yielded the pyrone acid (XIII), $C_9H_{10}O_4$, m. p. 199°, which with ethereal diazoethane gave an ethyl ester obviously identical (m. p. and spectroscopic properties) (see Table 3) with Vandewalle's ethyl 6-ethyl-3-methyl-4-pyrone-2-carboxylate (XV). As a precaution, we also esterified some of the pyrone acid (XIII) with diazomethane and confirmed that the methyl ester was identical with that originally obtained from the condensation mother-liquors. These

TABLE 2

Principal infrared maxima ($cm.^{-1}$) (for *a* KBr disc, *b* Nujol mull)

	O–H	C=O C=C	C–H and skeletal vibrations
(I) [a]	3279	1721, 1658 infl., 1626s	2959, 1462, 1429, 1370s, 1333w, 1316w, 1282, 1244w, 1215w, 1190s, 1131s, 1025w, 997, 952w, 909, 885w, 833s, 790, 725b
(II) [a]	3290	1718, 1650 infl., 1616s	2941, 1439, 1429w, 1370s, 1351w, 1318s, 1266w, 1238, 1200s, 1171, 1135s, 1120w, 1085s, 1049w, 1022w, 1000, 909, 824b, 781, 719b
(III) [a]	3247	1709, 1650 infl., 1621s	2950, 1425, 1362s, 1330w, 1276, 1208s, 1157s, 1106, 1070, 1025w, 1010, 997, 969w, 952w, 922w, 897, 883, 828b, 792, 724b
(IV) [b]	3367	1727, 1631s	1429, 1326, 1205, 1176, 1163, 1093, 1074, 1000w, 909, 833, 826, 796, 781w, 714
(V) [b]	3165	1712, 1613s	1323, 1235, 1176, 1124s, 1031, 990, 880, 820b, 790, 750w, 722b
(VIII) [a]	3226	1724, 1667 infl., 1618s	3000, 1466, 1429w, 1389s, 1359, 1323s, 1316w, 1280w, 1259w, 1250w, 1235s, 1176, 1124s, 1064, 1020, 942w, 853, 822b, 790w, 768, 754w, 723b
(IX) [a]	3226	1792, 1748 infl., 1667 infl., 1639s	3030 infl., 1493w, 1445w, 1397s, 1351s, 1282, 1235s, 1167, 1094s, 1029, 950w, 898, 866, 806, 780w, 735b, 690
(X) [b]	2353b	1736s, 1639s, 1560b	3125, 1889b, 1284s. 1240s, 1218, 1053, 990bw, 943s, 918, 881, 840w, 792w, 779s, 685b
(XIII) [a]	2571b	1724s, 1637s, 1582 infl., 1563s	3125w, 2778, 1905b, 1408s, 1351w, 1260s, 1190, 1128w, 1060, 1000bw, 940, 880s, 790w, 746w, 716s
(XI) [b]		1718s, 1647s, 1618s	3125w, 1418, 1282s, 1232w, 1099, 1058w, 981w, 938s, 901, 886w, 860, 811w, 781
(XIV) [a]		1730s, 1650s, 1626	3125w, 2941, 1439, 1400s, 1370, 1360, 1290s, 1259s, 1189s, 1164, 1121, 1068s, 1008w, 962, 936, 879s, 789, 765w, 748, 730s
(XII) [b]		1736s, 1656s, 1618	3077, 1408, 1282s, 1240, 1122w, 1100, 1020, 939s, 866, 781
(XV) [a]		1724s, 1650s, 1613, 1587w	3000, 1466, 1389, 1362, 1333, 1247s, 1190, 1174, 1136w, 1111w, 1075s, 1064w, 1021w, 986, 930, 910w, 894, 870, 786, 751, 740

w = weak, s = strong, b = broad, infl. = inflexion.

See also chelidonic acid and meconic acid (Sadtler Standard Spectra 20112 and 20113).

evidently contained the pyrone ethyl ester, as Vandewalle *et al.*, found, and our methanol–acid treatment had effected, as hoped, transesterification to the more easily crystallised higher-melting methyl ester (XIV). The p.m.r. characteristics of this were the same within experimental error as those recorded by Vandewalle *et al* for their " monomethyl enol ether." Furthermore, our results showed that their acidic product was the pyrone acid (XIII). Their p.m.r. data (on p. 368 in ref. 1) indicate that the products from their other oxalate condensations were pyrone-2-carboxylic acids and thence methyl esters: none of their data refers to acylcyclopentanetriones.

Our experiments confirmed that the oxalate condensations lead to a mixture of acylcyclopentanetrione and ethyl pyronecarboxylate as expected for mechanistic reasons, and showed that the authors of the method failed to characterise the acylcylopentanetrione products.

The Enolisation of Cyclopentanetriones.—The simple 3-acylcyclopentane-1,2,4-triones (VIII) and (IX) [5] were shown by their p.m.r. spectra to be dienolised in [^{2}H]chloroform. Each showed a low-field enol signal of intensity corresponding to two protons. There was no signal which could be attributed to a ring-proton and, equally important, the 5-methyl

groups in these compounds gave unsplit singlets (Table 3). The further analogue 3-acetyl-5-methylcyclopentane-1,2,4-trione (V) [2e] dissolved in [^{2}H]chloroform only on addition of pyridine. The possibility of measuring the intensity of the enol signal was then spoiled because of the difficulty of excluding water, but the spectrum again showed a sharp singlet from the 5-methyl group and no signal attributable to a ring proton. Hence the acylcyclopentanetrione (V) was also dienolic.

TABLE 3

Proton magnetic resonance results (for 5—10% solutions in *a* $CDCl_3$, *b* Me_2SO, *c* dioxan, containing 0·2% $SiMe_4$)

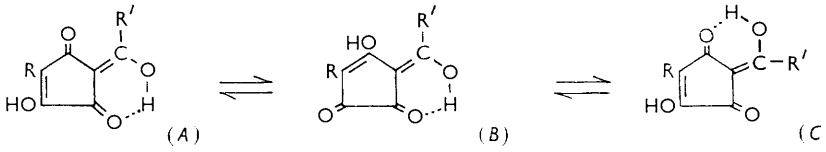
Compound	τ	Intensity, splitting * (J) (c./sec.)	Assignment
(XI)	5·98 [a]	3s	ester Me
	3·53	1dd (2·7, 6·0)	5-H
	2·90	1d (2·7)	3-H
	2·12	1d (6·0)	6-H
(XII)	8·58 [a]	3t (7·0)	Me of ester
	5·55	2q (7·0)	CH_2 of ester
	3·55	1dd (2·5, 6·0)	5-H
	2·92	1d (2·5)	3-H
	2·05	1d (6·0)	6-H
(X) †	3·53 [b]	1dd (2·5, 5·9)	5-H
	3·09	1d (2·5)	3-H
	1·74	1d (5·9)	6-H
(XVI)	8·53 [a]	6t (7·1)	Me's of ester
	5·52	4q (7·1)	CH_2's of ester
	2·87	2s	3-, 5-H's
(XIV)	8·73 [a]	3t (7·5)	Me at 6
	7·38	2q (7·5)	CH_2 at 6
	7·73	3s	3-Me
	6·02	3s	ester Me
	3·78	1s	5-H
(XV)	8·72 [a]	3t (7·5)	Me at 6
	7·38	2q (7·5)	CH_2 at 6
	8·58	3t (7·0)	Me of ester
	5·58	2q (7·0)	CH_2 of ester
	7·73	3s	3-Me
	3·78	1s	5-H
(XIII) †	8·71 [a] 8·79 [c]	3t (7·5)	Me at 6
	7·32 7·46	2q (7·5)	CH_2 at 6
	7·64 7·83	3s	3-Me
	3·53 3·83	1s	5-H
(VIII)	8·80 [a] 8·84 [c]	3t (7·5)	Me at 3
	7·25 7·30	2q (7·5)	CH_2 at 3
	8·12 8·21	3s	5-Me
	0·17	2b, 2·3 p.p.m.	OH's
(IX)	8·60 [a]	3t (7·5)	Me of ester
	5·57	2q (7·5)	CH_2 of ester
	8·05	3s	5-Me
	1·22	2b, 0·2 p.p.m.	OH's
(V)	8·13 [a] ‡	s	5-Me
	7·72	s	Me at 3
(XVII)	8·00 [a]	3t (1·0)	Me at 3
	6·98	2q (1·0)	5-H_2
	1·67	1b, 0·4 p.p.m.	OH

* s = singlet, d = doublet, t = triplet, q = quadruplet, dd = double doublet, b = broad (the total width being given in p.p.m.). † τ_{CO_2H} not given (solvents unsuitable). ‡ Trace of pyridine added (hence τOH not given).

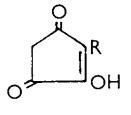
For compounds (V), (VIII), and (IX) to be dienolic, they must exist either as acyldihydroxycyclopentadienones or in the exocyclic enolic form. The former possibility seems unlikely: cyclopentadienone appears incapable of existence,[6] and moreover, neither cyclopentene-3,5-dione nor methylcyclopentene-4,5-dione are enolised (the enolic forms would

[6] Hafner and Goliasch, *Chem. Ber.*, 1961, **94**, 2909.

be hydroxycyclopentadienones).[7] Hence the second possibility is favoured and we regard the compounds (V), (VIII), and (IX) as existing in the exocyclic enolic form for which there are three tautomers (*A*), (*B*), and (*C*).



We previously concluded[4] that the fine structures of iso-(I), isoco-(II), and dehydrohumulinic acid (III) were best represented by the tautomers (*A*) and (*B*) because these compounds showed two separate low-field enol signals. If the tautomeric form (*C*) contributed to the equilibria then a third enol signal would be expected. In the simple analogues (V), (VIII), and (IX) proton exchange is more rapid so that only single enol signals are given, and it is probable that all three of the tautomeric forms are present.



(XVII : R = Me)
(XVIII : R = $[CH_2]_2 \cdot CHMe_2$)

Whilst the p.m.r. spectra unambiguously demonstrated that 3-acylcyclopentane-1,2,4-triones are dienolic, the compounds titrated in aqueous methanol with sodium hydroxide as monobasic acids (cf. refs. 2*a* and 3), presumably because the second dissociation is so weak. Table 4 lists pK_a results for isohumulinic acid (I), dehydrohumulinic acid (III), and the

TABLE 4

pK_a values (pH at half-neutralisation) for 10^{-2}M-solutions in 1 : 1 aqueous methanol at 25° by titration with 0·05N-NaOH

Comanic acid (X)	3·05	Isohumulinic acid (I)	4·77
(XIII)	3·37	Dehydrohumulinic acid (III)	3·76
(VIII)	3·83		
(IX)	3·18, 5·25 *		

* Resulting from hydrolysis of ester group.

simple acylcyclopentanetrione analogues (VIII) and (IX), as well as for the pyrone-2-carboxylic acid (XIII) and comanic acid (X) which are only slightly stronger acids.

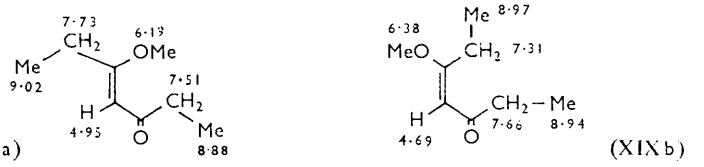
Yet another indication that cyclopentadienone tautomers play no part in the fine structures of cyclopentane-1,2,4-triones comes from the p.m.r. spectrum of 3-methylcyclopentane-1,2,4-trione (XVII) which shows that this is only monoenolised (Table 3). Also of interest is the fact that the enolisation involves only the two oxygen functions which flank the 3-methyl substituent. A similar observation was made for 3-(3-methylbutyl)-cyclopentane-1,2,4-trione (XVIII).[8] The p.m.r. spectrum of the 3-methyl-trione (XVII) shows a two-proton signal at τ 6·98 from the 5-methylene group and no other signal which could be attributed to a ring-proton. The methylene signal is split as a 1 : 3 : 3 : 1-quadruplet and the signal from the 3-methyl group as a 1 : 2 : 1-triplet, with $J = 1{\cdot}0$ c./sec. No observable effect on the splitting followed addition of an excess of trifluoroacetic acid. (expected to catalyse prototropy). Addition of an excess of triethylamine (expected to yield a mesomeric anion) caused only a slight increase in the coupling to 1·1 c./sec. It

[7] De Puy and Zaweski, *J. Amer. Chem. Soc.*, 1959, **81**, 4920; Gutowsky, Karplus, and Grant, *J. Chem. Phys.*, 1959, **31**, 1278; De Puy, Lyons, and Rodewald, *J. Amer. Chem. Soc.*, 1965, in the press.
[8] Burton, Elvidge, and Stevens, *J.*, 1965, 1276.

seems therefore most likely that the compound (XVII) undergoes very rapid tautomerism in solution, (*D*) $\rightleftharpoons$ (*E*), and is best regarded as not having a single fixed-bond structure (such as *D*) because otherwise protonation and anion-formation should alter $J_{2\text{-Me},5H}$, significantly.

Isomerism of the Heptane-3,5-dione Enol Ether (XIX).—We confirmed that the preparation of this ether (XIX) from methanolic heptane-3,5-dione and diazomethane yielded a mixture of geometrical isomers.[9] Eistert *et al.*[9] suggested that the higher-boiling form (b. p. 84—86°/10 mm.) was the *cis*-enol ether: it reverted in a few hours to a lower-boiling *trans*-enol ether (b. p. 58—59°/10 mm.). The p.m.r. spectra confirmed this conclusion. When the resonance lines were assigned to the two geometrical isomers in the various possible ways, it was found that only the assignments shown in (XIXa) and (XIXb) were fully self-consistent irrespective of whether s-*cis*- or s-*trans*-forms were employed. The higher-boiling isomer had the lower methoxyl chemical shift and the higher-field olefinic proton and so this must be the *trans*-olefin, *i.e.*, the *cis*-enol ether (XIXa). Within 3 hr. at room temperature in carbon tetrachloride solution, inversion to the stable isomer was

$\tau(CCl_4)$



(Each ethyl group shows J = 7·5 c./sec.)

complete. This had the higher methoxyl chemical shift and the lower-field olefinic proton and so must be the *cis*-olefin (XIXb). The *cis*-olefin is the more stable form, presumably because resonance is facilitated by the all-*trans* arrangement of the bonds between the two oxygen atoms.

Experimental

5-Methyl-3-propionylcyclopentane-1,2,4-trione (VIII).—(1) *Acylation of 3-methylcyclopentane-1,2,4-trione.* The trione [5] (1·08 g.) was suspended in propionic anhydride (10 ml.) and rapidly saturated with boron trifluoride. A slow stream of gas was then passed for a further 2 hr. The mixture was evaporated under reduced pressure and ethanol added, and the process repeated (3 ×) to give a crystalline residue. Filtration with the aid of methanol–water (4 : 1) afforded the *trione* (VIII) m. p. 190—193° (0·42 g.) (Found: C, 58·9; H, 5·4. $C_9H_{10}O_4$ requires C, 59·3; H, 5·5%; *M* 182). The mother-liquors afforded a further crop of trione (VIII) (0·1 g.; total yield 33%) and then by sublimation at 200°/0·5 mm. a small amount of starting material was recovered.

(2) *Condensation of ethyl oxalate with 5-methoxyhept-4-en-3-one* (XIX). (*a*) Ethyl oxalate (10·3 g.) interacted with the *trans*-enol ether (*cis*-olefin) (10 g.) and potassium ethoxide (from 5·46 g. of metal) in 3 : 1 ether–ethanol (40 ml.) under nitrogen for 2 days. Water (100 ml.) was added, followed by an excess of hydrochloric acid. Repeated extraction of the mixture with chloroform (50 ml. portions) and evaporation of the extracts afforded a partly crystalline viscous residue. Filtration was facilitated by addition of dry ether, and the solid was washed with a minimum of ether. The yellow product (0·47 g.) had m. p. 191° and mixed m. p. 192° with 5-methyl-3-propionylcyclopentane-1,2,4-trione. Dilution of the filtrate with ether (150 ml.) precipitated an amorphous solid (0·61 g.; softened from 160°) which was rejected.

[9] Eistert, Arndt, Loewe, and Ayça, *Chem. Ber.*, 1951, **84**, 156.

Evaporation of the filtrate gave a partly crystalline syrup from which, by treatment with ether as before, solid was collected: repetitions gave 0·36 g. of the acylcyclopentanetrione, m. p. 187—192°. Attempted distillation of the residue at up to 200°/0·5 mm. afforded a sublimate of the yellow acylcyclopentanetrione (0·605 g.), m. p. 193°; the remaining material decomposed and polymerised.

(*b*) Ethyl oxalate (10·3 g.) in benzene (10 ml.) was run into a dispersion of sodium hydride (3·38 g.) in benzene (20 ml.), stirred under nitrogen, and then the *cis*-enol ether (*trans*-olefin) (10 g.; b. p. 108—112°/25 mm., n_D^{22} 1·4726) in benzene (20 ml.) was slowly added. After 3 hr. (with cooling when needed), acetic acid (6 ml.) was added. The mixture was shaken with water (100 ml.) and the benzene separated and evaporated to give a dark reddish oil *X* (5 g.). The aqueous layer was acidified (to Thymol Blue) with hydrochloric acid and repeatedly extracted with chloroform (50 ml. portions), evaporation of which gave a partly crystalline syrup. Treatment with ether, evaporation of the filtrates, and repetition of these operations, several times afforded yellow 5-methyl-3-propionylcyclopentane-1,2,4-trione (0·65 g.), m. p. 174—177°, raised to 195° (with sublimation) by crystallisations from methanol (charcoal) and methanol–water [Found: C, 59·6; H, 5·8%; *M* (ebullioscopic in acetone), 176].

After this compound (100 mg.) had been kept for 48 hr. in methanol (10 ml.) containing concentrated hydrochloric acid (3 ml.), it was recovered by evaporation (95 mg.), m. p. and mixed m. p. 194—195°.

The oil *X* (above) was dissolved in methanol (80 c.c.) and concentrated hydrochloric acid (10 c.c.) added. After 4 days, yellow 5-methyl-3-propionylcyclopentane-1,2,4-trione (0·56 g.) was collected, and the filtrate evaporated under reduced pressure to give a mainly crystalline residue. By addition of light petroleum (b. p. 60—80°) containing ether, gum was removed and the solid was then collected (2·15 g.), m. p. 75—80°. Crystallisations from light petroleum (b. p. 60—80°) gave *methyl 6-ethyl-4-pyrone-2-carboxylate* (XIV) as needles, m. p. 86—87° [Found: C, 61·0; H, 6·1%; *M* (ebullioscopic in benzene), 199. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·2%; *M*, 196].

Hydrolysis of the Ester (XIV) *to the Pyrone Acid, and Re-esterification.*—The pyrone methyl ester (XIV) (1 g.) was refluxed with 4N-hydrochloric acid (15 ml.) for 20 min., the solution was cooled in ice, and the product collected. From dioxan–light petroleum (b. p. 60—80°), the *6-ethyl-3-methyl-4-pyrone-2-carboxylic acid* (XIII) (0·95 g.) crystallised as prismatic needles, m. p. 199° [Found: C, 59·6; H, 5·6%; *M* (ebullioscopic in methanol), 188; equiv. by titration, 178. $C_9H_{10}O_4$ requires C, 59·3; H, 5·5%; *M* and equiv., 182].

The acid in ethanol was treated with an excess of ethereal diazoethane for 1 hr. Evaporation under reduced pressure and crystallisation from light petroleum (b. p. 40—60°) gave ethyl 6-ethyl-3-methyl-4-pyrone-2-carboxylate (XV) as needles, m. p. 60—61° (lit.,[1] m. p. 59·5—61°) (Found: C, 62·5; H, 6·6. Calc. for $C_{11}H_{14}O_4$: C, 62·8; H, 6·7%).

Similarly the acid in methanol with ethereal diazomethane reafforded the methyl ester, m. p. and mixed m. p. 85—87°.

Methyl Comanate.—Comanic acid suspended in methanol passed into solution on addition of ethereal diazomethane (effervescence). Evaporation, and crystallisation from carbon tetrachloride gave *methyl comanate*, m. p. 90° (Found: C, 54·2; H, 3·8. $C_7H_6O_4$ requires C, 54·55; H, 3·9%).

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(J. A. E.) Chemistry Department, Imperial College of Science and Technology, South Kensington, London S.W.7.
(R. S.) Brewing Industry Research Foundation, Nutfield, Surrey.

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