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FURAN TETRACARBOXYLIC ACID

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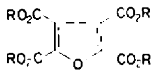
Abstract—Furan tetracarboxylic acid is a surprisingly strong acid. It forms well defined salts with a variety of bases. Its structure, and that of an intermediate in its preparation, is discussed in relation to its ultra-violet and infra-red spectra.

DURING the course of another investigation in which furan tetracarboxylic acid (F.T.C.A., I; R = H) was required as an intermediate, we were attracted to the properties of this acid. It may conveniently be prepared[1–4] by the bromination of ethyl sodiooxaloacetate to give a tetracarboxylic ester variously described as II,[1] III,[2] and IV,[4] followed by treatment of the tetraester with sulphuric acid to give I (R = Et). Of these structures IV is to be preferred since the tetraester gives no ferric reaction, but it shows strong hydroxyl absorption at 3500 cm^{-1} in the infra-red. Again, the tetraester shows strong absorption at 1775 and 1765 cm^{-1} which may be attributed to unconjugated ester groups, 1704 cm^{-1} arising from a conjugated ester and a fairly strong maximum at 1650 cm^{-1}. The intensity of the latter maximum is characteristic[5] of the C=C—O group. Thus dihydropyran shows a strong maximum at 1650 cm^{1}, and compound V[5] shows a strong maximum at 1627 cm^{-1} attributable to the C=C—O group. Furthermore the tetraester absorbs maximally at 2470 Å, log ε 3·86 in good agreement with the maximum absorption of V at 2480 Å, log ε 4·1.

However the tetraester does not absorb bromine and only decolourizes permanganate slowly. These may be characteristics of the unsaturated system in IV, although maleic ester reacts instantaneously with permanganate. Furthermore a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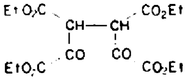
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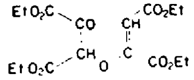
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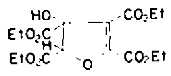
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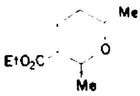
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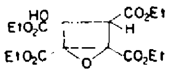
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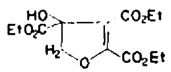
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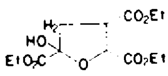
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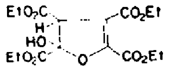
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[1] H. Sutter, *Liebigs Ann.* **499**, 56 (1932).
[2] T. Reichstein, A. Grussner, K. Schindler and E. Hardmeyer, *Helv. Chim. Acta* **16**, 276 (1933).
[3] H. Gilman, H. J. Oatfield and W. H. Kirkpatrick, *Proc. Iowa Acad. Sci.* **40**, 113 (1933).
[4] A. P. Dunlop and C. D. Hurd, *J. Org. Chem.* **15**, 1160 (1950).
[5] F. E. Bader, *Helv. Chim. Acta* **36**, 215 (1953).

compound of structure IV might be expected to be more unstable than is the case in view of its β-hydroxyester structure and the stability of the furan system. We therefore suggest that structure VI should not be overlooked pending the completion of further work.

A structure analogous to IV namely VII is preferred[cf.6] for the tricarboxylic ester (which shows similar infra-red characteristics to IV) formed by the condensation of ethyl bromopyruvate and ethyl sodio-oxaloacetate. The conversion of the tricarboxylic ester to triethyl furan-2:3:4-tricarboxylate with sulphuric acid eliminates the alternative structure VIII. The structure IX for the tetraester discussed above can by analogy be reasonably eliminated.

Hydrolysis of I(R = Et) to I(R = H) is usually performed[2] with hydrochloric acid. We used alcoholic potash for this purpose and after acidification of the alkaline solution a crystalline monopotassium salt of F.T.C.A. was obtained instead of the expected acid. The salt is not very soluble (14·54 g/l. at 18°) in cold water, and it may be crystallized from hot water. It may be crystallized unchanged from concentrated hydrochloric acid or 50 per cent sulphuric acid, but it is decomposed by 20 per cent perchloric acid. F.T.C.A. may however be quantitatively recovered from the monopotassium salt on passage in aqueous solution, or better in a solution of sodium carbonate, through a column of Zeo–Karb 225 ion exchange resin.

F.T.C.A. is a strong acid (see below) and it forms a series of well defined mono salts, which are stable to hydrochloric acid, with a variety of bases. The acid itself is very soluble in water, but it may conveniently be recrystallized from concentrated hydrochloric acid, in which it is largely unionised.

The apparent dissociation constants (pK) of F.T.C.A. were determined by the potentiometric method, the pH changes being followed by means of a Radiometer pH meter 23 using a type G 202 B glass electrode and a saturated potassium chloride–calomel electrode. Dissociation constants were measured only at one concentration of F.T.C.A., but change of concentration is not likely seriously to affect their order of magnitude. Table 1 summarizes the dissociation constants of F.T.C.A. and a number of analogous acids

Table 1

Acid	K_1	K_2	K_3	K_4	K_5	K_6
F.T.C.A.	$4{\cdot}2 \times 10^{-1}$ (p$K_1 = 1{\cdot}37$	$8{\cdot}0 \times 10^{-2}$ (p$K_2 = 2{\cdot}1$	$1{\cdot}86 \times 10^{-3}$ (p$K_3 = 3{\cdot}73$	$1{\cdot}96 \times 10^{-7}$ (p$K_4 = 7{\cdot}7$		
Phthalic[7]	$1{\cdot}05 \times 10^{-3}$	$5{\cdot}2 \times 10^{-6}$				
Pyromellitic[7]	$1{\cdot}2 \times 10^{-2}$	$1{\cdot}34 \times 10^{-3}$	$3{\cdot}2 \times 10^{-5}$	$2{\cdot}35 \times 10^{-6}$		
Prehitnic[7]	$4{\cdot}2 \times 10^{-3}$	$3{\cdot}1 \times 10^{-4}$	$3{\cdot}6 \times 10^{-5}$	$1{\cdot}55 \times 10^{-6}$		
Mellophanic[7] (112:3:4)	$8{\cdot}8 \times 10^{-3}$	$5{\cdot}6 \times 10^{-4}$	$1{\cdot}87 \times 10^{-5}$	$6{\cdot}1 \times 10^{-7}$		
pentacarboxylic[7]	$1{\cdot}6 \times 10^{-2}$	$1{\cdot}85 \times 10^{-3}$	$1{\cdot}08 \times 10^{-4}$	$5{\cdot}6 \times 10^{-6}$	$3{\cdot}5 \times 10^{-7}$	
Mellitic[7]	$4{\cdot}0 \times 10^{-2}$	$6{\cdot}4 \times 10^{-3}$	$4{\cdot}9 \times 10^{-4}$	$1{\cdot}65 \times 10^{-5}$	$1{\cdot}28 \times 10^{-6}$	$1{\cdot}1 \times 10^{-7}$
Maleic[8]	$1{\cdot}2 \times 10^{-2}$	$6{\cdot}0 \times 10^{-7}$				

Concentration of F.T.C.A. = 0·001 M N/5 NaOH used as titrant

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[6] E. C. Kornfield and R. G. Jones, *J. Org. Chem.* **19**, 16 (1954).

[7] W. R. Maxwell and J. R. Partington, *Trans. Faraday Soc.* **33**, 670 (1937).

[8] W. L. German, G. H. Jeffery and A. I. Vogel, *Phil. Mag.* **22**, 790 (1936).

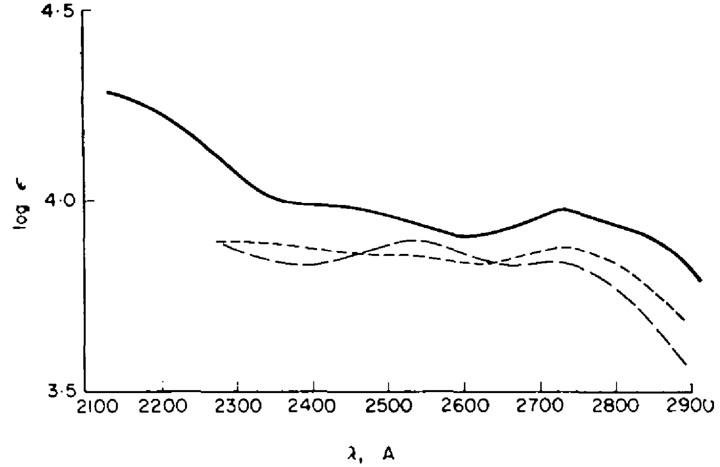

FIG. 1. Ultra-violet light absorption of F.T.C.A. in water.
- - - 0·00012 mole/l; λ_{max} 2520 Å. log ε 3·90 inflex. 2720 Å
. . . . . 0·000037 mole/l; λ_{max} 2720 Å. log ε 3·87
——— 0.000012 mole/l; λ_{max} 2720 Å. log ε 3·97

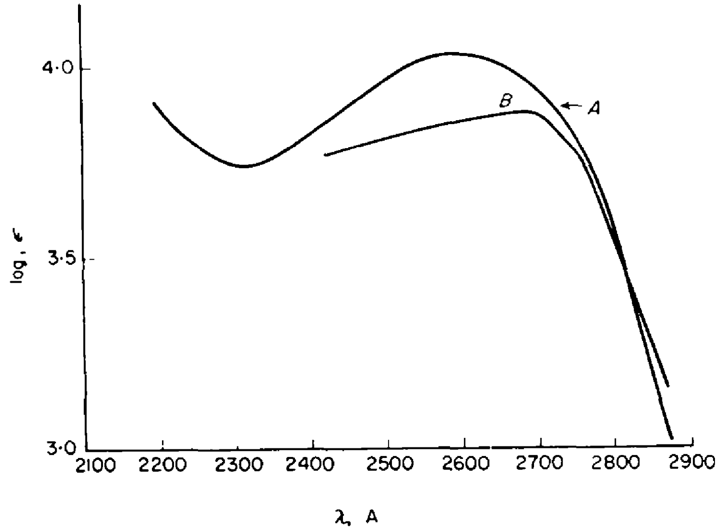

FIG. 2. Ultra-violet light absorption of F.T.C. A.
A—In N HCl λ_{max} 2590 Å log ε 4·03.
B—In MeOH λ_{max} 2700 Å log ε 3·89.

It is clear from the above data that F.T.C.A. is ten times as strong as mellitic acid and considerably stronger than maleic acid. F.T.C.A. is in fact comparable in strength with dichloroacetic acid (p*K* 1·29).[9]

As is only to be expected aqueous solutions of F.T.C.A. do not obey Beer's law. The values of p*K* given above indicate that three of the carboxyl groups are completely ionized at pH 7. Figs. 1 and 2 show the ultra-violet spectrum of the acid and its tetramethyl ester under various conditions. With change in concentration the acid

[9] L. F. Fieser and M. Fieser, *Organic Chemistry* (3rd Ed.) p. 163. Reinhold, New York (1956).

shows the development and suppression of peaks at about 2520 and 2720 Å as is only to be expected with change in the ionic species present. The tetramethyl ester shows a single maximum at 2590 Å. Dissolved in N-hydrochloric acid, in which one carboxyl alone is ionized to a slight extent and the others unionized, F.T.C.A. shows a single maximum at 2590 Å, and in aqueous solution at a concentration of 0·00012 mole/l. the acid shows two maxima, one at 2520 Å. The maximum in the 2520 to 2590 Å range can only be attributed to a largely unionized species. At all concentrations of F.T.C.A. used and in methanol, F.T.C.A. shows a maximum at 2700–2720 Å which we attribute to an ionised form.

The spectra of other furan carboxylic acids warrant comparison. Furan 2-carboxylic acid in water absorbs[10] maximally at 2450 and 2150 Å. In ethanol[11] the longer wavelength absorption occurs at 2480 Å whilst in hexane in which the acid is is unionized this band occurs at 2580 Å. Furan 2:5-dicarboxylic acid in aqueous solution absorbs[11] at 2625, (2370), and 1920 Å. Thus in water there is a bathochromic effect of about 175 Å in passing from the mono to the dicarboxylic acid. A further bathochromic shift of about 220 Å takes place in passing from the latter to the tetracarboxylic acid. This information is summarised in Table 2.

TABLE 2. ULTRA-VIOLET SPECTRA OF FURAN CARBOXYLIC ACIDS AND DERIVATIVES

	λ_{max} (Å) in H_2O	λ_{max} (Å) in EtOH	λ_{max} (Å) in hexane	λ_{max} (Å) in N HCl
Furan 2-carboxylic acid	2450, 2150	2480	2580	
Furan 2,5-dicarboxylic acid	2625, (2370), 1920			
Furan 2,3,4,5-tetra-carboxylic acid	2520, 2720	2720[a]		2590
Tetraethyl furan-2,3,4,5-tetracarboxylate		2590		

[a] Measured in MeOH

In the infra-red F.T.C.A. shows (in paraffin) a different spectrum from its mono potassium salt. The acid shows only weak absorption at 3500 cm^{-1} but strong absorption at 2466 cm^{-1} and 2375 cm^{-1} and medium strong absorption at 1887 cm^{-1}. Considerable hydrogen bonding is thus indicated. Strong maxima at 1694 and 1643 cm^{-1} shown by the acid may be assigned to hydrogen bonded carboxyl, whilst strong bands at 1606 and 1515 cm^{-1} may be attributed to aromatic type unsaturation.

In contrast to the acid, the mono potassium salt shows stronger absorption at 3570 cm^{-1}. Maleic acid and its mono potassium salt behave similarly.[12] However the potassium salt of F.T.C.A. shows some absorption at 2300 cm^{-1} not displayed by potassium hydrogen maleate. Hydrogen bonding of a type different from that shown by the latter is therefore present in the former. The potassium salt of F.T.C.A. shows strong absorption at 1734 and 1720 cm^{-1} absent from F.T.C.A. and potassium

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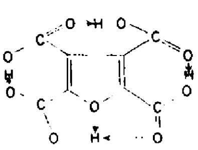
[10] G. Mackinney and O. Temmer, *J. Amer. Chem. Soc.* **70**, 3586 (1948).
[11] K. W. Hausser, R. Kuhn, A. Smakula, and A. Deutsch, *Z. Phys. Chem.* **29**, 378 (1935B).
[12] H. M. E. Cardwell, J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.* 3740 (1953).

hydrogen maleate, which must be attributed to carboxyl. Other strong bands shown by the potassium salt of F.T.C.A. are at 1575 cm^{-1} (CO_2^-) and at 1556 and 1534 cm^{-1} in the region of absorption by aromatic type unsaturation.

The tetramethyl ester of F.T.C.A. when examined in paraffin shows strong bands at 1766, 1747 and 1728 cm^{-1} and a weaker band at 1759 cm^{-1}. These bands can only be attributed to the methoxycarbonyl groups. A fairly strong band at 1612 cm^{-1} indicates aromatic type unsaturation, but this band is less intense than the corresponding band in F.T.C.A. The displacement of this band from around 1610 cm^{-1} in ester and acid to 1556 cm^{-1} in the salt has some significance not obvious to us at present.

The considerable hydrogen bonding shown by F.T.C.A. can be best accommodated in the symmetrical structure X but models show that the distance shown by the broken arrow is too great for hydrogen bond formation. All the other hydrogen bonds are capable of formation. F.T.C.A. may therefore exist as XI. Whilst it is very likely that the carboxyl group in the 2-position is the strongest of the four and therefore will initially form the anion we feel that the most likely structure for the potassium salt is XII incorporating the suggestion of Cardwell *et al.*[12] Besides being the most symmetrical form XII has two "exposed" carbonyl groups which may be responsible for the bands shown by the potassium salt in the infra-red at 1734 and 1720 cm^{-1}. Full elucidation of fine structure of the acid and salt will however have to await their X-ray examination.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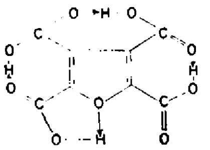
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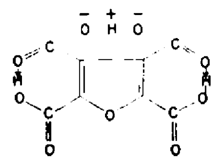
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EXPERIMENTAL

Salts of furan tetracarboxylic acid. A mixture of molar quantities of the acid and the base was heated with sufficient water to effect solution at 100°. The solution was cooled and the salt was deposited. It was collected, washed with ice-cold water and dried. Alternatively, water insoluble bases were dissolved in a minimum of conc HCl, a molar quantity of furan tetracarboxylic acid was added, the mixture was heated to 100°, and water was added at this temp until solution was effected. In all cases except that of the dimethylformamide salt the mono salt was formed whether the reaction was carried out either in presence or absence of HCl. With dimethylformamide the mono salt was obtained when HCl was present, and a di salt when mineral acid was absent.

Potassium salt. Ethyl furan tetracarboxylate (I; R = Et)(10 g) was refluxed for 1 hr with a solution of potassium hydroxide (70 g) in water (200 cc). The solution was filtered and acidified to congo red with HCl. On cooling the hydrated mono potassium salt was deposited (8·5 g; 95%). Crystallization from water gave long needles, m.p. 261° (dec) (Found, without drying to constant weight, C, 30·5; H, 2·9. E, 103. $C_8H_3O_9K$. $2H_2O$ requires: C, 30·2; H, 2·2% E, 106. Found after drying at 160° in a vacuum C, 33·4; H, 1·0; K, 13·8. $C_8H_3O_9K$ requires: C, 34·0; H, 1·1; K, 13·8%).

Furan tetracarboxylic acid. The potassium salt (4 g) was dissolved with 3 g sodium carbonate in water (100 cc) and passed through a column of Zeo-Karb 225 which was then washed with water. Concentration of the eluate in a vacuum gave furan tetracarboxylic acid (3.1 g), m.p. 235° (dec), which on crystallization gave the acid as rhombs, m.p. 248° (dec).[3]

TABLE 3. SALTS OF FURAN TETRACARBOXYLIC ACID

Base	M.p. and crystalline form of salt		
Rb	275° (dec)	needles (H_2O)	C, 28·2; H, 1·0. $C_8H_3O_9Rb\frac{1}{2}H_2O$ requires: C, 28·4; H, 1·2%
$MeNH_2$	237–238°	needles ($MeOH/H_2O$)	C, 38·9; H, 3·6. $C_9H_9O_9N$ requires: C, 39·3; H, 3·3%
$EtNH_2$	203–204°	needles (MeOH)	C, 41·3; H, 3·8; N, 5·1. $C_{10}H_{11}O_9N$ requires: C, 41·5; H, 3·8; N, 4·8%
$NH_2(CH_2)_2NH_2$	262° (dec)[a]	rhombs (H_2O)	C, 39·7; H, 3·3; N, 5·2. $C_{18}H_{16}O_{18}N_2$ requires: C, 39·4; H, 2·9; N, 5·1%
NH_2NH_2	212° (dec)	needles ($MeOH/H_2O$)	C, 31·5, 31·8; H, 3·7, 3·7. $C_8H_8O_9N_2$ $1\frac{1}{2}$ H_2O requires: C, 31·7; H, 3·6%
$NH_2NHCONH_2$	200–201° (dec)	needles (H_2O)	C, 33·4; H, 2·9. $C_9H_9O_{10}N_3$ requires: C, 33·9; H, 2·8%
NH_2CONH_2	170°	needles (MeOH)	C, 32·8; H, 3·1. $C_9H_8O_{10}N_2$ $1\frac{1}{2}$ H_2O requires: C, 32·7; H, 3·3%
$HCONMe_2$	251° (dec)[b]	prisms ($MeOH/H_2O$)	C, 41·8; H, 3·9. $C_{11}H_{11}O_{10}N$ requires; C, 41·6; H, 3·5%
	190–191°[c]	needles (EtOH)	C, 43·1; H, 4·6. $C_{14}H_{18}O_{11}N_2$ requires: C, 43·1; H, 4·6%
Piperidine	196–197°	needles (MeOH)	C, 47·8; H, 4·7. $C_{13}H_{15}O_9N$ requires: C, 47·4; H, 4·6%
Pyridine	250° (dec)	needles ($MeOH/H_2O$)	C, 47·4; H, 2·7. $C_{13}H_9O_9N$ $\frac{1}{2}$ H_2O requires; C, 47·0; H, 3·0%
Quinoline	207–208°	needles (C_6H_6)	C, 54·3; H, 3·2. $C_{17}H_{11}O_9N$ requires; C, 54·7; H, 3·0%
$C_6H_5NH_3$	171° (dec)	prisms (H_2O)	C, 50·5; H, 3·6. $C_{14}H_{11}O_9N$ requires: C, 49·9; H, 3·3%
C_6H_5NHMe	216°	rhombs ($MeOH/H_2O$)	C, 51·6; H, 4·0. $C_{15}H_{13}O_9N$ requires: C, 51·3; H, 3·7%
$pMeC_6H_4NH_2$	187° (dec), loses H_2O at 150°	needles (H_2O)	C, 49·6; H, 4·5. $C_{15}H_{13}O_9NH_2O$ requires: C, 48·9; H, 4·0%

[a] refers to a bis salt of $NH_2(CH_2NH_{22})$
[b] refers to a mono $HCONMe_2$ salt
[c] refers to a di $HCONMe_2$ salt
All salts were dried on the water bath at about 90°

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