83. *Physical Properties and Chemical Constitution. Part I. Esters of Normal Dibasic Acids and of Substituted Malonic Acids.*

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THE objects of this series of investigations are to obtain accurate values of certain physical properties (densities, refractive indices, molecular dispersions, surface tensions, dipole moments, viscosities, and heats of combustion) of a variety of highly purified organic compounds with a view to test known relationships between these properties and chemical constitution and to deduce new ones. Such a reinvestigation is all the more necessary in that many physical data in the literature have been obtained with compounds for which no criteria of purity are given.

Measurements of the refractive indices, $n_C^{20°}$, $n_D^{20°}$, $n_F^{20°}$, $n_{G'}^{20°}$, and of the density and surface tension over a range of temperature of a homologous series of methyl and ethyl esters of normal dibasic acids, and of the methyl esters of substituted malonic acids, are now recorded. All the esters were prepared from the pure acids of definite and sharp m. p. Karvonen (*Acad. Sci. Fennicae*, 1918, **10A**, No. 5, 1) carried out a series of careful measurements of the refractive indices and of $d_{4°}^{20°}$ for the esters of the normal dibasic acids, which are in good agreement with the present results, but apart from this work and from certain isolated determinations [molecular refractivities of methyl dimethyl- and diethyl-malonates (von Auwers, *Ber.*, 1913, **46**, 511; compare Smyth and Walls, *J. Amer. Chem. Soc.*, 1931, **53**, 529) and parachors of methyl malonate, ethyl malonate, succinate, and sebacate (see *Rep. Brit. Assoc.*, 1932, 264, which contains a complete bibliography)], no systematic attempt to investigate the physical properties of these three series of compounds appears to have been made.

Whilst the present work was in progress, Beck, Macbeth, and Pennycuick (J., 1932, 2258) determined the parachors *inter alia* of methyl (282·5) and ethyl malonate (360·4), methyl dimethyl- (354·0), ethyl- (364·2), and *n*-propyl-malonates (393·3). Surface tensions were determined by the maximum bubble-pressure method (Sugden, J., 1922, **121**, 858; 1924, **125**, 27), and the densities in " pycnometers of different capacities " at 30° for methyl and ethyl malonates, but no details of temperature, surface tension, or density are given for the substituted malonates. In the absence of criteria of purity of the esters, there is little to be gained in discussing the measurements, but the parachor values are given in parentheses for comparison with those deduced in the present paper.

The results for the methyl and ethyl esters of the normal dibasic acids are summarised in Tables I and II. Table I contains the molecular refractivities for the C, D, F, and G′ lines at 20°; the mean differences for CH_2 in the two series are in sufficiently close agreement with the widely employed constants of Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 585; 1912, **79**, 129), *viz.*, H_C 4·598, Na_D 4·618, H_F 4·668, $H_{G'}$, 4·710, to justify the use of the latter

TABLE I.

Substance.	$[R_L]_C$.	Δ.	$[R_L]_D$.	Δ.	$[R_L]_F$.	Δ.	$[R_L]_{G'}$.	Δ.
Methyl malonate ...	28·49		28·62		28·92		29·19	
,, succinate ...	32·86	4·37	33·01	4·39	33·35	4·43	33·64	4·45
,, glutarate......	37·27	4·41	37·43	4·42	37·83	4·48	38·16	4·52
,, adipate	41·99	4·72	42·18	4·75	42·61	4·78	42·98	4·82
,, pimelate ...	46·66	4·67	46·87	4·69	47·37	4·76	47·72	4·74
,, suberate......	51·32	4·66	51·55	4·68	52·10	4·73	52·56	4·84
,, azelate	55·90	4·58	56·14	4·59	56·72	4·62	57·24	4·68
	Mean	4·57		4·59		4·63		4·675
Ethyl malonate	37·72		37·89		38·30		38·62	
,, succinate	42·16	4·44	42·35	4·46	42·80	4·50	43·18	4·56
,, glutarate	46·73	4·57	46·93	4·58	47·43	4·63	47·83	4·65
,, adipate.........	51·28	4·55	51·51	4·58	52·05	4·62	52·50	4·67
,, pimelate	55·97	4·69	56·23	4·72	56·80	4·75	57·30	4·80
,, suberate	60·64	4·67	60·93	4·70	61·56	4·76	62·08	4·78
,, sebacate	69·89	2×4·63	70·18	2×4·63	70·93	2×4·69	71·52	2×4·72
	Mean	4·59		4·61		4·66		4·70

figures, for the present, in the computation of molecular refractivities. Swarts (*J. Chim. physique*, 1923, **20**, 33) found H_C 4·618, H_F 4·688, and $H_{G'}$, 4·725 at 20°, as deduced by temperature correction of determinations at 79·5°, and Mercks, Verhulst, and Bruylants (*Bull. Soc. chim. Belg.*, 1933, **42**, 177) found H_C 4·615, Na_D 4·632, H_F 4·685, and $H_{G'}$ 4·721 at 15°. Table II contains the values of the molecular refraction coefficients, $Mn_D^{20°}$ (Eisenlohr, *Fortschr. Chem.*, 1925, **18**, *B*, Heft 9), the parachors, and the dispersions $[R_L]_{F-C}$ and $[R_L]_{G'-C}$. The mean value for CH_2 of $Mn_D^{20°}$ is 20·63. Eisenlohr (*loc. cit.*) gives 20·56 and his constants will therefore be retained pending the accumulation of further data. The mean increment for CH_2 in the parachor is 40·3, which is appreciably higher than that (39·0) employed by Sugden (J., 1924, **125**, 1180; "The Parachor and Valency," 1929, 34; *Rapports Institut Internat. Chim. Solvay*, 1931, **4**, 296) as a basis for his calculations of atomic and structural parachors. Mumford and Phillips (J., 1929, 2112) have pointed out that Sugden's low value may be partly due to his use of CH_2 differences derived from both normal and branched-chain compounds and suggest that a more probable value, based largely on Hunten and Maass's surface-tension determinations on a series of fatty acids (*J. Amer. Chem. Soc.*, 1929, **51**, 153), is 40 units. On this basis they have recalculated the atomic and structural parachor constants and have also introduced new "strain constants." Their values, although more accurate than those of Sugden, will doubtless require slight modification, but this will be discussed as trustworthy data accumulate in subsequent papers of this series.

Table II.

Substance.	$Mn_D^{20°}$.	Δ.	Parachor.	Δ.	$[R_L]_{F-C}$.	$[R_L]_{G'-C}$.
Methyl malonate	186·71		283·0		0·43	0·70
,, succinate	207·39	20·58	321·3	38·3	0·49	0·78
,, glutarate	228·01	20·62	361·4	40·1	0·56	0·89
,, adipate	248·70	20·69	401·8	40·4	0·62	0·99
,, pimelate	269·16	20·46	443·3	41·5	0·71	1·06
,, suberate	289·73	20·57	484·4	41·1	0·78	1·24
,, azelate	310·43	20·70	524·6	40·2	0·82	1·34
	Mean	20·60		40·3		
Ethyl malonate	226·37		361·5		0·58	0·90
,, succinate	247·19	20·82	400·0	38·5	0·64	1·02
,, glutarate	267·89	20·70	439·6	39·6	0·70	1·10
,, adipate	288·58	20·69	480·2	40·6	0·77	1·22
,, pimelate	309·08	20·50	520·5	40·3	0·83	1·33
, suberate	329·71	20·63	562·8	42·3	0·92	1·44
,, sebacate	370·94	2 × 20·62	643·8	2 × 40·5	1·04	1·63
	Mean	20·66		40·3		

Hennant-Roland and Lek (*Bull. Soc. chim. Belg.*, 1931, **40**, 177; Lek, Diss., Bruxelles, 1930) have carried out measurements on a series of homologous *n*-alkyl bromides, iodides, and chlorides from which the parachors have been calculated (*Rep. Brit. Assoc.*, *loc. cit.*). Their results are collected in Table III. The mean difference for CH_2 is greater than 39·0 and the figures support the view that Sugden's original value is too low.

Table III.

	Bromides.		Iodides.		Chlorides.	
	P.	Δ.	*P*.	Δ.	*P*.	Δ.
C_2H_5X	165·7		187·0		151·6	
C_3H_7X	205·3	39·6	226·0	39·0	187·0	36·0
C_4H_9X	243·5	38·2	264·7	38·7	230·5	42·5
$C_5H_{11}X$	283·6	40·1	—	2 × 39·7		
$C_6H_{13}X$	322·8	39·2	344·1			
$C_7H_{15}X$	363·0	40·2	384·5	40·4		
$C_8H_{17}X$	402·4	39·4				

The atomic parachor for hydrogen calculated from the most authoritative values for the normal hydrocarbons is 14·4 (Table IV); the corresponding value for carbon is therefore 11·5. The figures for the last three hydrocarbons have been added for purposes of comparison and indicate clearly that the constants apply to compounds of high molecular weight. These constants differ considerably from the values H = 17·1 and C = 4·8 originally calculated by Sugden (*loc. cit.*). It should, however, be pointed out that the new values of the atomic parachors based on CH_2 = 40·3 are regarded as preliminary and will be considered again when the investigation of other homologous series has been completed. The atomic parachor for carbon is very sensitive to small differences in the CH_2 value and further independent determinations are therefore necessary.

TABLE IV.

Deduction of Atomic Parachor of Hydrogen.

Compound.	Observers.	*P*, obs.	$n \times CH_2$.	2 H.
C_2H_6	M. and W. (1, 2)	110·5	80·6	29·9
C_3H_8	M. and W. (1, 2)	150·8	120·9	29·9
n-C_4H_{10}	C. and M. (2)	190·3	161·2	29·1
n-C_6H_{14}	H.-R. and L. (3)	270·4	241·8	28·6
n-C_7H_{16}	E. and C. (2)	310·8	282·1	28·7
n-C_8H_{18}	H.-R. and L. (3)	351·0	322·4	28·6
n-$C_{10}H_{22}$	H.-R. and L. (3)	429·7	403·0	26·7
			Mean	28·8
n-$C_{26}H_{54}$	S. and K. (2, 3)	1082	1048	24
n-$C_{32}H_{66}$	H. and M. (2, 3)	1322	1290	32
n-$H_{60}H_{122}$	S. and K. (2, 3)	2480	2418	62

The initials give the reference to the observers, and the number in parentheses that of the parachor calculation.

M. and W., Maass and Wright, *J. Amer. Chem. Soc.*, 1921, **43**, 1098; C. and M., Coffin and Maass, *ibid.*, 1928, **50**, 1427; H.-R. and L., Hennant-Roland and Lek, *loc. cit.*; E. and C., Edgar and Calingaert, *J. Amer. Chem. Soc.*, 1929, **51**, 1540; S. and K., Schenk and Kintzinger, *Rec. trav. chim.*, 1923, **42**, 759; H. and M., Hunten and Maass, *loc. cit.*; (1), Sugden; (2), Mumford and Phillips; (3), *Rep. Brit. Assoc.*; *locc. cit.*

The results for the methyl esters of the substituted malonic acids, including the cyclic 1 : 1-dicarboxylic acids, are summarised in Table V. The calculated values of $Mn_D^{20°}$ and $[R_L]_D$ were derived from Eisenlohr's constants; no allowance was made for the presence of ring systems. The significance of these results will be discussed in connexion with those of the corresponding substituted glutaric acids in the next paper of this series. Attention is, however, directed to the CH_2 differences for the parachor in the series malonic, methyl-, ethyl-, and *n*-propyl-malonic esters, which are 38·9, 38·3, and 37·7 respectively; these are, in qualitative accordance with the valency-deflexion effect, less than the normal value (40·3) in a polymethylene chain.

TABLE V.

	$Mn_D^{20°}$.		$[R_L]_D$.				
Methyl ester.	Obs.	Calc.	Obs.	Calc.	*P*.	$[R_L]_{F-C}$.	$[R_L]_{G'-C}$.
Malonate	186·71	187·65	28·62	28·60	283·0	0·43	0·70
Methylmalonate	206·61	208·20	33·36	33·22	321·9	0·49	0·80
Ethylmalonate	227·09	228·76	37·97	37·83	360·2	0·58	0·91
n-Propylmalonate	247·50	249·32	42·52	42·45	397·9	0·65	1·12
Dimethylmalonate	226·55	228·76	37·73	37·83	355·8	0·47	0·90
Methylethylmalonate	247·54	249·32	42·13	42·45	391·3	0·61	1·00
Methyl-*n*-propylmalonate	267·98	269·88	46·88	47·07	431·2	0·71	1·11
Ethyl-*n*-propylmalonate	289·07	290·44	51·44	51·69	468·8	0·77	1·16
Di-*n*-propylmalonate	311·94	310·95	56·07	56·31	505·1	0·84	1·35
*cyclo*Propane-1 : 1-dicarboxylate	227·75	233·76	36·39	35·63	339·3	0·59	0·85
*cyclo*Butane-1 : 1-dicarboxylate	248·01	254·32	40·59	40·25	374·8	0·62	1·00
*cyclo*Pentane-1 : 1-dicarboxylate	269·37	274·88	44·82	44·87	408·0	0·66	1·05
*cyclo*Hexane-1 : 1-dicarboxylate	291·23	295·44	49·16	49·49	442·2	0·73	1·14

The methyl esters were selected partly owing to the comparative ease of their preparation and partly in the hope that reduction in the volume of the ester groupings would render the influence of substituents on the central carbon atom more apparent.

EXPERIMENTAL.

Measurement of Refractive Indices and Dispersions.—These were carried out on the latest type of Zeiss Pulfrich refractometer. For the D-line a Hilger sodium lamp was used in the early determinations, which was later replaced by a Zeiss electric sodium lamp. An H-type of Geissler hydrogen tube was employed for the measurements at the C, F, and G′ lines. All the determinations were carried out at 20° ± 0·05°, unless otherwise stated; accurate temperature control was ensured by surrounding the cell containing the liquid under investigation with a hollow cylinder in addition to the usual silver-plated cylinder immersed almost to the surface of the liquid in the cell, and water at 20°, from an electrically controlled thermostat, was circulated through both by means of a small pump.

Measurement of Surface Tension and of Density over a Range of Temperature.—The surface tension was determined by the method of Richards, Speyers, and Carver (*J. Amer. Chem. Soc.*, 1924, **46**, 1196) in an apparatus constructed entirely of Pyrex glass, modified as previously described by the author (J., 1928, 2027). The Pyrex capillary tubes were carefully selected from a large batch of specially drawn tubing for the uniformity of their bore.

The difference in capillary rise was measured by means of a travelling microscope, provided with spirit levels both on the observation tube and on the base, reading directly to 0·01 mm. Both meniscuses could be observed simultaneously, and adjustment to the central cross wires was made by means of a specially designed fine adjustment screw. The constant of the apparatus, K, was determined both with conductivity water ($\gamma_{20^\circ} = 72{\cdot}80$, and temperature coefficient = 0·15 dyne/cm./degree) and with different samples of benzene (Kahlbaum's " pure for molecular weight determinations " and sodium-dried A.R.) ($\gamma_{20^\circ} = 28{\cdot}88$, and values at other temperatures from Sugden, J., 1924, **125**, 27), and the corrections for the meniscus were applied by means of Poisson's equation as before (J., 1928, 2028); the corrected difference in height between the meniscuses in the capillary tubes, H, is obtained from the observed difference, h (in mm.), by subtracting 0·24. The mean values for the three apparatus employed were: A, 1·8545; B, 2·5142; and C, 1·8725.

Measurements were conducted at room temperature and at those of boiling chloroform and of boiling trichloroethylene, and the exact temperature in each of the last two cases was measured on a small Anschütz thermometer with enclosed graduations immersed in the liquid under examination. Before the measurements at room temperature, the surface-tension apparatus was inclined several times to ensure thorough " wetting " of the sides of the capillaries. Between each series the apparatus was rinsed with rectified spirit, then with water, kept in dichromate mixture for 24 hours, thoroughly washed successively with water, rectified spirit, and absolute alcohol, and finally dried at 100°. Both the rectified spirit and the absolute alcohol were distilled through a plug of purified glass wool to remove any finely divided solids present: the first and last 10% of the distillate were discarded.

The densities were determined with a silica or Pyrex pycnometer of about 1·5 c.c. capacity, which was calibrated with conductivity water. Measurements at 20° were carried out by immersion in a thermostat at 20° ± 0·01°, and at other temperatures by completely surrounding the pycnometer by a closely fitting double-walled glass vessel, the annular space being filled with a suitable vapour. The exact temperature was read on a small Anschütz thermometer immersed in the vapour.

In the tabulated results below, t is the temperature, h the observed difference in height (in mm.) in the two arms of the U-tube, H the corrected value, $d_{4^\circ}^{t^\circ}$ the density (g./c.c.; calculated from the observed densities by assuming a linear variation with temperature), and γ is the surface tension (dynes/cm.) computed from the equation $\gamma = KHd$. In calculating the parachor, the density of the vapour has been neglected. The number in parentheses following the value of γ_{20° is the temperature coefficient of surface tension.

Preparation of Acids.—The preparations of those marked with an asterisk have already been described (J., 1929, 1478, 1488), and only improvements are indicated. The preparations marked with a dagger were carried out by Mr. G. H. Jeffery.

**Malonic acid.* M. p. 135° (decomp.).

†*Succinic acid.* Prepared by the hydrolysis of succinonitrile, m. p. 54°, with 50% sulphuric acid (see below); recrystallised from acetone, m. p. 185—185·5°.

†*Glutaric acid.* αγ-Dibromopropane, b. p. 163—167°/771 mm., was converted into the nitrile (" Organic Syntheses," 1925, **5**, 103) in 60% yield. A middle fraction, b. p. 149—150°/14 mm., was hydrolysed by heating under reflux for 10 hours with 15 times its weight of 50% sulphuric acid, and the acid isolated by ether extraction after saturation with ammonium sulphate; the

yield of crude product, m. p. 97—97·5°, was 85%. Recrystallisation from chloroform gave m. p. 97·5—98°.

†*Adipic acid.* A commercial sample was recrystallised from acetone; m. p. 151—152°.

†**Pimelic acid.* From αε-dibromopentane (Vogel, J., 1929, 728); m. p. 105—106°.

†*Suberic acid.* Ethyl adipate, b. p. 138°/19 mm., was reduced with sodium and absolute alcohol to hexamethylene glycol, b. p. 144—146°/15 mm., the latter converted successively into the dibromide, b. p. 134—136°/20 mm., the dinitrile (by aqueous-alcoholic potassium cyanide), b. p. 178—180°/15 mm., and suberic acid (by 50% sulphuric acid). Recrystallised from acetone, it had m. p. 141—142°.

†**Azelaic acid.* Prepared by the oxidation of ricinoleic acid with potassium permanganate by Maquenne's method (*Bull. Soc. chim.*, 1899, **21**, 1061). The crude product was recrystallised three times from benzene–light petroleum (b. p. 40—60°), and the resultant acid, m. p. 98—100°, was converted into the methyl ester, b. p. 154—155°/18 mm., which was hydrolysed with excess of ethyl-alcoholic potassium hydroxide, and the acid recrystallised successively from A.R. formic acid (*d* 1·2), and benzene–light petroleum. It then had m. p. 106—107°.

†*Sebacic acid.* Boots's pure acid was recrystallised from acetone, m. p. 132—133°.

*Methylmalonic acid, m. p. 132° (decomp.), and *ethylmalonic acid, m. p. 115° (decomp.), gave satisfactory analyses by combustion.

†n-*Propylmalonic acid.* Ethyl malonate was converted into ethyl *n*-propylmalonate, b. p. 220—222°/758 mm., and the latter hydrolysed with excess of ethyl-alcoholic potassium hydroxide for 6 hours. The acid was recrystallised from benzene, m. p. 95—96° (decomp.).

*Dimethylmalonic acid, m. p. 193·5° (decomp.), *methylethylmalonic acid, m. p. 121°, *diethylmalonic acid, m. p. 127°, *ethyl-*n*-propylmalonic acid, m. p. 116°, and *di-*n*-propylmalonic acid, m. p. 161° (decomp.).

*Methyl-*n*-propylmalonic acid* (with R. J. TUDOR, M.Sc.). Ethyl methylmalonate was converted by sodium ethoxide and *n*-propyl iodide into ethyl methyl-*n*-propylmalonate, b. p. 220—223°. Solutions of the ester (37 g.) in rectified spirit (74 g.) and potassium hydroxide (38 g.) in water (76 g.) were mixed, and the mixture refluxed for 48 hours, the product neutralised with concentrated hydrochloric acid (litmus) and a saturated solution of calcium chloride (20 g.) added; the calcium salt of the acid was precipitated. The filtrate was extracted repeatedly with ether, the calcium salt suspended in the ethereal extract, and concentrated hydrochloric acid added slowly until the solid was decomposed. The acid, m. p. 95—96° (25·5 g.; 93% yield), from the dried ethereal extract was recrystallised from benzene–light petroleum (b. p. 60—80°) and then from dry benzene. It had m. p. 96°, unaffected by further recrystallisation. Stiassny (*Monatsh.*, 1891, **12**, 593) gives m. p. 106—107°.

†cyclo*Propane*-1 : 1-*dicarboxylic acid.* An equimolecular mixture of redistilled ethylene dibromide and ethyl malonate was added to sodium ethoxide solution (from absolute alcohol distilled over calcium), the whole stirred and refluxed for 5 hours, and the alcohol distilled off. Water was then added, the precipitated oil isolated by ether extraction, dried, and distilled three times under ordinary pressure, the fraction, b. p. 216—220°/764 mm., being collected (32% yield). This was hydrolysed by refluxing for 24 hours with excess of aqueous-alcoholic potassium hydroxide; the alcohol was removed, the residue extracted with ether, the extract acidified with dilute sulphuric acid, and the acid isolated by ether extraction. On recrystallisation from benzene–ether–light petroleum (b. p. 60—80°), it melted at 135—136°, softening at 120°, the softening occurring at 127° after two triturations with boiling benzene. The acid was then esterified by refluxing for 7 hours with a mixture of dry methyl alcohol, benzene, and concentrated sulphuric acid, and the ester, b. p. 196—198°/757 mm., hydrolysed as above to an acid, which, after one crystallisation from benzene–ether–light petroleum (b. p. 60—80°), had m. p. 136—137°.

†cyclo*Butane*-1 : 1-*dicarboxylic acid.* αγ-Dibromopropane was condensed with ethyl sodiomalonate and the product worked up as described under the *cyclo*propane acid. A fraction, b. p. 110—115°/17 mm., after two distillations, was obtained in 38% yield; this was hydrolysed with 4 mols. of aqueous-alcoholic potassium hydroxide for 18 hours, and the acid crystallised once from benzene–ether–light petroleum (b. p. 60—80°) and twice from benzene–ether to remove the last traces of any malonic acid; m. p. 157°.

†*cyclo*Pentane*-1 : 1-*dicarboxylic acid.* Tetramethylene glycol, b. p. 127—129°/12 mm., was obtained in 70% yield by the reduction of ethyl succinate with sodium and absolute alcohol (compare Bennett and Mosses, J., 1931, 1697 : the quantities of sodium and alcohol recommended by these authors for 0·1 mol. of ester can be employed for 0·4 mol. without appreciably affecting the yield), and then converted in the dibromide, b. p. 82—84°/12 mm., in 72% yield by refluxing

with excess of constant b. p. hydrobromic acid containing 40% sulphuric acid [compare Kamm and Marvel, *J. Amer. Chem. Soc.*, 1920, **42**, 307; the use of a greater proportion of sulphuric acid (Goldsworthy, J., 1931, 482) leads to charring and reduction of yield to 48%] and isolation by extraction with light petroleum (b. p. 40—60°) in which the glycol is insoluble. The dibromide was condensed with ethyl sodiomalonate as described above, and the fraction, b. p. 115—125°/20 mm. (largely 120°/20 mm.), isolated in 55% yield. This was hydrolysed with aqueous-alcoholic potassium hydroxide, and the acid crystallised twice from benzene–ether–light petroleum (b. p. 40—60°), and once from benzene–ether; m. p. 187°.

†*cyclo*Hexane*-1 : 1-*dicarboxylic acid*. From αε-dibromopentane and ethyl sodiomalonate; m. p. 178° (decomp.).

Preparation of Esters.—These were prepared by refluxing the acid with a mixture of the pure dry alcohol, pure sodium-dried benzene, and concentrated sulphuric acid for several hours (compare Vogel, J., 1928, 2021); thrice the volume of water was added, and the benzene layer containing most of the ester separated. The aqueous solution was saturated with sodium chloride and extracted twice with ether, and the ethereal extract combined with the benzene solution. After drying (sodium sulphate) and removal of solvents, the ester was usually distilled under diminished pressure. For the determination of the physical properties, the pure esters were redistilled and a middle fraction collected. The yields were satisfactory except for methyl malonate and methylmalonate, which are being investigated further. For the highly substituted esters somewhat longer refluxing was necessary to ensure a good yield. The methyl alcohol was a synthetic product, containing less than 0·1% of acetone, and was dried over lime, and the large middle fraction employed. Ethyl alcohol was Burroughs's absolute ethyl alcohol.

It was soon noticed that the pure esters changed slightly, as indicated by the refractive index, when preserved in vessels of ordinary glass. All operations were therefore conducted in Pyrex vessels, in which the specimens remained unchanged.

Methyl malonate. M = 132·06; b. p. 180°/770 mm.; n_C 1·41172, n_D 1·41376, n_F 1·41880, $n_{G'}$ 1·42318. Densities determined : $d^{20^\circ}_{4^\circ}$ 1·1527, $d^{63\cdot4^\circ}_{4^\circ}$ 1·1066, $d^{86\cdot4^\circ}_{4^\circ}$ 1·0774.

γ_{20° = 37·31 (0·125). App. B.

t.	*h.*	*H.*	$d^{t^\circ}_{4^\circ}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d^{t^\circ}_{4^\circ}$.	γ.	*P.*
15·1°	13·27	13·03	1·1576	37·92	283·1	85·4°	11·13	10·89	1·0784	29·53	282·2
62·6	11·73	11·49	1·1074	31·99	283·6					Mean	283·0

Methyl succinate. M = 146·08; b. p. 194°/754 mm.; n_C 1·41757, n_D 1·41965, n_F 1·42468, $n_{G'}$, 1·42888. Densities determined : $d^{20^\circ}_{4^\circ}$ 1·1192, $d^{63\cdot2^\circ}_{4^\circ}$ 1·0757, $d^{85\cdot0^\circ}_{4^\circ}$ 1·0548.

γ_{20° = 35·61 (0·119). App. B.

22·9	13·16	12·92	1·1163	36·26	321·1	85·0	11·14	10·90	1·0548	28·91	321·1
63·5	11·86	11·62	1·0754	31·42	321·6					Mean	321·3

Methyl glutarate. M = 160·10; b. p. 109°/21 mm.; n_C 1·42208, n_D 1·42415, n_F 1·42925, $n_{G'}$ 1·43362. Densities determined : $d^{20^\circ}_{4^\circ}$ 1·0874, $n^{63\cdot3^\circ}_{4^\circ}$ 1·0450, $d^{85\cdot6^\circ}_{4^\circ}$ 1·0239.

γ_{20° = 36·23 (0·120). App. A.

22·7	18·09	17·85	1·0847	35·91	361·3	85·0	15·28	15·04	1·0245	28·58	361·3
62·7	16·29	16·05	1·0456	31·12	361·7					Mean	361·4

Methyl adipate. M = 174·11; b. p. 122°/20 mm.; n_C 1·42600, n_D 1·42815, n_F 1·43330, $n_{G'}$ 1·43763. Densities determined : $d^{20^\circ}_{4^\circ}$ 1·0625, $d^{63\cdot4^\circ}_{4^\circ}$ 1·0208, $d^{85\cdot0^\circ}_{4^\circ}$ 0·9966.

γ_{20° = 35·66 (0·112). App. B.

23·0	13·50	13·26	1·0595	35·32	400·6	85·0	11·55	11·31	0·9966	28·34	403·1
62·5	12·26	12·02	1·0217	30·88	401·7					Mean	401·8

Methyl pimelate. M = 188·13; b. p. 128°/16 mm.; n_C 1·42853, n_D 1·43065, n_F 1·43588, $n_{G'}$ 1·43967. Densities determined : $d^{20^\circ}_{4^\circ}$ 1·0383, $d^{62\cdot8^\circ}_{4^\circ}$ 1·0012, $d^{85\cdot6^\circ}_{4^\circ}$ 0·9817.

γ_{20° = 35·58 (0·104). App. B.

17·6	13·94	13·70	1·0406	35·84	442·4	85·1	11·93	11·69	0·9822	28·87	444·0
62·4	12·58	12·34	1·0016	31·08	443·5					Mean	443·3

Methyl suberate. M = 202·14; b. p. 148°/20 mm.; n_C 1·43105, n_D 1·43326, n_F 1·43864, $n_{G'}$ 1·44308. Densities determined : $d^{20^\circ}_{4^\circ}$ 1·0198, $d^{63\cdot2^\circ}_{4^\circ}$ 0·9839, $d^{85\cdot6^\circ}_{4^\circ}$ 0·9606.

γ_{20° = 35·43 (0·107). App. A.

17·4°	19·08	18·84	1·0221	35·71	483·5	85·6	16·17	15·93	0·9606	28·38	485·7
64·4	17·06	16·82	0·9828	30·66	484·0					Mean	484·4

Methyl azelate. M = 216·16; b. p. 156°/20 mm.; n_C 1·43386, n_D 1·43607, n_F 1·44134, $n_{G'}$ 1·44588. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0069, $d_{4^\circ}^{63·4^\circ}$ 0·9680, $d_{4^\circ}^{86·3^\circ}$ 0·9490.

γ_{20° = 35·35 (0·109). App. A.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*
15·6°	19·35	19·11	1·0109	35·83	523·1	87·6°	16·28	16·04	0·9478	28·19	525·5
63·1	17·30	17·06	0·9683	30·63	525·2					Mean	524·6

Ethyl malonate. M = 160·10; b. p. 197°/759 mm.; n_C 1·41179, n_D 1·41386, n_F 1·41897, $n_{G'}$ 1·42313. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0550, $d_{4^\circ}^{62·2^\circ}$ 1·0104, $d_{4^\circ}^{85·3^\circ}$ 0·9878.

γ_{20° = 31·84 (0·105). App. B.

17·0	12·33	12·09	1·0580	32·16	360·1	85·3	10·33	10·09	0·9878	25·06	362·4
62·2	11·01	10·77	1·0104	27·36	362·1					Mean	361·5

Ethyl succinate. M = 174·11; b. p. 108°/17 mm.; n_C 1·41763, n_D 1·41975, n_F 1·42484, $n_{G'}$ 1·42912. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0398, $d_{4^\circ}^{63·4^\circ}$ 0·9948, $d_{4^\circ}^{86·6^\circ}$ 0·9683.

γ_{20° = 31·75 (0·104). App. A.

19·3	16·73	16·49	1·0405	31·82	397·4	85·3	14·19	13·95	0·9696	25·08	401·9
63·4	14·97	14·73	0·9948	27·18	399·6					Mean	400·0

Ethyl glutarate. M = 188·13; b. p. 118°/15 mm.; n_C 1·42188, n_D 1·42395, n_F 1·42916, $n_{G'}$ 1·43331. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0229, $d_{4^\circ}^{63·6^\circ}$ 0·9833, $d_{4^\circ}^{86·0^\circ}$ 0·9610.

γ_{20° = 32·34 (0·102). App. B.

17·5	12·88	12·64	1·0252	32·59	438·4	86·0	10·87	10·63	0·9610	25·68	440·7
63·1	11·53	11·29	0·9838	27·93	439·6					Mean	439·6

Ethyl adipate. M = 202·14; b. p. 132°/15 mm.; n_C 1·42548, n_D 1·42765, n_F 1·43284, $n_{G'}$ 1·43711. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0090, $d_{4^\circ}^{62·4^\circ}$ 0·9663, $d_{4^\circ}^{84·2^\circ}$ 0·9485.

γ_{20° = 32·58 (0·100). App. C.

17·0	17·89	17·65	0·9956	32·93	520·1	85·8	15·04	14·80	0·9360	25·94	521·2
63·2	15·91	15·67	0·9562	28·06	520·3					Mean	520·5

Ethyl pimelate. M = 216·16; b.p. 149°/18 mm.; n_C 1·42770, n_D 1·42985, n_F 1·43494, $n_{G'}$ 1·43929. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9929, $d_{4^\circ}^{64·2^\circ}$ 0·9553, $d_{4^\circ}^{85·2^\circ}$ 0·9365.

γ_{20° = 32·63 (0·101). App. C.

17·0	17·89	17·65	0·9956	32·93	520·1	85·8	15·04	14·80	0·9360	25·94	521·2
63·2	15·91	15·67	0·9562	28·06	520·3					Mean	520·5

Ethyl suberate. M = 230·18; b. p. 164°/22 mm.; n_C 1·43013, n_D 1·43236, n_F 1·43762, $n_{G'}$ 1·44178. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9807, $d_{4^\circ}^{62·7^\circ}$ 0·9460, $d_{4^\circ}^{86·1^\circ}$ 0·9269.

γ_{20° = 32·79 (0·102). App. B.

21·3	13·50	13·26	0·9797	32·66	561·7	86·3	11·57	11·33	0·9267	26·40	563·0
63·6	12·32	12·08	0·9453	28·71	563·6					Mean	562·8

Ethyl sebacate. M = 258·21; b. p. 183°/20 mm.; n_C 1·43445, n_D 1·43657, n_F 1·44194, $n_{G'}$ 1·44621. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9631, $d_{4^\circ}^{63·2^\circ}$ 0·9298, $d_{4^\circ}^{86·0^\circ}$ 0·9124.

γ_{20° = 33·17 (0·097). App. B.

20·0	13·94	13·70	0·9631	33·17	643·4	85·5	11·97	11·73	0·9129	26·92	644·3
62·4	12·62	12·38	0·9305	28·96	643·7					Mean	643·8

Methyl methylmalonate. M = 146·08; b. p. 176—177°/735 mm.; n_C 1·41226, n_D 1·41436, n_F 1·41930, $n_{G'}$ 1·42360; $[R_L]_C$ 33·21, $[R_L]_D$ 33·36, $[R_L]_F$ 33·70, $[R_L]_{G'}$ 34·01. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0952, $d_{4^\circ}^{64·3^\circ}$ 1·0473, $d_{4^\circ}^{86·1^\circ}$ 1·0237.

γ_{20° = 32·81 (0·120). App. B.

19·0	12·55	12·31	1·0693	33·93	321·6	86·6	10·34	10·10	1·0232	25·98	322·1
64·3	11·03	10·79	1·0473	28·41	322·0					Mean	321·9

Methyl ethylmalonate. M = 160·10; b. p. 189°/760 mm.; n_C 1·41632, n_D 1·41845, n_F 1·42356, $n_{G'}$ 1·42776; $[R_L]_C$ 37·80, $[R_L]_D$ 37·97, $[R_L]_F$ 38·38, $[R_L]_{G'}$ 38·71. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0637, $d_{4^\circ}^{62·8^\circ}$ 1·0227, $d_{4^\circ}^{86·0^\circ}$ 0·9973.

γ_{20° = 32·72 (0·111). App. B.

19·5	12·49	12·25	1·0642	32·78	360·0	87·0	10·38	10·14	0·9963	25·40	360·8
64·0	11·05	10·81	1·0215	27·76	359·8					Mean	360·2

Methyl n-*propylmalonate.* M = 174·11; b. p. 203°/756 mm.; n_C 1·41930, n_D 1·42155, n_F 1·42658, $n_{G'}$ 1·43203; $[R_L]_C$ 42·31, $[R_L]_D$ 42·52, $[R_L]_F$ 42·96, $[R_L]_{G'}$ 43·43. Densities determined: $d_{4°}^{20°}$ 1·0398, $d_{4°}^{62·6°}$ 0·9984, $d_{4°}^{85·6°}$ 0·9756.

$\gamma_{20°}$ = 31·62 (0·103). App. B.

22·1	12·27	12·03	1·0379	31·39	397·1	86·1	10·34	10·10	0·9751	24·76	398·3
62·3	11·09	10·85	0·9987	27·24	398·3					Mean	397·9

Methyl dimethylmalonate. M = 160·10; b. p. 78·5°/20 mm.; n_C 1·41292, n_D 1·41505, n_F 1·42001, $n_{G'}$ 1·42421; $[R_L]_C$ 37·57, $[R_L]_D$ 37·73, $[R_L]_F$ 38·14, $[R_L]_{G'}$ 38·47. Densities determined: $d_{4°}^{20°}$ 1·0624, $d_{4°}^{61·8°}$ 1·0200, $d_{4°}^{85·8°}$ 0·9928.

$\gamma_{20°}$ = 31·05 (0·111). App. A.

24·7	15·80	15·56	1·0577	30·52	355·8	85·8	13·12	12·88	0·9928	23·71	355·9
63·2	14·12	13·88	1·0186	26·22	355·7					Mean	355·8

Methyl methylethylmalonate. M = 174·11; b. p. 90°/21 mm.; n_C 1·41956, n_D 1·42175, n_F 1·42663, $n_{G'}$ 1·43096; $[R_L]_C$ 41·94, $[R_L]_D$ 42·13, $[R_L]_F$ 42·55, $[R_L]_{G'}$ 42·94. Densities determined: $d_{4°}^{20°}$ 1·0497, $d_{4°}^{62·6°}$ 1·0040, $d_{4°}^{85·2°}$ 0·9835.

$\gamma_{20°}$ = 30·84 (0·110). App. B.

23·5	11·82	11·58	1·0459	30·45	391·1	85·6	9·87	9·63	0·9831	23·80	391·2
62·0	10·57	10·33	1·0046	26·09	391·7					Mean	391·3

Methyl diethylmalonate. M = 188·13; b. p. 97°/17 mm.; n_C 1·42551, n_D 1·42765, n_F 1·43269, $n_{G'}$ 1·43705; $[R_L]_C$ 46·30, $[R_L]_D$ 46·51, $[R_L]_F$ 46·98, $[R_L]_{G'}$ 47·40. Densities determined: $d_{4°}^{20°}$ 1·0400, $d_{4°}^{61·8°}$ 0·9951, $d_{4°}^{85·8°}$ 0·9694.

$\gamma_{20°}$ = 31·07 (0·110). App. A.

21·9	16·27	16·03	1·0380	30·86	427·1	85·5	13·57	13·33	0·9694	23·97	429·2
62·0	14·54	14·30	0·9949	26·38	428·5					Mean	428·3

Methyl methyl-n-*propylmalonate.* M = 188·13; b. p. 101°/20 mm.; n_C 1·42229, n_D 1·42445, n_F 1·42969, $n_{G'}$ 1·43375; $[R_L]_C$ 46·67, $[R_L]_D$ 46·88, $[R_L]_F$ 47·38, $[R_L]_{G'}$ 47·78. Densities determined: $d_{4°}^{23°}$ 1·0250, $d_{4°}^{62·8°}$ 0·9870, $d_{4°}^{89·6°}$ 0·9640.

$\gamma_{20°}$ = 30·49 (0·100). App. B.

26·0	11·92	11·66	1·0196	29·89	431·4	88·2	10·00	9·76	0·9625	23·62	430·9
64·0	10·76	10·52	0·9861	26·08	431·2					Mean	431·2

Methyl ethyl-n-*propylmalonate.* M = 202·14; b. p. 107°/17 mm.; n_C 1·42782, n_D 1·43005, n_F 1·43517, $n_{G'}$ 1·43898; $[R_L]_C$ 51·20, $[R_L]_D$ 51·44, $[R_L]_F$ 51·97, $[R_L]_{G'}$ 52·36. Densities determined: $d_{4°}^{20°}$ 1·0154, $d_{4°}^{62·8°}$ 0·9756, $d_{4°}^{82·0°}$ 0·9510.

$\gamma_{20°}$ = 30·53 (0·102). App. B.

17·0	12·29	12·05	1·0181	30·84	468·0	85·0	10·24	10·00	0·9510	23·91	470·0
62·4	10·90	10·66	0·9760	26·16	468·3					Mean	468·8

Methyl di-n-*propylmalonate.* M = 216·16; b. p. 120·5°/20 mm.; n_C 1·42972, n_D 1·43196, n_F 1·43712, $n_{G'}$ 1·44155; $[R_L]_C$ 55·81, $[R_L]_D$ 56·07, $[R_L]_F$ 56·65, $[R_L]_{G'}$ 57·16. Densities determined: $d_{4°}^{20°}$ 0·9999, $d_{4°}^{63·2°}$ 0·9630, $d_{4°}^{85·0°}$ 0·9388.

$\gamma_{20°}$ = 20·28 (0·085). App. B.

21·0	11·86	11·62	0·9990	29·19	502·9	85·5	10·17	9·93	0·9383	23·43	506·8
63·2	10·87	10·63	0·9630	25·74	505·6					Mean	505·1

Methyl cyclo*propane*-1 : 1-*dicarboxylate.* M = 158·08; b. p. 95°/20 mm.; n_C 1·43833, n_D 1·44070, n_F 1·44647, $n_{G'}$ 1·45126; $[R_L]_C$ 36·21, $[R_L]_D$ 36·39, $[R_L]_F$ 36·80, $[R_L]_{G'}$ 37·06. Densities determined: $d_{4°}^{20°}$ 1·1466, $d_{4°}^{62·1°}$ 1·1028, $d_{4°}^{86·1°}$ 1·0771.

$\gamma_{20°}$ = 36·42 (0·118). App. A.

23·3	17·24	17·00	1·1430	36·03	338·9	85·9	14·58	14·34	1·0774	28·65	339·5
62·1	15·60	15·36	1·1028	31·41	339·4					Mean	339·3

Methyl cyclo*butane*-1 : 1-*dicarboxylate.* M = 172·10; b. p. 102°/21 mm.; n_C 1·43881, n_D 1·44110, n_F 1·44661, $n_{G'}$ 1·45217; $[R_L]_C$ 40·41, $[R_L]_D$ 40·59, $[R_L]_F$ 41·03, $[R_L]_{G'}$ 41·41. Densities determined: $d_{4°}^{20°}$ 1·1198, $d_{4°}^{62·5°}$ 1·0780, $d_{4°}^{85·8°}$ 1·0509.

$\gamma_{20°}$ = 35·31 (0·117). App. B.

20·0	12·78	12·54	1·1198	35·31	374·6	85·1	10·68	10·44	1·0516	27·60	375·1
62·5	11·44	11·20	1·0780	30·36	374·8					Mean	374·8

Methyl cyclo*pentane*-1 : 1-*dicarboxylate.* $M = 186{\cdot}11$; b. p. 113°/21 mm.; n_C 1·44519, n_D 1·44742, n_F 1·45287, $n_{G'}$ 1·45740; $[R_L]_C$ 44·63, $[R_L]_D$ 44·82, $[R_L]_F$ 45·29, $[R_L]_{G'}$ 45·68. Densities determined: $d_{4°}^{20°}$ 1·1104, $d_{4°}^{62{\cdot}2°}$ 1·0738, $d_{4°}^{86{\cdot}2°}$ 1·0428.

$\gamma_{20°} = 35{\cdot}20$ (0·114). App. A.

20·4	17·30	17·06	1·1111	35·15	408·2	85·8	14·60	14·36	1·0432	27·78	409·6
62·2	15·55	15·31	1·0738	30·49	407·3					Mean	408·0

Methyl cyclo*hexane*-1 : 1-*dicarboxylate.* $M = 200{\cdot}13$; b. p. 126·5°/20 mm.; n_C 1·45297, n_D 1·45522, n_F 1·46081, $n_{G'}$ 1·46531; $[R_L]_C$ 48·96, $[R_L]_D$ 49·16, $[R_L]_F$ 49·69, $[R_L]_{G'}$ 50·10. Densities determined: $d_{4°}^{20°}$ 1·1046, $d_{4°}^{64{\cdot}0°}$ 1·0654, $d_{4°}^{85{\cdot}4°}$ 1·0463.

$\gamma_{20°} = 35{\cdot}53$ (0·109). App. A.

20·0	17·58	17·34	1·1046	35·53	442·2	85·9	14·97	14·73	1·0455	28·56	442·5
62·5	15·81	15·57	1·0667	30·80	442·0					Mean	442·2

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