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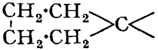
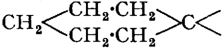
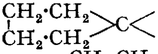
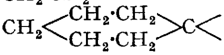
385. *Physical Properties and Chemical Constitution. Part II. Esters of ββ-Substituted Glutaric Acids.*

By Arthur I. Vogel.

The present work was undertaken with the objects (1) of providing certain physicochemical data (surface tension, density, refractive index) for a comprehensive series of glutaric esters, and (2) of discovering new evidence for the valency-deflexion hypothesis based on relationships involving these quantities. It is clear that the difference between any of the properties of the ββ-substituted glutaric and those of the corresponding malonic esters will yield values for 2 × CH_2 and these may be compared with the value for CH_2 determined

Table I.

Substituent.	Malonic series. Parachor.	Glutaric series. Parachor.	Diff. for $2CH_2$.	Malonic series. $[R_L]_D$.	Glutaric series. $[R_L]_D$.	Diff. for $2CH_2$.
H, H	283·0	361·4	78·4	28·62	37·58	8·96
Me, H	321·9	399·9	78·0	33·36	42·36	9·00
Me, Me	355·8	431·8	76·0	37·73	46·88	9·15
Me, Et	391·3	466·8	75·5	42·13	51·18	9·05
Et, Et	428·3	500·7	72·4	46·51†	55·74	9·23
Me, Pr^a	431·2	505·9	74·7	46·88	56·14	9·26
Et, Pr^a	468·8	539·8	71·0	51·44	60·48	9·04
Pr^a, Pr^a	505·1	575·9	70·8	56·07	65·03	8·96
 $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<$	408·0	482·3	74·3	44·82	53·86	9·04
 $CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<$	444·2	517·4	75·2	49·16	58·26	9·10

Substituent.	Malonic series. $Mn_D^{20°}$.	Glutaric series. $Mn_D^{20°}$.	Diff. for $2CH_2$.	Malonic series. $[R_L]_{F-C}$.	Malonic series. $[R_L]_{G'-C}$.	Glutaric series. $[R_L]_{F-C}$.	Glutaric series. $[R_L]_{G'-C}$.
H, H	186·71	228·01	41·30	0·43	0·70	0·56	0·89
Me, H	206·61	248·20	41·59	0·49	0·80	0·64	0·97
Me, Me	226·55	268·83	42·28	0·47	0·90	0·71	1·08
Me, Et	247·54	290·13	42·59	0·61	1·00	0·77	1·17
Et, Et	268·59†	311·80	43·21	0·68†	1·10†	0·84	1·26
Me, Pr^a	267·98	310·71	42·73	0·71	1·11	0·85	1·31
Et, Pr^a	289·07	332·05	42·98	0·77	1·16	0·91	1·38
Pr^a, Pr^a	309·08*	352·40	43·32	0·84	1·35	0·97	1·50
 $\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<$	269·37	311·78	42·41	0·66	1·05	0·73	1·23
 $CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<$	291·23	333·97	42·74	0·73	1·14	0·86	1·31

* Original value 311·94 (this vol., p. 334) was miscalculated.

† The line for this ester was omitted from Table V of Part I (this vol., p. 335); it included these data and also $[R_L]_C$ 46·30, $R[_L]_F$ 46·98, and $R[_L]_{G'}$ 47·40.

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for the normal dibasic esters. Any divergence between these values may be attributed directly to valency deflexion, since all other variables are the same in the two series. This method has the great advantage that a knowledge of the individual atomic and structural constants is unnecessary. The results of such a comparison for the methyl esters are in Table I, the data in Part I (this vol., p. 333) for the malonic series being employed.

It will be seen that only the parachor and the molecular refraction coefficients * exhibit real divergencies from the normal CH_2 differences of 40·3 and 20·63 respectively (Part I, *loc. cit.*): irregular differences are obtained for the refractivities and dispersions. The valency angles would thus appear to be in the order $Pr^{a},Pr^{a} < Et,Pr^{a} < Et,Et < Me,Pr^{a} < Me,Et < Me,Me < Me,H < H,H$, and the difference between Et,Et, Et,Pr^{a}, and Pr^{a},Pr^{a} would also appear to be small.

Table II records data for a number of sets of isomeric esters investigated by the author.

TABLE II.

Ester.	*P*.	$Mn_{D}^{20°}$.	$[R_L]_D$.	$[R_L]_{F-C}$.	$[R_L]_{G'-C}$.
Et malonate	361·5	226·37	37·89	0·58	0·90
Me glutarate	361·4	228·01	37·58	0·56	0·89
Me dimethylmalonate	355·8	226·55	37·73	0·57	0·90
Me ethylmalonate	360·2	227·09	37·97	0·58	0·91
Et succinate	400·0	247·19	42·35	0·64	1·02
Me adipate	401·8	248·69	42·23	0·62	0·99
Me methylethylmalonate	391·3	247·54	42·13	0·61	1·00
Me methylglutarate	399·9	248·20	42·36	0·64	0·97
Et glutarate	439·6	267·89	46·93	0·70	1·10
Me pimelate	443·3	269·19	46·89	0·71	1·06
Me diethylmalonate	428·3	268·58	46·51	0·68	1·10
Me methyl-*n*-propylmalonate	431·2	267·98	46·88	0·71	1·11
Me dimethylglutarate	431·8	268·83	46·88	0·71	1·08
Et adipate	480·2	288·58	51·51	0·77	1·22
Me suberate	484·4	289·81	51·55	0·78	1·24
Me ethyl-*n*-propylmalonate	468·8	289·07	51·44	0·77	1·16
Me methylethylglutarate	466·8	290·13	51·18	0·77	1·17
Et pimelate	520·5	309·08	56·23	0·83	1·33
Me azelate	524·6	310·43	56·14	0·82	1·34
Me di-*n*-propylmalonate	505·1	311·94	56·07	0·84	1·35
Me diethylglutarate	500·7	311·80	55·74	0·84	1·26
Me methyl-*n*-propylglutarate	505·9	310·71	56·14	0·85	1·31
Et dimethylglutarate	510·6	308·71	55·98	0·86	1·28
Me *cyclo*hexane-1 : 1-diacetate	517·2	330·97	58·26	0·86	1·31
Me 3-methyl*cyclo*pentane-1 : 1-diacetate	519·4	331·42	58·62	0·87	1·34
Et *cyclo*hexane-1 : 1-diacetate	595·5	373·67	67·65	1·02	1·54
Et 3-methyl*cyclo*pentane-1 : 1-diacetate	599·0	371·16	67·99	1·02	1·58
Me 3-methyl*cyclo*hexane-1 : 1-diacetate	555·2	353·86	63·27	0·96	1·47
Me 4-methyl*cyclo*hexane-1 : 1-diacetate	553·9	353·86	63·04	0·94	1.42
Et 3-methyl*cyclo*hexane-1 : 1-diacetate	633·3	393·53	72·48	1·09	1·64
Et 4-methyl*cyclo*hexane-1 : 1-diacetate	630·9	393·55	72·31	1·10	1·68

The most remarkable and unexpected feature of these results is the large variation in the parachor in several series; this must be attributed largely to valency deflexion. It is of interest that Sugden (see " The Parachor and Valency," 1930, p. 33) originally based the additivity of the parachor on its values for isomeric substances, those which differed only in the position of groups or linkages in the molecule being deemed to give identical parachors. Other examples of the variation of the parachor for isomeric compounds are known (*Rep. Brit. Assoc.*, 1932, 264; compare Mumford and Phillips, J., 1929, 2112), so Sugden's generalisation is no longer acceptable.

Smaller but not parallel variations are present in the molecular refraction coefficients but these are not large enough to justify any useful conclusions. The dispersions $[R_L]_{F-C}$ and $[R_L]_{G'-C}$ would seem to be approximately the same for isomeric compounds.

EXPERIMENTAL.

Preparation of ββ-Substituted Glutaric Acids by the Guareschi Reaction.—This reaction has been widely employed for work in connexion with the valency-deflexion hypothesis but no

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* The difference in $Mn_{D}^{20°}$ for the diethyl series appears anomalous.

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complete details have been published (compare Guareschi, *Atti Accad. Sci. Torino*, **1900—1901**, **36**, 443; Kon and Thorpe, J., 1919, **115**, 693). In view of the expensive nature of the materials involved, full details are given of the preparation of the dicyano-imides from fourteen ketones, and also an improved method of hydrolysis of these to the corresponding substituted glutaric acids.

Preparation of dicyano-imides. 400 C.c. of absolute ethyl alcohol absorb *ca.* 52 g. (3 g.-mols.) of anhydrous ammonia at 0°, the solution expanding to approximately 600 c.c. A mixture of 1 g.-mol. of the dry ketone and 2 g.-mols. of pure ethyl cyanoacetate, contained in a large (1500 c.c.) wide-mouthed glass-stoppered bottle and cooled to − 5°, is treated with 400 c.c. of absolute alcohol, previously saturated at − 5° (5—6 hours) in an all-glass wash bottle with ammonia, derived from a cylinder and dried by passage through lime. The whole is kept at 0° for 1—7 days (the time depends upon the ketone employed) with the stopper held down by means of a heavy weight, and then the separated ammonium salt of the dicyano-imide is filtered off and washed with alcohol, followed by ether (*cyclo*pentanone, 3-methyl*cyclo*pentanone, *cyclo*hexanone, 3- and 4-methyl*cyclo*hexanone, *trans*-β-decalone, *trans*-hexahydro-β-hydrindone, acetone, methyl ethyl ketone, and methyl-*n*-propyl ketone). The solid ammonium salt is dissolved in the minimum quantity of boiling water (*ca.* 1—1·5 l.), a large excess of concentrated hydrochloric acid (300—500 c.c.) added, and the precipitated dicyano-imide collected after 12 hours and dried at 100°. The products from the dicyclic ketones must be boiled with dilute hydrochloric acid, since the ammonium salts are sparingly soluble in water. For diethyl, ethyl *n*-propyl, and di-*n*-propyl ketones some cyanoacetamide but very little ammonium salt separates, and the filtered solution is therefore diluted with 1·5 times its volume of water, extracted four times with ether (*ca.* 1 l.), the aqueous solution strongly acidified with concentrated hydrochloric acid, and the separated solid collected after 24 hours and dried at 100°.

Ketones. These were usually dried over anhydrous sodium sulphate before use, and were obtained from the following sources:

Acetone. B.D.H. " A.R.," dried over calcium chloride; b. p. 56—56·6°.

Methyl ethyl ketone. A purified commercial specimen was fractionated and the portion, b. p. 79—80°, collected.

The higher aliphatic ketones were prepared from the purified acids (fractionation only) by passage over manganous oxide at 300—350°, and had the following b. p.'s: Diethyl ketone, 100—103°; methyl *n*-propyl ketone, 101·5—103·5°; ethyl *n*-propyl ketone, 121—125°; di-*n*-propyl ketone, 143—145°.

*cyclo*Pentanone. Prepared from adipic acid (compare Vogel, J., 1928, 1021; 1929, 727); b. p. 131°.

*cyclo*Hexanone. Commercially " pure " specimens vary considerably in purity and give widely different yields of the dicyano-imide. *cyclo*Hexanol may be removed by standing over calcium chloride (compare Hückel, Neunhoeffer, Gercke, and Frank, *Annalen*, 1929, **477**, 99). The best method is to purify it through the bisulphite compound prepared with aqueous-alcoholic sodium bisulphite solution (Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, **9**, 339), and after the solid has been washed with ether to remove any *cyclo*hexanol present, it is decomposed in a separating-funnel with 10% sodium hydroxide solution, and the liberated ketone extracted with ether; b. p. 156—157°.

3-Methyl*cyclo*pentanone. From pure β-methyladipic acid, derived from the oxidation of 4-methyl*cyclo*hexanol with nitric acid (Vogel, J., 1931, 912; Desai, *ibid.*, p. 1219); b. p. 143—145°.

3- and 4-Methyl*cyclo*hexanones. Pure products from Deutsche Hydrierwerke.

trans-β-Decalone. From pure trans-β-decalol, m. p. 74—75° (see Tudor and Vogel, this vol., p. 1251, for references); b. p. 117°/16 mm.

trans-Hexahydro-β-hydrindone. From *trans*-*cyclo*hexane-1 : 2-diacetic acid, m. p. 167° (Tudor and Vogel, *loc. cit.*); b. p. 91—92°/13 mm.

The yields of dicyano-imides from the various ketones (1 g.-mol.) and ethyl cyanoacetate (2 g.-mols.) were as follows (the time of standing in the ice-chest is shown in parentheses): Acetone, 129 g., 68% (3 days); methyl ethyl ketone, 130 g., 63% (42 hours); diethyl ketone, 97 g., 44% (7 days); methyl *n*-propyl ketone, 140 g., 64% (5 days); ethyl *n*-propyl ketone, 39 g., 17% (7·5 days); di-*n*-propyl ketone, 500 c.c. of alcohol employed, 47 g., 19% (8 days); *cyclo*pentanone, 120 g., 55% (24 hours); *cyclo*hexanone, *ex* bisulphite compound, 165 g., 73% (4 days); *cyclo*hexanone, best sample of commercially " pure," 126 g., 55% (4 days); 3-methyl*cyclo*pentanone, 116 g., 50% (4 days); 3-methyl*cyclo*hexanone, 142 g., 58% (4 days); 4-methyl*cyclo*hexanone, 168 g., 69% (2·5 days); *trans*-β-decalone, 188·5 g., 66% (7 days); *trans*-hexahydro-β-

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hydrindone, 195 g., 72% (7 days). The most expensive cyclic ketones may be largely recovered from the alcoholic filtrate from the ammonium salts by adding a large excess of water, filtering if necessary, saturating with ammonium sulphate, and extracting several times with ether.

Hydrolysis of the dicyano-imides to the corresponding 1 : 1-*diacetic acids.* The following method gives nearly theoretical yields of the *crude* acid. 1 G.-mol. of the *finely divided* imide is dissolved in 480 c.c. of concentrated sulphuric acid in a spacious, Pyrex, round-bottomed flask (*gentle* warming is usually necessary and a clear reddish-brown solution is obtained), the solution is kept over-night, and then 450 c.c. of water are slowly added with frequent shaking. The whole is heated under reflux for 12—24 hours, very cautiously at first owing to the attendant frothing which subsides after 2—3 hours. It is essential to shake the flask well at intervals of about 3 hours. The acid separates on cooling and is collected upon a large sintered Jena-glass funnel. For the dicyano-imides from *trans*-β-decalone and *trans*-hexahydro-β-hydrindone, the best proportions are respectively 750 c.c. sulphuric acid, 700 c.c. water, and 1350 c.c. acid, 1200 c.c. water. Very little acid is contained in the sulphuric acid mother-liquors in the preparation of the cyclic acids, and the proportion is less than 5% for the aliphatic acids. The crude acids are usually dried at 100° (the dimethyl acid at 90°, and the other higher aliphatic acids at 50°), and are purified by extraction with sodium bicarbonate solution, any imide present being thus removed (potassium bicarbonate must be employed for *trans*-decahydronaphthalene-2 : 2-diacetic acid owing to the sparing solubility of the sodium salt), and strong acidification with concentrated hydrochloric acid. The cyclic acids are all almost quantitatively precipitated, but for the alkyl-substituted acids considerable quantities remain in solution and it is therefore best to saturate with ammonium sulphate and to isolate the acid by three or four extractions with ether.

The details of the subsequent purification of the various acids are given below.

ββ-*Dimethylglutaric acid.* The crude acid was converted into the anhydride by refluxing with excess of acetic anhydride for 7 hours and subsequent distillation; b. p. 156—157°/20 mm., m. p. 125°, *ex* light petroleum (b. p. 100—120°) (Perkin, J., 1896, **69**, 1475, gives m. p. 124—125°; Perkin and Thorpe, J., 1899, **75**, 54, give b. p. 181°/25 mm.). The anhydride (29·5 g.) was refluxed for 2·5 hours with aqueous potassium hydroxide (35 g., 3 mols., in 55 g. of water), acidified with concentrated hydrochloric acid, extracted thrice with ether after saturation with ammonium sulphate, dried with anhydrous sodium sulphate, the ether removed, and the residue recrystallised from concentrated hydrochloric acid and dried at 70°; m. p. 101° (Guareschi, *loc. cit.*, gives m. p. 103—104°; Thole and Thorpe, J., 1911, **99**, 435, give m. p. 101°).

β-*Methyl*-β-*ethylglutaric acid.* Recrystallised twice from dry benzene; m. p. 85° (Guareschi, 87°; Thole and Thorpe, 86°).

ββ-*Diethylglutaric acid.* Recrystallised successively from dry benzene and from chloroform–light petroleum (b. p. 40—60°); m. p. 106° (Guareschi, 108°).

β-*Methyl*-β-n-*propylglutaric acid.* Recrystallised twice from dry benzene; m. p. 92—93° (Guareschi, 92°).

β-*Ethyl*-β-n-*propylglutaric acid.* Recrystallised from benzene–light petroleum (b. p. 40—60°), m. p. 62·5—63·5°, then from hot water (the solution was poured off from a small quantity of oil), m. p. 67—68°, and another recrystallisation from hot water gave m. p. 69°, unaffected by further crystallisation (Guareschi, 71—72°).

Di-n-*propylglutaric acid.* Recrystallised from benzene; m. p. 117° (Guareschi, *Gazzetta*, 1919, **49**, 124, gives m. p. 112—113°; Bains and Thorpe, J., 1923, **123**, 1209, m. p. 114·5—115°).

cyclo*Pentane*-1 : 1-*diacetic acid.* The crude acid was converted into the anhydride, m. p. 68°, with acetic anhydride (Kon and Thorpe, J., 1919, **115**, 701, give m. p. 68°) and then into the acid as described above for the dimethyl acid. Recrystallised from hot water; m. p. 176—177° (Kon and Thorpe, *loc. cit.*, give m. p. 176—177°).

cyclo*Hexane*-1 : 1-*diacetic acid.* The crude acid was purified through the anhydride and had m. p. 181° after recrystallisation from dilute alcohol (Thole and Thorpe, J., 1911, **99**, 445, give m. p. 181°).

3-*Methyl*cyclo*pentane*-1 : 1-*diacetic acid.* Purified through the anhydride; m. p. 135° (compare Vogel, J., 1931, 913; Desai, J., 1931, 1220).

3-*Methyl*cyclo*hexane*-1 : 1-*diacetic acid.* Recrystallised successively from hot water and 20% alcohol; m. p. 142° (Thorpe and Wood, J., 1913, **103**, 1597, give m. p. 143°).

4-*Methyl*cyclo*hexane*-1 : 1-*diacetic acid.* Purified as for the 3-methyl acid; m. p. 158—159° (Thorpe and Wood, *loc. cit.*, give m. p. 158°).

trans-*Decahydronaphthalene*-2 : 2-*diacetic acid.* Recrystallised from rectified spirit or from acetone; m. p. 175° (Rao, J., 1929, 1962, gives m. p. 175°).

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trans-*Hexahydrohydrindene*-2 : 2-*diacetic acid.* Recrystallised from rectified spirit; m. p. 224° (Kandiah, J., 1931, 943, gives m. p. 224°).

β-*Methylglutaric acid.* This was prepared by Day and Thorpe's method (J., 1920, **117**, 1465) and recrystallised from chloroform; m. p. 88° (Day and Thorpe give m. p. 87°).

Preparation of Esters.—These were obtained by refluxing the pure 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; 1933, 338).

Measurement of Refractive Indices and Dispersions.—These determinations were carried out at 20° ± 0·05° on a new Pulfrich refractometer. A Zeiss electric sodium lamp and an **H**-type of Geissler hydrogen tube were used as the sources of illumination. The latter must be checked periodically with a standard liquid, such as ethyl succinate, since the G′ line becomes relatively indistinct after some use, due possibly to the gases evolved from the aluminium electrodes, and other lines appear. This difficulty is largely overcome by the use of Guild's form of hydrogen vacuum tube (*Proc. Physical Soc.*, 1916, **28**, 69; compare Hilger's Catalogue, 1929, F11).

All the measurements described in Part I have been checked with the new refractometer, and revised figures for a few liquids are given at the end of this paper.

Measurement of Surface Tension and of Density over a Range of Temperatures.—The technique has already been described (Part I, this vol., p. 336). Three surface-tension apparatus, A, B, and C, were employed, the constants of which were 1·8545, 2·5142, and 1·8725 respectively.

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, $d^{t^\circ}_{4^\circ}$ the density (calculated from the observed densities by assuming a linear variation with temperature), γ the surface tension (dynes/cm.) computed from the equation $\gamma = KHd$, P the parachor (density of the vapour was neglected in the calculation), M the molecular weight, and $Mn^{20^\circ}_{\mathrm{D}}$ the molecular refraction coefficient. The number in parentheses following the value of γ_{20° is the temperature coefficient of surface tension. The following abbreviations are employed: $d^{20^\circ}_{4^\circ}$ for $d^{20\cdot0^\circ}_{4^\circ}$; R_{C}, R_{D}, R_{F}, and $R_{\mathrm{G'}}$, for $[R_L]_{\mathrm{C}}$, $[R_L]_{\mathrm{D}}$, $[R_L]_{\mathrm{F}}$, and $[R_L]_{\mathrm{G'}}$, respectively. Data for $[R_L]_{\mathrm{D}}$, $Mn^{20^\circ}_{\mathrm{D}}$, $[R_L]_{\mathrm{F-C}}$, and $[R_L]_{\mathrm{G'-C}}$, already given in Tables I and II, are not repeated in the constants for each compound.

Assistance in the preparations and measurements marked with an asterisk was given by R. J. Tudor, M.Sc.

Methyl β-*methylglutarate* (Found: C, 55·1; H, 8·0. $C_8H_{14}O_4$ requires C, 55·1; H, 8·1%); M = 174·11; b. p. 110°/19 mm.; n_{C} 1·42334, n_{D} 1·42556, n_{F} 1·43073, $n_{\mathrm{G'}}$ 1·43452; R_{C} 42·16, R_{F} 42·80, $R_{\mathrm{G'}}$ 43·13. Densities determined: $d^{20^\circ}_{4^\circ}$ 1·0523, $d^{63\cdot8^\circ}_{4^\circ}$ 1·0147, $d^{85\cdot0^\circ}_{4^\circ}$ 0·9929.

γ_{20° = 33·77 (0·106). App. B.

t.	*h.*	*H.*	$d^{t^\circ}_{4^\circ}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d^{t^\circ}_{4^\circ}$.	γ.	*P.*
24·0°	12·89	12·65	1·0487	33·25	399·0	86·9°	10·91	10·67	0·9912	26·59	398·9
63·8	11·67	11·43	1·0147	29·16	398·7					Mean	399·9

Methyl ββ-*dimethylglutarate*, M = 188·13; b. p. 111°/20 mm.; n_{C} 1·42679, n_{D} 1·42897, n_{F} 1·43424, $n_{\mathrm{G'}}$ 1·43809; R_{C} 46·67, R_{F} 47·38, $R_{\mathrm{G'}}$ 47·75. Densities determined: $d^{20^\circ}_{4^\circ}$ 1·0345; $d^{61\cdot8^\circ}_{4^\circ}$ 0·9944, $d^{85\cdot7^\circ}_{4^\circ}$ 0·9742.

γ_{20° = 31·44 (0·098). App. A.

23·9	16·49	16·25	1·0306	31·06	430·9	85·4	14·12	13·88	0·9745	25·08	432·0
61·8	15·06	14·82	0·9944	27·33	432·6					Mean	431·8

Methyl* β-*methyl*-β-*ethylglutarate*, M = 202·14; b. p. 124°/21 mm. (Dickens, Kon, and Thorpe, J., 1922, **121, 1503, give b. p. 128°/19 mm.); n_{C} 1·43312, n_{D} 1·43530, n_{F} 1·44062, $n_{\mathrm{G'}}$ 1·44446; R_{C} 50·95, R_{F} 51·72, $R_{\mathrm{G'}}$ 52·12. Densities determined: $d^{20^\circ}_{4^\circ}$ 1·0313, $d^{62\cdot6^\circ}_{4^\circ}$ 0·9981, $d^{85\cdot7^\circ}_{4^\circ}$ 0·9693.

γ_{20° = 31·97 (0·097). App. A.

23·9	16·81	16·57	1·0281	31·59	466·1	84·5	14·44	14·20	0·9703	25·55	468·4
62·2	15·38	15·14	0·9984	28·03	465·9					Mean	466·8

**Methyl* ββ-*diethylglutarate*, M = 216·16; b. p. 135°/20 mm. (Dickens, Kon, and Thorpe, *loc. cit.*, give b. p. 131°/16 mm.); n_{C} 1·44023, n_{D} 1·44245, n_{F} 1·44780, $n_{\mathrm{G'}}$ 1·45173; R_{C} 55·49, R_{F} 56·33, $R_{\mathrm{G'}}$ 56·75. Densities determined: $d^{20^\circ}_{4^\circ}$ 1·0270, $d^{62\cdot0^\circ}_{4^\circ}$ 0·9924, $d^{85\cdot8^\circ}_{4^\circ}$ 0·9732.

γ_{20° = 31·74 (0·089). App. B.

23·0	12·47	12·23	1·0236	31·47	500·2	85·3	10·83	10·59	0·9736	25·92	501·0
62·0	11·46	11·22	0·9924	28·00	501·0					Mean	500·7

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**Methyl* β-*methyl*-β-n-*propylglutarate* (Found : C, 60·9 ; H, 9·3. $C_{11}H_{20}O_4$ requires C, 61·1 ; H, 9·3%), M = 216·16 ; b. p. 130°/17 mm. ; n_{C} 1·43522, n_{D} 1·43741, n_{F} 1·44281, $n_{\mathrm{G'}}$ 1·44677 ; R_{C} 55·89, R_{F} 56·74, $R_{\mathrm{G'}}$ 57·20. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0095, $d_{4^\circ}^{62\cdot4^\circ}$ 0·9776, $d_{4^\circ}^{86\cdot2^\circ}$ 0·9567.

γ_{20° = 31·17 (0·092). App. B.

t.	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*
27·3	12·34	12·10	1·0037	30·53	506·3	85·4	10·71	10·47	0·9573	25·20	505·9
62·4	11·35	11·11	0·9776	27·31	505·5					Mean	505·9

**Methyl* β-*ethyl*-β-n-*propylglutarate* (Found : C, 62·6 ; H, 9·6. $C_{12}H_{22}O_4$ requires C, 62·6 ; H, 9·6%), M = 230·17 ; b. p. 142°/20 mm. ; n_{C} 1·44041, n_{D} 1·44265, n_{F} 1·44806, $n_{\mathrm{G'}}$ 1·45207 ; R_{C} 60·21, R_{F} 61·12, $R_{\mathrm{G'}}$ 61·59. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0083, $d_{4^\circ}^{63\cdot0^\circ}$ 0·9765, $d_{4^\circ}^{87\cdot4^\circ}$ 0·9569.

γ_{20° = 31·37 (0·090). App. B.

19·0	12·64	12·40	1·0091	31·46	540·2	86·0	10·79	10·55	0·9580	25·41	539·4
62·7	11·47	11·23	0·9767	27·58	540·0					Mean	539·8

**Methyl di*-n-*propylglutarate* (Found : C, 63·7 ; H, 9·9. $C_{13}H_{24}O_4$ requires C, 63·9 ; H, 9·9%), M = 244·19 ; b. p. 151°/20 mm. ; n_{C} 1·44092, n_{D} 1·44315, n_{F} 1·44856, $n_{\mathrm{G'}}$ 1·45256 ; R_{C} 64·74, R_{F} 65·71, $R_{\mathrm{G'}}$ 66·24. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9958, $d_{4^\circ}^{63\cdot6^\circ}$ 0·9626, $d_{4^\circ}^{86\cdot8^\circ}$ 0·9443.

γ_{20° = 30·53 (0·090). App. A.

19·5	16·79	16·55	0·9962	30·58	576·4	85·4	14·36	14·12	0·9454	24·76	576·1
63·6	15·06	14·82	0·9626	26·46	575·3					Mean	575·9

Methyl cyclo*pentane*-1 : 1-*diacetate*, M = 214·14 ; b. p. 141°/17 mm. (Dickens, Kon, and Thorpe, J., 1922, **121**, 1503, give b. p. 162°/15 mm. : this is definitely high) ; n_{C} 1·45366, n_{D} 1·45597, n_{F} 1·46163, $n_{\mathrm{G'}}$ 1·46580 ; R_{C} 53·61, R_{F} 54·34, $R_{\mathrm{G'}}$ 54·84. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0810, $d_{4^\circ}^{61\cdot8^\circ}$ 1·0476, $d_{4^\circ}^{85\cdot8^\circ}$ 1·0269.

γ_{20° = 35·40 (0·107). App. A.

23·4	17·77	17·53	1·0779	35·04	483·3	85·8	15·18	14·94	1·0269	28·45	481·6
61·8	16·15	15·91	1·0476	30·91	482·0					Mean	482·3

**Methyl* 3-*methyl*cyclo*pentane*-1 : 1-*diacetate* (Found : C, 63·1 ; H, 8·8. $C_{12}H_{20}O_4$ requires C, 63·2 ; H, 8·8%), b. p. 148°/19 mm. ; M = 228·16 ; n_{C} 1·45031, n_{D} 1·45257, n_{F} 1·45814, $n_{\mathrm{G'}}$ 1·46225 ; R_{C} 58·36, R_{F} 59·23, $R_{\mathrm{G'}}$ 59·70. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0513, $d_{4^\circ}^{63\cdot4^\circ}$ 1·0171, $d_{4^\circ}^{84\cdot3^\circ}$ 1·0003.

γ_{20° = 32·56 (0·087). App. B.

20·4	12·55	12·31	1·0510	32·53	518·5	85·3	10·97	10·73	0·9993	26·96	520·3
64·6	11·44	11·20	1·0161	28·61	519·3					Mean	519·4

Methyl cyclo*hexane*-1 : 1-*diacetate*, M = 228·16 ; b. p. 159°/21 mm. (Dickens, Kon, and Thorpe, J., 1922, **121**, 1503, give b. p. 164°/26 mm.) ; n_{C} 1·46136, n_{D} 1·46374, n_{F} 1·46946, $n_{\mathrm{G'}}$ 1·47364 ; R_{C} 58·01, R_{F} 58·87, $R_{\mathrm{G'}}$ 59·32. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0801, $d_{4^\circ}^{62\cdot4^\circ}$ 1·0460, $d_{4^\circ}^{84\cdot4^\circ}$ 1·0283. This specimen (in App. B) gave γ_{20° = 36·10 (0·102) ; P = 517·4. A redistilled specimen, b. p. 155°/18 mm., gave $d_{4^\circ}^{20^\circ}$ 1·0801, $d_{4^\circ}^{62\cdot2^\circ}$ 1·0468, $d_{4^\circ}^{85\cdot2^\circ}$ 1·0283.

γ_{20° = 35·83 (0·098). App. A.

23·0	18·02	17·78	1·0777	35·54	516·9	85·9	15·69	15·45	1·0278	29·45	517·1
62·5	16·51	16·27	1·0466	31·58	516·8					Mean	516·9

**Methyl* 3-*methyl*cyclo*hexane*-1 : 1-*diacetate* (Found : C, 64·5 ; H, 9·2. $C_{13}H_{22}O_4$ requires C, 64·4 ; H, 9·2%), M = 242·18 ; b. p. 155°/15 mm. ; n_{C} 1·45881, n_{D} 1·46115, n_{F} 1·46687, $n_{\mathrm{G'}}$ 1·47115 ; R_{C} 62·99, R_{F} 63·95, $R_{\mathrm{G'}}$ 64·46. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0506, $d_{4^\circ}^{62\cdot9^\circ}$ 1·0187, $d_{4^\circ}^{85\cdot0^\circ}$ 1·0009.

γ_{20° = 33·28 (0·080). App. C.

20·6	17·14	16·90	1·0501	33·23	553·7	85·8	15·01	14·77	1·0003	27·67	555·3
62·9	15·98	15·74	1·0187	30·02	556·5					Mean	555·2

**Methyl* 4-*methyl*cyclo*hexane*-1 : 1-*diacetate* (Found : C, 64·4 ; H, 9·2%), M = 242·18 ; b. p. 164°/20 mm. ; n_{C} 1·45879, n_{D} 1·46115, n_{F} 1·46685, $n_{\mathrm{G'}}$ 1·47102 ; R_{C} 62·77, R_{F} 63·71, $R_{\mathrm{G'}}$ 64·19. Densities determined : $d_{4^\circ}^{20^\circ}$ 1·0547, $d_{4^\circ}^{63\cdot2^\circ}$ 1·0204, $d_{4^\circ}^{85\cdot6^\circ}$ 1·0038.

γ_{20° = 33·27 (0·079). App. B.

16·9	1·285	12·61	1·0572	33·52	551·2	85·6	11·36	11·12	1·0038	28·06	555·3
63·9	11·88	11·64	1·0198	29·84	551·1					Mean	553·9

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**Methyl* trans-*decahydronaphthalene*-2 : 2-*diacetate*, M = 282·21; b. p. 193°/14 mm. (Rao, J., 1929, 1962, gives b. p. 190°/12 mm.); n_C 1·47946, n_D 1·48195, n_F 1·48799, $n_{G'}$ 1·49253; R_C 74·49, R_D 74·81, R_F 75·61, $R_{G'}$ 76·21; $R_{G'-C}$ 1·72, R_{F-C} 1·12; $Mn_D^{20^\circ}$ 418·22. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0753, $d_{4^\circ}^{64{\cdot}2^\circ}$ 1·0418, $d_{4^\circ}^{83{\cdot}2^\circ}$ 1·0247.

γ_{20° = 36·44 (0·097). App. A.

t.	*h.*	*H.*	$d^{t^\circ}_{\circ}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d^{t^\circ}_{4^\circ}$.	γ.	*P.*
17·2	18·61	18·37	1·0777	36·71	644·6	84·0	16·23	15·99	1·0241	30·37	646·9
61·8	16·93	16·69	1·0437	32·30	644·6					Mean	645·4

**Methyl* trans-*hexahydrohydrindene*-2 : 2-*diacetate*, M = 268·19; b. p. 179°/12 mm. (Kandiah, J., 1931, 943, gives b. p. 172°/15 mm., $d_{4^\circ}^{19{\cdot}0^\circ}$ 1·074, $n_{4^\circ}^{19{\cdot}0^\circ}$ 1·4769); n_C 1·47297, n_D 1·47538, n_F 1·48137, $n_{G'}$ 1·48580; R_C 70·09, R_D 70·39, R_F 71·16, $R_{G'}$ 71·71; $R_{G'-C}$ 1·62, R_{F-C} 1·07; $Mn_D^{20^\circ}$ 395·68. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0734, $d_{4^\circ}^{63{\cdot}0^\circ}$ 1·0404, $d_{4^\circ}^{86{\cdot}6^\circ}$ 1·0221.

γ_{20° = 35·67 (0·093). App. C.

21·9	17·96	17·72	1·0698	35·50	611·9	87·1	15·64	15·40	1·0217	29·46	611·5
62·5	16·49	16·25	1·0408	31·67	611·3					Mean	611·6

Ethyl ββ-*dimethylglutarate*, M = 216·16; b. p. 126°/17 mm.; n_C 1·42600, n_D 1·42817, n_F 1·43346, $n_{G'}$ 1·43718; R_C 55·98, R_F 56·84, $R_{G'}$ 57·26. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9893, $d_{4^\circ}^{63{\cdot}0^\circ}$ 0·9519, $d_{4^\circ}^{85{\cdot}4^\circ}$ 0·9319.

γ_{20° = 29·68 (0·095). App. B.

18·5	12·21	11·97	0·9907	29·82	509·9	85·1	10·37	10·13	0·9322	23·74	511·7
62·7	10·89	10·65	0·9522	25·50	510·1					Mean	510·6

Ethyl cyclo*pentane*-1 : 1-*diacetate*, M = 242·18; b. p. 153°/14 mm. (Kon, J., 1922, **121**, 525, gives b. p. 157—158°/16 mm.); n_C 1·44916, n_D 1·45147, n_F 1·45698, $n_{G'}$ 1·46115; R_C 62·92, R_D 63·20, R_F 63·87, $R_{G'}$ 64·38; $R_{G'-C}$ 1·46, R_{F-C} 0·95; $Mn_D^{20^\circ}$ 351·52. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0326, $d_{4^\circ}^{62{\cdot}4^\circ}$ 0·9982, $d_{4^\circ}^{85{\cdot}6^\circ}$ 0·9789.

γ_{20° = 32·84 (0·098). App. B.

15·7	13·01	12·77	1·0360	33·26	561·4	85·6	11·01	10·77	0·9789	26·51	561·3
62·4	11·66	11·42	0·9982	28·66	561·4					Mean	561·4

**Ethyl* 3-*methyl*cyclo*pentane*-1 : 1-*diacetate*, M = 256·19; b. p. 164°/21 mm. (Vogel, J., 1931, 914, gives b. p. 155·5°/15 mm., $n_D^{20^\circ}$ 1·4485, $d_{4^\circ}^{15^\circ}$ 1·0602, the last figure is definitely high and requires correction; Desai, J., 1931, 1220, gives b. p. 156°/15 mm., $n_D^{20^\circ}$ 1·44933, $d_{4^\circ}^{20^\circ}$ 1·009); n_C 1·44648, n_D 1·44876, n_F 1·45427, $n_{G'}$ 1·45850; R_C 67·69, R_F 68·71, $R_{G'}$ 69·27. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0102, $d_{4^\circ}^{62{\cdot}3^\circ}$ 0·9780, $d_{4^\circ}^{85{\cdot}6^\circ}$ 0·9608.

γ_{20° = 31·12 (0·088). App. B.

18·2	12·54	12·30	1·0116	31·28	598·9	85·6	10·76	10·52	0·9608	25·41	598·7
62·3	11·39	11·15	0·9780	27·41	599·4					Mean	599·0

Ethyl cyclo*hexane*-1 : 1-*diacetate*, M = 256·19; b. p. 165°/14 mm. (Thole and Thorpe, J., 1911, **99**, 446, give b. p. 288°/733 mm.); n_C 1·45626, n_D 1·45856, n_F 1·46423, $n_{G'}$ 1·46836; R_C 67·36, R_F 68·38, $R_{G'}$ 68·90. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0344, $d_{4^\circ}^{64{\cdot}2^\circ}$ 1·0007, $d_{4^\circ}^{86{\cdot}4^\circ}$ 0·9833.

γ_{20° = 33·48 (0·095). App. B.

18·6	13·15	12·91	1·0355	33·61	595·7	86·4	11·26	11·02	0·9830	27·24	595·4
63·6	11·88	11·64	1·0012	29·30	595·3					Mean	595·5

**Ethyl* 3-*methyl*cyclo*hexane*-1 : 1-*diacetate* (Found: C, 66·6; H, 9·7. $C_{15}H_{26}O_4$ requires C, 66·6; H, 9·7%), M = 270·21; b. p. 177°/21 mm.; n_C 1·45405, n_D 1·45637, n_F 1·46205, $n_{G'}$ 1·46617; R_C 72·17, R_F 73·26, $R_{G'}$ 73·81. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0142, $d_{4^\circ}^{63{\cdot}2^\circ}$ 0·9815, $d_{4^\circ}^{84{\cdot}2^\circ}$ 0·9568.

γ_{20° = 31·70 (0·092). App. B.

19·4	12·69	12·45	1·0147	31·76	632·1	85·7	10·89	10·65	0·9556	25·59	635·8
62·5	11·51	11·27	0·9821	27·83	631·9					Mean	633·3

**Ethyl* 4-*methyl*cyclo*hexane*-1 : 1-*diacetate* (Found: C, 66·5; H, 9·7%), M = 270·21; b. p. 178°/21 mm.; n_C 1·45402, n_D 1·45647, n_F 1·46212, $n_{G'}$ 1·46633; R_C 71·98, R_F 73·08, $R_{G'}$ 73·66. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0166, $d_{4^\circ}^{63{\cdot}2^\circ}$ 0·9845, $d_{4^\circ}^{84{\cdot}7^\circ}$ 0·9674.

γ_{20° = 31·72 (0·089). App. C.

18·0	16·97	16·73	1·0182	31·90	630·7	86·2	14·55	14·31	0·9662	25·89	630·8
63·2	15·42	15·18	0·9845	27·98	631·3					Mean	630·9

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**Ethyl* trans-*hexahydrohydrindene*-2 : 2-*diacetate*, $M = 296{\cdot}22$; b. p. 196°/14 mm. (Kandiah, J., 1931, 943, gives b. p. 182°/16 mm., $n_D^{19°}$ 1·4687, $d_4^{19°}$ 1·043); n_C 1·46700, n_D 1·46938, n_F 1·47528, $n_{G'}$ 1·47963; R_C 79·31, R_D 79·65, R_F 80·53, $R_{G'}$ 81·15; $R_{G'-C}$ 1·84, R_{F-C} 1·22; $Mn_D^{20°}$ 435·26. Densities determined : $d_{4°}^{20°}$ 1·0362, $d_{4°}^{63{\cdot}2°}$ 1·0022, $d_{4°}^{87{\cdot}2°}$ 0·9846.

$\gamma_{20°} = 33{\cdot}95$ (0·094). App. B.

t.	*h.*	*H.*	$d_{4°}^{°}$.	γ.	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{°}$.	γ.	*P.*
22·3	13·21	12·97	1·0343	33·73	690·2	85·6	11·50	11·26	0·9859	27·91	690·6
63·2	12·06	11·82	1·0022	29·78	690·5					Mean	690·4

**Ethyl* trans-*decahydronaphthalene*-2 : 2-*diacetate*, $M = 310{\cdot}24$; b. p. 208°/17 mm. (Rao, J., 1929, 1958, gives b. p. 209°/16 mm., $n_{4°}^{16{\cdot}8°}$ 1·47702, $d_{4°}^{16{\cdot}8°}$ 1·04115); n_C 1·47313, n_D 1·47558, n_F 1·48154, $n_{G'}$ 1·48598; R_C 83·66, R_D 84·04, R_F 84·93, $R_{G'}$ 85·61; $R_{G'-C}$ 1·95, R_{F-C} 1·27; $Mn_D^{20°}$ 457·78. Densities determined : $d_{4°}^{20°}$ 1·0405, $d_{4°}^{64{\cdot}0°}$ 1·0054, $d_{4°}^{84{\cdot}1°}$ 0·9894.

$\gamma_{20°} = 34{\cdot}43$ (0·096). App. B.

18·9	13·43	13·19	1·0414	34·54	722·2	84·1	11·69	11·45	0·9894	28·48	724·4
63·5	12·15	11·19	1·0058	30·12	722·6					Mean	723·1

Revised Data.—Methyl glutarate. $M = 160{\cdot}10$; b. p. 109°/21 mm.; n_C 1·42208, n_D 1·42415, n_F 1·42925, $n_{G'}$ 1·43362; R_C 37·42, R_F 37·98, $R_{G'}$ 38·31.

Methyl adipate. $M = 174{\cdot}11$; b. p. 119°/17 mm.; n_C 1·42616, n_D 1·42835, n_F 1·43340, $n_{G'}$ 1·43772; R_C 42·04, R_F 42·66, $R_{G'}$ 43·03.

Methyl pimelate. $M = 188{\cdot}13$; b. p. 128°/16 mm.; n_C 1·42872, n_D 1·43088, n_F 1·43614, $n_{G'}$ 1·43989; R_C 46·68, R_F 47·39, $R_{G'}$ 47·74.

Methyl suberate. $M = 202{\cdot}14$; b. p. 148°/20 mm.; n_C 1·43145, n_D 1·43370, n_F 1·43892, $n_{G'}$ 1·44274; R_C 51·36, R_F 52·13, $R_{G'}$ 52·51.

The figures in Tables I and II (Part I, this vol., p. 335) must accordingly be amended; the mean value of $Mn_D^{20°}$ for the methyl esters is 20·62.

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