STUDIES IN ESTERIFICATION.

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In continuation of the work on the relations between the esterification constants of carboxylic acids and their structure [1] the constants of the following acids have been determined at 25° in the presence of excess of anhydrous ethyl alcohol and using hydrogen chloride as catalyst :—

1. *n*-Valeric, 2. caproic, 3. nonoic, 4. decoic, 5. lauric, 6. myristic, 7. palmitic, 8. stearic, 9. erucic, 10. brassidic, 11. allylacetic, 12. hydrocinnamic, 13. *iso*propylacetic, 14. *iso*butylacetic, 15. *iso*amylacetic, 16. methyl-*n*-propylacetic, 17. methylallylacetic, 18. methyl-*n*-butylacetic, 19. methylbenzylacetic, 20. methyl*iso*propylacetic, 21. methyl*iso*butylacetic, 22. ethyl-*n*-butylacetic, 23. di-*n*-propylacetic, 24. *cyclo*heptanemonocarboxylic, 25. *bicyclo*heptanemonocarboxylic, 26. *cyclo*hexylacetic, 27. *cyclo*hexeneacetic, 28. *cyclo*hexylideneacetic, 29. *p*-methyl*cyclo*hexylacetic, 30. *p*-methyl*cyclo*hexeneacetic, 31. *p*-methyl*cyclo*hexylideneacetic, 32. Δ^1-tetrahydrobenzoic, 33. Δ^2-tetrahydrobenzoic, 34. *cyclo*heptatrienecarboxylic, 35. *o*-toluic, 36. *m*-toluic, 37. *p*-toluic, 38. hexahydro-*m*-toluic, 39. hexahydro-*p*-toluic, 40. β-*cyclo*hexylpropionic, 41. Δ^2-*cyclo*hexeneacetic, 42. adipic, 43. pimelic, 44. suberic, 45. α-*cyclo*geranic, 46. β-*cyclo*geranic.

The constants have all been calculated with the aid of Goldschmidt and Udby's formula [2]

$$k_c\, t = (r + a)\ \log_e a/(a - x)$$

where $r = 0{\cdot}15$, as constant values cannot be obtained when the usual equation for a unimolecular reaction is employed, owing to the disturbing action of the water formed during the course of the reaction.[3] In the tables which follow k_1 is used to denote the value of k calculated according to this formula and then recalculated for 0·1 N hydrochloric acid assuming that k_c is proportional to the concentration of the catalyst.

The results given in the present paper, in combination with a few earlier results, lead to the following generalisations.

[1] *Ber.*, 1894, 27, 510, 1580, 3146. *J. Chem. Soc.*, 1898, 73, 81 ; 1899, 75, 476 ; 1904, 85, 534 ; 1905, 87, 1840 ; 1907, 91, 1033 ; 1909, 95, 315, 975 ; 1911, 99 2307 ; 1912, 101, 237, 1227. *This Journal*, 1923, 6, 41.

[2] *Z. physikal. Chem.*, 1907, 60, 728.

[3] More recently Goldschmidt, *ibid.*, 1920, 94, 235, has recommended using $r = 0{\cdot}25$ as the values for k then agree even better. This value has not been used in the present paper, as we wished to compare our values with some earlier values obtained by using $r = 0{\cdot}15$.

A. Saturated Monobasic Aliphatic Acids.

1. *Normal chain acids.*—In 1908 attention was drawn to the fact that in the series of normal fatty acids the esterification constant falls from formic to butyric acid and then remains fairly constant as far as stearic acid. The values given at that date refer to methyl alcohol at 15° and were obtained by using the usual equation for a unimolecular reaction.[1]

Table I gives the values for the esterification constants of the same acids calculated with the aid of Goldschmidt and Udby's formula for anhydrous ethyl alcohol at 25° and using 0·1 N hydrogen chloride as catalyst.

TABLE I.

Normal fatty acid	k_1
Acetic	0·796[2]
Propionic	0·550[2]
Butyric	0·270[2]
Valeric	0·268
Caproic	0·267
Nonoic	0·270
Decoic	0·269
Lauric	0·272
Myristic	0·269
Palmitic	0·276
Stearic	0·276
Allylacetic	0·274
Erucic	0·279
Brassidic	0·273

These values show that the constant falls from acetic to butyric and then remains practically constant, the values for the acids examined between butyric and stearic vary by only 1·5 per cent. The last three values given in Table I are of interest as they show that an olefine linking in the molecule of a normal fatty acid has little or no effect on the rate of esterification provided it is sufficiently far removed from the carboxylic group.

2.—*The effect on the rate of esterification of attaching a methyl group to the penultimate carbon atom in the molecule of a normal fatty acid.*—The figures given in Table II illustrate this effect.

[1] *J. Chem. Soc.*, 1908, 93, 211.
[2] Goldschmidt and Udby, *Z. physikal. Chem.*, 1908, 60, 743.

Gyr[1] has determined the esterification constants of certain acids in methyl alcohol at 15°. The constants are calculated by the usual formula for unimolecular reactions and are as follows:—

Phenylacetic ...	... 3·44	Diphenylacetic ...	... 0·201
p-Methylphenylacetic	... 3·66	Phenyl-*p*-tolylacetic	... 0·212

4. *Influence of cyclic olefine linkings on the rate of esterification of a monobasic acid.*—In earlier papers[2] attention has been drawn to the inhibiting effect on esterification produced by the introduction of an αβ-olefine linking in the case of a monobasic aliphatic acid, whereas the presence of a βγ-linking in such an acid has a slight accelerating effect. The values obtained when such linkings are present in the case of cyclic acids are given in Table X.

TABLE X.

Acid	*Formula*	k_1
*Cyclo*hexylacetic	... $CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>CH\cdot CH_2\cdot CO_2H$	... 0·0809
*Cyclo*hexeneacetic	... $CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH}{CH_2\cdot CH_2}\gg C\cdot CH_2\cdot CO_2H$	... 0·108
*Cyclo*hexylideneacetic	... $CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>C{:}CH\cdot CO_2H$	... 0·00228
p-methyl-*cyclo*hexeneacetic	... $CH_3\cdot CH<\genfrac{}{}{0pt}{}{CH_2\cdot CH}{CH_2\cdot CH_2}\gg C\cdot CH_2\cdot CO_2H$	... 0·118
p-methyl-*cyclo*hexylideneacetic	... $CH_3\cdot CH<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>C{:}CH\cdot CO_2H$	... 0·00234
Δ²-tetrahydrobenzoic	... $CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH{:}CH}>CH\cdot CO_2H$	... 0·0829
Δ¹-tetrahydrobenzoic	... $CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH}\gg C\cdot CO_2H$	... 0·00220
Δ²-*cyclo*hexeneacetic acid	... $CH_2<\genfrac{}{}{0pt}{}{CH{:}CH}{CH_2\cdot CH_2}>CH\cdot CH_2\cdot CO_2H$	... 0·0731

[1] *Ber.*, 1907, 41, 4318.
[2] *J. Chem. Soc.*, 1905, 87, 1840; 1907, 91, 1033; 1909, 95, 315; 1911, 99, 2307.

The following ratios are of interest:—

TABLE XI.

Ratio of k *for saturated acid to* k *for βγ-unsaturated acid.*

Saturated	*βγ-unsaturated*	*Ratio*
n-Hexoic	Hydrosorbic	1 : 1·32
γ-Phenyl-*n*-butyric	βγ-Phenylcrotonic	1 : 1·57
n-Valeric	Ethylidenepropionic	1 : 1·40
d-Phenyl-*n*-valeric	β-Phenylethylidenepropionic	1 : 2·07
*Cyclo*hexylacetic	*Cyclo*hexeneacetic	1 : 1·33
Hexahydrobenzoic	Δ^{2}-Tetrahydrobenzoic	1 : 1·02

TABLE XII.

Ratio of k *for saturated acid to* k *for αβ-unsaturated acid.*

Saturated	*Unsaturated*	*Ratio*
n-Butyric	Crotonic	39 : 1
β-Phenylpropionic	Cinnamic	50 : 1
Methyl hydrogen succinate	Methyl hydrogen maleate	20 : 1
n-Valeric	β-Ethylacrylic	36 : 1
Hydratropic	Atropic	51 : 1
*iso*Valeric	Dimethylacrylic	43 : 1
Methyl-*iso*propylacetic	Trimethylacrylic	30 : 1
β-Furfurylpropionic	β-Furfurylacrylic	61 : 1
d-Phenyl-*n*-valeric	Phenylpropylideneacetic	30 : 1
*Cyclo*hexylacetic	*Cyclo*hexylideneacetic	35 : 1
p-Methyl-*cyclo*hexylacetic	*p*-Methyl-*cyclo*hexylideneacetic	38 : 1
Hexahydrobenzoic	Δ^{1}-Tetrahydrobenzoic	37 : 1

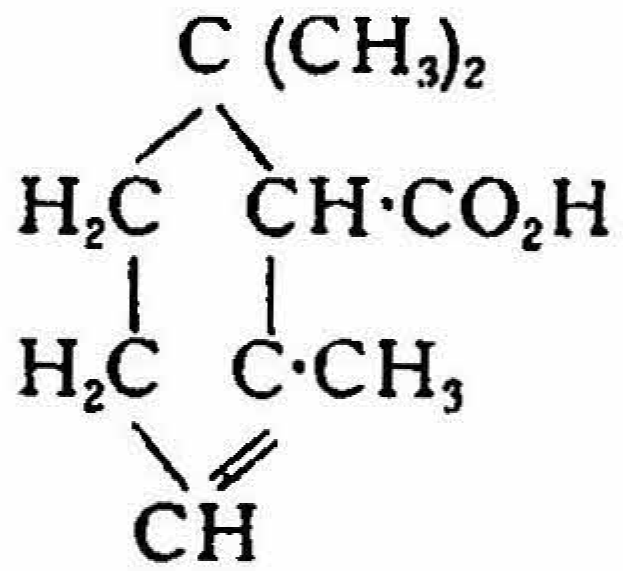
A comparison of the values for benzoic and *cyclo*hepta-$\Delta^{1:3:5}$-triene-carboxylic acids is of interest. The Kekulé formula for benzoic acid has a conjugate αβ-linking and in addition a βγ-olefine linking, whereas the triene-acid has the one conjugate linking but no βγ-linking. From this it would follow that the triene-acid should have a lower constant than the benzoic acid, and as *cyclo*hexanecarboxylic acid has a higher value than *cyclo*heptanecarboxylic acid this should augment the difference. The actual values are benzoic acid = 0·00240 and *cyclo*heptatriene-1-carboxylic acid = 0·00184 giving a ratio 1 : 0·78.

5. *Influence of di-ortho-substituents.*—In the benzoic series it is well known that two ortho-substituents inhibit esterification by the catalytic process at temperatures between 0° and 70°. So far no

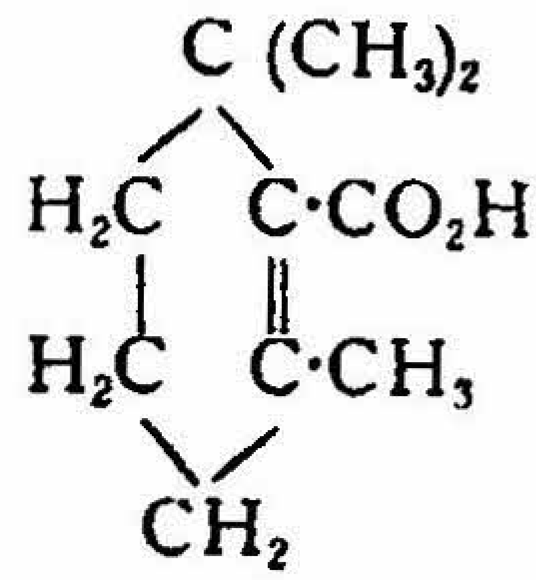
experiments have been made with di-ortho-substituted *cyclo*hexanecarboxylic acids. We took up the study of the esterification of the α and β-*cyclo*geranic acids with the object of studying the effects of the αβ and βδ-unsaturated linkings on the rate of esterification; but at 25° with hydrogen chloride as catalyst no ester had been formed at the end of 30 days.

These results show that the ortho-methyl substituents in these acids, as in the benzoic series, have a marked inhibiting effect on esterification.

α



β



EXPERIMENTAL.

PREPARATION OF ACIDS.

The following acids were purchased and were purified by distillation or crystallisation:—Propionic, *iso*valeric, caproic, nonoic, decoic, lauric, myristic, palmitic, stearic, erucic, brassidic, benzoic, *o*-toluic, *m*-toluic, *p*-toluic, suberic and adipic. The melting or boiling points of these and of all the other acids after purification and as actually used for esterification are given in Table XIII.

The remaining acids were prepared in these laboratories and the following notes are of value:—

Allylacetic acid.—Allylmalonic acid was obtained in 80 per cent. yield by hydrolysing the ethyl ester with a 50 per cent. excess of alcoholic potash, and when distilled gave an almost theoretical yield of crude allylacetic acid boiling at [illegible]186°. When fractionated the pure acid was obtained boiling at 185–186° under a pressure of 685 mm.

iso*Amylacetic acid.*—[illegible] per cent. yield of ethyl *iso*amylmalonate was obtained by Hoffmann's method[1] from ethyl malonate and *iso*amyl bromide. The ester was hydrolysed with alcoholic potash and the dibasic acid and distillation gave a 90 per cent. yield of crude *iso*amylacetic acid boiling at 200–206° under a pressure of 685 mm.

[1] *Ber.*, 1890, 28, 1498.

Dialkylated acetic acids.—Most of the acids of this series were prepared by introducing alkyl groups into the ethyl malonate molecule hydrolysing the esters by Perkin's method [1] and distilling the dibasic acid so obtained.

In the preparation of the alkylated malonic esters it was found that the water-content of the alcohol employed had a marked effect on the yield of condensation product, as shown by the following results:—In the preparation of ethyl *n*-butylmalonate the yield was 20 per cent. using 95 per cent. alcohol, but rose to 74 per cent. of the theoretical when 99·9 per cent. alcohol was used. In the case of ethyl *iso*propylmalonate the yield was 58 per cent. of theoretical with 99·7 alcohol and 68 per cent. with 99·9 per cent. alcohol.

For the hydrolysis of the esters the following procedure was adopted:—One part by weight of ester was hydrolysed with twice the theoretical amount of potassium hydroxide dissolved in two parts by weight of 50 per cent. alcohol. The ester was added gradually to the alkali and the whole well shaken. Usually the potassium ethyl salt separated during the course of the reaction and the mixture was heated on the water-bath until this had disappeared, an operation which usually required 4–5 hours. The product was diluted with its own volume of water, evaporated to its original volume and shaken with ether, to remove traces of unsaponified ester; the aqueous solution was acidified with dilute sulphuric acid and again extracted with ether. This method usually gave yields of from 80 to 85 per cent. of the theoretical.

*Methyl-*n*-butylacetic acid.*—*n*-Butyl iodide was prepared by Linnemann's method [2] from the corresponding alcohol, care being taken to pass in dry hydrogen iodide slowly especially at the beginning of the reaction. The yield was 73 per cent. of the theoretical and the boiling point 125–127° under a pressure of 685 mm. Rasetti's method [3] was used for the condensation and the yield of dibasic ester was 74 per cent. of the theoretical. The yield of monobasic acid was practically theoretical.

*Ethyl-*n*-butylacetic acid.*—A yield of 74 per cent. of ethyl ethyl-*n*-butylmalonate was obtained as compared with 53 given by Raper.[4] An 80 per cent. yield of crude monobasic acid boiling at 220–225° under 685 mm. pressure was obtained.

*Methyl-*n*-propylacetic acid.*—An 80 per cent. yield was obtained by heating the dibasic acid at 180° and then distilling.

[1] *J. Chem. Soc.*, 1896, 69, 1477.
[2] *Annalen*, 1872, 161, 198.
[3] *Bull. Soc. chim.*, 1905, [111], 33, 688.
[4] *J. Chem. Soc.*, 1907, 91, 1837.

Methyl-iso*propylacetic acid*.—The methods, details and yields were much the same as those given by Perkin.[1]

Methyl-iso*butylacetic* acid was prepared by the method given by Burrows and Bentley.[2]

Methylallylacetic acid.—The ester of the dibasic acid was prepared by methylating ethyl allylmalonate according to the following process:—60 grams of ethyl allylmalonate are added to a well-cooled solution of 7 grams of sodium in 75 cc. of 99·9 per cent. alcohol and to this mixture 50 grams of methyl iodide are added gradually so that the temperature does not rise above 40° and the whole is kept over night. Next day the alcohol is removed, the residue diluted with water and extracted with ether when a 74 per cent. yield of ethyl methylallylmalonate is obtained boiling at 222–226° under 685 mm. pressure. The dibasic acid obtained by hydrolysis with alcoholic potash (1·5 mols.) and subsequent crystallisation from benzene forms leaflets, melting at 98–99°.

0·127 gram required 17·3 cc. of 0·09069N. potassium hydroxide. Equivalent = 79·1. Theory for $C_7H_{10}O_4 = 79$.

When heated for an hour at 160° and then distilled, it yields crude methylallylacetic acid, which after three fractionations was obtained as a colourless liquid boiling at 188–189° under a pressure of 683 mm. 0·2020 gram required 19·1 cc. of the same alkali for neutralisation. Equivalent = 114·2. Theory for $C_6H_{10}O_2 = 114$.

Cyclo*heptane*-1-*carboxylic acid* was prepared by Zelinsky's method[3] from suberic acid by the following series of reactions:— suberic acid ⟶ suberone ⟶ suberol ⟶ suberyl bromide ⟶ magnesium compound ⟶ *cyclo*pentanecarboxylic acid. The yield of suberone was the same as that given by Mager,[4] viz., 30 to 35 per cent. of the theoretical, and the yield of suberol 80 per cent. when prepared by Markownikoff's method.[5] The yield of suberyl bromide obtained by heating suberol with hydrobromic acid (sp. gr. 1·92) for five hours at 100° was 65 per cent. of the theoretical and the yield of cyclic acid from the bromide, 40 per cent. In this way from 100 grams of suberic acid it is possible to obtain only 5 grams of *cyclo*heptanecarboxylic acid.

[1] *J. Chem. Soc.*, 1896, 69, 1477.
[2] *Ibid.*, 1895, 67, 511.
[3] *Ber.*, 1902, 35, 2691.
[4] *Annalen*, 1893, 275, 357.
[5] *Ibid.*, 1903, 327, 63.

Cyclo*hexylacetic acid*, $CH_2 \left< \begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix} \right> CH\cdot CH_2\cdot CO_2H$, has been obtained by Wallach [1] by reducing ethyl *cyclo*hexanolacetate with zinc dust, hydrogen bromide and glacial acetic acid with a yield of 48 per cent. of the weight of the ester taken. It has also been prepared by Perkin [2] by condensing *cyclo*hexyl bromide with ethyl sodiomalonate, hydrolysing and removing carbon dioxide; but the yield of dibasic ester is only 33 per cent. of the theoretical. A third method consists in using ethyl cyanoacetate in place of ethyl malonate, but the yields are even lower. The method we have adopted and found convenient is the treatment of Robinson's *cyclo*hexylmalonamic acid [3] with sodium nitrite in 90 per cent. sulphuric acid solution.

$$CH_2 \left< \begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix} \right> CH\cdot CH \left< \begin{matrix} CO\cdot NH_2 \\ CO_2H \end{matrix} \right. + HNO_2 \longrightarrow$$

$$CH_2 \left< \begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix} \right> CH\cdot CH_2\cdot CO_2H + N_2 + CO_2$$

For this purpose 25 grams of *cyclo*hexylmalonamic acid were dissolved in 380 cc. of 90 per cent. sulphuric acid and heated on the water bath until the evolution of carbon dioxide ceased. After cooling to 0°, 15 grams of sodium nitrite in 20 cc. of water was added gradually with continuous stirring; after one hour, the solution was gradually warmed on the water bath and well stirred until evolution of nitrogen and carbon dioxide ceased. On cooling, the mass was diluted with three times its volume of water and extracted three times with ether, the ethereal solution dried and the ether removed. The residue was extracted with sodium carbonate to separate the acid from small amounts of amide which remained undissolved, the clear solution acidified and extracted with ether. A 60 per cent. yield of the crude acid was obtained as a colourless liquid boiling at 228–230° under a pressure of 685 mm.

Attempts were made to reduce the volume of sulphuric acid, but it was found that under such conditions part of the amic acid separated and escaped action.

Cyclo*hexeneacetic acid*, $CH_2 \left< \begin{matrix} CH_2\cdot CH \\ CH_2\cdot CH_2 \end{matrix} \right> C\cdot CH_2\cdot CO_2H$, was prepared by Wallach's method from *cyclo*hexanone by the three stages[4]:—

*Cyclo*hexanone ⟶ methyl *cyclo*hexan-1-ol-1-acetate ⟶ methyl*cyclo*hexeneacetate ⟶ *cyclo*hexeneacetic acid, potassium hydrogen sulphate

[1] *Annalen*, 1907, 353, 205.
[2] *J. Chem. Soc.*, 1909, 95, 1363.
[3] *Ibid.*, 1924, 125, 227.
[4] Wallach, *Annalen*, 1906, 347, 345.

being used at the second stage and the yield at each stage being 70–80 per cent. of the theoretical.

p-Methyl-*cyclo*hexeneacetic acid[1] was prepared in a similar manner from *p*-methyl*cyclo*hexanone and the yields were much the same.

Cyclo*hexylideneacetic acid*, $CH_2\left\langle\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\right\rangle C:CH\cdot CO_2H$, and the corresponding *p*-methyl derivative were obtained by heating the hydroxy-acids (2 grams) with acetic anhydride (5 grams) and the yield of unsaturated acid was 2 grams.[2]

When the experiments were started, no methyl bromoacetate was available and attempts were made to utilise the corresponding ethyl ester, but with boiling benzene as diluent no condensation occurred. It was found, however, that by replacing the benzene by toluene the ethyl bromoacetate, zinc and ketone reacted readily, and the reaction became so brisk that external cooling was necessary. The yield of ethyl *cyclo*hexanolacetate was 77 per cent. of the theoretical and it formed a colourless liquid boiling at 132–135° under a pressure of 11 mm.

Cyclo*hepta-*$\Delta^{1:3:5}$*-triene-*1*-carboxylic acid*, was prepared by Buchner's method[3] and the yield was slightly less than that given by this author.

Bicyclo*heptanecarboxylic acid* or 1-B 1:3, cyclo*heptane-*2*-carboxylic acid*, $\left.\begin{matrix}CH_2\cdot CH_2\cdot CH\\ | \qquad\qquad |\\ CH_2\cdot CH_2\cdot CH\end{matrix}\right\rangle CH\cdot CO_2H$.—The ester of this acid was prepared by condensing ethyl diazoacetate with tetrahydrobenzene obtained from *cyclo*hexanol and potassium hydrogen sulphate as recommended by Brunel.[4]

Fifteen grams of the tetrahydrobenzene and 7·5 of the diazo-ester were heated in a sealed tube at 130–135° for eight hours. The tetrahydrobenzene was distilled off on the water bath, the residue steam-distilled and the distillate extracted three times with ether. The residue after removal of the ether was distilled and the fraction boiling at 112–115° under a pressure of 11 mm. collected separately. From 25 grams of diazo-ester 8 grams of the bicyclic ester were obtained, a yield considerably higher than that obtained by condensing benzene with ethyl diazoacetate. For the hydrolysis of the ester the following process was adopted:—8 grams of the ester were boiled

[1] Wallach, *Annalen*, 1909, 365, 263.
[2] Wallach, *Annalen*, 1909, 365, 261, 266.
[3] *Ber.*, 1901, 34, 990.
[4] *Bull. Soc. chim.*, 1905, [III], 33, 270.

on the water bath with 10 grams of potassium hydroxide, 20 cc. of water and 10 cc. of alcohol for two hours, the mixture was then made faintly acid with dilute hydrochloric acid and again just alkaline with dilute sodium carbonate. The alcohol was removed by evaporation on the water bath. The residue was cooled to 0° and oxidized with 1 per cent. permanganate solution until a permanent pink colour was obtained, the hydrated manganese oxide was removed and carefully washed and the clear filtrate acidified with dilute hydrochloric acid. The precipitate (4 grams), which melted at 70° after drying, was crystallised twice from 50 per cent. alcohol and obtained as feathery long needles melting at 97·5–98°.

The yield of acid obtained by hydrolysing the ester with sodium ethoxide was not so good.

0·1012 grs. of the acid required 15·3 cc. of 0·09279 N. sodium hydroxide solution. Equivalent = 140. $C_8H_{12}O_2$ requires 140.

Δ^1-*Tetrahydrobenzoic acid* was prepared by Aschan's method of removing hydrogen bromide from α-bromo-hexahydrobenzoic acid.[1] The yield of bromo-acid was 70 per cent. of the theoretical and the yield of crude tetrahydro-acid 80 per cent. of the theoretical.

Δ^2-*Tetrahydrobenzoic acid* was obtained by reducing benzoic acid by Aschan's method.[2]

*p-Methyl*cyclo*hexylacetic acid*, $CHMe\langle\begin{smallmatrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{smallmatrix}\rangle CH\cdot CH_2CO_2H$. —The method adopted was that due to Hope and Perkin,[3] but as they give few details, the following notes may be of value :—A 60 per cent. yield of β-bromo-*p*-methyl*cyclo*hexylacetic acid was obtained by treating the corresponding β-hydroxy-acid with aqueous hydro bromic acid saturated at 0°.

10 grams of the bromo-acid were dissolved in 10 cc. of 98 per cent. alcohol together with 5 cc. of glacial acetic acid and a few drops of concentrated hydrochloric acid; 2·1 grams of magnesium turnings were added and the temperature kept below 30°. When all the magnesium had dissolved, the product was steam-distilled and the distillate treated with cold dilute permanganate to destroy any unsaturated acid present. The yield of saturated acid was 4 grams or 57 per cent. of the theoretical.

[1] *Annalen*, 1892, 271, 267.
[2] *Ibid.*, 234.
[3] *J. Chem. Soc.*, 1908, 93, 1080.

Δ^2-Cyclo-*hexeneacetic acid*, $CH_2\langle{}^{CH:CH}_{CH_2\cdot CH_2}\rangle CH\cdot CH_2\cdot CO_2H$, was prepared by van Eykmann's method.[1] Tetrahydrobenzene dissolved in its own volume of dry chloroform was treated at 0° with the theoretical quantity of dry bromine in the form of a 20 per cent. chloroform solution. The yield of 1:2-dibromo*cyclo*hexane[2] was 95 per cent. of the theoretical and this was treated in the usual manner with ethyl disodiomalonate (1 mol.) in absolute alcohol, and an 84 per cent. yield of ethyl Δ^2-*cyclo*hexenemalonate was obtained, boiling at 150–152° under 3 mm. pressure; the dibasic acid melting at 164° was obtained by hydrolysing the ester with alcoholic potash and was decomposed by heating with a free flame for 30 minutes under a pressure of 30 mm. and finally distilled under a pressure of 8 mm. At 105–115° the lactone distilled over and at 125–127° the monobasic acid in a yield of 62 per cent. of the theoretical.

β-Cyclo*hexylpropionic acid*, $C_6H_{11}\cdot CH_2\cdot CH_2\cdot CO_2H$.—Zelinsky's method[3] was adopted. The yields in the various stages were as follows:—

$C_6H_{11}MgBr + CH_2O \longrightarrow C_6H_{11}\cdot CH_2\cdot OH$. 60 per cent.[4]

$C_6H_{11}\cdot CH_2\cdot OH + PI_3 \longrightarrow C_6H_{11}\cdot CH_2I$. 75 per cent.

$C_6H_{11}\cdot CH_2I + CHNa(CO_2Et)_2 \longrightarrow C_6H_{11}\cdot CH_2\cdot CH(CO_2Et)_2 \longrightarrow$

$C_6H_{11}\cdot CH_2\cdot CH(CO_2H)_2$, 75 per cent. and in the decomposition of the dibasic to the monobasic acid the yield was nearly theoretical.

Hexahydro-m-*toluic acid*.—Zelinsky's method[5] was adopted and the yields were similar to those given by this author.

Hexahydro-p-*toluic acid*.—This was prepared from *p*-methyl*cyclo*hexyl bromide[6] by means of magnesium and carbon dioxide in dry ethereal solution. From 40 grams of bromide only 4 grams of *trans*hexahydro-*p*-toluic acid melting at 110° were obtained.[7]

α and *β*-cyclo*geranic* acids were prepared by Tiemann's method.[8]

[1] *Chem. Week.*, 1909, 6, 699.
[2] Baeyer, *Annalen*, 1894, 278, 108.
[3] *Ber.*, 1908, 41, 2676.
[4] *Bull. Soc. chim.*, 1906, [III]. 35, 547.
[5] *Ber.*, 1902, 35, 2689.
[6] Hope and Perkin, *J. Chem. Soc.*, 1909, 95, 1367.
[7] Cf. Perkin, *ibid.*, 1911, 99, 536.
[8] *Ber.* 1893, 26, 2716; 1900, 33, 881.

TABLE XIII.

No.	Acid	Boiling point in degrees Centigrade	Pressure in mm. (unc.)	Melting point in degrees Centigrade	Esterification constant k_1 for 0·1 hydrochloric acid
1	*n*-Valeric	180–181	685	...	0·268
2	*n*-Caproic	198–199	685	...	0·267
3	Nonoic	245–246	685	...	0·270
4	Decoic	148–150	9	...	0·269
5	Lauric	...	...	43-43·5	0·272
6	Myristic	...	...	53·5	0·269
7	Palmitic	...	...	61–62	0·276
8	Stearic	...	...	68·5–69	0·276
9	Erucic	...	...	32-32·5	0·279
10	Brassidic	...	...	58·5-59	0·273
11	Allylacetic	184–185	683	...	0·274
12	Hydrocinnamic	...	...	47·5	0·321
13	*iso*Propylacetic	151–152	683	...	0·0518
14	*iso*Butylacetic	199–201	683	...	0·247
15	*iso*Amylacetic	205–207	683	...	0·267
16	Methyl-*n*-propylacetic	190–191	683	...	0·0393
17	Methylallylacetic	188–189	683	...	0·0421
18	Methyl-*n*-butylacetic	203–205	683	...	0·0345
19	Methylbenzylacetic	150–152	8	...	0·0553
20	Methyl-*iso*propylacetic	184–186	683	...	0·0110
21	Methyl-*iso*butylacetic	203–204	683	...	0·0318
22	Ethyl-*n*-butylacetic	221–222	683	...	0·00283
23	Di-*n*-propylacetic	219–220	683	...	0·00285
24	*cyclo*Heptanecarboxylic... ...	137–139	14	...	0·0499
25	*bicyclo*Heptanecarboxylic ...	...	...	97·5–98	0·0137
26	*cyclo*Hexylacetic	230–231	683	...	0·0809
27	*cyclo*Hexeneacetic	137–138	11	36–37	0·108
28	*cyclo*Hexylideneacetic	...	...	91·5–92	0·00228
29	*p*-Methyl*cyclo*hexylacetic ...	...	...	71–72	0·0999
30	*p*-Methyl*cyclo*hexeneacetic ...	130–132	10	39–40	0·118
31	*p*-Methyl*cyclo*hexylideneacetic ...	...	...	62–63	0·00234
32	Δ^1-Tetrahydrobenzoic	238–240	683	...	0·00220
33	Δ^2-Tetrahydrobenzoic	130–132	30	...	0·0829
34	*cyclo*Heptatrienecarboxylic ...	...	...	55–56	0·00184
35	*o*-Toluic	...	...	102	0·000718
36	*m*-Toluic	...	...	110	0·00261
37	*p*-Toluic	...	...	176–177	0·00197
38	Hexahydro-*m*-toluic	128–130	11	...	0·0827
39	Hexahydro-*p*-toluic	134–136	15	110	0·0850
40	β-*cyclo*Hexylpropionic	140–142	10	...	0·141
41	Δ^2-*cyclo*Hexeneacetic	125–127	8	...	0·0731
42	Adipic	...	...	149–150	0·301
43	Pimelic	...	...	103	0·282
44	Suberic	...	...	140	0·264
45	α-*cyclo*Geranic	...	...	93	nil.
46	β-*cyclo*Geranic	...	...	104–105	nil.

In this table all temperatures given were determined with the aid of short normal thermometers, so that the temperatures given may be taken as corrected temperatures.

In the following tables dealing with the acids 1–44 the various columns 1–5 indicate:—

Column
- 1 = Time in hours.
- 2 = Value of $a-x$ in cc.
- 3 = Percentage conversion into ester.
- 4 = Value of k calculated from the usual equation for a unimolecular reaction.
- 5 = Value of k_r calculated from equation on p. 89.
- A = Normality of the organic acid.
- B = Normality of the alkali used for titration.
- C = Normality of the hydrogen chloride.
- a = Number of cc. of the alkali required for neutralising the organic acid in 10 cc. of the solution at zero time.[1]

1. n-*Valeric Acid.*

A=0·07099 N B=0·09279 N			C=0·0886 N a=7·65		A=0·07950 N B=0·08738 N			C=0·04282 N a=9·1	
1	2	3	4	5	1	2	3	4	5
0·1	6·60	13	0·642	0·229	0·20	7·9	13	0·307	0·110
0·2	5·65	26	0·658	0·247	0·50	6·3	30	0·320	0·119
0·3	4·90	35	0·645	0·243	0·75	5·4	40	0·302	0·116
0·5	3·80	50	0·607	0·238	1·00	4·6	49	0·296	0·117
0·9	2·40	68	0·559	0·231	1·50	3·5	61	0·276	0·114
1·5	1·20	84	0·536	0·233	2·00	2·6	71	0·272	0·115

Mean value of k_r =0·237 ... =0·115
Mean value of k_1 =0·267 ... =0·268

[1] In a few cases, marked with an asterisk in the tables, 20 cc. were used.

2. n-*Caproic Acid.*

A=0·1272 N, B=0·06425 N		C=0·0408 N, a=19·8			A=0·1217 N, B=0·06425 N		C=0·06646 N, a=18·95		
1	2	3	4	5	1	2	3	4	5
0·30	16·35	17	0·277	0·103	0·25	14·70	22	0·441	0·168
0·50	14·35	27	0·280	0·108	0·60	10·45	45	0·431	0·179
0·74	12·50	37	0·270	0·109	0·83	8·45	55	0·421	0·183
1·15	9·95	49	0·260	0·110	1·00	7·35	61	0·411	0·183
1·70	7·65	61	0·243	0·109	1·25	6·05	68	0·397	0·182
2·50	5·25	73	0·236	0·110	1·75	4·15	78	0·378	0·180
...	...	...	...	...	2·40	2·65	82	0·356	0·179

Mean value of k_c =0·108 =0·179
Mean value of k_1 =0·265 =0·269

3. n-*Nonoic Acid.*

A = 0·1838 N, B = 0·06425 N		C = 0·0395 N, a = 28·60			A = 0·09668 N, B = 0·06425 N		C = 0·03534 N, a = 15·05		
1	2	3	4	5	1	2	3	4	5
0·17	25·6	10	0·281	0·104	0·20	13·30	11	0·268	0·0960
0·40	22·1	22	0·280	0·111	0·57	10·70	28	0·259	0·0985
0·67	19·3	32	0·255	0·106	0·87	9·25	38	0·243	0·0951
1·00	16·8	41	0·231	0·102	1·10	8·10	46	0·244	0·0984
1·40	14·0	51	0·222	0·603	1·40	7·15	52	0·231	0·0948
1·80	11·9	58	0·212	0·103	2·20	4·90	67	0·222	0·0962
...	...	...	...	...	3·33	2·90	80	0·215	0·0985

Mean value of k_c = 0·105 = 0·0968
Mean value of k_1 = 0·266 = 0·274

6. *Myristic Acid.*

A = 0·09057 N B = 0·06425 N		C = 0·0385 N a = 14·1			A = 0·1047 N B = 0·06425 N		C = 0·03212 N a = 16·3		
1	2	3	4	5	1	2	3	4	5
0·25	12·10	14	0·266	0·0995	0·17	14·90	8·5	0·234	0·0845
0·42	10·60	24	0·278	0·0984	0·40	13·20	19·0	0·229	0·0868
0·75	9·00	36	0·260	0·100	0·97	10·10	38	0·223	0·0887
1·08	7·55	46	0·250	0·104	1·40	8·25	49	0·211	0·0876
1·33	6·60	53	0·252	0·104	1·75	7·05	56	0·208	0·0885
1·67	5·60	60	0·241	0·104	2·25	5·70	65	0·203	0·0886
1·83	4·40	68	0·231	0·104	3·00	4·25	73	0·195	0·0884

Mean value of k_c = 0·102 = 0·0876
Mean value of k_1 = 0·265 = 0·272

7. *Palmitic Acid.*

A = 0·02891 N B = 0·06425 N		C = 0·02212 N a = 4·5			A = 0·02859 N B = 0·06425 N		C = 0·04015 N a = 4·45		
1	2	3	4	5	1	2	3	4	5
0·20	4·10	9	0·202	[0·0704]	0·20	3·85	13	0·315	0·110
0·50	3·65	18	0·180	0·0640	0·40	3·35	24	0·308	0·109
0·85	3·20	28	0·174	0·0620	0·60	2·90	34	0·310	0·111
1·20	2·85	36	0·165	0·0593	1·00	2·15	51	0·316	0·115
1·40	2·65	41	0·164	0·0592	1·25	1·85	57	0·305	0·112
2·10	2·05	54	0·164	0·0595	2·50	0·85	80	0·289	0·109

Mean value of k_c = 0·0608 = 0·111
Mean value of k_1 = 0·275 = 0·276

8. *Stearic Acid.*

A = 0·0157 N, B = 0·03077 N	C = 0·06276 N, a = 5·1				A = 0·0185 N, B = 0·0355 N	C = 0·02308 N, a = 5·2			
1	2	3	4	5	1	2	3	4	5
0·1	4·6	10	0·448	[0·156]	0·25	4·60	12	0·213	[0·0740]
0·3	3·6	30	0·504	0·177	0·80	3·70	29	0·185	0·0650
0·5	3·0	41	0·461	0·163	1·25	3·05	41	0·185	0·0658
0·7	2·4	53	0.468	0·166	1·75	2·50	52	0·182	0·0650
0·9	1·9	63	0·477	0·171	2·50	1·90	63	0·175	0·0632
1·5	1·0	80	0·471	0·172	3·50	1·25	73	0·177	0·0646

Mean value of k_c = 0·170 = 0·0647
Mean value of k_1 = 0·271 = 0·280

9. *Erucic Acid.*

A = 0·03918 N, B = 0·06425 N	C = 0·04318 N, a = 6·1				A = 0·04336 N, B = 0·06425 N	C = 0·07516 N, a = 6·75			
1	2	3	4	5	1	2	3	4	5
0·17	5·30	13	0·358	0·126	0·25	4·8	28	0·592	0·214
0·40	4·50	26	0·330	0·118	0·60	2·8	58	0·637	[0·241]
0·70	3·65	40	0·318	0·117	1·00	1·9	72	0·551	0·214
1·00	2·90	52	0·323	0·120	1·20	1·5	77	0·544	0·214
1·30	2·40	60	0·312	0·118	1·80	0·8	88	0·515	0·208
2·00	1·50	72	0·305	0·118	2·50	0·5	92	0·521	0·216

Mean value of k_c = 0·119 = 0·213
Mean value of k_1 = 0·275 = 0·283

10. *Brassidic Acid.*

A = 0·01296 B = 0·0355 N			C = 0·02165 N a = 7·3*		A = 0·01526 N B = 0·0355 N			C = 0·02165 N a = 4·3	
1	2	3	4	5	1	2	3	4	5
0·50	5·8	20	0·200	[0·0687]	0·25	3·90	9	0·170	0·0589
1·25	4·4	39	0·176	0·0616	0·75	3·20	25	0·171	0·0600
2·20	3·2	56	0·163	0·0578	1·35	2·55	40	0·168	0·0594
2·70	2·6	64	0·166	0·0592	2·10	1·90	55	0·169	0·0602
3·25	2·2	69	0·160	0·0573	2·70	1·55	63	0·164	0·0589
4·50	1·4	80	0·159	0 0575	3·5	1·10	74	0·169	[0·0612]

Mean value of k_c = 0·0587 = 0·0595
Mean value of k_1 = 0·271 = 0·275

11. *Allylacetic Acid.*

A = 0·1104 N B = 0·08726 N			C = 0·07575 N a = 12·65		A = 0·1081 N B = 0·08726 N			C = 0·02790 N a = 12·4	
1	2	3	4	5	1	2	3	4	5
0·1	10·05	20	0·589	0·214	0·10	11·8	4·8	0·215	[0·0699]
0·3	8·55	32	0·567	[0·221]	0·33	10·55	14	0·210	0·0767
0·5	6·95	45	0·520	0·213	0·67	9·1	26	0·202	0·0762
0·7	5·60	55	0·505	0·212	1·00	7·9	36	0·196	0·0764
1·1	3·85	69	0·469	0·211	1·50	6·6	46	0·183	0·0748
1·5	2·80	77	0·400	0·205	2·50	5·2	58	0·168	0·0730

Mean value of k_c = 0·211 = 0·0754
Mean value of k_1 = 0·278 = 0·270

* 20 cc. of solution used for titrating

12. Hydrocinnamic Acid.

A = 0·09603 N B = 0·09281 N		C = 0·0808 N a = 10·35			A = 0·1206 N B = 0·09348 N			C = 0·0934 a = 12·9	
1	2	3	4	5	1	2	3	4	5
0·1	8·75	15	0·728	0·264	0·1	10·7	17	0·812	0·300
0·2	7·50	27	0·698	0·263	0·2	9·0	30	0·782	0·304
0·4	5·80	43	0·628	0·250	0·3	7·6	41	0·766	0·311
0·7	3·80	63	0·621	0·257	0·5	5·8	55	0·692	0·293
1·0	2·70	73	0·583	0·259	0·7	4·5	63	0·653	0·295
1·4	1·70	83	0·560	0·260	1·4	2·1	83	0·564	[0·280]

Mean value of k_c = 0·259 = 0·301
Mean value of k_1 = 0·320 = 0·322

13. iso Valeric Acid.

A = 0·1494 N B = 0·09279 N		C = 0·09128 N a = 16·1			A = 0·1229 N B = 0·09279 N			C = 0·0385 N a = 13·25	
1	2	3	4	5	1	2	3	4	5
0·5	13·9	13	0·128	0·0471	0·25	12·7	4·6	0·0736	[0·0258]
1·0	12·2	24	0·120	0·0468	1·00	11·65	12	0·0558	0·0202
2·0	9·7	39	0·113	0·0462	2·00	10·35	21	0·0537	0·0203
3·5	6·8	57	0·107	0·0491	3·50	8·85	33	0·0500	0·0198
5·0	5·2	67	0·098	0·0475	5·00	7·65	42	0·0477	0·0196
7·0	3·6	77	0·093	0·0475	6·00	6·95	47	0·0467	0·0196

Mean value of k_c = 0·0473 = 0·0199
Mean value of k_1 = 0·0518 = 0·0517

14. iso*Butylacetic Acid.*

A = 0·09603 N, B = 0·09281 N			C = 0·1109 N, a = 10·35		A = 0·05475 N, B = 0·09281 N			C = 0·0689 N, a = 5·9	
1	2	3	4	5	1	2	3	4	5
0·25	7·05	31	0·666	[0·255]	0·1	5·30	10	0·466	0·164
0·50	4·85	53	0·658	0·271	0·3	4·20	28	0·492	0·180
0·75	3·70	64	0·595	[0·255]	0·6	3·15	46	0·454	0·172
0·90	2·95	71	0·606	0·267	1·1	1·90	67	0·438	0·177
1·00	2·50	75	0·617	0·277	1·5	1·40	76	0·417	0·168
1·50	1·45	85	0·579	0·267	3·3	0·30	94	0·393	0·169

Mean value of k_c = 0·271 = 0·172
Mean value of k_1 = 0·244 = 0·249

15. iso*Amylacetic Acid.*

A = 0·08760 N, B = 0·08718 N			C = 0·0777 N, a = 10·05		A = 0·09763 N, B = 0·08718 N			C = 0·0425 N, a = 11·2	
1	2	3	4	5	1	2	3	4	5
0·1	8·65	13	0·650	[0·234]	0·2	9·70	13	0·312	0·113
0·2	7·75	22	0·563	0·208	0·4	8·50	24	0·302	0·112
0·4	6·10	39	0·542	0·211	0·7	7·00	37	0·292	0·114
0·6	4·90	51	0·519	0·210	1·0	5·90	47	0·278	0·113
0·8	3·85	61	0·518	0·217	1·5	4·55	59	0·261	0·111
1·1	3·05	69	0·471	0·202	2·5	2·70	75	0·247	0·111

Mean value of k_c = 0·210 = 0·112
Mean value of k_1 = 0·270 = 0·264

16. *Methyl-n-propylacetic Acid.*

A = 0·1256 N B = 0·1004 N			C = 0·0930 N a = 25·03*		A = 0·1187 N B = 0·1004 N			C = 0·09565 N a = 23·65 *	
1	2	3	4	5	1	2	3	4	5
1	19·58	21	0·1066	[0·0403]	1	18·40	22	0·1090	[0·0411]
2	16·08	35	0·0961	0·0385	2	15·00	36	0·0987	0·0394
3	13·58	45	0·0883	0·0371	3	12·45	47	0·0928	0·0387
4	11·48	54	0·0846	0·0367	4	10·55	55	0·0876	0·0378
5	9·88	60	0·0807	0·0360	5	8·95	62	0·0844	0·0375
6	8·58	65	0·0777	0·0354	6	7·70	67	0·0812	0·0369
8	6·48	74	0·0736	0·0349	8	5·85	73	0·0758	0·0358

Mean value of k_c = 0·0364 = 0·0377
Mean value of k_1 = 0·0391 = 0·0394

17. *Methylallylacetic Acid.*

A = 0·1308 N B = 0·09281 N			C = 0·1058 N a = 14·1		A = 0·08886 N B = 0·09354 N			C = 0·1098 N a = 9·5	
1	2	3	4	5	1	2	3	4	5
0·40	12·60	10	0·122	0·0441	0·5	8·15	14	0·133	0·0478
1·10	10·50	25	0·116	0·0448	1·0	7·2	24	0·120	0·0446
1·70	9·00	31	0·115	0·0463	1·5	6·3	33	0·119	0·0455
2·35	7·80	44	0·109	0·0460	2·0	5·5	42	0·118	0·0466
3·60	6·05	57	0·102	0·0452	3·0	4·4	53	0·111	0·0454
4·50	5·10	63	0·098	0·0450	4·5	3·1	66	0·108	0·0461
6·00	4·10	70	0·089	0·0423	...	...	...	...	...

Mean value of k_c = 0·0448 = 0·0460
Mean value of k_1 = 0·0423 = 0·0419

* 20 cc. solution used for titrating.

18. *Methyl-n-butylacetic Acid.*

A = 0·1079 N B = 0·06425 N			C = 0·09637 N a = 16·8		A = 0·06725 N B = 0·1004 N			C = 0·1013 N a = 13·4 *	
1	2	3	4	5	1	2	3	4	5
1·00	13·70	18	0·0854	[0·0308]	1·0	10·65	20	0·0999	0·0361
2·00	11·40	32	0·0842	0·0321	2·0	8·45	36	0·1001	[0·0376]
3·00	9·50	44	0·0825	0·0334	3·0	7·10	47	0·0919	0·0353
4·25	7·70	54	0·0796	0·0335	5·0	5·25	60	0·0814	[0·0325]
5·00	6·80	59	0·0785	0·0338	7·0	3·45	74	0·0843	0·0350
7·00	5·05	69	0·0745	0·0335	9·0	2·55	80	0·0806	0·0340
9·00	3·90	76	0·0705	0·0326	10·5	1·95	84	0·0706	0·0345

Mean value of k_c = 0·0332 = 0·0350
Mean value of k_1 = 0·0344 = 0·0345

19. *Methylbenzylacetic Acid.*

A = 0·1086 N B = 0·09279 N			C = 0·0897 N a = 11·7		A = 0·1494 N B = 0·09279 N			C = 0·0837 N a = 16·1	
1	2	3	4	5	1	2	3	4	5
0·4	10·5	10	0·118	[0·0421]	0·2	15	6·8	0·154	[0·0547]
1·0	8·6	26	0·134	0·0507	0·5	13·9	13	0·128	0·0471
1·6	7·8	33	0·125	[0·0429]	1·0	12·2	24	0·121	0·0468
2·1	6·6	43	0·118	0·0480	2·0	9·7	39	0·110	0·0462
3·0	5·3	54	0·114	0·0484	3·4	6·8	57	0·110	[0·0505]
5·0	3·4	62	0·107	0·0485	5·0	5·2	68	0·098	0·0473
...	...	...	...	...	7·0	3·6	77	0·070	0·0475

Mean value of k_c = 0·0488 = 0·0470
Mean value of k_1 = 0·0544 = 0·0561

* 20 cc. of solution used for titrating.

20. *Methylisopropylacetic Acid.*

A = 0·1136 N B = 0·08738 N		C = 0·1183 N a = 13·0			A = 0·1199 N B = 0·08718 N			C = 0·0681 N a = 13·75	
1	2	3	4	5	1	2	3	4	5
2·0	11·1	14	0·0343	0·0126	1·0	13·10	4·7	0·0210	0·00742
4·0	9·4	27	0·0352	0·0135	2·5	12·35	10	0·0186	[0·00676]
6·6	7·9	39	0·0329	0·0131	6·0	11·55	16	0·0126	[0·00465]
9·0	6·6	49	0·0327	0·0132	10·0	8·95	34	0·0186	0·00742
13·0	5·2	60	0·0306	0·0133	15·0	7·45	45	0·0177	0·00740
23·0	3·2	75	0·0261	0·0123	20·0	6·20	55	0·0172	0·00745

Mean value of k_c = 0·0130 = 0·00742
Mean value of k_1 = 0·0110 = 0·0109

21. *Methylisobutylacetic Acid.*

A = 0·09928 N B = 0·09279 N		C = 0·1030 N a = 10·7			A = 0·09371 N B = 0·09279			C = 0·1013 N a = 10·1	
1	2	3	4	5	1	2	3	4	5
0·7	9·20	14	0·0939	0·0335	0·6	8·90	11	0·0915	0·0329
1·2	8·40	21	0·0875	0·0326	1·2	7·85	22	0·0911	0·0337
2·2	7·00	34	0·0837	0·0324	2·0	6·70	33	0·0891	0·0341
3·0	6·25	41	0·0777	0·0309	3·0	5·80	42	0·0803	0·0317
4·5	4·80	55	0·0773	0·0324	3·8	5·10	49	0·0780	0·0316
6·0	3·80	64	0·0749	0·0323	5·5	3·90	61	0·0751	0·0317

Mean value of k_c = 0·0324 = 0·0326
Mean value of k_1 = 0·0314 = 0·0322

22. *Ethyl-n-butylacetic Acid.*

A = 0·1702 N B = 0·1004 N			C = 0·2510 N a = 16·95		A = 0·1004 N B = 0·1004 N			C = 0·1815 N a = 10·0	
1	2	3	4	5	1	2	3	4	5
4	14·10	17	0·0200	[0·00759]	7·58	7·55	25	0·0166	[0·00609]
8	12·30	21	0·0174	0·00702	18·66	5·75	42	0·0129	0·00515
12	10·65	37	0·0167	0·00710	27·00	4·65	53	0·0123	0·00510
24	7·35	56	0·0151	0·00713	43·00	3·15	68	0·0119	0·00510
32	5·95	64	0·0142	0·00703	70·00	1·65	83	0·0115	0·00525

Mean value of k_c = 0·00707 = 0·00515
Mean value of k_1 = 0·00282 = 0·00283

23. *Dipropylacetic Acid.*

A = 0·1131 N B = 0·1004 N			C = 0·1729 N a = 22·55*		A = 0·1772 N B = 0·1004 N			C = 0·1835 N a = 17·65	
1	2	3	4	5	1	2	3	4	5
7·00	18·40	17	0·0126	0·00467	6·00	14·85	15	0·0125	[0·00472]
13·75	15·05	33	0·0122	0·00500	17·25	10·95	37	0·0121	0·00515
23·00	12·00	46	0·0119	0·00492	24·00	9·05	54	0·0121	0·00551
30·00	10·05	55	0·0117	0·00500	30·20	8·05	60	0·0112	0·00531
37·00	8·75	61	0·0110	0·00486	41·25	6·35	64	0·0103	0·00516
48·00	7·05	68	0·0106	0·00475	50·00	5·45	69	0·0102	0·00525

Mean value of k_c = 0·00487 = 0·00528
Mean value of k_1 = 0·00281 = 0·00288

* 20 cc. of solution used for titrating.

24. cyclo*Heptanecarboxylic Acid.*

A = 0·07484 N B = 0·09354 N		C = 0·09354 N a = 8·0			A = 0·08886 N B = 0·09354			C = 0·09354 N a = 9·5	
1	2	3	4	5	1	2	3	4	5
0·5	6·9	13	0·128	0·0460	0·5	8·15	14	0·133	0·0479
1·0	6·0	25	0·125	0·0460	1·0	7·20	24	0·120	0·0447
1·5	5·1	36	0·130	0·0490	1·5	6·30	33	0·119	0·0455
2·0	4·5	43	0·124	0·0483	2·0	5·50	42	0·118	0·0466
3·0	3·6	55	0·115	0·0461	3·0	4·40	53	0·111	0 0454
4·5	2·4	70	0·121	0·0480	4·5	3·10	67	0·108	0·0461
6·0	1·7	78	0·112	0·0482	...	...	...	...	...

Mean value of k_c = 0·0473   = 0·0460
Mean value of k_1 = 0·0506   = 0·0491

25. bicyclo*Heptanecarboxylic Acid.*

A = 0·07377 N B = 0·09279 N		C = 0·1109 N a = 7·95			A = 0·1116 N B = 0·09279 N			C = 0·2610 N a = 12·0	
1	2	3	4	5	1	2	3	4	5
3	6·05	23	0·0401	0·0145	0·2	11·4	5	0·1115	[0·0393]
5	4·90	38	0·0420	0·0149	0·6	10·4	13	0·1036	0·0377
7	4·25	46	0·0385	0·0151	1·1	9 4	22	0·0964	0·0361
10	3·35	57	0·0375	0·0150	1·9	8·0	33	0·0926	0·0362
22	1·35	83	0·0350	0·0152	3·8	5·7	63	0·0851	0·0359
30	0·75	90	0·0341	0·0153	6·5	3·7	69	0·0786	0·0355

Mean value of k_c = 0·0150   = 0·0363
Mean value of k_1 = 0·0135   = 0·0139

26. cyclo*Hexylacetic Acid.*

A = 0·1199 N B = 0·08718 N			C = 0·0929 N a = 13·75		A = 0·1173 N B = 0·08718 N			C = 0·09337 N a = 13·45	
1	2	3	4	5	1	2	3	4	5
0·10	13·10	4·7	0·210	0·0739	0·25	11·85	11	0·220	0·0794
0·25	12·35	10	0·186	[0·0673]	0·50	10·05	25	0·251	[0·0966]
0·40	11·55	16	0·191	0·0697	1·00	8·70	35	0·189	0·0751
1·00	8·95	34	0·186	0·0743	1·50	7·10	47	0·185	0·0768
1·50	7·45	45	0·177	0·0739	2·00	5·90	56	0·178	0·0772
2·00	6·20	55	0·172	0·0750	2·75	4·40	67	0·177	0·0800
...	...	...	...	...	4·25	2·90	78	0·157	0·0753

Mean value of k_c = 0·0734   = 0·0773
Mean value of k_1 = 0·0790   = 0·0828

27. cyclo*Hexeneacetic Acid.*

A = 0·09874 N B = 0·08738 N			C = 0·1013 N a = 11·3		A = 0·1126 N B = 0·8738 N			C = 0·1084 N a = 12·9	
1	2	3	4	5	1	2	3	4	5
0·17	10·0	14	0·312	0·112	0·2	11·1	13	0·325	0·119
0·40	8·6	26	0·296	0·111	0·4	9·4	27	0·344	0·131
0·70	7·2	38	0·279	0·109	0·7	7·9	38	0·304	0·122
1·00	6·2	47	0·261	0·105	1·0	6·6	48	0·291	0·121
1·50	4·8	59	0·248	0·104	1·5	5·2	59	0·263	0·114
2·20	3·3	71	0·243	0·107	3·0	3·2	75	0·201	0·094

Mean value of k_c = 0·108   = 0·117
Mean value of k_1 = 0·107   = 0·108

28. cyclo*Hexylideneacetic Acid.*

A = 0·1054 N, B = 0·08718 N		C = 0·2504 N, a = 12·1			A = 0·1064 N, B = 0·08718 N		C = 0·1920 N, a = 12·2		
1	2	3	4	5	1	2	3	4	5
3	10·8	10	0·0164	0·00591	3·25	11·1	9	0·0126	0·00451
7	9·4	22	0·0159	0·00585	7	10	18	0·0123	0·00454
11	8·4	30	0·0144	0·00554	11	9·15	25	0·0113	0·00429
22	6·1	49	0·0135	0·00558	22	7·1	41	0·0107	0·00429
31	4·6	61	0·0132	0·00585	30	5·9	51	0·0105	0·00439
47	3·1	74	0·0126	0·00573	71	2·8	77	0·0090	0·00416
72	1·8	85	0·0114	0·00551	...	...	...	...	...

Mean value of k_c = 0·00571 = 0·00436
Mean value of k_1 = 0·00228 = 0·00227

29. p-*Methyl*cyclo*hexylacetic Acid.*

A = 0·09535 N, B = 0·09348 N		C = 0·08863 N, a = 10·2			A = 0·1019 N, B = 0·09348 N		C = 0·09135 N, a = 10·9		
1	2	3	4	5	1	2	3	4	5
0·2	9·20	10	0·224	0·0798	0·2	9·8	10	0·231	0·0823
0·4	8·30	18	0·224	0·0821	0·5	8·5	22	0·216	0·0804
0·9	6·70	33	0·203	0·0781	0·9	7·0	35	0·214	0·0837
1·6	5·05	50	0·191	0·0777	1·4	5·6	48	0·207	0·0844
2·5	3·60	64	0·181	0·0775	2·2	4·1	62	0·193	0·0830
3·5	2·50	74	0·177	0·0780	3·5	2·5	77	0·183	0·0835

Mean value of k_c = 0·0789 = 0·0829
Mean value of k_1 = 0·0890 = 0·0908

30. p-*Methyl*cyclo*hexeneacetic Acid.*

A = 0·1013 N, B = 0·08738 N		C = 0·1013 N, a = 11·6			A = 0·09949 N, B = 0·08738 N		C = 0·1013 N, a = 11·1		
1	2	3	4	5	1	2	3	4	5
0·25	9·60	17	0·329	0·120	0·2	9·50	14	0·338	0·124
0·50	8·05	30	0·317	0·120	0·4	8·20	26	0·328	0·126
1·00	5·90	48	0·294	0·120	0·7	6·70	39	0·313	0·125
1·50	4·50	60	0·274	0·118	1·0	5·60	49	0·297	0·123
2·00	3·40	70	0·266	0·118	1·5	4·40	60	0·268	0·115
3·00	2·20	80	0·240	0·112	2·0	3·35	69	0·260	0·116

Mean value of k_c = 0·118   = 0·121
Mean value of k_1 = 0·117   = 0·119

31. p-*Methyl*cyclo*hexylideneacetic Acid.*

A = 0·09249 N, B = 0·08718 N		C = 0·1920 N, a = 10·6			A = 0·09598 N, B = 0·08718 N		C = 0·1920 N, a = 11·0		
1	2	3	4	5	1	2	3	4	5
4	9·4	11	0·0130	0·00467	3	9·85	10	0·0160	[0·00592]
8	8·4	20	0·0127	0·00465	7	8·95	18	0·0129	0·00470
22	6·2	41	0·0114	0·00417	11	8·20	25	0·0117	0·00435
33	4·6	56	0·0113	0·00455	22	6·10	44	0·0115	0·00464
48	3·3	66	0·0105	0·00459	30	5·25	52	0·0107	0·00439
72	2·1	80	0·0099	0·00442	51	3·50	68	0·0099	0·00424
...	...	...	...	...	72	2·70	75	0·0098	[0·00380]

Mean value of k_c = 0·00451   = 0·00447
Mean value of k_1 = 0·00235   = 0·00232

32. Δ^1-Tetrahydrobenzoic Acid.

A = 0·1038 N, B = 0·09348 N		C = 0·1197 N, a = 11·1			A = 0·1720 N, B = 0·09348 N		C = 0·1197 N, a = 18·4		
1	2	3	4	5	1	2	3	4	5
10	9·5	14	0·00676	[0·00245]	10	15·5	15	0·00745	[0·00281]
20	8·1	27	0·00684	0·00259	20	13·5	26	0·00673	0·00270
30	7·0	36	0·00667	0·00262	30	11·9	35	0·00631	0·00266
61	4·7	57	0·00612	0·00259	40	10·5	42	0·00609	0·00267
110	2·6	76	0·00573	0·00263	50	9·6	47	0·00565	0·00254
152	1·6	85	0·00561	0·00265	100	5·5	70	0·00524	0·00268

Mean value of k_c = 0·00262   = 0·00265
Mean value of k_1 = 0·00219   = 0·00221

33. Δ^2-Tetrahydrobenzoic Acid.

A = 0·1395 N, B = 0·09363 N		C = 0·0975 N, a = 14·9			A = 0·1374 N, B = 0·09348 N		C = 0·0975 N, a = 14·7		
1	2	3	4	5	1	2	3	4	5
0·25	13·2	11	0·210	[0·0766]	0·2	13·30	9·5	0·217	0·0782
0·60	11·2	24	0·206	0·0800	0·4	12·20	17	0·202	[0·0754]
0·90	9·8	34	0·202	0·0817	0·8	10·00	31	0·209	0·0836
1·30	8·4	43	0·191	0·0806	1·1	8·95	39	0·196	0·0808
1·90	6·7	55	0·182	0·0814	1·5	7·55	48	0·192	0·0832
2·30	5·8	61	0·178	0·0817	2·0	6·50	55	0·177	0·0789
3·40	4·1	72	0·164	0·0801	...	...	...	...	...

Mean value of k_c = 0·0809   = 0·0809
Mean value of k_1 = 0·0829   = 0·0829

34. β-*cycloHeptatrienecarboxylic Acid.*

A = 0·09372 N B = 0·09279 N			C = 0·2210 N a = 10·1		A = 0·08351 N B = 0·09279 N			C = 0·2210N a = 9·0	
1	2	3	4	5	1	2	3	4	5
5	8·8	13	0·0120	0·00430	6	7·7	14	0·0113	0·00406
10	7·9	22	0·0108	0·00394	16	6·0	33	0·0110	0·00417
30	5·1	49	0·0099	0·00400	34	4·2	53	0·0097	0·00392
40	4·2	58	0·0095	0·00398	46	3·1	66	0·0101	0·00423
72	2·3	77	0·0090	0·00400	70	2·1	77	0·0090	0·00394
100	1·4	86	0·0086	0·00401	105	1·0	89	0·0091	0·00413

Mean value of k_c = 0·00404 = 0·00408
Mean value of k_1 = 0·00183 = 0·00185

35. o-*Toluic Acid.*

A = 0·1021 N B = 0·09279 N			C = 0·1485 N a = 11·0		A = 0·09001 N B = 0·09279 N			C = 0·1485 N a = 9·7	
1	2	3	4	5	1	2	3	4	5
24	9·40	14	0·00284	0·00103	24	8·30	14	0·00282	0·00102
47	8·10	26	0·00283	0·00106	49	6·95	28	0·00295	0·00111
74	6·95	36	0·00269	0·00105	73	6·00	38	0·00285	0·00111
96	6·10	44	0·00266	0·00108	119	4·70	51	0·00264	0·00107
120	5·40	50	0·00257	0·00106	144	4·10	57	0·00259	0·00107
200	3·70	66	0·00236	0·00104	216	2·70	72	0·00257	0·00112
...	...	...	...	...	264	2·20	77	0·00244	0·00109

Mean value of k_c = 0·00105 = 0·00108
Mean value of k_1 = 0·000710 = 0·000725

36. m-*Toluic Acid.*

A = 0·09835 N, B = 0·09279 N; C = 0·02002 N, a = 10·6					A = 0·1048 N, B = 0·09279 N; C = 0·2877 N, a = 11·3				
1	2	3	4	5	1	2	3	4	5
4	9·35	11	0·0136	[0·00489]	1·5	10·5	7	0·0212	0·00753
10	7·70	27	0·0138	0·00523	5·0	9·0	20	0·0197	0·00733
25	5·10	51	0·0127	0·00523	12·0	6·8	39	0·0184	0·00743
30	4·40	58	0·0127	0.00536	27·0	3·8	66	0·0175	0·00771
36	3·80	64	0·0123	0·00516	38·0	2·8	75	0·0159	0·00729
53	2·50	76	0·0118	0·00536	46·0	2·1	81	0·0158	0·00747
62	2·10	80	0·0113	0·00521	...	...	...	...	...

Mean value of k_c = 0·00526   = 0·00746
Mean value of k_1 = 0·00263   = 0·00259

37. p-*Toluic Acid.*

A = 0·1267 N, B = 0·09279 N; C = 0·1485 N, a = 13·65					A = 0·1011 N, B = 0·09279 N; C = 0·04463 N, a = 10·9				
1	2	3	4	5	1	2	3	4	5
5	12·4	9	0·0083	0·00299	24	9·5	12	0·00248	0·000897
21	9·5	30	0·0075	0·00294	70	7·4	32	0·00240	0·00 0925
33	7·9	42	0·0072	0·00297	95	6·7	38	0·00222	0·000876
45	6·7	50	0·0068	0·00294	119	6·0	44	0·00217	0·000877
70	4·9	64	0·0063	0·00289	160	5·0	54	0·00211	0·000880
94	3·8	72	0·0059	0·00279	216	4·0	63	0·00201	0·000869
118	3·0	78	0·0057	0·00279	...	...	...	...	...

Mean value of k_c = 0·00290   = 0·000887
Mean value of k_1 = 0·00195   = 0·00199

38. *Hexahydro*-m-*toluic Acid.*

A = 0·1113 N B = 0·09348 N		C = 0·0888 N a = 11·9			A = 0·1337 N B = 0·09348 N		C = 0·09556 N a = 14·3		
1	2	3	4	5	1	2	3	4	5
0·2	10·9	8·4	0·191	[0·0679]	0·4	12·0	16	0·190	[0·0706]
0·5	9·5	20	0·196	0·0729	0·5	11·3	21	0·204	0·0775
0·7	8·8	26	0·187	0·0712	1·0	9·1	37	0·196	0·0796
1·1	7·4	37	0·187	0·746	1·7	7·0	52	0·182	0·0791
2·0	5·4	54	0·172	0·728	2·1	6·0	59	0·180	0·0803
3·0	3·8	68	0·166	0·742	3·4	3·9	74	0·166	0·0798

Mean value of k_c = 0·0731 = 0·0793

Mean value of k_1 = 0·0823 = 0·0830

39. *Hexahydro*-p-*toluic Acid.*

A = 0·1113 N B = 0·09348 N		C = 0·1009 N a = 11·9			A = 0·09627 N B = 0·09348 N		C = 0·09348 N a = 10·3		
1	2	3	4	5	1	2	3	4	5
0·20	10·6	10	0·251	0·0903	0·2	9·30	9·7	0·222	0·0789
0·40	9·6	19	0·233	0·0864	0·4	8·40	18	0·221	0·0810
0·75	8·1	31	0·222	0·0866	0·9	6·75	34	0·204	0·0776
1·00	7·2	39	0·218	0·0874	1·6	5·10	50	0·191	0·0778
1·50	5·8	51	0·208	0·0872	2·4	3·60	65	0·190	0·0816
2·00	4·9	58	0·192	0·0832	3·3	2·60	74	0·181	0·0809
3·00	3·4	71	0·181	0·0826	...	...	...	...	...

Mean value of k_c = 0·0857 = 0·0796

Mean value of k_1 = 0·0849 = 0·0851

40. β-*cycloHexylpropionic Acid.*

A = 0·1214 N B = 0·09348 N			C = 0·0811 N a = 13·0		A = 0·0888 N B = 0·09348 N			C = 0·1430 N a = 9·5	
1	2	3	4	5	1	2	3	4	5
0·2	11·1	15	0·343	[0·126]	0·10	8·3	13	0·586	0·210
0·5	9·4	28	0·281	0·109	0·20	7·4	20	0·542	0·200
0·8	7·9	39	0·270	0·109	0·35	6·2	35	0·529	0·203
1·1	6·6	49	0·267	0·113	0·50	5·3	44	0·507	0·200
1·5	5·2	60	0·265	0·117	0·70	4·1	57	0·521	0·214
2·5	3·2	75	0·243	0·116	1·10	2·9	70	0·468	0·202

Mean value of k_c = 0·113 = 0·205
Mean value of k_1 = 0·139 = 0·143

41. Δ^2*cycloHexeneacetic Acid.*

A = 0·1225 N B = 0·09279 N			C = 0·2070 N a = 13·2		A = 0·1117 N B = 0·09348 N			C = 0·09743 N a = 11·95	
1	2	3	4	5	1	2	3	4	5
0·2	11·0	16	0·396	0·146	0·20	10·8	9·6	0·202	[0·0788]
0·4	9·1	31	0·404	0·158	0·45	9·8	17	0·195	0·0714
0·6	7·9	40	0·372	0·151	0·80	8·5	28	0·185	0·0712
0·9	6·3	52	0·357	0·153	1·60	6·4	46	0·170	0·0697
1·4	4·4	66	0·341	0·155	2·00	5·5	53	0·168	0·0714
1·9	3·3	75	0·317	0·151	4·00	2·9	75	0·153	0·0715

Mean value of k_c = 0·152 = 0·0710
Mean value of k_1 = 0·0734 = 0·0728

42. *Adipic Acid.*

A = 0·1206 N B = 0·09348 N		C = 0·1009 N a = 12·9			A = 0·09545 N B = 0·08718 N		C = 0·0804 N a = 10·95		
1	2	3	4	5	1	2	3	4	5
0·1	10·7	17	0·812	0·300	0·10	9·50	13	0·617	0·223
0·2	9·0	30	0·782	0·305	0·25	7·60	30	0·634	0·242
0·3	7·6	41	0·766	0·312	0·45	5·85	46	0·605	0·243
0·5	5·8	55	0·694	0·300	0·70	4·25	61	0·587	0·249
0·7	4·5	65	0·653	0·295	1·00	3·05	72	0·555	0·245
1·3	2·1	83	0·606	0·300	1·50	1·65	84	0·548	0·256

Mean value of k_c = 0·302   = 0·243
Mean value of k_1 = 0·300   = 0·302

43. *Pimelic Acid.*

A = 0·1337 N B = 0·09348 N		C = 0·0488 N a = 14·3			A = 0·08786 N B = 0·09348 N		C = 0·0989 N a = 9·4		
1	2	3	4	5	1	2	3	4	5
0·20	12·0	16	0·381	0·141	0·10	7·9	15	0·755	0·273
0·30	11·1	22	0·367	0·140	0·20	6·7	29	0·736	0·276
0·60	9·1	36	0·327	0·133	0·30	5·7	39	0·724	0·281
0·75	8·1	43	0·329	0·138	0·40	4·9	47	0·707	0·281
0·95	7·0	51	0·310	0·142	0·65	3·5	62	0·651	0·276
1·50	5·3	62	0·287	0·132	1·00	2·2	76	0·631	0·278

Mean value of k_c = 0·138   = 0·278
Mean value of k_1 = 0·283   = 0·281

44. *Suberic Acid.*

A = 0·1194 N B = 0·08718 N			C = 0·09337 N a = 13·7		A = 0·07932 N B = 0·08718 N			C = 0·04345 a = 9·1	
1	2	3	4	5	1	2	3	4	5
0·1	11·70	14	0·685	0·251	0·20	7·9	13	0·307	0·110
0·2	10·05	22	0·673	0·259	0·50	6·3	30	0·319	0·120
0·4	7·80	41	0·612	0·251	0·75	5·4	40	0·302	0·116
0·7	5·60	59	0·555	0·244	1·00	4·6	49	0·296	0·117
1·0	4·10	70	0·524	0·241	1·50	3·5	61	0·278	0·114
1·4	2·70	80	0·504	0·244	2·00	2·6	71	0·272	0·115

Mean value of k_c = 0·247 = 0·115
Mean value of k_1 = 0·264 = 0·264

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