212. *Chemical Constitution and the Dissociation Constants of Mono-carboxylic Acids. Part VI.* (a) *The Polarity of Vinyl and Phenyl Groups.* (b) *An Apparent Linear Relationship between Dissociation Constants and Dipole Moments.*

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DISSOCIATION constants of further monobasic acids have been determined by the procedure already described (J., 1934, 161, 1888; 1936, 644). The following table contains the classical and the thermodynamic dissociation constants of nine acids in water at 25°, together with corresponding mobility data. In the last column all previous values in the literature are recorded; these were derived by the simple classical procedure, and confirmation was desirable to ensure complete reliance in the data, especially where differences between the strengths of acids in a series are relatively small, *e.g.*, the olefinic acids.

Acid.	Λ_0 (Na salt).	Λ_0 (acid).	$10^5 K_{class.}$	$10^5 K_{therm.}$	Earlier values.
p-Tolylacetic	80·0	379·6	4·35	4·27	
β-Phenylpropionic	80·4,* 80·8 *	380·2	2·23	2·19	2·27,[1] 2·2 [2]
γ-Phenylbutyric	79·0	378·6	1·78	1·75	
trans-Cinnamic	80·4,* 80·6 *	380·1	3·72	3·65	3·5,[1] 3·7,[4] 3·82,[3] 3·8 [5]
cis-Cinnamic (*allo*)	82·5, 82·9	382·3	13·5₅	13·2	14·2,[6] 14·1 [7]
Cinnamylideneacetic	78·2	377·8	3·80	3·75	
Acrylic	87·5, 87·5	387·1	5·74	5·56	5·6 [1]
Vinylacetic	84·9, 84·9	384·3	4·76	4·62	3·83,[8] 4·65,[9] 4·48 [10] †
Allylacetic	83·1	382·7	2·17₅	2·11₅	2·09,[8] 2·10 [10] †

* The measurements in these cases were made on specimens of the isolated salts.
† These are thermodynamic constants, but the rest are classical values.

[1] Ostwald, *Z. physikal. Chem.*, 1889, **3**, 389.   [2] Springer and Jones, *Amer. Chem. J.*, 1912, **48**, 440.   [3] Schaller, *Z. physikal. Chem.*, 1898, **25**, 517.   [4] White and Jones, *Amer. Chem. J.*, 1910, **44**, 188.   [5] Roth and Stoermer, *Ber.*, 1913, **46**, 270.   [6] Biilmann, *Ber.*, 1910, **43**, 571.   [7] J. Meyer, *Z. Elektrochem.*, 1911, **17**, 982.   [8] Fichter and Pfister, *Annalen*, 1904, **334**, 201.   [9] Zelinsky and Isgarischew, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1387.   [10] Ives, Linstead, and Riley, J., 1933, 561.

Our thermodynamic constants for vinylacetic and allylacetic acids are in harmony with those of Ives, Linstead, and Riley (*loc. cit.*). $K_{class.}$ for *trans*-cinnamic acid approximates to that recorded by White and Jones (Ostwald's determination is appreciably lower), and $K_{class.}$ for the *cis*-acid (*allo*) is about 4% below the values of Biilmann and J. Meyer.

The mobility data are particularly interesting. The values of Λ_0 for phenylacetic and β-phenylpropionic acids appear to be identical (within the limits of experimental accuracy), but that for γ-phenylbutyric acid is distinctly less. It was to be expected that *trans*-cinnamic acid would have a mobility comparable with that for phenylpropionic acid, but the value for *cis*-cinnamic acid is 2 units higher than that of the isomeride; this may be due

to the smaller resistance offered by the more compact anion, although the diminution is comparatively large. Introduction of p-methyl into phenylacetic acid causes a fall of about 1 unit in mobility. With increasing anion size the Λ_0 values for the olefinic acids steadily fall. A considerable decrease is experienced in going from acrylic to vinylacetic acid, and that from the first to the third member is 4·4 units. Satisfactory mobilities for these acids could not be obtained with solutions made from the isolated salts : this procedure invariably led to values of Λ_0 several units high. It is possible that in the process of evaporation, during the preparation of the salts, sufficient alkali is present to facilitate isomeric change; although this scarcely provides an explanation of our observations, since the resultant isomeric anions here would not be expected to possess mobilities widely different from those of the original ions. The difficulty was overcome by making the stock salt solutions directly from the acids without intermediate isolation; more reasonable results were then obtained.

EXPERIMENTAL.

All stock solutions of acids were made up to 250 c.c., and both acid and salt solutions were prepared from water of specific conductivity 0·9—1·0 gemmho. Details of the measurements made on the acid solutions are recorded in the tables below.

Cell constant.	$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$
		p-Tolylacetic acid.		
0·07423	1·812	55·31	4·41	4·32
	1·301	63·72	4·39	4·31
	0·9236	73·58	4·31	4·23
	0·8917	75·06	4·35	4·27
	0·5983	89·10	4·31	4·24
	0·3961	106·2	4·31	4·24

6 Determinations; limits of $10^5K_{therm.}$: 4·23—4·32.

Cell constant.	$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$
		β-Phenylpropionic acid.		
0·1363	4·201	26·97	(2·27$_5$)	2·21$_5$
	2·130	36·99	2·24	2·19
	1·657	41·27	2·19	2·15
0·07319	1·588	42·61	2·24	2·20$_5$
	0·8294	57·53	2·24	2·20

15 Determinations; limits of $10^5K_{therm.}$: 2·15—2·21$_5$.

Cell constant.	$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$
		γ-Phenylbutyric acid.		
0·1356	3·801	25·01	1·77$_5$	1·73$_5$
	2·525	30·47	1·77	1·74
	1·708	36·87	1·79$_5$	1·76
0·07318	1·076	45·68	1·78	1·75$_5$
	0·8358	51·14	1·76$_5$	1·73$_5$

9 Determinations; limits of $10^5K_{therm.}$: 1·73$_5$—1·76.

Cell constant.	$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$
		trans-Cinnamic acid.		
0·1363	3·100	39·55	3·75	3·67
	1·523	54·48	3·68	3·60
	1·256	60·33	3·76	3·68
0·07319	0·9488	67·69	3·68$_5$	3·62
	0·7958	73·43	3·68	3·62$_5$

14 Determinations; limits of $10^5K_{therm.}$: 3·60—3·70.

Cell constant.	$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$
		cis-Cinnamic acid.		
0·1363	2·770	76·43	13·8$_5$	13·3$_5$
	1·206	108·4	13·5$_5$	13·2
	0·9028	121·5	13·3$_5$	13·0$_5$
0·07319	0·7017	134·9	13·5	13·2
	0·5030	153·2	13·5	13·2$_5$
	0·4973	153·8	13·4$_5$	13·2

17 Determinations; limits of $10^5K_{therm.}$: 13·0$_5$—13·4.

Cell constant.	$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$
		Cinnamylideneacetic acid.		
0·07905	0·5254	89·59	3·87	3·81
	0·2948	113·4	3·79$_5$	3·75
0·05421	0·1700	139·8	(3·69$_5$)	(3·66)
	0·09232	176·5	3·78	3·75
	0·07144	192·6	3·78$_5$	3·76

10 Determinations; limits of $10^5K_{therm.}$: 3·75—3·81.

Cell constant.	$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$
		Acrylic acid.		
0·1387	12·92	25·03	5·78	5·53
	9·506	28·95	5·75	5·53
	5·776	36·73	5·75	5·55
	4·089	43·13	5·72	5·54
	1·667	65·05	5·67	5·55
	1·329	72·15	5·67	5·55

16 Determinations; limits of $10^5K_{therm.}$: 5·53—5·61.

Cell constant.	$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$
		Vinylacetic acid.		
0·1387	12·16	23·54	4·86	4·67
	6·257	32·12	4·77	4·59
	4·672	37·01	4·80	4·67
	3·463	42·13	4·68	4·57
	1·353	65·15	4·68	4·58
	1·350	65·20	4·68	4·58

13 Determinations; limits of $10^5K_{therm.}$: 4·56—4·67.

Cell constant.	$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$		$10^3 C.$	$\Lambda.$	$10^5K_{class.}$	$10^5K_{therm.}$
			Allylacetic acid.						
0·1363	16·61	13·55	2·16	2·07$_5$		4·255	26·45	2·18$_5$	2·12
	8·676	18·83	2·21	2·13		3·364	29·73	2·20	2·13$_5$
	6·831	21·00	2·17$_5$	2·10		2·396	34·84	2·18$_5$	2·13$_5$
	4·883	24·56	2·14	2·07$_5$					

13 Determinations; limits of $10^5K_{therm.}$: 2·07$_5$—2·13$_5$.

Materials.—*p*-Tolylacetic acid was prepared by the hydrolysis of *p*-toluonitrile.   *p*-Methyl-benzyl bromide (1·6 g.; 1 mol.) and sodium cyanide (1·5 g.; 3—4 mols.) in alcohol (20 c.c.) were heated at 100° for 30 hours.   The oil remaining after evaporation and washing with water was hydrolysed by heating with 10 c.c. of dilute sulphuric acid (3 parts acid : 2 parts water) for 6 minutes, and the hot liquid filtered through glass wool; on standing, crystals of the tolyl acid separated.

Cinnamylideneacetic acid was derived from cinnamylideneacetone (Diehl and Einhorn, *Ber.*, 1885, **18**, 2321) by the haloform reaction.   The ketone was shaken at 100° with an excess of fresh bleaching powder and saturated sodium carbonate solution.   When evolution of chloroform had ceased, concentrated hydrochloric acid was added, and the deposit of cinnamyl-ideneacetic acid filtered off (25% yield).

β-Phenylpropionic and *trans*-cinnamic acids were supplied by British Drug Houses, Ltd., *cis*-cinnamic and acrylic acids by L. Light and Co., and vinylacetic and allylacetic acids by Schering-Kahlbaum.   γ-Phenylbutyric acid was kindly provided by Dr. E. L. Martin, to whom we are grateful.

All specimens of acids were rigorously purified.   The solids (except *cis*-cinnamic acid) were finally purified by successive recrystallisation from conductivity water.   The *cis*-cinnamic acid was of the *allo*-modification; it was supplied in very pure condition, and precautions were taken not to isomerise it.   The liquids were redistilled until satisfactory fractions were obtained. Equivalents were determined throughout.   The corrected physical constants are tabulated below, together with the best values in the literature.

Acid.	M. p. (or b. p.).	M. p. (or b. p.) from literature.
p-Tolylacetic	94°	94° (Strassmann, *Ber.*, 1889, **22**, 1230).
β-Phenylpropionic ...	50	48·5—49·5 (Thomas and Sudborough, *J.*, 1912, **101**, 323).
γ-Phenylbutyric	50·5	51 (Fischer and Schmitz, *Ber.*, 1906, **39**, 2212).
trans-Cinnamic	136·5	136·8 (Kendall, *J. Amer. Chem. Soc.*, 1914, **36**, 1726).
cis-Cinnamic	68	68 (Liebermann, *Ber.*, 1890, **23**, 2510).
Cinnamylideneacetic	166	166 (Hinrichsen and Triepel, *Annalen*, 1904, **336**, 197).
Acrylic	b. p. 140·5—141/755 mm.	b. p. 140·8—141/atm. press. (Biilmann, *J. pr. Chem.*, 1900, **61**, 494).
Vinylacetic	b. p. 70·5—71/12—13 mm.	b. p. 71/12—14 mm. (Fichter and Sonneborn, *Ber.*, 1902, **35**, 938).
Allylacetic	b. p. 82—83/9·5 mm.	b. p. 90—92/16—17 mm. (Wohlgemuth, *Ann. Chim.*, 1914, **2**, 322).

DISCUSSION.

(a) *The Polarity of Vinyl and Phenyl Groups.*—The effect of the vinyl group on the strengths of aliphatic acids has led inevitably to the conclusion that this group possesses an intrinsic attraction for electrons (Flürscheim, *J. pr. Chem.*, 1902, **66**, 321; *J.*, 1909, **95**, 718; Ashworth and Burkhardt, *J.*, 1928, 1791; Lowry, *Trans. Faraday Soc.*, 1923, **19**, 496; Henrich, " Theories of Organic Chemistry," English transl., p. 145; Ingold, *Chem. Reviews*, 1934, **15**, 239).   It is also accepted that phenyl possesses a similar polar character (Ash-worth and Burkhardt, *loc. cit.*; Nathan and Watson, *J.*, 1933, 219; Ingold, *loc. cit.*), and accurate measurements of dissociation constants of acids ($10^5 K_{therm.}$ * : acetic, 1·76; phenylacetic, 4·88; diphenylacetic, 11·5) have provided sound confirmation for this (Dippy and Williams, *J.*, 1934, 161, 1888; Jeffery and Vogel, *J.*, 1934, 166) (compare depression in the strengths of bases measured by Carothers, Bickford, and Hurwitz, *J. Amer. Chem. Soc.*, 1927, **49**, 2908).†   In addition, the vinyl and the phenyl group, when present in a conjugate system undergoing reaction, are concerned in electromeric displacements; on demand of the reagent, movement of electrons takes place in either direction.

The permanent polarisation associated with the phenyl and the vinyl group is shown in dipole moment measurements.   The well-known difference between the moments of

* Distinction should be made between values of $K_{therm.}$ and $K_{class.}$.   Many of the latter are accept-able in discussion (chiefly as confirmatory evidence), but comparisons should be consistent.   To give clarity, values of $K_{class.}$ have been italicised; all constants are $10^5 K$.

† It is hardly possible to ascribe to phenyl a $+ I$ effect as suggested by Waters (*Chem. Reviews*, 1930, **7**, 415).

aliphatic and aromatic compounds (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668 ; cf. Bennett and Glasstone, *ibid.*, 1934, *A*, **145**, 71) demonstrates that the benzene nucleus makes some contribution to the measured moment, whilst the following data (in D) due to Höjendahl (taken from *Trans. Faraday Soc.*, Sept. 1934, Appendix) point to a similar permanent effect in the case of vinyl :—

Vinyl bromide	1·48	Allyl bromide	1·93	Allyl chloride	1·97
Ethyl bromide	2·09	*n*-Propyl bromide	2·15	*n*-Propyl chloride	2·11

Although the origin of this polarisation effect exhibited by both groups has still to be understood, it probably arises from their unsaturated character. In this connexion it is noteworthy that the introduction of a triple bond enhances the strength of an acid much more than does a double bond (phenylpropiolic acid, *590*; Ostwald, *loc. cit.*); moreover, Wilson and Wenzke (*J. Amer. Chem. Soc.*, 1935, **57**, 1265) have recently drawn attention to the marked influence of the triple bond on dipole moments.

The dissociation constants of unsaturated and phenyl-substituted acids may be interpreted on the basis of this combination of polarisation and polarisability effects.
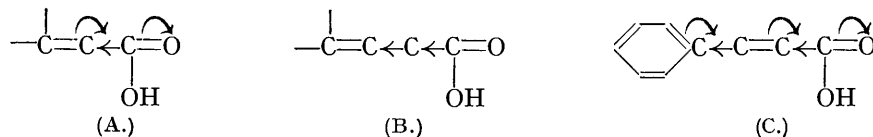
Fichter and his co-workers (*Annalen*, 1904, **334**, 201; *Ber.*, 1909, **42**, 4703) assigned classical constants to series of isomeric unsaturated aliphatic acids, noting that the order was $\beta\gamma>\alpha\beta>\gamma\delta$, and Ives, Linstead, and Riley (*J.*, 1933, 561) confirmed these observations : *e.g.*, *n*-hexenoic acids—$\alpha\beta$, 1·98; $\beta\gamma$, 3·05; $\gamma\delta$, 1·91. The following evidence has a similar significance :

*cyclo*Hexanecarboxylic acid, *1·34*;[1] Δ^1- and Δ^2-tetrahydrobenzoic acids, *2·14* and *3·05* respectively.[2]

*cyclo*Heptanecarboxylic acid, *1·22*;[1] Δ^1- and Δ^2-*cyclo*heptenecarboxylic acids, *0·992* and *2·61*.[3]

[1] Zelinsky and Isgarischew, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1379. [2] Collan, *Annalen*, 1892, **271**, 237, 271. [3] Roth, *Ber.*, 1900, **33**, 2033.

The influence of the vinyl group is observed most favourably, however, where terminal alkyl groups do not interfere, *viz.*, in acrylic, vinylacetic, and allylacetic acids. Comparable data for these acids are therefore desirable; Ives, Linstead, and Riley did not redetermine the dissociation constant of acrylic acid, while earlier values for vinylacetic acid differed greatly. The order of strengths is actually $\alpha\beta>\beta\gamma>\gamma\delta$, although the difference between $\alpha\beta$ and $\beta\gamma$ acids is less than that between $\beta\gamma$ and $\gamma\delta$ acids. These authors (*loc. cit.*, p. 563) advance the view that the double bond polarises on demand of the attacking reagent. Since the available facts are more easily interpreted, however, by supposing that an *inherent* electrical attraction *can* be associated with the vinyl group, the explanation along these lines appears more probable. The polarisation effect alone should lead to the order $\alpha\beta\gg\beta\gamma>\gamma\delta$ (cf. chloro-aliphatic acids) but actually in the $\alpha\beta$ acid (A) a conflicting effect can operate by the tautomeric mechanism so as to reduce acid strength even to the extent of producing a different order in some instances. Where the double bond and carboxyl group are not included in a conjugate system (B) there is only one influence exerted.

$$-\text{C}=\text{C}\leftarrow\text{C}=\text{O} \qquad -\text{C}=\text{C}\leftarrow\text{C}\leftarrow\text{C}=\text{O} \qquad \text{C}\leftarrow\text{C}=\text{C}\leftarrow\text{C}=\text{O}$$
$$\underset{\text{OH}}{} \qquad \underset{\text{OH}}{} \qquad \underset{\text{OH}}{}$$

(A.)   (B.)   (C.)

When phenyl is attached to the terminal carbon of a fatty acid its permanent effect (called $-I$ for simplicity) alone operates, and this gradually diminishes as the chain lengthens {Ph·CH$_2$·CO$_2$H, 4·88; Ph·[CH$_2$]$_2$·CO$_2$H, 2·19; Ph·[CH$_2$]$_3$·CO$_2$H, 1·75; cf. CH$_3$·CO$_2$H, 1·76; C$_2$H$_5$·CO$_2$H, 1·336; CH$_3$·[CH$_2$]$_2$·CO$_2$H, 1·523 (the last two measurements are due to Harned, *J. Amer. Chem. Soc.*, 1933, **55**, 2379; 1934, **56**, 2039)}. This influence is also illustrated in the strengths of phenyl-substituted aliphatic primary amines (Carothers, Bickford, and Hurwitz, *ibid.*, 1927, **49**, 2908). In this system it has been shown that the

effect is still propagated from the ε-position, although it is probably correct to regard the ε-position here as comparable to the δ-position in the above acids.

Saturation of the aromatic nucleus, however, causes the strength of an acid to fall to approximately that of the fatty acids (*cyclo*hexanecarboxylic acid, *1·34*). Results comparable to this have been obtained with bases (p_{K_B}: aniline, 4·6; *cyclo*hexylamine, 10·61; methylamine, 10·64; cf. pyridine, 5·21; and piperidine, 11·13; Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3482). This supports the suggestion made above, that the — *I* effect of phenyl arises from its unsaturated nature.

It appears that abnormality occurs in the strengths of the first members of both the vinyl and the phenyl-substituted series. The difference exhibited between the strengths of phenylacetic and β-phenylpropionic acids would suggest a constant for benzoic acid far
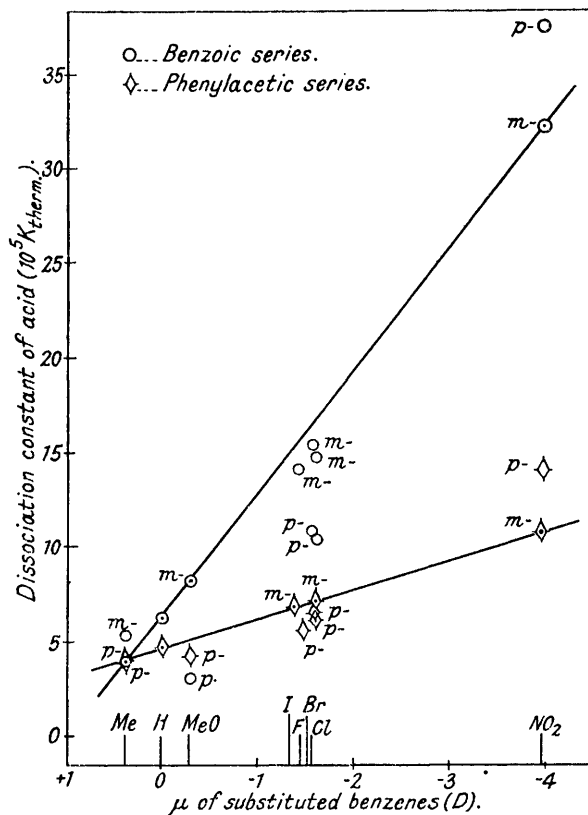
in excess of the value actually observed (cf. strengths of aniline, benzylamine, and β-phenylethylamine; Carothers, Bickford, and Hurwitz, *loc. cit.*). The explanation is on the same lines as that provided in the case of αβ-unsaturated acids.

Phenyl, when situated conjugately in an olefinic acid, *diminishes* the strength (acrylic, 5·56; *trans*-cinnamic, 3·65); doubtless the electromeric (or mesomeric) effect of phenyl preponderates here (C).

The constant for *cis*-cinnamic acid is 4 times that of the *trans*-isomeride, and is also much in excess of that of the parent acrylic acid. Here an additional " steric " effect exists; the phenyl group is adjacent to carboxyl in the same sense as the substituent in an *o*-substituted benzoic acid, where abnormally large constants have long been observed (see Hey, J., 1928, 231; cf. Sudborough and Lloyd, J., 1898, **73**, 93, on esterification).

The strength of cinnamylideneacetic acid is very similar to that of *trans*-cinnamic acid, which is not surprising since opposing effects operate here owing to the additional ethylenic linkage.

In contrast to the evidence of the acids, there are instances where the polar influence of phenyl appears to be subordinate to that of methylene, the best known being in the *op*-substitution of diphenylmethane, the relative stabilities of cyanohydrins (Lapworth and Manske, J., 1930, 1976), and the nitration of guaiacol benzyl ethers (Allan, Oxford, Robinson, and Smith, J., 1926, 401).

It is manifest, therefore, that the individual effects associated with the polarisation and polarisability of phenyl are exhibited in varying degree, according to the system in which the group is present and the nature of the reaction.

(b) *An Apparent Linear Relationship between Dissociation Constants and Dipole Moments.*—A further quantitative examination of the connexion between dipole moments and dissociation constants has been made (cf. Dippy, *Nature*, 1937, **139**, 591) since Dippy and Watson (*Chem. and Ind.*, 1935, **54**, 735) showed that the thermodynamic constants of certain substituted benzoic acids (K) and dipole moments of substituted benzenes (μ) are related by the equation $\log K = \log K_0 - C(\mu + a\mu^2)$ (see Nathan and Watson, J., 1933, 893), where K_0 is the dissociation constant of benzoic acid. If K (instead of $\log K$) is plotted against μ, a straight line can be drawn through the points involved in the earlier relationship, *viz.*, *m*-nitro-, *m*-methoxy-, unsubstituted, and *p*-methyl-benzoic acids (see fig.). It is noteworthy that *p*-toluic acid falls on the line; it appears, therefore, that the dipole moment of toluene is a measure of both the inductive effect and the permanent displacement of nuclear electrons.

The points representing *m*-nitro-, *m*-chloro-, *m*-iodo-, unsubstituted, and *p*-methyl-phenylacetic acids are also found to be collinear, although the slope of the line is much smaller. The divergence shown by the halogens in the benzoic series (discussed by Dippy and Watson, *loc. cit.*) has been so diminished that it is not noticeable here.

Any connexion this relationship may have with the earlier equation proposed by Nathan and Watson does not seem obvious. It may transpire that the linear equation is only an approximation to the ultimate true relationship, but nevertheless it has the undoubted advantage of being simple to apply. The conformity of the *p*-methyl substituted acids did not become clear until now.

It is interesting that the strengths of *p*-toluic and *p*-tolylacetic acids are almost identical; from the figure it is seen that the benzoic and phenylacetic straight lines intersect at a point representing these two acids. This is fortuitous, and arises, no doubt, from the fact that although phenylacetic acid is weaker than benzoic acid, yet the depressing effect of *p*-methyl in the former is appreciably less on account of the damping effect of the intervening methylene grouping.