72. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part IX.* Monosubstituted β-Phenylpropionic and Cinnamic Acids.*

By J. FREDERICK J. DIPPY and JAMES E. PAGE.

The thermodynamic dissociation constants of 23 substituted β-phenylpropionic and cinnamic acids in aqueous solution have been determined conductometrically, and these data are discussed in relation to the strengths of the corresponding benzoic and phenylacetic acids, from the point of view of the electronic theory of valency.

The linear relationship shown to exist between dissociation constants and dipole moments of substituted benzenes (Dippy, *Nature*, 1937, **139**, 591) has been satisfactorily re-examined in the light of new values of dipole moments. The substituted phenylpropionic acids also appear to conform, but in the case of the cinnamic acids there is definitely no agreement.

EARLIER papers in this series (J., 1934, 161, 1888; 1935, 343; 1936, 644; 1937, 1008) have recorded thermodynamic constants for a representative number of monosubstituted benzoic and phenylacetic acids, and the study has now been extended to the β-phenylpropionic and cinnamic series. It was expected that the acids of the phenylpropionic class would provide confirmation of the influences observed in the phenylacetic series, and this anticipation has been realised although the relative differences are naturally smaller. The *m*- and *p*-substituted cinnamic acids (all of which possess the *trans*-form) are, in the main, comparable to the corresponding benzoic acids. It has also been shown that " ortho-effects " are restricted to the benzoic series.

Table I, showing the strengths ($10^5 K_{\text{therm.}}$) of methyl-, methoxy-, chloro-, and nitro-acids in the four series, provides a fairly complete set of data. For reference purposes the

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* Two previous papers, *viz.*, J., 1937, 1426, 1774, which appeared under other titles are regarded as Parts VII and VIII of this series.

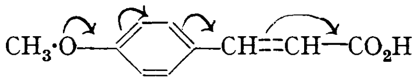
ratios $K/K_{\text{unsub.}}$ are included ($K_{\text{unsub.}}$, the thermodynamic constant of the parent acid in each series, is shown in parentheses in each heading); these simplify the examination of the relative effects of substituents from system to system.

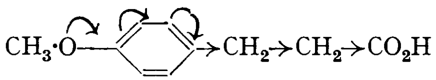
TABLE I.

	Me.		MeO.		Cl.		NO_2.	
	$10^5 K$.	$K/K_{\text{unsub.}}$.	$10^5 K$.	$K/K_{\text{unsub.}}$.	$10^5 K$.	$K/K_{\text{unsub.}}$.	$10^5 K$.	$K/K_{\text{unsub.}}$.
			Benzoic acids (H, 6·27 × 10^{-5}).					
o-	$12{\cdot}3_5$	1·97	8·06	1·29	114	18·2	671	107
m-............	5·35	0·87	8·17	1·30	14·8	2·36	32·1	5·19
p-	4·24	0·68	3·38	0·54	$10{\cdot}5_5$	1·68	37·6	6·00
			Phenylacetic acids (H, 4·88 × 10^{-5}).					
o-	—	—	—	—	8·60	1·76	9·90	2·03
m-............	—	—	—	—	7·24	1·48	10·8	2·21
p-	4·27	0·87	4·36	0·89	6·45	1·32	14·1	2·89
			β-Phenylpropionic acids (H, 2·19 × 10^{-5}).					
o-	2·17	1·00	1·57	0·72	2·65	1·21	$3{\cdot}13_5$	1·44
m-............	$2{\cdot}10_5$	0·96	2·22	1·01	2·60	1·19	—	—
p-	2·07	0·94	$2{\cdot}04_5$	0·94	2·47	1·13	$3{\cdot}36_5$	1·54
			Cinnamic acids (H, 3·65 × 10^{-5}).					
o-	$3{\cdot}16_5$	0·87	3·45	0·94	5·83	1·60	7·07	1·94
m-............	$3{\cdot}61_5$	1·00	4·21	1·15	$5{\cdot}08_5$	1·39	7·58	2·08
p-	2·73	0·75	2·89	0·79	3·86	1·06	8·99	2·46

Except in the case of *o*-toluic acid, where an "ortho-effect" exists, introduction of methyl into *o*-, *m*-, or *p*-positions in all four acids leads to a decrease in strength. A marked fall in effect is observed in passing from *p*-toluic to the corresponding phenylacetic acid, and very little further decrease in the β-phenylpropionic acid, but *p*-methyl substitution in cinnamic acid causes a diminution as marked as in the benzoic acid; this must be attributed to the existence of the conjugate system, which permits transfer of the electromeric displacements set up by methyl. With regard to *o*-substitution, *o*-methyl-phenylpropionic and -cinnamic acids, in contrast to *o*-toluic acid, tend to be weaker than the parent acids.

The strength of *m*-methoxy-β-phenylpropionic acid is identical with that of the parent acid; the — *I* effect of methoxyl is too weak to influence carboxyl at that distance. In the less rigid cinnamic acid system, however, *m*-methoxyl enhances the strength appreciably. The order of strengths throughout the four series is *m*-OMe > H > *o*- and *p*-OMe (except with *o*-methoxybenzoic acid, which is stronger than the parent acid), and this is in harmony with the known influence of methoxyl which combines — *I* and + *T* effects. The latter is pronounced, *e.g.*, in (I), and can lead to an inductively transmitted effect in a saturated side chain, *e.g.*, in (II) (cf. J., 1935, 346). It is strange, indeed, that *o*-methoxyl causes a much greater relative fall in strength in β-phenylpropionic than in cinnamic acid.

(I.) 

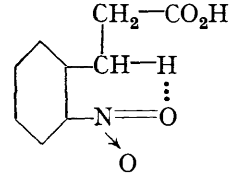
(II.) 

The strengths of *o*- and *m*-hydroxycinnamic acids have also been determined ($10^5K_{\text{therm.}}$ = 2·44 and $4{\cdot}00_5$ respectively), and from these data it may be concluded that there is greater electron recession from *o*-hydroxyl than from *o*-methoxyl, and smaller electron accession to *m*-hydroxyl than to *m*-methoxyl. Comparison of the strengths of *m*- and *p*-hydroxy- and -methoxy-benzoic acids (in water or aqueous alcohol) leads to a similar conclusion (for obvious reasons *p*-methoxyl is considered here in place of *o*-methoxyl). Branch and Yabroff (*J. Amer. Chem. Soc.*, 1934, **56**, 2568) published the following values of $10^5K_{\text{therm.}}$ for 25% ethyl-alcoholic solution at 25° : H, 2·29; *m*-OH, 2·43; *p*-OH, 0·750; *m*-OCH_3, 2·87; *p*-OCH_3, 1·16. On fundamental grounds, methyl, when substituted in hydroxyl, should produce results quite contrary to these. This observation is not without parallel; Groves and Sugden (J., 1937, 1992) have shown that hydroxyl, when attached to the benzene nucleus, possesses a greater mesomeric moment than methoxyl, and again, it is well known that phenol undergoes substitution far more readily than anisole. It is not possible to explain the anomalous order of strengths, *p*-OMe > *p*-OH and *m*-OMe > *m*-OH in these aromatic acids on the basis of ionisation of the hydroxyl group. This ionisation would lead to relatively ***high*** constants in the hydroxy-acids, whereas low constants are actually the case. Moreover, the second dissociation constant of salicylic acid has been shown by Senter and Bulle (J., 1912, **101**, 2532) to be of the order of 1×10^{-13} (cf. Branch and Yabroff, *loc. cit.*), and it is likely that other phenolic acids are comparable in this respect.

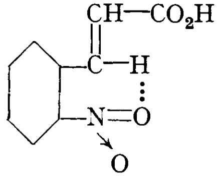
In all four series the order of strengths of chloro-acids is *o*- > *m*- > *p*- > H, and as far as we have determined, the other halogeno-acids preserve a similar order. The much discussed " mesomeric " effect of halogen (compare in this connection the work of Groves and Sugden, *loc. cit.*) contributes to the order *m*- > *p*-, but there seems to be no particular reason why the *o*-acid should consistently be the strongest of the three. In accordance with anticipation, the ratio $K/K_{\text{unsub.}}$ is greater in benzoic and cinnamic acids than in phenylacetic and phenylpropionic acids, irrespective of whether the chlorine occupies the *o*-, *m*-, or *p*-position.

The order of strengths of the nitro-acids (the abnormal *o*-nitrobenzoic acid being omitted) is *p*- > *m*- > *o*- > H, but on the basis of the operation of the $-I$ and the $-T$ effect of nitroxyl, it is reasonable to suppose that the *o*-nitro-acids should be comparable with the *p*-nitro-isomerides in being stronger than the *m*-acids (the phenylacetic and phenylpropionic acids are included in this because the $-T$ effect of nitroxyl is believed to be transmitted inductively through a saturated side chain; see reference to methoxyl above). Dippy and Lewis (J., 1937, 1426), studying the nitrophenylacetic acids, first showed the *o*-isomeride to be the weakest, and to account for this feature they suggested that the molecule was chelated along the lines already suggested for *o*-nitrotoluene by Sidgwick and Callow (J., 1924, **125**, 538). This chelation may also occur in *o*-nitrophenylpropionic (III) and *o*-nitrocinnamic acids (IV), and it is significant that the constants of these acids are now found to be anomalous.

(III.)

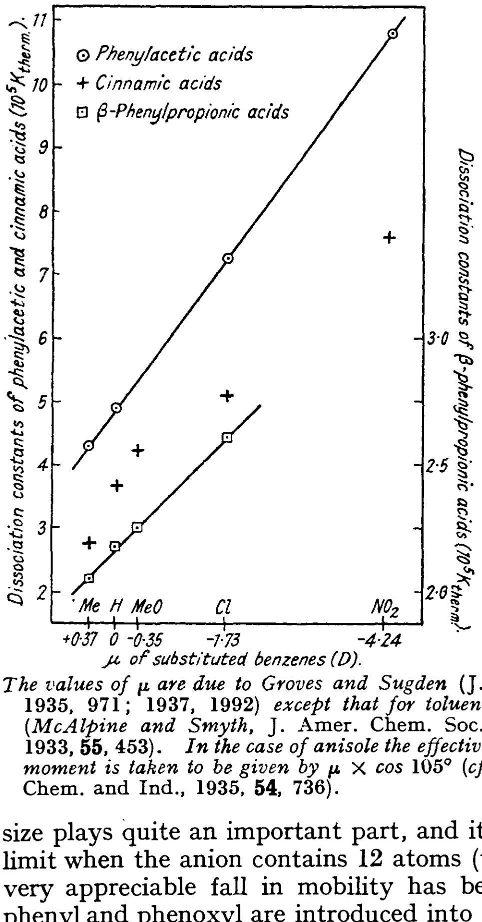


(IV.)



The strength of 3-nitro-*o*-toluic acid has been determined by us ($10^2K_{\text{therm.}} = 1{\cdot}335$), and this demonstrates that the introduction of a second *o*-substituent into an acid further enhances the strength abnormally. The increase brought about in *o*-toluic acid (which itself exhibits an " ortho-effect ") by substituting nitroxyl in the *o*-position to the carboxyl group is even greater than that observed in going from benzoic to *o*-nitrobenzoic acid. The dissociation constants of two other 2 : 6-disubstituted benzoic acids may be found in the literature, *viz.*, the dihydroxy- ($10^2K_{\text{class.}} = 5{\cdot}0$; Ostwald, *Z. physikal. Chem.*, 1889, **3**, 249) and the dinitro- ($10^2K_{\text{class.}} = 8{\cdot}15$; Sirks, *Rec. trav. chim.*, 1908, **27**, 221) acid, and these also indicate the trend observed above. It should be noted that the thermodynamic dissociation constant for 3-nitro-*o*-toluic acid is substantially greater than that of the classical constant ($1{\cdot}135 \times 10^{-2}$), and this may be expected in an acid of this order of strength (compare remarks on *o*-nitrobenzoic acid, J., 1937, 1426). Further, the values of $K_{\text{therm.}}$ for the other diortho-substituted acids cited here would be greatly in excess of the recorded values, which are in terms of $K_{\text{class.}}$; this favours still more the foregoing observation.

Quantitative Correlation.—It has already been pointed out by one of us (*Nature*, 1937, **139**, 591) that a linear relationship exists between the dissociation constants ($K_{\text{therm.}}$) of *m*-nitro-, *m*-chloro-, *m*-methoxy-, *p*-methyl, and unsubstituted benzoic and phenylacetic acids and the dipole moments of substituted benzenes (the values were all comparable but referred to benzene solution; see J., 1937, 1008, for figure). This relationship is now re-examined in the light of recent measurements on the vapours of these substituted benzenes and the results are included in the figure. The benzoic and phenylacetic acids give excellent conformity; the relationship has also been tested with β-phenylpropionic acids, as far as data permit, and found to hold good. In the case of the phenylacetic and β-phenylpropionic acids it can be shown that if the dipole moments of substituted toluenes (data for benzene solution) are taken, a straight line is also obtained. From this it follows that, where the side chain of the acid is composed of methylene links, the dipole moments of substituted benzenes constitute a satisfactory basis for correlation. It is seen from the figure, however, that the points representing the cinnamic acids are irregular, meaning that the permanent polar influences operating in the acids here are not reflected truly in these dipole moments; this is not surprising, since the existence of a double bond in the side chain must considerably affect the polarity of the molecule. The effect of introducing two methylene carbon atoms into a chain is very different from that of introducing vinyl, which is recognised to possess a strong intrinsic attraction for electrons (this is illustrated in the strengths of unsaturated acids; Dippy and Lewis, J., 1937, 1008). Unfortunately, dipole-moment data for the appropriate styrenes do not exist, and so further examination of the cinnamic acids cannot be made.



The values of μ are due to Groves and Sugden (J., 1935, 971; 1937, 1992) *except that for toluene* (*McAlpine and Smyth,* J. Amer. Chem. Soc., 1933, **55**, 453). *In the case of anisole the effective moment is taken to be given by μ × cos* 105° (*cf.* Chem. and Ind., 1935, **54**, 736).

The Mobilities of Anions.—A comprehensive survey of the mobilities of the anions of common aromatic monobasic acids is now possible. It has been made abundantly clear that isomeric ions differ in mobility, although there does not appear to be any rule as to the effect on the speed of migration brought about by moving the position of the substituent; examination of ion mobilities in the four series fails to reveal any consistent order. Constitutive influences must be partly responsible for the movement of anions, since it is obvious that considerations of bulk and weight do not always provide an explanation. It is seen that the mobilities of methyl- and methoxyl-substituted ions are, on the whole, smaller than might be expected, when compared with the mobilities of halogen- and nitro-substituted anions. Nevertheless, ion size plays quite an important part, and it has been shown that the speed does not reach a limit when the anion contains 12 atoms (the original postulate of Ostwald). Actually, a very appreciable fall in mobility has been observed when bulky substituents such as phenyl and phenoxyl are introduced into the benzoate ion (a decrease of 33·4 to 23·5 and 23·3, respectively; Dippy and Lewis, *loc. cit.*).

EXPERIMENTAL.

Conductivity measurements were made on aqueous solutions of 24 acids and their salts at 25° by the procedure described earlier (Parts I—III). The cells were calibrated frequently, and the constants calculated on the customary Parker–Parker basis. The conductivity water employed throughout had a specific conductivity of 0·9—1·0 gemmho.

The stock solutions of almost all the phenylpropionic acids were made up to 500 ml., whereas those of most of the cinnamic acids were made up to 1 l. The only acids soluble enough to permit the preparation of 250 ml. of solution were 3-nitro-*o*-toluic and *o*-chloro-β-phenylpropionic acids; it is indeed surprising that the disubstituted benzoic acid has such a relatively high solubility.

Values of Λ_0 (salt) were computed from the sodium salt measurements by the method of Dippy and Williams (see Parts I and II).

TABLE II.

Cell const.	10^3 C.	Λ.	10^5 $K_{\text{class.}}$.	10^5 $K_{\text{therm.}}$.
o-*Methyl-β-phenylpropionic acid.*				
0·1347	1·002	52·01	2·20$_5$	2·16$_5$
	0·5835	66·21	2·17$_5$	2·14
	0·5595	67·81	2·19$_5$	2·15$_5$
0·07288	0·4094	77·38	2·16	2·13
	0·2814	91·49	2·18	2·15$_5$
12 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·13—2·21; Λ_0 (acid) = 377·8.				
p-*Methyl-β-phenylpropionic acid.*				
0·1365	0·7537	58·01	2·09$_5$	2·06
	0·5584	66·46	2·09$_5$	2·06
	0·4139	75·58	2·06$_5$	2·04
0·07394	0·2650	92·15	2·08	2·05$_5$
	0·1969	104·5	2·08	2·05$_5$
15 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·03—2·11; Λ_0 (acid) = 378·1.				
m-*Methoxy-β-phenylpropionic acid.*				
0·1349	0·4977	72·63	(2·29)	2·25$_5$
	0·2828	92·51	2·25$_5$	2·23
	0·1902	109·3	2·25	2·23
0·07288	0·1716	113·4	2·22	2·20
	0·1051	137·7	2·21	2·19
11 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·19—2·25$_5$; Λ_0 (acid) = 377·0.				
o-*Chloro-β-phenylpropionic acid.*				
0·1347	0·6699	68·69	2·70	2·65$_5$
	0·3229	95·04	2·72	2·69
	0·2803	100·1	2·67$_5$	2·64
0·07288	0·2202	110·4	2·65$_5$	2·62
	0·1795	120·4	2·67$_5$	2·64$_5$
10 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·62—2·69; Λ_0 (acid) = 378·1.				
p-*Chloro-β-phenylpropionic acid.*				
0·1347	0·5139	74·50	2·49$_5$	2·46
	0·2509	101·7	2·50	2·47
	0·2439	102·3	2·46	2·43$_5$
0·07288	0·1758	118·4	2·52	2·49$_5$
	0·08921	153·9	2·50$_5$	2·48$_5$
11 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·43$_5$—2·49$_5$. Λ_0 (acid) = 377·4.				
p-*Nitro-β-phenylpropionic acid.*				
0·07214	0·3421	102·6	3·44	3·39
	0·2667	114·2	3·46$_5$	3·42
	0·2122	123·8	3·36$_5$	3·33
0·05284	0·1724	135·0	3·40	3·36$_5$
	0·1393	146·1	3·36$_5$	3·33
12 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 3·33—3·42$_5$. Λ_0 (acid) = 379·0.				
m-*Methylcinnamic acid.*				
0·1343	0·6459	80·17	3·66$_5$	3·61
	0·3210	108·6	3·69$_5$	3·65
	0·2878	113·9	3·71$_5$	3·66$_5$
0·07295	0·2044	130·3	3·68	3·63
	0·1499	146·6	3·65$_5$	3·60
	0·1353	152·3	3·65	3·60
11 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 3·56—3·67; Λ_0 (acid) = 379·1.				
o-*Hydroxycinnamic acid.*				
0·1347	0·7233	63·90	2·49	2·45
	0·5229	73·41	2·45	2·41$_5$
	0·4179	81·00	2·44$_5$	2·41$_5$
0·07288	0·2873	95·94	2·48$_5$	2·45$_5$
	0·1682	119·9	2·48	2·45$_5$
11 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·41$_5$—2·45$_5$; Λ_0 (acid) = 377·8.				

Cell const.	10^3 C.	Λ.	10^5 $K_{\text{class.}}$.	10^5 $K_{\text{therm.}}$.
m-*Methyl-β-phenylpropionic acid.*				
0·1338	0·5024	70·86	2·18	2·14$_5$
	0·3925	78·48	2·14	2·11$_5$
	0·2492	95·79	2·15	2·12$_5$
0·07214	0·1515	116·7	2·09	2·07
	0·1110	133·1	2·13	2·11$_5$
10 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·06$_5$—2·14$_5$; Λ_0 (acid) = 377·6.				
o-*Methoxy-β-phenylpropionic acid.*				
0·1349	0·5134	60·91	1·59$_5$	1·57$_5$
	0·4663	63·74	1·60$_5$	1·58$_5$
	0·3177	75·67	1·60$_5$	1·58
0·07254	0·2140	89·54	1·58	1·56$_5$
	0·1768	97·16	1·58	1·56$_5$
12 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 1·54$_5$—1·58$_5$; Λ_0 (acid) = 377·2.				
p-*Methoxy-β-phenylpropionic acid.*				
0·1349	0·5822	64·91	2·08$_5$	2·05$_5$
	0·4818	70·84	2·09$_5$	2·06$_5$
	0·4490	72·88	2·08	2·05$_5$
	0·3697	79·68	2·09$_5$	2·07
0·07254	0·2773	89·86	2·07	2·04$_5$
	0·2070	101·6	2·06	2·04
11 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·02—2·07; Λ_0 (acid) = 377·0.				
m-*Chloro-β-phenylpropionic acid.*				
0·1338	0·3902	86·72	2·67	2·63$_5$
	0·3087	95·50	2·64	2·61
	0·2292	107·6	2·60	2·57
0·07214	0·2107	111·0	2·57$_5$	2·55
	0·1548	126·4	2·60$_5$	2·58
11 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·55—2·63$_5$; Λ_0 (acid) = 377·8.				
o-*Nitro-β-phenylpropionic acid.*				
0·1347	0·3897	93·89	3·19	3·14$_5$
	0·2888	106·5	3·18$_5$	3·14$_5$
	0·2335	116·1	3·17	3·13$_5$
0·07288	0·1613	134·8	3·17$_5$	3·14
	0·1413	142·0	3·18$_5$	3·15
10 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 3·12—3·15; Λ_0 (acid) = 378·4.				
o-*Methylcinnamic acid.*				
0·07288	0·09350	166·2	3·17$_5$	3·15
	0·07391	180·1	3·15$_5$	3·13
0·05347	0·06112	192·1	3·16	3·14
	0·05319	202·1	3·21$_5$	3·19$_5$
8 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 3·13—3·23; Λ_0 (acid) = 380·0.				
p-*Methylcinnamic acid.*				
0·07246	0·1234	142·9	2·81$_5$	2·79$_5$
	0·1060	151·5	2·82	2·80
	0·1019	154·4	2·85	2·83
0·05319	0·07787	168·1	2·74$_5$	2·73
	0·06871	171·7	(2·57$_5$)	(2·56)
10 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 2·64—2·83; Λ_0 (acid) = 379·1.				
m-*Hydroxycinnamic acid.*				
0·1347	0·5610	88·9	4·06	3·99$_5$
	0·3290	111·5	4·06	4·00
	0·2994	115·2	(4·00)	3·95
0·07288	0·2152	133·5	4·14$_5$	4·09$_5$
	0·1769	142·8	4·05$_5$	4·01
10 Detmtns.; limits of 10^5 $K_{\text{therm.}}$ 3·95—4·09$_5$; Λ_0 (acid) = 378·0.				

TABLE II (*contd.*).

o-*Methoxycinnamic acid.*

Cell const.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.
0·07246	0·1331	150·9	$3{\cdot}53_5$	$3{\cdot}49_5$
	0·1326	150·7	3·51	3·47
	0·1278	149·4	$3{\cdot}30_5$	$(3{\cdot}26_5)$
	0·1140	158·4	$3{\cdot}45_5$	3·42
0·05319	0·09452	169·3	3·44	3·41
	0·07741	182·0	$3{\cdot}46_5$	3·43

10 Detmtns.; limits of $10^5 K_{therm.}$ $3{\cdot}38_5$—3·54; Λ_0 (acid) = 377·8.

p-*Methoxycinnamic acid.*

Cell const.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.
0·07254	0·1163	147·2	$2{\cdot}92_5$	2·90
	0·1069	153·9	3·02	3·00
	0·09033	165·8	$(3{\cdot}11_5)$	$(3{\cdot}09_5)$
0·05319	0·07467	171·6	2·85	2·83
	0·06236	186·2	3·01	2·99

11 Detmtns.; limits of $10^5 K_{therm.}$ 2·84—3·00; Λ_0 (acid) = 376·6.

o-*Nitrocinnamic acid.*

Cell const.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.
0·1351	0·3181	143·0	7·34	7·24
	0·2629	153·4	7·30	7·20
	0·1759	175·7	7·11	7·03
0·7278	0·1279	194·5	6·99	6·93
	0·07668	199·7	7·22	7·17

10 Detmtns.; limits of $10^5 K_{therm.}$ 6·87—7·24; Λ_0 (acid) = 377·8.

p-*Nitrocinnamic acid.*

Cell const.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.
0·07259	0·07252	248·9	9·20	9·15
	0·06146	258·9	9·14	9·09
	0·05198	267·9	8·95	8·90
0·05351	0·05129	269·2	9·02	8·98
	0·04141	280·9	8·89	8·86

9 Detmtns.; limits of $10^5 K_{therm.}$ 8·75—9·15; Λ_0 (acid) = 378·1.

m-*Methoxycinnamic acid.*

Cell const.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.
0·1347	0·3483	110·8	$4{\cdot}25_5$	$4{\cdot}19_5$
	0·2400	128·8	$4{\cdot}25_5$	$4{\cdot}20_5$
	0·1952	140·3	4·30	4·25
0·07288	0·1498	154·1	$4{\cdot}23_5$	4·19
	0·1074	175·8	$4{\cdot}22_5$	4·18

12 Detmtns.; limits of $10^5 K_{therm.}$ 4·18—$4{\cdot}25_5$; Λ_0 (acid) = 377·1.

m-*Chlorocinnamic acid.*

Cell const.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.
0·07259	0·1539	163·2	5·09	5·05
	0·1346	173·3	(5·26)	(5·21)
	0·1276	175·9	5·21	5·16
0·05351	0·1050	186·9	5·12	5·09
	0·09942	190·5	5·14	5·10

10 Detmtns.; limits of $10^5 K_{therm.}$ 4·94—5·16; Λ_0 (acid) = 377·0.

m-*Nitrocinnamic acid.*

Cell const.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.
0·07285	0·1264	203·7	7·80	7·73
	0·1170	208·8	7·78	7·72
	0·1162	208·6	7·74	7·67
	0·09768	217·9	(7·49)	7·43
	0·07914	233·5	7·72	7·67

12 Detmtns.; limits of $10^5 K_{therm.}$ 7·38—7·73; Λ_0 (acid) = 380·5.

3-*Nitro*-o-*toluic acid.*

Cell const.	$10^3 C$.	Λ.	$10^5 K_{class.}$.	$10^5 K_{therm.}$.
0·1347	0·7667	354·0	1110	1265
	0·4369	362·4	1043	1275
	0·3708	366·7	1285	(1575)
0·07288	0·2435	369·1	1115	1500
	0·1593	370·8	(937·5)	1340

15 Detmtns.; limits of $10^5 K_{therm.}$ 1230—1500; Λ_0 (acid) = 377·0. A higher degree of accuracy could not be achieved for this highly-conducting acid.

Table II contains details of the experimental results on acids. In each case a representative run is included, together with the mean value of Λ_0 (acid) obtained by employing the usual sodium and hydrogen mobilities; the concentration C refers to g.-equivs. per litre.

The values in parentheses in the above table were not taken into account in the calculation of mean constants.

Preparation of Materials.—All the β-phenylpropionic acids, except the nitro-derivatives, were obtained by reduction of aqueous solutions of salts of the corresponding cinnamic acids. In each case the cinnamic acid (1 mol.) was dissolved in sodium hydroxide solution and treated with 2½% sodium amalgam (4 atoms) in small portions with intermittent shaking. The whole was then heated for 1 hour on a steam-bath to ensure complete reaction of the sodium amalgam, the aqueous layer decanted and treated with concentrated hydrochloric acid in the cold, and the precipitated phenylpropionic acid washed and recrystallised from water. Yields of 80—90% were frequently obtained.

o- and *p*-Nitro-β-phenylpropionic acids had to be prepared by nitration of the parent acid with a mixture of concentrated and fuming nitric acid (Konek and Pascu, *Ber.*, 1918, **51**, 858). The yields of pure acid were 20% and 50% respectively.

o- and *p*-Methyl-, *m*-hydroxy-, and *o*-, *m*-, and *p*-methoxy-cinnamic acids were prepared by the Knoevenagel synthesis, which proved to be clean and economical. The general procedure was as follows : An alcoholic solution of the substituted benzaldehyde (1 mol.) and malonic acid (1·5 mols.) was treated with 7% alcoholic ammonia solution (1 mol. of NH_3), and allowed to stand for 24 hrs. The alcohol was evaporated, and the residue (intermediate malonic acid derivative) decomposed by heating to 100—120°. The remaining acid was extracted with sodium carbonate solution and recovered by acidification. Precautions had to be taken with *o*-hydroxybenzaldehyde to exclude air to the utmost, since oxidation occurred very readily. Yields of 70—80% of substituted cinnamic acid were obtained throughout.

Attempts to prepare these acids by the haloform reaction met with little success. Hitherto, the Perkin synthesis has been applied almost exclusively.

m-Methoxycinnamic acid had to be prepared by methylation, and the method described here is superior to those in the literature. *m*-Hydroxycinnamic acid (1 mol.) was dissolved in a large excess of concentrated sodium hydroxide solution, and methyl sulphate (4 mols.) added gradually with shaking; after being warmed on the steam-bath for 2 hrs., the solution was extracted with ether and the aqueous layer acidified, whereupon the methoxy-acid was precipitated (70% yield).

We are indebted to Professor F. Böck of the Technische Hochschule, Vienna, for specimens of *m*-methyl-, *m*-chloro-, and *o*-, *m*-, and *p*-nitro-cinnamic acids, and to Professor L. P. Hammett, of Columbia University, for the 3-nitro-*o*-toluic acid.

All acids were finally purified by recrystallisation several times from conductivity water and drying in a vacuum desiccator. They were kept out of contact with light as far as possible; certain of the substituted cinnamic acids (*e.g.*, the nitro-acid) develop a reddish colour after long exposure to daylight. Details of the purity of the dry acids used in the measurements are included in Table III. The equivalents of all acids were determined by titration.

TABLE III.

	M. p. (corr.).	M. p. (best in lit.).	
β-Phenylpropionic acids.			
o-Me	102°	102°	(Young, *Ber.*, 1892, **25**, 2104)
m-Me	43	42—43	(v. Miller and Rohde, *ibid.*, 1890, **23**, 1899)
p-Me	122	120	(Kröber, *ibid.*, p. 1033)
o-OMe	92	92	(Perkin, J., 1881, **39**, 415)
m-OMe	52	51	(Tiemann and Ludwig, *Ber.*, 1882, **15**, 2052)
p-OMe	107	104—105	(Borsche and Gerhardt, *ibid.*, 1914, **47**, 2914)
o-Cl	99	97	(Stoermer, *ibid.*, 1911, **44**, 659)
m-Cl	77	77—78	(Gabriel and Herzberg, *ibid.*, 1883, **16**, 2039)
p-Cl	126	124	(*Idem, ibid.*)
o-NO_2	115	115	(Jaenisch, *ibid.*, 1923, **56**, 2448)
p-NO_2	168	163—164	(Beilstein and Kuldberg, *Annalen*, 1872, **163**, 132)
Cinnamic acids.			
o-Me	169	174—175	(v. Auwers, *ibid.*, 1917, **413**, 265)
		169	(Böck, Lock, and Schmidt, *Monatsh.*, 1934, **64**, 399)
m-Me	119	118	(*Idem, ibid.*)
p-Me	199	198—199	(Hanzlik and Bianchi, *Ber.*, 1899, **32**, 1289)
		199	(Böck, Lock, and Schmidt, *loc. cit.*)
o-OH	209	214	(Stoermer, *Ber.*, 1911, **44**, 643)
		208	(Fittig and Ebert, *Annalen*, 1884, **226**, 351)
m-OH	194	193	(Posner, *J. pr. Chem.*, 1910, **82**, 428)
o-OMe	186	185—186	(Reychler, *Bull. Soc. chim.*, 1908, **3**, 552)
m-OMe	120	117	(Bauer and Vogel, *J. pr. Chem.*, 1913, **88**, 340)
p-OMe	174	173·8	(Prins, *Z. physikal. Chem.*, 1909, **67**, 718)
m-Cl	167	176	(Gabriel and Herzberg, *loc. cit.*)
		165	(Böck, Lock, and Schmidt, *loc. cit.*)
o-NO_2	242	242	(*Idem, ibid.*)
m-NO_2	202	201	(*Idem, ibid.*)
p-NO_2	288	288	(Drewsen, *Annalen*, 1882, **212**, 151; Böck, Lock, and Schmidt, *loc. cit.*)
3-Nitro-*o*-toluic acid	154	153—154	(Treffers and Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1709)

The strengths ($10^5 K_{\text{class.}}$) of only three of the above acids have hitherto been measured. Roth and Stoermer (*Ber.*, 1913, **46**, 267) recorded a value of 2·1 for both *o*- and *p*-methoxycinnamic acids, whereas we found classical constants of 3·47 and $2{\cdot}91_5$ respectively; the value of Λ_0 (acid) in each case, *viz.*, 369, was also very considerably lower than our figure. The dissociation constant of *o*-hydroxycinnamic acid has been given as 2·14 and 2·7 by Ostwald (*Z. physikal. Chem.*, 1889, **3**, 277) and Springer and Jones (*Amer. Chem. J.*, 1912, **48**, 441), respectively (our classical constant is 2·48).

The following points are also noteworthy: (1) the order of m. p.'s of the above isomeric acids is *p*- > *o*- > *m*- (excluding the methoxycinnamic acids), (2) the sodium salt solution prepared from *o*-hydroxycinnamic acid exhibited a pronounced yellow-green fluorescence (cf. Zwenger, *Annalen*, 1872, Suppl. **8**, 23).

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THE TECHNICAL COLLEGE, CARDIFF.

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