205. *The Influence of Solvents and of Other Factors on the Rotation of Optically Active Compounds. Part XXXVII. Asymmetric Solvent Action* (continued).

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From the work herein described it appears that (1) *l*-nicotine and ethyl *d*-tartrate have a considerable mutual solvent influence, (2) the tartrate raises the rotation of the nicotine (in an absolute sense), (3) similarly the nicotine raises the rotation of the tartrate, (4) ethyl *i*-tartrate has a slightly greater effect than ethyl racemate, (5) the *iso*butyl tartrates show a generally similar and consistent behaviour, as compared with the ethyl derivatives.

Experiments described in Part XXXVI (J., 1937, 1453) dealt with the changes of volume which occur when two unsymmetrical compounds are mixed. In that investigation, the rotational changes observed were only briefly referred to, but those for mixtures of *l*-nicotine with ethyl tartrate and with the *iso*butyl tartrates are now described more fully. Previous work would lead one to expect that, on mixing ethyl tartrate and nicotine, the rotation of both should be mutually influenced to a considerable extent; and that the change in the rotation of the mixture might be strikingly great in cases where the contributions of the two components were of the same sign, or comparatively small if the contributions of the components happened to be of opposite sign. Although, unfortunately, it is clear, *a priori*, that no definitive solution to the problem is yet to be expected, the present data are of interest in this connexion.

The ethyl tartrate used was prepared by the hydrogen chloride saturation method and had $\alpha_{5461}^{20^\circ} + 9{\cdot}45^\circ$. The nicotine was purified by means of the zinc chloride double salt, $C_{10}H_{14}N_2,2HCl,ZnCl_2,H_2O$ (Patterson and Fulton, J., 1925, **127**, 2493; Lowry and Lloyd, J., 1929, 1381). Its rotation and density agreed closely with the data given by Jephcott (J., 1919, **115**, 104), Patterson and Fulton (*loc. cit.*), Lowry and Singh (*Compt. rend.*, 1925, **181**, 910), and Lowry and Lloyd (*loc. cit.*). It was distilled in an atmosphere of nitrogen at 10—15 mm. pressure, atmospheric pressure being finally restored by admission of nitrogen instead of air; and during later work the distillate was shaken vigorously in the nitrogen-filled receiver before removal and use. This was remarkably efficient in preventing oxidation. The nicotine used had $\alpha_{5461}^{20^\circ} -206{\cdot}2^\circ$. With these samples of ethyl tartrate and nicotine the rotations and densities of three mixtures were determined for three colours of light, at a number of temperatures between 0° and 100°.

The discussion of the experimental data presents difficulty, inasmuch as it is necessary first to adopt some criterion of what may be considered analogous conditions under which comparisons may be made. We shall not discuss other possibilities, but describe only that one adopted in the sequel, and recorded in the Table. The various solutions were made up to certain definite percentages by weight; *e.g.*, solution I contained 7·88% of nicotine and 92·12% of ethyl tartrate. The *specific rotation* of such a solution, containing two active substances, can have no useful meaning here, so that for comparison of the rotations of the constituents with the rotation of the mixed solution, it is necessary to use observed rotations.* If 10 g. of the above solution be supposed divided into its two constituent parts, the 0·788 g. of nicotine at 0° would occupy 0·7716 c.c. and the 9·212 g. of ethyl tartrate would occupy 7·5169 c.c.; the sum of these volumes is 8·2885 c.c. If these two quantities were placed one behind the other, so that they could not mix, in a tube of 1 cm.² cross-section,† the observed rotation, for light of $\lambda = 5461$, due to the nicotine (which would occupy a length of 7·716 mm. of the tube) would be $-15{\cdot}98^\circ$, *i.e.*, $0{\cdot}07716 \times -207^\circ$ (length of column, in dcm., $\times$ observed rotation of nicotine at 0°), and that due to the ethyl tartrate would similarly be $+4{\cdot}135^\circ$, *i.e.*, $0{\cdot}75169 \times 5{\cdot}5^\circ$. The sum

* In the Experimental Data, when *both* constituents of a solution are active, observed rotations only are recorded. If only one constituent is active, the specific rotation is mostly recorded, as this value is often useful and, from it, the observed rotation can easily be calculated.

† In order to reduce the data to the usual standards of comparison.

TABLE.

	(A) Nicotine.*	(B) Ethyl tartrate.	(C) Ethyl racemate.	(D) Ethyl *i*-tartrate.	(E) *iso*Butyl *d*-tartrate.	(F) *iso*Butyl *l*-tartrate.	(G) *iso*Butyl racemate.	(H) *iso*Butyl *i*-tartrate.
$d^{0°}$	1·0212	1·2255	1·2252	—	—	—	—	—
$d^{99°}$	0·9453	1·1249	1·1260	1·1387	1·0099 (now re-determined)	1·0099 (J., 1913, **103**, 175)	1·0099	1·0225
$\alpha_{5461}^{0°}$	− 207·1°	+ 5·5°	—	—	—	—	—	—
$\alpha_{5461}^{99°}$	− 195·9°	+ 15·75	—	—	+ 23·56° (J., 1916, **109**, 1162)	− 23·56° (assumed same as *d*-compd.)	—	—

No. of solution.	*t*.	*d*.	*W*. Weight (g.) in 10 g. of soln.	*X*. Vol. (c.c.) in 10 g. of soln.	*Y*. Obs. rotation (λ = 5461) of separate components.	*Z*. Obs. rotation (λ = 5461) of actual mixture for total vol. shown in Col. *X*.	Δ = *Z* − *Y*.
I	0°	1·2125	*A* = 0·788	0·7716	− 15·98°		
			B = 9·212	7·5169	+ 4·13		
			10·000	8·2885	− 11·85	− 4·84°	+ 7·01°
	99	1·1125	ditto	0·8336	− 16·33		
				8·2080	+ 12·93		
				9·0416	− 3·40	− 0·99	+ 2·41
II	0	1·1629	*A* = 3·333	3·2638	− 67·59		
			B = 6·667	5·4403	+ 2·99		
			10·000	8·7041	− 64·60	− 45·78	+ 18·82
	99	1·0166	ditto	3·5259	− 69·07		
				5·9404	+ 9·36		
				9·4663	− 59·71	− 51·11	+ 8·60
III	0	1·1089	*A* = 6·019	5·8940	− 122·06		
			B = 3·981	3·2485	+ 1·79		
			10·000	9·1425	− 120·27	− 103·0	+ 17·3
	99	1·0657	ditto	6·3673	− 124·73		
				3·5472	+ 5·59		
				9·9145	− 119·14	− 110·9	+ 8·2
IV	0	1·2092	*A* = 0·788	0·7716	− 15·98		
			C = 9·212	7·5187	0		
			10·000	8·2903	− 15·98	− 13·20	+ 2·78
	99	1·1117	ditto	0·8336	− 16·33		
				8·1810	0		
				9·0146	− 16·33	− 14·96	+ 1·37
V	0	1·1635	*A* = 3·333	3·2638	− 67·59		
			C = 6·667	5·4415	0		
			10·000	8·7053	− 67·59	− 59·10	+ 8·49
	99	1·0662	ditto	3·5259	− 69·07		
				5·9209	0		
				9·4468	− 69·07	− 65·37	+ 3·70

* From Patterson and Fulton (J. 1925, **127**, 2444).

TABLE (*continued*).

No. of solution.	*t.*	*d.*	*W.* Weight (g.) in 10 g. of soln.	*X.* Vol. (c.c.) in 10 g. of soln.	*Y.* Obs. rotation (λ = 5461) of separate components.	*Z.* Obs. rotation (λ = 5461) of actual mixture for total vol. shown in Col. *X*.	$\Delta = Z - Y$.
VI	0°	1·1089	*A* = 6·02	5·8951	− 122·09°		
			C = 3·98	3·2484	0		
			10·00	9·1435	− 122·09	− 113·6°	+ 8·5°
	99	1·0172	ditto	6·3684	− 124·76		
				3·5346	0		
				9·9030	− 124·76	− 120·7	+ 4·1
VII	99	1·0215	*A* = 6·0197	6·3681	− 124·75		
			D = 3·9803	3·4954	0		
			10·0000	9·8635	− 124·75	− 119·7	+ 5·1
VIII	99	0·9770	*A* = 6·02	6·3684	− 124·76		
			E = 3·98	3·9409	+ 9·29		
			10·00	10·3093	− 115·47	− 109·2	+ 6·3
IX	99	0·9775	*A* = 6·0201	6·3686	− 124·76		
			F = 3·9799	3·9408	− 9·28		
			10·0000	10·3094	− 134·04	− 137·0	− 3·0
X	99	0·9770	*A* = 6·02	6·3684	− 124·76		
			G = 3·98	3·9409	0		
			10·00	10·3093	− 124·76	− 123·0	+ 1·8
XI	99	0·9815	*A* = 6·0196	6·3680	− 124·75		
			H = 3·9804	3·8927	0		
			10·0000	10·2607	− 124·75	− 122·4	+ 2·4

of the separate rotations would therefore be −11·85°. If the two solutions were now mixed, the volume would become 8·247 c.c., so that there is a slight contraction, which, meantime at least, may be neglected. The change in rotation, however, is considerable; the rotation of the mixed solution (−4·84°) is higher than the sum of the two separate rotations (−11·85°) by 7·01°.

Data calculated in this way for three such solutions are given in the Table for 0° and 99°,* and it will be seen from the last column that there is in all cases a considerable difference between the observed and the calculated values. The differences are greater at 0° than at 99°. We think it probable that with further increase of temperature these differences would fall to zero and then increase again.

In the Table are also shown the results for three similar solutions of nicotine with ethyl racemate. In solution IV at 0° the rotation of 0·788 g. (= 0·771 c.c.) of nicotine would be, as before, −15·98°, and, the rotation of the ethyl racemate being *presumably* zero, the total rotation for a length of 82·903 mm. should be −15·98°. The actual rotation *for* 100 *mm.* was found to be −15·92° and therefore for 82·903 mm., −13·20°, *i.e.*, 2·78° higher than would be expected if the phenomenon were purely additive. Similar differences were found for the other solutions and temperatures.

If it be assumed for the moment that *l*-nicotine exerts the same influence upon the rotation of ethyl *d*-tartrate as it does upon that of ethyl *l*-tartrate, so that the rotation of *l*-nicotine dissolved in either of them is, from experiment (IV), −13·20°, then the rotation

* This temperature was chosen as it happened to be that for which the rotation of nicotine was directly observed (Patterson and Fulton, J., 1925, **127**, 2444). The other data are taken mostly from graphs by extrapolation.

of the *d*-ester in a solution of this concentration must be +8·36°, *i.e.*, —4·84°, the rotation of I, minus that of IV. Hence nicotine appears to raise the rotation of ethyl *d*-tartrate from +4·13° in the homogeneous condition, for the quantity now under consideration (l = 75·17 mm.), to +8·36°, under the conditions of solution IV at 0°.

On the other hand since the observed rotation of the undiluted *l*-nicotine in IV at 0° is —15·98° and in the mixed solution IV it is —13·2°, ethyl racemate raises considerably (makes less negative) the rotation of *l*-nicotine. Thus the rotation of ethyl *d*-tartrate would presumably become more positive, and that of ethyl *l*-tartrate more negative, by solution in *dl*-nicotine, whereas the rotation of *l*-nicotine becomes less negative and that of *d*-nicotine would become less positive by solution in ethyl *dl*-tartrate.

Since ethyl *i*-tartrate is a solid of m. p. 57°, it was only possible to examine this ester in a solution of composition corresponding to solutions III and VI, and only to compare these at 99°. As is shown in the Table, solution VII, *l*-nicotine (6·0197 g.) in ethyl *i*-tartrate (3·9803 g.) at 99°, changes its observed rotation from —124·75° to —119·7°, which is 1° more than the change produced by ethyl *dl*-tartrate (—120·7°). The influence is in the same direction.

We also examined similar solutions of nicotine in *iso*butyl *d*-, *l*-, *dl*-, and *i*-tartrate, and again, since these esters are solids at room temperature, comparison of rotation values can only be made, directly, at higher temperatures. The data obtained are also shown in the Table.

Dealing with solutions VIII, IX, and X in the same way as with I—VI, but making the actual comparisons at 99°, we find that: (1) in all cases there is a distinct and, since it is mostly suffered by the much less active constituent of the solutions, considerable change of rotation when the two active substances are mixed; (2) from the data for X, it appears that the change of rotation of nicotine owing to admixture with *iso*butyl racemate is comparatively slight, 1·8°, but, as with ethyl racemate (VI), it is again in an upward direction; (3) from the value for VIII (—109·2°) minus that for X (—123°), the value +13·8° is found as the apparent observed rotation at this concentration, for *iso*butyl *d*-tartrate in *l*-nicotine (for 103·093 mm. length of column); and similarly from IX and X the value —14° for the apparent observed rotation of *iso*butyl *l*-tartrate in *l*-nicotine is found, numbers which agree as closely with each other as could be expected. Thus *l*-nicotine raises the rotation of *iso*butyl *d*-tartrate and depresses (makes more negative) that of the *l*-ester; whereas *iso*butyl tartrate (presumably both *d*- and *l*-) raises slightly (makes less negative) the rotation of *l*-nicotine.

In all cases temperature–rotation curves for these solutions have been plotted and analysed, but the only point in regard to them that need be mentioned here is that a minimum rotation, which appears distinctly in the *iso*butyl *dl*-tartrate solution (X) at a temperature of about 25°, is not quite reached in the corresponding *i*-tartrate (XI) at zero, but clearly would appear on further cooling.

Similar results to those given above—but using *specific* rotation and the temperature 0°—are obtained by the method adopted in Part XXXVI (*loc. cit.*). If from the present data for VIII the specific rotation at 0° be calculated as if the whole rotation were due to the *iso*butyl *d*-tartrate (p = 39·8), we find the composite value $x - y$ = —104·85/(0·398 × 1·0653) = —247·3°, where x may be supposed to be the part of this specific rotation, due to the *d*-tartrate, and from IX for the *l*-tartrate $-x - y$ = —141·45/(0·395 × 1·0658) = —333·5°. Then, by elimination, $x = \pm$43·1°.

Similarly, from the data for the same two solutions but calculated with reference to the nicotine (p = 60·2), or by eliminating y in the above equations and multiplying the result by 39·8/60·2, we find the specific rotation of the nicotine in these solutions to be —192·0°.

By extrapolation, the specific rotation of homogeneous *iso*butyl *d*-tartrate at 0° should be about +15·3° (J., 1913, **103**, 174; 1916, **109**, 1147, 1162), so that *l*-nicotine appears to raise considerably the specific rotation of *iso*butyl *d*-tartrate, whilst, since the specific rotation of homogeneous *l*-nicotine at 0° is —198° (solution X), *iso*butyl *dl*-tartrate appears to raise slightly the rotation of *l*-nicotine.

Comparing VI and X at 99°, we find that ethyl racemate raises the rotation of *l*-nicotine more than does *iso*butyl racemate (4·1° as against 1·8°); and, from VII and XI, that ethyl *i*-tartrate raises the rotation of *l*-nicotine more than does *iso*butyl *i*-tartrate (5·1° as compared with 2·4°).

Experimental Data.

Wave lengths of light used :

	r_1.	r_2.	*y*.	*g*.	*b*.	*v*.
λ	6716	6234	5790	5461	4916	4359

Ethyl tartrate : observed rotation, $\alpha^{t°}_{5461}$ (100 mm.).

t	14·0°	16·0°	20·0°	24·8°	27·5°	36·0°
a	8·18°	8·57°	9·45°	10·26°	10·53°	11·62°

Ethyl tartrate and nicotine : observed rotations (100 mm.).

t.	$d^{t°}_{4°}$.	r_1.	r_2.	*y*.	*g*.	*b*.	*v*.
	Solution I. Ethyl tartrate, p = 92·12 ; nicotine, q = 7·88.						
0°	1·2125 *	− 1·18°	− 2·30°.	− 3·97°	− 5·84°	− 11·42°	− 24·36°
22	1·1989	− 0·12	− 1·00	− 2·35	− 4·07	− 8·96	− 20·86
44	1·1675	+ 0·78	+ 0·24	− 0·90	− 2·32	− 6·83	− 17·40
66	1·1454	+ 1·58	+ 1·14	+ 0·15	− 1·09	− 4·90	− 14·69
89·5	1·1215	+ 2·16	+ 1·82	+ 0·99	− 0·06	− 3·47	− 12·29
	Solution II. Ethyl tartrate, p = 66·67 ; nicotine, q = 33·33.						
0	1·1629 *	− 30·41	− 36·71	− 44·79	− 52·60	− 71·14	—
20·8	1·1425	− 31·24	− 37·33	− 45·47	− 53·52	− 72·04	—
43·5	1·1203	− 31·41	− 37·87	− 46·17	− 54·14	− 73·01	—
66	1·0979	− 31·65	− 38·08	− 46·35	− 54·36	− 72·91	—
90	1·0745	− 31·64	− 38·03	− 46·22	− 54·21	—	—
	Solution III. Ethyl tartrate, p = 39·81 ; nicotine, q = 60·19.						
0	1·1089 *	− 67·56	− 80·8	− 97·37	− 112·8	—	—
20·0	1·0900	− 67·94	− 81·15	− 98·22	− 113·56	—	—
44·75	1·0670	− 68·63	− 81·73	− 98·53	− 113·78	—	—
66·0	1·0472	− 68·28	− 81·65	− 98·23	− 113·60	—	—
89·5	1·0253	− 69·36	− 81·98	− 97·47	− 112·56	—	—

Ethyl racemate and nicotine.

Temp.	$d^{t°}_{4°}$.	r_1.	r_2.	*y*.	*g*.	*g*.	*b*.	*v*.
		[α].				α (100 mm.).	[α].	
	Solution IV. Ethyl racemate, p = 92·12 ; nicotine, q = 7·88.							
0°	1·2092 *	−102·8°	−121·6°	−144·1°	−167·0°	−15·92°	−218·3°	−306·8°
18·8	1·1921	105·5	124·7	148·9	172·2	16·18	224·7	314·2
44·0	1·1676	109·6	129·8	155·0	179·3	16·51	233·2	325·2
66·9	1·1443	111·8	133·8	160·0	184·6	16·65	240·1	334·9
90·7	1·1202	115·4	136·8	163·2	188·5	16·64	243·9	338·5
	Solution V. Ethyl racemate, p = 66·67 ; nicotine, q = 33·33.							
0	1·1635 *	−105·9	−126·7	−151·4	−175·1	−67·88	−228·8	−320·0
19·0	1·145 *	111·1	131·2	156·7	180·9	69·08	236·1	330·2
29·2	1·1346	111·6	133·2	159·4	183·8	69·48	239·4	334·9
54·2	1·1093	116·9	138·6	164·0	189·9	70·18	247·1	344·4
86·3	1·0783	119·9	141·4	168·0	194·3	69·85	253·4	352·6
	Solution VI. Ethyl racemate, p = 39·80 ; nicotine, q = 60·20.							
0	1·1077 *	−133·4	−135·0	−161·2	−186·2	−124·20	−242·3	−340·8
23·0	1·0869	116·8	138·8	165·5	191·2	125·13	247·9	348·6
44·8	1·0669	119·4	141·3	168·7	194·8	125·13	252·9	355·2
67·4	1·0461	121·1	143·3	170·9	197·2	124·28	255·0	358·1
90·2	1·0253	121·9	144·4	172·3	198·9	122·75	254·2	360·7

* By extrapolation.

Ethyl *i*-tartrate was prepared by Frankland and Aston's continuous method (J., 1901, **79**, 517) from dehydrated *meso*tartaric acid, m. p. 143°. The ester, crystallised from carbon disulphide and subsequently distilled, melted at 57° with slight preliminary softening from 54°. Kühn and Wagner-Jauregg give m. p. 55° (*Ber.*, 1928, **61**, 503).

The *iso*butyl *d*-, *l*-, and *dl*-esters were prepared by the Fischer–Speier method, purified by crystallisation from benzene, and, finally, distillation at 5—8 mm. pressure (Patterson and

Lamberton, J., 1937, 1458). iso*Butyl* i-*tartrate*, prepared and purified in the same manner, had m. p. 81—82°, b. p. 176—178°/12 mm. (Found: C, 55·3; H, 8·5. $C_{12}H_{22}O_6$ requires C, 54·9; H, 8·5%); solubility, 17 g. of ester in 100 g. of benzene at 20°.

Densities determined (of molten ethyl and *iso*butyl *i*-tartrates). Ethyl *i*-tartrate: $d_{4°}^{60·7°}$ 1·1783, $d_{4°}^{70·4°}$ 1·1674, $d_{4°}^{80·5°}$ 1·1586, $d_{4°}^{81·8°}$ 1·1568, $d_{4°}^{88·5°}$ 1·1499, $d_{4°}^{93·9°}$ 1·1441; whence $d_{4°}^{100°}$ = 1·1384. *iso*Butyl *i*-tartrate: $d_{4°}^{83·4°}$ 1·0356, $d_{4°}^{85·0°}$ 1·0348, $d_{4°}^{87·7°}$ 1·0327, $d_{4°}^{91·6°}$ 1·0296, $d_{4°}^{94·5°}$ 1·0258, $d_{4°}^{95·2°}$ 1·0261, $d_{4°}^{97·3°}$ 1·0236; whence $d_{4°}^{100°}$ = 1·0216.

Ethyl meso*tartrate and nicotine.*

Solution VII. Ethyl *meso*tartrate, p = 39·803; nicotine, q = 60·197.

Temp.	$d_{4°}^{t°}$.	r_1.	r_2.	y.	g.	g.	b.	v.
		[α].				α (100 mm.).	[α].	
0°	1·1116 *	−113·6°	−134·0°	−160·3°	−185·3°	−124·00°	−240·1°	−338·8°
17·8	1·0953 *	—	—	—	188·5	124·28	244·1	—
20·5	1·0928	115·8	137·0	163·4	188·7	124·13	—	345·0
43·4	1·0723	117·6	139·5	166·8	192·3	124·15	249·6	350·1
66·1	1·0516	119·4	141·3	168·8	195·0	123·43	252·0	354·7
89·9	1·0297	120·7	142·9	170·6	196·8	121·98	253·7	357·4

iso*Butyl* d-*tartrate and nicotine.*

Solution VIII. *iso*Butyl *d*-tartrate, p = 39·800; nicotine, q = 60·200. α (100 mm.).

Temp.	$d_{4°}^{t°}$.	r_1.	r_2.	y.	g.	b.	v.
0°	1·0653 *	−63·30°	−74·93°	−90·55°	−104·85°	−137·43°	−197·33°
18·4	1·0484	64·23	75·88	91·68	106·18	139·08	199·15
42·4	1·0275	64·73	76·68	92·40	107·05	138·90	199·40
66·5	1·0061	64·93	76·83	92·38	107·13	139·65	199·25
90·7	0·9842	64·55	76·25	92·08	106·38	138·28	197·33

iso*Butyl* l-*tartrate and nicotine.*

Solution IX. *iso*Butyl *l*-tartrate, p = 39·799; nicotine, q = 60·201. α (100 mm.).

0	1·0658 *	−87·70	−103·25	−122·93	−141·45	−181·45	−251·68
21·2	1·0473	87·23	102·85	122·40	140·85	179·53	250·03
44·8	1·0258	86·50	101·85	121·03	139·25	178·38	247·58
66·5	1·0061	85·13	100·15	119·20	137·13	176·80	243·90
89·3	0·9862	83·48	98·00	116·75	134·35	171·68	239·65

iso*Butyl racemate and nicotine.*

Solution X. *iso*Butyl racemate, p = 39·8; nicotine, q = 60·2.

Temp.	$d_{4°}^{t°}$.	r_1.	r_2.	y.	g.	g.	b.	v.
		[α].				α (100 mm.).	[α].	
0°	1·0653 *	−117·6°	−139·1°	−166·1°	−191·9°	−123·03°	−249·4°	−350·3°
20·6	1·0470	120·2	141·9	169·2	196·0	123·50	253·9	357·2
46·0	1·0245	122·3	144·8	172·9	199·5	123·05	258·4	364·1
65·2	1·0071	122·8	145·9	174·4	201·4	122·10	260·3	366·2
86·2	0·9885	124·0	146·7	175·4	202·3	120·50	261·9	367·5

iso*Butyl* meso*tartrate and nicotine.*

Solution XI. *iso*Butyl *meso*tartrate, p = 39·804; nicotine, q = 60·196.

0	1·0680 *	−117·6	−139·1	−166·2	−191·9	−123·50	−248·8	−351·0
18·5	1·0518	119·8	140·8	168·9	194·6	123·25	252·4	354·8
41·0	1·0325	121·2	143·1	170·9	197·4	122·75	256·0	359·7
65·8	1·0107	122·5	145·1	173·2	199·9	121·93	257·9	363·1
89·3	0·9902	123·9	145·9	174·3	201·2	119·93	259·6	364·5

* By extrapolation.

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