56. *Aqueous Solubilities of* r- *and* l-*Mandelic Acids and Three* O-*Acyl*-r-*mandelic Acids.*

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The aqueous solubilities of *r*-mandelic, and of acetyl-, propionyl-, and benzoyl-*r*-mandelic acids at 5° intervals from 0° to 50°, and of *l*-mandelic acid from 25° to 70°, have been determined. Substitution causes a lowering of solubility, and that of the racemic acid is greater than that of the active acid at the same temperature. In geometrical and stereoisomerides the form with the lower m. p. has the greater solubility.

Existing data on the solubility of *r*-mandelic acid comprise isolated determinations at one temperature only. When these results are expressed in the same units they agree fairly well with each other and with those now communicated. Solubility, *S*, is expressed in g. per 100 g. of water.

Temp.	Reference.	*S*.	Temp.	Reference.	*S*.
20°	Lewkowitsch (*Ber.*, 1883, **16**, 1566)	15·97	25°	Knox and Richards (J., 1919, **115**, 516)	22·10
	Schlossberg (*Ber.*, 1900, **33**, 1056)	15·95		Ross and Morrison (J., 1933, 1016)	20·4
	Authors	16·21		Authors	21·95
24·7	Rimbach (*Ber.*, 1899, **32**, 2388) ...	20·85			

Recorded values for the solubility of *l*-mandelic acid are somewhat higher than those now reported. They are: at 20°, Lewkowitsch (*loc. cit.*), 8·64; at 25°, Campbell and Garrow (*Trans. Faraday Soc.*, 1930, **26**, 560), 10·98; Ross, Morrison, and Johnson (J., 1937, 608), 12·68. No data are on record for the solubilities of the substituted acids.

Experimental.

The acids were purified by the methods described in the preceding paper.

The solubilities of the racemic compounds were determined by a method closely resembling that of Dalman (*J. Amer. Chem. Soc.*, 1937, **59**, 2547). Round-bottomed glass tubes of 50-c.c. capacity, fitted with ground glass stoppers, were charged with 40 c.c. of water and sufficient excess of acid to ensure saturation at the appropriate temperature. The tubes were clamped to the rotating stirrer of an electrically-heated thermostat and rotated until equilibrium had been attained (10—20 hrs.). Samples were transferred at intervals to tared vessels, and analysed by titration with standard alkali of suitable concentration. Table I shows the solubilities of (*a*) *r*-mandelic acid, (*b*) acetyl-*r*-, (*c*) propionyl-*r*-, and (*d*) benzoyl-*r*-mandelic acids at various temperatures, θ. Several values were obtained for each solute at each temperature; for *r*-mandelic acid the results were reproducible to 0·5%, and for the substituted acids to 1%.

Table I.

θ.	(*a*).	(*b*).	(*c*).	(*d*).	θ.	(*a*).	(*b*).	(*c*).	(*d*).
0°	8·79	0·57	0·29	0·51	37°	109·4	—	—	—
10	11·68	0·68	0·35	0·60	40	163·2	3·18	1·22	1·27
15	13·40	0·76	0·37	0·65	42·5	192·4	—	—	—
20	16·19	0·96	0·38	0·73	45	247·0	5·74	1·85	1·57
25	21·95	1·14	0·52	0·79	47	274·2	—	—	—
30	37·46	1·39	0·59	0·92	50	373·0	13·50	3·46	1·88
35	81·8	1·99	0·74	1·04					

The amount of *l*-mandelic acid available was relatively small and the solubility was, therefore, determined by Kuriloff's sealed-tube method (*Z. physikal. Chem.*, 1897, **23**, 547). The mean values of several observations at each temperature are given in Table II. Although the precision of this method is much less than that of the analytical method employed for the other acids, the results were reproducible to 2%.

Table II.

θ	24·5°	27·5°	31·5°	37·0°	41·5°	44·0°	46·5°
S	8·9	10·9	14·3	20·8	30·0	39·8	55·7
θ	48·5°	50·5°	52·5°	54·5°	57·0°	60·5°	68·0°
S	74·0	94·4	112·8	129·1	155·1	194·0	289·2

All thermometers were checked against N.P.L. certified instruments.

Discussion.—The solubility curves of all these substances, except benzoyl-*r*-mandelic acid, show a similarity in shape. Up to a certain temperature (approx. 30—40°) the solubility increases slowly, but thereafter it increases rapidly with temperature. The substituted acids are much less soluble than mandelic acid, owing to acylation of the strongly hydrophilic hydroxyl group; and, in passing from acetyl- to propionyl-*r*-mandelic acid there is further diminution.

Both *r*- and *l*-mandelic acid have essentially similar solubility curves, but the solubility of the former is considerably greater than that of the latter at the same temperature and increases more rapidly with temperature. Scarcity of *l*-acid has prevented us from determining the solubility of the active forms of the other compounds.

The results for mandelic acid, however, fall into line with previous data on the solubility of geometrical and stereoisomerides in that the form with the lower m. p. is the more soluble; *e.g.*, for maleic (m. p. 130°) and fumaric (m. p. 300°) acids, Weiss and Downs (*J. Amer. Chem. Soc.*, 1923, **45**, 1003) give the solubility at 25°

as 78·8 and 0·70, respectively. Further, examination of Findlay and Campbell's data (J., 1928, 1768) on tartaric acid and tartrates reveals that, in each case, the more soluble form has the lower m. p. It is hoped to extend this investigation.

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