CLXI.—*The Amygdalins. Part I.*

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In a previous communication by one of us (Walker, Trans., 1903, **83**, 472) it was demonstrated that *l*-amygdalin is converted rapidly at the ordinary temperature by a very small quantity of an alkaline solution into a much more soluble substance, which yields on hydrolysis by concentrated hydrochloric acid, not *l*-mandelic, but *r*-mandelic acid. Although the new material was termed provisionally *r*-amygdalin, proof was wanting that it is even a homogeneous substance, since it could not be obtained crystalline. The author stated that it was still under examination, and consequently was much surprised to find Dakin (Trans., 1904, **85**, 1512) claiming to have isolated it in crystalline form. It may be well therefore to state here that its study had been continued; that a very soluble, crystalline substance had already been isolated from aqueous or aqueous-alcoholic solution, which proved not to be *r*-amygdalin, since it yielded mandelic acid possessed of a high lævorotation; that this

substance yielded on fractional crystallisation ordinary or *l*-amygdalin; that the mother liquor on acid hydrolysis gave a large preponderance of *d*-mandelic acid; that the racemised solution, as was to be anticipated, gave benzaldehyde and hydrocyanic acid with emulsin; and that the mandelic acid obtained from the racemised solution was in no case absolutely inactive, but always contained a small excess of the dextro-variety. There were, however, a number of questions which for a long time defied the attempts made to elucidate them, and some of these we have only as yet been able to answer in part satisfactorily.

Regarding the nomenclature to be adopted, we shall employ that indicated in the former communication, considering it preferable to the *iso*-amygdalin of Dakin or the *neo*-amygdalin of Tutin (Trans., 1909, **95**, 663), and designate ordinary amygdalin as *l*-amygdalin, since it yields *l*-mandelic acid and the isomeride which only differs from it in yielding *d*-mandelic acid on hydrolysis as *d*-amygdalin, leaving to their discoverer the task of assigning names to the similar compounds which contain the different varieties of *d*- and *l*-glucose.

In the former communication the simplest assumption was made regarding the nature of the change induced in the molecule of amygdalin by alkalis, namely, that it consists only in the racemisation of the mandelic asymmetric carbon atom, although further change, for example, that of a β- into an α-glucoside, was not excluded. We have reason now to conclude that a partial change of that nature does occur during racemisation, and to a much greater extent on protracted concentration of the solution, especially in presence of barium carbonate. This of course complicates the problem, and renders it difficult to decide whether the small excess of dextro-acid which is invariably found on hydrolysis represents a displacement of the equilibrium in the transformation lævo $\rightleftarrows$ dextro beyond the middle point. We have proved, however, that the rotation of the racemised solution is independent of the nature and of the concentration of the alkali, and that the equilibrium point is independent of temperature and of the concentration of the amygdalin. In studying the fractional crystallisation of the racemised solution, we find that the less soluble fraction yields on hydrolysis mandelic acid containing 78 per cent. of the lævo-variety, and that the more soluble fraction obtained by suitable means from the mother liquor gives mandelic acid containing 75 per cent. of the dextro-variety. These figures point to the presence of the respective compounds $(3l+d)$- and $(3d+l)$-amygdalin, but their rotations are not quite in conformity with this supposition, nor is the behaviour of the second, when subjected to the action of emulsin, such as we would expect from a compound having the composition $(3d+l)$-amygdalin. We are driven therefore to the conclusion that

the second compound at least does not contain the substance which we have termed *d*-amygdalin, and that the change induced in *l*-amygdalin by alkalis is of a much more complicated nature than has been hitherto assumed.

Experimental.

The material employed throughout this investigation was Kahlbaum's preparation. Analyses showed that it possesses the formula

$$C_{20}H_{27}O_{11}N,2H_2O,$$

and that when it is allowed to crystallise from aqueous solution the air-dried material contains 3 molecules of water of crystallisation. Its specific rotation, and that of its racemised solution, were determined at different temperatures and concentrations. The results contained in the following tables, as well as all that follow, refer to the anhydrous substance.

Table I.

l-*Amygdalin*.

t.	$[\alpha]_D$.
	$c=18\cdot54$.
20·5°	−38·0°
29·0	37·1
42 0	35·8
	$c=9\cdot27$.
8·0°	41·6°
16·0	40·1
20·0	39·3
25·0	38·8
28·5	38·3
40·0	36·8
48·0	35·8

Table II.

r-*Amygdalin*

t.	$[\alpha]_D$.
	$c=17\cdot657$.
13·0°	−54·4
40·0	50·8
	$c=8\cdot9$.
23·0°	−52·8°
38·0	51·0
	$c=6\cdot39$.
26·0°	−52 4°
	$c=4\cdot414$.
23·0°	−52·6°

Table III.

l-*Amygdalin*. $t=28\cdot5°$.

c.	$[\alpha]_D$.	*c*.	$[\alpha]$.
18 54	−37·1°	4·472	−39·0°
9·27	38·3	2·236	39·4
6·71	37·8		

These observations show a large and approximately equal variation with temperature for both substances. The variation with concentration is much smaller in the case of *l*-amygdalin and negligible for *r*-amygdalin.

The Equilibrium between Laevo- and Dextro-amygdalin.—Since the two forms are not optical antipodes, there seems no reason to expect

that the equilibrium point should lie exactly midway between the two, and even in the former communication it was noted, as has been confirmed by Dakin, that after complete hydrolysis of the racemised solution with hydrochloric acid, the ethereal extract did possess a slight activity, pointing to the production of a slight excess of *d*-amygdalin, although Liebig and Wöhler's amygdalinic acid gave quite inactive mandelic acid. This has been fully confirmed in a large number of subsequent experiments in which the hydrolysis was performed both at the ordinary temperature and on the boiling-water bath. If the equilibrium point, however, were not situated midway between the two extremes, it is probable that by varying the conditions of racemisation there would be a consequent displacement of the equilibrium point. Of the four variable factors which may influence the equilibrium point, namely, temperature, concentration of the amygdalin, and the nature and concentration of the alkali, the last two will be excluded if it can be shown that the reaction is purely catalytic, and this was roughly done in the previous communication. It has been considered advisable therefore to obtain more accurate proof of the catalytic nature of the change. The alkali, however, may also slowly hydrolyse both varieties of amygdalin to their respective amygdalinic acids, and, if it does so at unequal rates, but with a velocity at all comparable to that of racemisation, the dextro-variety, if more rapidly hydrolysed by alkalis, as Dakin has shown (*loc. cit.*), than it is by acids, would be continuously produced from the lævo-. It was therefore considered necessary to examine also the velocity of the change of amygdalin into amygdalinic acid in alkaline solution, although the facts recorded formerly, namely, that no ammonia could be detected after racemisation, and that amygdalinic acid yields *r*-amygdalinic acid, were strong evidence that alkaline hydrolysis is not responsible for the excess of mandelic acid obtained. The velocity of racemisation was observed in the 2-dcm. tube at 16°. The first three solutions were prepared by adding 1 c.c. of the alkaline solution to 25 c.c. of a 10 per cent. solution of recrystallised *l*-amygdalin, the fourth by adding 1 c.c. of alkali to 50 c.c.

TABLE IV.

Catalyst, Barium Hydroxide. 1 c.c. added to 25 c.c.

Observed rotation.	Time (in minutes).	$A-x$.	K.
−6·86° (calculated)	0	2·24	—
7·72	2	1·38	0·105
8·31	4	0·79	0·113
8·65	6	0·45	0·116
8·88	9	0·22	0·112
9·09	14	0·10	0·168

TABLE IV (*continued*).

Catalyst, Potassium Hydroxide. 1 c.c. added to 25 c.c.

Observed rotation.	Time (in minutes).	$A-x$.	K.
−6·86°	0	2·24	—
7·75	2	1·35	0·110
8·28	4	0·82	0·109
8·59	6	0·51	0·107
8·85	9	0·25	0·106
9·03	14	0·07	0·108
9·11	20	—	—
9·11	30	—	—

Catalyst, Lithium Hydroxide. 1 c.c. added to 25 c.c.

−6·86°	0	2·24	—
7·72	2	1·38	0·105
8·25	4	0·85	0·105
8·63	6	0·47	0·113
8·86	9	0·24	0·108
9·08	14	0·02	0·146
9·10	20	—	—

Catalyst, Lithium Hydroxide. 1 c.c. added to 50 c.c.

−7·00° (calculated)	0	2·24	—
7·43	2	1·81	0·046
7·88	4	1·35	0·054
8·21	6	1·03	0·056
8·54	9	0·70	0·057
8·88	14	0·36	0·056
9·11	22	0·13	0·073
9·24	38	—	—
9·25	58	—	—

The mean total change of rotation is 2·24°, and as the slight deviations are well within the limit of experimental error this may be taken as a measure of the total chemical action. The values of K, calculated by means of the unimolecular equation, are seen to be in satisfactory agreement in experiments I, II, and III, whilst that in experiment IV is just half value. Consequently all the alkalis examined racemise amygdalin with the same velocity in equivalent solutions, and when their concentation is halved the velocity of their action is also reduced to half. These are the criteria for a catalytic action. It is further important to note that, within the limits studied, the concentration of the alkali has no influence on the end point. As these limits are, however, somewhat narrow, it was considered advisable to extend them. In the following experiments, which were done at 25°, the volumes of water and barium hydroxide (1 c.c. = 0·0122 gram

$Ba(OH)_2$·) specified were added to 20 c.c. of a 10 per cent. solution of *l*-amygdalin and the final rotation examined in the 1-dcm. tube :

C.c. water.	C.c. baryta.	Final value of α_D.
8	1	−3·35°
4	5	3·35
3	6	3·35
1	8	3·35

It is obvious that the concentration of the alkali is without influence. At 25° the velocity of racemisation was so great that the change was almost complete by the time that the first reading could be taken.

The velocity of hydrolysis of amygdalin to amygdalinic acid was also examined polarimetrically, using a solution of sodium hydroxide containing 0·1 gram-molecule in 50 c.c. For this purpose 10 grams of recrystallised *l*-amygdalin were dissolved in water containing five equivalents of sodium hydroxide and diluted to 50 c.c., the change of rotation being followed at 20° in the 2-dcm. tube :

TABLE V.

Time.	α_D.	$A-x$.	K.
0	(−18·80°)	5·76	—
14	19·40	5·16	0·00012
27	20·00	4·56	0·00013
77	21·40	3·16	0·00012
147	22·30	2·26	0·00010
297	23·54	1·02	0·00010
387	23·80	0·76	0·00009
1360	24·56	0·00	—

The initial reading, namely, −18·80°, obtained by plotting the subsequent values and exterpolating, corresponds with a specific rotation for anhydrous *r*-amygdalin of $[\alpha]_D$ −52·5°, which is identical with that given in Table II, showing that the equilibrium point of the reaction is the same even at this concentration of alkali as in the very dilute. The values of K, calculated from the equation for a bimolecular reaction, are in good agreement, and it is evident that the time taken is about 1000 times as long as that for racemisation, even although the alkali is now more than 300 times stronger. It is certain therefore that hydrolysis plays no part during racemisation and is not responsible for any excess of *d*-mandelic acid obtained on acid hydrolysis. Concurrent experiments to be described later on the fractional crystallisation of *r*-amygdalin had led us to look upon the dextro-variety as an extremely soluble substance compared with its lævo-isomeride, which could be isolated by fractional crystallisation from the racemised solution, and it seemed natural to associate the over-production of the dextro-variety with its great solubility. If this were the

case we should expect to find that, by racemising in a very concentrated solution, a greater excess of the dextro-variety would be produced. Consequently a series of experiments were made in which the concentration of the amygdalin varied from $c = 17{\cdot}657$ to $4{\cdot}414$ and the rotations of the resulting racemised solutions were observed. The results are contained in Table II. As already stated they show that the specific rotation of the racemised solution is independent of the concentration of the amygdalin. Even more concentrated solutions of *r*-amygdalin than these were produced by adding a small quantity of baryta solution to solid amygdalin. After acid hydrolysis and extraction with ether the mandelic acid obtained had always about the same specific rotation, namely, $+16°$, indicating therefore about 15 per cent. excess of dextro-acid. A somewhat higher result was obtained by the polarimetric study of the hydrolysis of *r*-amygdalin. The concentration of anhydrous material was $9{\cdot}442$ and the hydrolyst, hydrochloric acid ($D = 1{\cdot}1$). The change of rotation was followed in the 2-dcm. tube at 40°.

TABLE VI.

Time (in hours).	α_D.	Time (in hours).	α_D.
0·5	−19·76°	22	+3·64°
1·5	19·7	41	12·22
2·75	18·64	66	16·74
5·75	15·48	89	18·70
17·0	−0·88	114	20·16

There was no further change on prolonged heating at the same temperature. If inactive mandelic acid and dextrose be the sole products of hydrolysis, the final rotation of the solution should be $+15{\cdot}8°$. The excess of dextrorotation observed is $+4{\cdot}4°$, which corresponds with 21 per cent. excess of *d*-mandelic acid, since the specific rotation of the latter is $+168°$ when dissolved in that strength of hydrochloric acid. We have not yet been able to account for the difference in the results obtained by the two methods except on the assumption that the dextrose has also undergone some change.

The last factor which can influence the racemisation and produce excess of the dextro-variety is temperature; consequently, in order to investigate this point, two experiments were performed, one at 50°, the other at 100°, the amygdalin being racemised in each case with 10 c.c. of the baryta solution. After complete acid hydrolysis they were extracted with ether and a specific rotation taken of the dry acids. It was found in both cases to be 16°. Consequently temperature has no influence on the equilibrium point during racemisation. These facts, all taken in conjunction, point to the conclusion that there is actually a racemic compound in solution, and that the production of an excess

of *d*-mandelic acid from it is due to an inequality in the rates of hydrolysis of the two varieties by acid, accompanied by a slow racemisation in that medium also. The experiments now to be described on the fractional crystallisation of the racemised solution indicate, however, that the material contained in it may not be of such a simple nature.

The Partial Resolution of r-*Amygdalin.*—This had been effected before the last communication was published, but, owing to its incompleteness, it was reserved for further study and only the statement made that the racemic compound could not be obtained crystalline. Successive crops of crystals had been obtained, however, either from aqueous or alcoholic solution, but these, although showing a far greater solubility in water than *l*-amygdalin, were not constant in specific rotation, nor had the latter nearly so high a value as that of the racemised solution. Further, it was frequently found impossible to induce crystallisation at all, but the syrup obtained on evaporation would dry up to a glassy mass. It was found, however, that when a crop of very soluble crystals was obtained, it yielded on recrystallisation almost pure *l*-amygdalin, and that, after a large amount of gummy material had been precipitated from the alcoholic mother liquor by the addition of ether, the residue left on the evaporation of the ether yielded, when hydrolysed with hydrochloric acid, a sample of mandelic acid melting at 120—125° and showing a specific rotation of +99°. A partial separation had therefore been effected by fractional crystallisation and precipitation. In a very recent communication Tutin (Trans., 1909, **95**, 663) has shown that this may also be effected in the case of hepta-acetyl-*r*-amygdalin; but here also the separation is far from quantitative, for Tutin only obtained 9 grams of crystalline material from 20 grams of *r*-amygdalin instead of the theoretical 16·5 grams, and even that was evidently far from pure hepta-acetyl-*d*-amgydalin. This is exactly on a parallel with what we have observed in our very numerous experiments on the fractional crystallisation of *r*-amygdalin. We always obtain a considerable amount of uncrystallisable gum which yields excess of *d*-mandelic acid on acid hydrolysis. At first it seemed probable that this is due to some *l*-amygdalin separating with the less soluble fraction, thus leaving an excess of the non-crystallisable *d*-amygdalin in the mother liquor; but subsequent experiments involving a study of the action of emulsin on the different varieties, and of the electrical resistances of the solutions before and after evaporation, have led us to conclude that they may, according to the treatment which they have undergone, contain 50 per cent. or even more of something which is not one of the amygdalins. Our reasons for concluding that it may to that extent have undergone an isomeric change will appear in the description of a few of our experiments

bearing on that point. Assuming for the present that the solution contains only *l*- and *d*-amygdalin in equivalent amounts, it is evident from the specific rotations of *l*- and *r*-amygdalin, namely, $-39{\cdot}3°$ and $-53°$ in 10 per cent. solution at 20°, that the specific rotation of *d*-amygdalin must be $-66{\cdot}7°$ under the same conditions. We should have therefore for $(3l+d)$-amygdalin $[\alpha]_D - 46{\cdot}2°$ and for $(3d+l)$-amygdalin $[\alpha]_D - 59{\cdot}9°$. The best method yet devised for conducting the fractional crystallisation is as follows. After racemising 200 grams by baryta, the solution was saturated by carbon dioxide and the barium carbonate removed by filtration. The filtrate was evaporated to a syrup, and dissolved in a litre of 95 per cent. alcohol. After being kept at 0° for several hours, 80 grams of crystalline material were obtained. On drying over phosphoric oxide in a vacuum it lost weight equivalent to two molecules of water of crystallisation. The specific rotation of the anhydrous substance was $c = 9{\cdot}27$, $t = 28{\cdot}5°$, $\alpha_D - 8{\cdot}65°$; hence $[\alpha]_D - 46{\cdot}6°$. At 20°, therefore, its specific rotation must be $-47{\cdot}7°$, assuming that the temperature coefficient is the same for this substance as for the other two. This value is in fairly close agreement with that calculated above for a substance possessing the composition of $(3l+d)$-amygdalin. Ten grams of it were hydrolysed with hydrochloric acid (D 1·118), and the mandelic acid, after extraction with ether, was converted into the barium salt (3·7 grams). Analysis showed that it was almost pure barium mandelate. When dissolved in water and diluted to 50 c.c., it showed a rotation of $\alpha_D - 6{\cdot}8°$ at 20° in the 2-dcm. tube. The specific rotation of pure barium *l*-mandelate was found to be $[\alpha]_D - 80{\cdot}9°$ under the same conditions; hence the concentration of lævo-salt in excess in the above solution is $c = 6{\cdot}8 \times 100/80{\cdot}9 \times 2 = 4{\cdot}2$. Therefore 3·7 grams contain 2·1 grams of lævo-salt in excess and 1·6 grams of racemic salt or a total of 78·4 per cent. of the lævo- compound. That this crystalline material is mainly a definite compound and not a mixture of *l*- and *r*-amygdalin was evident from the extreme ease with which it dissolved in water. From the result of its hydrolysis, however, it evidently contained a small quantity of free *l*-amygdalin. After being twice crystallised from water, it gave, on acid hydrolysis, a sample of mandelic acid, showing the specific rotation $[\alpha]_D - 142{\cdot}5°$. It contained, therefore, less than 8 per cent. of *d*-mandelic acid. The original mother liquor from the 200 grams of amygdalin was concentrated to a syrup and then extracted with 300 c.c. of a boiling mixture containing one part of alcohol to three of ethyl acetate. The residue, obtained after evaporation of the solvent, was dried over sulphuric acid until constant in weight. It weighed 35 grams. As it was non-crystalline, we had no criterion that it was a chemical individual. It was therefore re-dissolved in 350 c.c. absolute alcohol, and this solution kept for some time at about $-18°$. The crystalline

material (10 grams) which separated was rapidly dried and transferred at once to weighing bottles. These precautions are necessary, for at a slightly higher temperature the crystals liquefy. The material in the weighing bottles rapidly melted, and was kept in a vacuum over sulphuric acid until constant in weight. In this way it lost 35 per cent. in weight, corresponding with 5·35 molecules of alcohol. The material dried over sulphuric acid was employed for determining its specific rotation with the following results: $c = 5·9$, $t = 29°$, $l = 1$-dcm., α_D $-3·25°$; hence $[\alpha]_D - 55·1°$. At 20°, therefore, its rotation will be about $-56°$. Ten grams of it, when hydrolysed as above, yielded 4·35 grams of barium mandelate, showing the rotation $c = 8·7$, $l = 2$-dcm., α_D $+7·25°$. It therefore contained 75·7 per cent. of dextro-salt. Its rotation, however, does not correspond with the value calculated for $(3d + l)$-amygdalin. The alcoholic solution from which this modification of amygdalin was obtained yielded further crops of the same material on evaporation.

Action of Emulsin on the Amygdalins.—When a solution of emulsin was added to the racemised solution of amygdalin and the mixture kept for several hours at 40° in a closed flask, it acquired a strong odour of oil of bitter almonds. This was also observed by Dakin (*loc. cit.*), but this qualitative observation is of no further value than to afford proof that the solution still contains *l*-amygdalin. A series of comparative experiments has therefore been conducted quantitatively to determine the action of emulsin on these different substances. The emulsin employed was Kahlbaum's preparation. After the solutions had been heated at 40—45° for twenty-four hours, the liberated hydrocyanic acid was estimated by the method described by Auld (Trans., 1908, **93**, 1277) and the dextrose by Fehling's solution. The former we found far from satisfactory, as the end point is by no means sharp, although accurate enough for comparative results. In the following table are given the averages of several determinations.

TABLE VII.

	0·2833 gram of substance required of *N*/50-iodine (in c.c.).	1·89 grams yielded of dextrose (in grams).
l-Amygdalin	52·3	1·5
r-Amygdalin	26·0	1·19
$(3d + l)$-Amygdalin (?)	18·0	—

Since the values of iodine for the first two are very nearly in the ratio 2 : 1, the conclusion seemed obvious that emulsin only liberates hydrocyanic acid from the *l*-amygdalin present, and, as the amounts of dextrose are approximately in the ratio 4 : 3, that it is only capable of removing one molecule of dextrose from the supposed *d*-amygdalin.

If it contains *d*-amygdalin, the second substance ought to yield, on partial hydrolysis by emulsin, *d*-mandelonitrile glucoside. But Caldwell and Courtauld (Trans., 1907, **91**, 673) have pointed out that the substance sambunigrin, isolated by Bourquelot and Danjou (*Compt. rend.*, 1905, **141**, 598) from elder leaves, must be *d*-mandelonitrile glucoside; consequently our solution ought to contain sumbunigrin. That it does not contain that substance, however, was proved by the fact that emulsin is unable to hydrolyse it, for no further change took place on heating at 40° for forty-eight hours longer. We therefore attempted to isolate the new substance by concentrating to a syrup and extracting with ethyl acetate, but the residue left after evaporating the ethyl acetate did not crystallise even after a long period. This result led us to conclude that some further change than simple racemisation had taken place in the amygdalin molecule; accordingly, another set of comparative experiments was made to determine whether it is contemporaneous with, or subsequent to, racemisation. The concentration of the emulsin was lower in these, so that it is improbable that hydrolysis was carried as far as in the previous experiments.

0·3 gram substance required of *N*/50-iodine:

(1)	Racemised without heating	42 c.c.
(2)	Racemised and dried for 4 hours on the water-bath	21 ,,

These results suggested an explanation of several difficulties, showing as they do that a profound change takes place when the solution is evaporated to dryness. They indicated a reason for the large quantities of uncrystallisable material which we frequently obtained, and pointed to a probable change in the rotatory power of the racemised solution by protracted evaporation. Our early determinations of this constant had shown considerable inexplicable divergences from each other. There are three possible directions in which the structure of the molecule may be affected by heating. It may suffer an isomeric change in one or both of its dextrose radicles, it may lose one dextrose radicle by hydrolysis, or it may be hydrolysed to the ammonium salt of amygdalinic acid. That dextrose was not liberated was shown by testing the evaporated material with Fehling's solution. The result was negative. As none of the ordinary methods of testing for the presence of an ammonium salt recommended themselves in this case, we finally decided to take the decrease in electrical resistance of the solution as a measure of the amount of such hydrolysis, and, at the same time, to measure the change in optical power. In the cell which we employed the ordinary distilled water of the laboratory had a resistance of 16,000 ohms at 19°, whilst a 5 per cent. solution of

the material employed, namely, $C_{20}H_{27}O_{11}N,3H_2O$, had a resistance of 2,444 ohms.

For the purpose of comparison 5 grams of the same sample were boiled with excess of baryta until all the ammonia was expelled; then carbon dioxide and ammonia were passed into the solution to precipitate all the barium as carbonate and give a solution of ammonium amygdalinate. This was thoroughly boiled to expel dissolved gases, diluted to 100 c.c., and found to be neutral in reaction and free from barium. Its specific rotation was $[\alpha]_D^{20}$ $-72°$, and its resistance 15 ohms. In the following three experiments 2·5 grams of *l*-amygdalin were racemised with baryta, and, after precipitation of the latter by carbon dioxide, were evaporated on the water-bath for the times specified. They were then diluted to 50 c.c., filtered, and their electrical resistances and specific rotations measured. In the first experiment 10 c.c. were hydrolysed by emulsin for twenty-four hours, and the liberated hydrocyanic acid was titrated with *N*/50-iodine.

TABLE VIII.

Time (in hours).	Ohms.	$[\alpha]_D$ (anhydrous).	C.c. *N*/50-iodine.
8	148	−61·0°	24
4	200	60·0	—
2	273	52·7	—

If we assume as an approximation that the resistance of a solution of ammonium amygdalinate is proportional to its concentration, the 5 per cent. solution of that salt would evidently require to be diluted to nearly ten times its volume to show a resistance equal to the first of these. That is to say, 10 per cent. at most of the amygdalin has been hydrolysed. When we examine the specific rotations, however, we find that $61 - 52/72 - 52 = 9/20$ths, or 45 per cent. has been changed, assuming hydrolysis to be the cause. In the third experiment, conditions are reversed, for there practically no change has occurred in the optical properties of the solution, although its resistance would indicate 5 per cent. of hydrolysis. Finally, without any assumption as to the nature of the change, when the amount of hydrocyanic acid liberated is compared with that produced under similar conditions from a racemised solution which has not been heated, we find that 66 per cent. has been changed, for such a solution required 70 c.c. *N*/50-iodine. We must conclude, therefore, that the chief change which takes place on protracted heating is not a hydrolytic one, but consists in some intramolecular transformation, a new isomeride of amygdalin being produced which probably bears to amygdalin the relationship of an α-glucoside to a β-glucoside. Our experiments are, however, not yet

decisive as to whether the freshly racemised solution contains *d*-amygdalin or not, but we are continuing the study of the subject.

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