CCCCXIX.—*Optical Activity dependent on Co-ordinated Beryllium, Copper, and Zinc.*

By WILLIAM HOBSON MILLS and REGINALD ARTHUR GOTTS.

IT was observed by Lowry and Burgess, in an examination of the properties of the metallic derivatives of benzoylcamphor (J., 1924, **125**, 2081), that beryllium benzoylcamphor when dissolved in benzene, chloroform, and other solvents showed mutarotation, and they referred this mutarotation to the gradual disappearance in solution of optical activity associated with the beryllium, since, as they pointed out, the beryllium atom in this compound would probably act as a centre of asymmetry in the same way as the central carbon atom of the ketodilactone of benzophenonetetracarboxylic acid (Mills and Nodder, J., 1920, **117**, 1407 ; 1921, **119**, 2094).

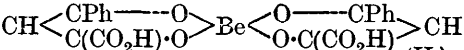
The experiments described in the present paper were carried out with the object of obtaining direct experimental proof that a dissymmetrically linked beryllium atom can, as thus indicated, give rise to optical activity.

We endeavoured to find a β-diketone, containing a salt-forming group, which would be itself devoid of molecular dissymmetry, but could be shown to acquire it on conversion into its beryllium derivative. Experiments directed towards the same end, which, however, did not yield positive results, have recently been described by Morgan and Porter (this vol., p. 1256).

After some exploratory work, we found in benzoylpyruvic acid (I) a compound with which this plan could be carried out.

Aqueous solutions of the sodium salt of this acid dissolved freshly-precipitated basic beryllium carbonate, the *sodium* salt of the beryllium derivative (II) * being formed.

$Ph\cdot CO\cdot CH_2\cdot CO\cdot CO_2H$
(I.)



$$CH\left<\begin{matrix}CPh\text{——}O\\C(CO_2H)\cdot O\end{matrix}\right>Be\left<\begin{matrix}O\text{——}CPh\\O\cdot C(CO_2H)\end{matrix}\right>CH$$

(II.)

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* The linkings in the six-membered rings in this formula are represented by single lines with the intention of indicating that the question of the nature of these bonds is left open, though we regard the beryllium atom as being linked to the four oxygen atoms in the way suggested by Sidgwick (J., 1923, **123**, 725

But while this salt crystallised well and reacted immediately with the mineral acid salts of the common alkaloids to give sparingly soluble alkaloid salts of the beryllium complex, the latter compounds could not be obtained crystalline in this manner. The alternative method of preparation was therefore tried of digesting the alkaloid salts of benzoylpyruvic acid in alcoholic solution with basic beryllium carbonate and by this means the *brucine* salt of the beryllium complex could be obtained in crystalline form without difficulty after crystalline nuclei had (with some little trouble) once been obtained.

The brucine salt crystallised with 8 molecules of water of crystallisation and was sufficiently soluble in aqueous alcohol for polarimetric examination, but no mutarotation could be observed in this solvent. It was realised, however, that any activity associated with the co-ordinated beryllium was likely to be exceedingly evanescent and that under these conditions the expected mutarotation might well have proceeded to completion before any observations could be taken. The salt was therefore dehydrated. The anhydrous compound proved to be exceedingly soluble in chloroform and moderately soluble in absolute alcohol and with these solutions we were able to observe changes of rotation of the type expected.

The solution of the anhydrous brucine salt in chloroform showed a very rapid mutarotation. Three minutes after wetting, the salt showed a specific rotation $[\alpha]_{5461}$ of + 25·0°, which decreased according to the unimolecular law and reached a steady value of + 5·0° within about ½ hour.

In alcohol, only very fleeting mutarotations were at first observed, but by taking greater and greater care in purification of the solvent, and by employing vessels of silica, the time required for the completion of the mutarotation was at length increased to 3 hours, the specific rotation $[\alpha]_{5461}$ decreasing during this period from 39·9° (observed 5 minutes after first wetting the salt) to the final value 13·1°.

Crystallisation of the brucine salt from aqueous alcohol thus gives a dextrorotatory salt the optical activity of which *decreases* in solution to a limiting value, and which is accordingly, on the hypothesis on which we were working, the brucine salt of the *d*-beryllium complex.

We also obtained the salt in an initially lævorotatory form in which the optical activity *increased* in solution to the same final positive value as was attained by the dextrorotatory salt and which we therefore regarded as the brucine salt of the *l*-beryllium complex. This modification was obtained by dissolving the anhydrous brucine *d*-acid salt in chloroform, allowing the solution to stand for 2 hours to racemise the beryllium complex, and then precipitating the salt in two fractions by adding ether. The first fraction consisted principally of the original initially dextrorotatory salt, but the second fraction showed in chloroform an initial lævorotation $[\alpha]_{5461}$ of $-11{\cdot}8°$, which rose in 25 minutes to $+5{\cdot}2°$ and this fraction was therefore regarded as the diastereoisomeric salt, brucine *l*-berylliobenzoylpyruvate.

The brucine salt had thus been obtained in two modifications showing opposite and (within the degree of approximation to be expected) equal mutarotations. It was then necessary to prove that these mutarotations were in fact due, as had been provisionally assumed, to the disappearance of an optical activity associated with the beryllium, for whilst brucine salts are lævorotatory in aqueous solution, a not inconsiderable number of the salts of this alkaloid with organic acids are dextrorotatory in organic solvents—for example, brucine benzoylpyruvate is dextrorotatory in chloroform or alcoholic solution. The rotatory power of brucine in its salts in solution in organic solvents is thus particularly sensitive to the acid with which it is associated, and, in the absence of proof to the contrary, the possibility would always remain that the observed mutarotation was due to the effect of tautomeric changes in the berylliobenzoylpyruvic acid on the optical activity of the brucine with which it was combined. To obtain this proof it was necessary to remove the brucine without destroying the very delicate optical activity depending on the co-ordination of the beryllium.

It appeared that this removal of the brucine could be most simply effected (and with sufficient completeness) by taking advantage of the sparing solubility of brucine hydrochloride in absolute alcohol, but in trying this method we were met with the difficulty that most of the salts of berylliobenzoylpyruvic acid are also sparingly soluble in this solvent. The dimethylammonium salt proved, however, to be sufficiently soluble for our purpose.

Brucine *d*-berylliobenzoylpyruvate was therefore added to a very carefully purified alcoholic solution of a considerable excess of dimethylamine hydrochloride. A precipitate formed which proved to be mainly brucine hydrochloride and had slightly more than the theoretical weight. The filtrate (observed as rapidly as possible) showed a dextrorotation, α_{5461} $+1{\cdot}13°$ $(l = 2)$, which, as was to be expected, was evanescent and sank to zero in about ¼ hour. The solution finally became faintly lævorotatory ($-0{\cdot}1°$), indicating the presence of a small amount of unremoved brucine hydrochloride. On evaporation, it left a crystalline residue from which analytically pure *dimethylammonium berylliobenzoylpyruvate* was isolated.

A similar experiment was made with the diastereomeric brucine *l*-acid salt. The solution showed, after the removal of the greater part of the brucine, a lævorotation α_{5461} of $-$ 0·63° which rose in 10 minutes to a final value of $-$ 0·06°.

Thus the greater part of the brucine could be removed from these solutions without a corresponding decrease in their unstable optical activity. This activity must therefore be a property of berylliobenzoylpyruvic acid and the molecule of this substance must be dissymmetric.

These observations show in the first place that the beryllium derivatives of the β-diketones are not simple beryllium salts of the enolic forms, $(R{\cdot}CO{\cdot}CH{:}CR{\cdot}O)_2Be$, since a beryllium derivative of benzoylpyruvic acid thus constituted could not exist in enantiomorphous modifications. They accordingly provide a new proof that these compounds are internally complex salts in which both oxygen atoms in each of the two diketone residues are directly linked to the beryllium atom as shown in formula (II).

FIG. 1.

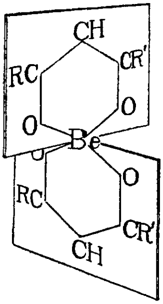
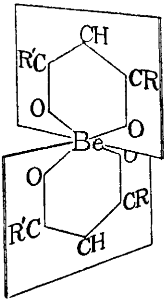


FIG. 2.



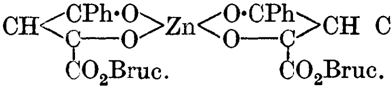
Moreover, to give dissymmetry of the molecule, the planes of the two rings between which the beryllium atom is shared must intersect as represented in Figs. 1 and 2.

The four oxygen atoms to which the beryllium atom is linked must therefore be disposed tetrahedrally about it.

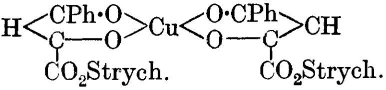
The arrangement of the attached atoms about the 4-co-ordinated beryllium atom, which these experiments establish for the dissolved molecule, thus corresponds with that deduced for the crystalline state by Bragg and Morgan from their study of the crystal structures of basic beryllium acetate (*Proc. Roy. Soc.*, 1923, *A*, **104**, 437).

After it had been shown that the mutarotation of the salts of berylliobenzoylpyruvic acid was due to the disappearance of an optical activity associated with the co-ordinated beryllium atom, we sought for evidence of the existence of optical activity similarly associated with other metals and found that analogous zinc and copper compounds showed a corresponding behaviour.

It proved possible to obtain the *copper* derivative of strychnine benzoylpyruvate and the *zinc* derivative of brucine benzoylpyruvate in crystalline form. Both these compounds, when anhydrous, are soluble in chloroform and their solutions showed definite mutarotations.



$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{CPh{\cdot}O}\\ \underset{\mathrm{CO_2Bruc.}}{\mathrm{C}}\text{——}\mathrm{O}\end{matrix}\right\rangle\mathrm{Zn}\left\langle\begin{matrix}\mathrm{O{\cdot}CPh}\\ \mathrm{O}\text{——}\underset{\mathrm{CO_2Bruc.}}{\mathrm{C}}\end{matrix}\right\rangle\mathrm{CH}$$



$$\mathrm{CH}\left\langle\begin{matrix}\mathrm{CPh{\cdot}O}\\ \underset{\mathrm{CO_2Strych.}}{\mathrm{C}}\text{——}\mathrm{O}\end{matrix}\right\rangle\mathrm{Cu}\left\langle\begin{matrix}\mathrm{O{\cdot}CPh}\\ \mathrm{O}\text{——}\underset{\mathrm{CO_2Strych.}}{\mathrm{C}}\end{matrix}\right\rangle\mathrm{CH}$$

For example, a chloroform solution of the zinc derivative gave an initial rotation, α_{5461}, of + 0·90° which sank in about a ¼ hour to + 0·18°. The copper derivative was difficult to examine polarimetrically on account of the colour of its solutions. The zone of maximum transparency (λ 5100—λ 5200) of the chloroform solution, however, lies not very far from the green mercury line (λ 5461) and in this light it was possible to get satisfactory measurements on 0·7—0·8% solutions in a 2-dcm. tube. Although, with such dilute solutions, the readings were necessarily small, the evidence for the mutarotation was quite definite. Thus in one experiment, the observed rotation, α_{5461}, fell in ½ hour from + 0·39° to + 0·06°, the limit of observational error being about 0·03°.

As the optical behaviour of these zinc and copper compounds resembles so closely that of the corresponding beryllium compound, we think it justifiable to conclude that the changes observed in their rotatory powers are due to the corresponding cause, namely, the disappearance of unstable optical activity associated with the co-ordinated zinc and copper atoms.

From the existence of this activity it is accordingly to be concluded that in these compounds the 4-co-ordinated metallic atoms and the four oxygen atoms to which each is attached do not lie in one plane.

This is of special interest in view of the fact that both copper and zinc are capable of forming compounds in which their co-ordination number is six. If the view is adopted that there are six fixed octahedrally disposed positions about these atoms in which alone other atoms can be attached, then the 4-co-ordinated compounds of zinc and copper must have either (1) the planar configuration (Fig. 3), in which the two vacant positions corresponding with the two latent valencies are at the ends of a diagonal, or (2) the configuration represented in Fig. 4, in which the vacant positions are on one edge of the octahedron.

Configuration (1), which corresponds with that assigned by Werner to the 4-co-ordinated compounds of platinum, and with that which, according to the observations of Vernon, belongs to the isomeric dimethyltellurium di-iodides (J., 1920, **117**, 86, 889), is excluded by our observations. Configuration (2), moreover, would seem improbable on general grounds, since it is difficult to see why the molecule should assume the form conditioned by this distribution of the valencies when the planar configuration, which would apparently give a so much better balanced system, was also possible. Although too much weight must not be assigned to considerations of this kind in view of the uneven distribution in space of the valencies of the doubly-linked nitrogen atom, as well as those of the sulphur in the thionyl radical (Phillips, J., 1925, **127**, 2552; Harrison, Kenyon, and Phillips, this vol., p. 2079), the most probable inference to be drawn from these observations would seem to be that the valencies of copper and zinc have not the same direction in compounds in which their co-ordination number is four as in those in which it is six. That is to say, when two of the valencies of the 6-co-ordinated atoms of these metals become latent, this change is accompanied by a change in the directions of the four valencies which remain active in the resulting 4-co-ordinated compounds, these four assuming a " tetrahedral " arrangement, so that it is most probable that in the molecules of the zinc and copper derivatives of the β-diketones, as in those of their beryllium derivatives, the four oxygen atoms are disposed tetrahedrally about the metallic atom.

FIG. 3.

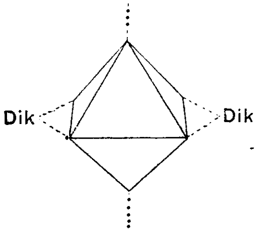


FIG. 4.

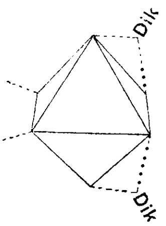


FIG. 5.

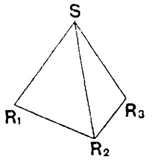
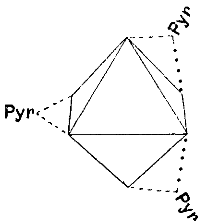


FIG. 6.



In the case of arsenic, a similar difference of valency direction must exist in the compounds of the co-ordination numbers four and six. In *p*-carboxyphenylmethylethylarsine sulphide, a compound of the type $R_1R_2R_3AsS$, resolved by one of us and R. Raper (J., 1925, **127**, 2479), the valencies have evidently a tetrahedral distribution (Fig. 5), whilst in tripyrocatechylarsenic acid, which was obtained in optically active forms by Rosenheim and Plato (*Ber.*, 1925, **58**, 2000), the valencies must be octahedrally disposed (Fig. 6).

EXPERIMENTAL.

Sodium Berylliobenzoylpyruvate, $Be(C_{10}H_6O_4Na)_2,H_2O$.—A solution of sodium benzoylpyruvate (Brömme and Claisen, *Ber.*, 1888,

21, 1131) in 10—12 parts of water is digested on the water-bath with the equivalent quantity of freshly-precipitated basic beryllium carbonate. The latter dissolves and, on cooling, the *sodium* salt of the beryllium derivative crystallises. Recrystallised from hot water, aqueous alcohol, or acetone, it forms slender needles containing one molecule of water of crystallisation (Found : Be, 1·9; Na, 10·2; H_2O, 4·25. $C_{20}H_{12}O_8Na_2Be,H_2O$ requires Be, 2·0; Na, 10·15; H_2O, 4·15%).

Brucine d-*Berylliobenzoylpyruvate*, $Be(C_{10}H_7O_4,C_{23}H_{26}O_4N_2)_2,8H_2O$.—Benzoylpyruvic acid (12·6 g.) and brucine (28 g.) were dissolved in warm alcohol (100 c.c.). The yellow solution was diluted with water (50 c.c.) and moist freshly-precipitated beryllium carbonate (from 5·4 g. of crystallised beryllium sulphate) was gradually stirred in. The carbonate dissolved slowly (15—20 minutes). The solution, acidified with a drop of glacial acetic acid, was filtered, allowed to cool slowly, and while still warm inoculated with a few crystals of brucine berylliobenzoylpyruvate previously obtained by slow cooling and scratching. The compound was deposited in crystalline form and was obtained by recrystallisation from warm 80% alcohol as clusters of pale yellow needles. It was completely dehydrated without losing its crystalline form by standing in a high vacuum over phosphorus pentoxide for 3 weeks in the cold, or by heating at 95—100°/20 mm. for 8 hours. The anhydrous salt melts at 212—215° (decomp.) and is very soluble in chloroform and rather sparingly soluble in absolute alcohol (Found : C, 66·9; H, 5·7; Be, 0·8. $C_{66}H_{66}O_{16}N_4Be$ requires C, 67·1; H, 5·6; Be, 0·8%. Found : H_2O, 10·6. $8H_2O$ requires 10·9%).

Mutarotation of Brucine d-*Berylliobenzoylpyruvate*.—(a) *In chloroform.* A solution of the salt (1·058 g.) in chloroform (17·34 g.) showed at 20° the following rotations ($l = 2$) ($[\alpha]^{20°}_{5461} = +$ 25·06° and + 5·00° for $t = 3$ and ∞, respectively) :

t (mins.).	$a^{20°}_{5461}$.	a calc. ($k =$ 0·0508).	t (mins.).	$a^{20°}_{5461}$.	a calc. ($k =$ 0·0508).	t (mins.).	$a^{20°}_{5461}$.	a calc. ($k =$ 0·0508).
3	+4·26°	(4·26°)	12	2·04°	2·04°	21	1·27°	1·27°
4	3·86	3·88	13	1·90	1·91	32	0·96	0·97
5	3·40	3·55	16	1·58	1·60	34	0·86	0·94
7	2·98	2·99	17	1·52	1·51	∞	0·85	(0·85)
8	2·76	2·75	18	1·45	1·44			

The numbers in the first column give the time in minutes from the first wetting of the salt. Those in the third column are calculated from the formula for the unimolecular reaction,

$$\log_{10}(\alpha_0 - \alpha_\infty)/(\alpha_t - \alpha_\infty) = kt,$$

substituting for α_0 and α_∞ the observed values 4·26° and 0·85° and giving k the value 0·0508. Their agreement with the observed numbers indicates that the mutarotation proceeds in accordance with the unimolecular law.

(b) *In alcohol.* A solution of the salt (0·4200 g.) in absolute alcohol made up to a volume of 50 c.c. at 20° showed the following rotations ($l = 4$) ($[\alpha]^{20°}_{5461} = +39{\cdot}9°$ and $+13{\cdot}1°$ for $t = 5$ and ∞, respectively) :

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=$ 0·0094).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=$ 0·0094).	(mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=$ 0·0094).
5	+1·34°	(1·34°)	30	0·96°	0·96°	150	0·46°	0·48°
7	1·30	1·30	60	0·73	0·71	∞	0·44	(0·44)
10	1·20	1·25	90	0·60	0·58			
20	1·09	1·09	120	0·50	0·51			

The correspondence between the observed values and those calculated from the above formula (column iii) shows that in this solvent also the mutarotation proceeds in accordance with the unimolecular law. As has been explained, the relative rate is greatly dependent on the purity of the solvent; in alcohol of the purity that we were able to obtain,* it was much slower than in chloroform ($k = 0{\cdot}0094$ for alcohol as against 0·0508 for chloroform).

Brucine 1-*Berylliobenzoylpyruvate.*—A solution of anhydrous brucine *d*-berylliobenzoylpyruvate (8 g.) in anhydrous chloroform (25 c.c.), after being kept for 2 hours, was cooled to —5°, and ether (40 c.c.) added. On vigorous shaking, a part of the salt (4·5 g.) was deposited as a microcrystalline mass which mostly adhered to the sides of the vessel. The mother-liquor was quickly filtered into more ether (100 c.c.); a second fraction of the salt (2·6 g.) was then precipitated.

The first fraction consisted chiefly of brucine *d*-berylliobenzoylpyruvate, since a solution of 1·166 g. in chloroform (18·655 g.) gave the following rotations ($l = 2$) ($[\alpha]^{20°}_{5461} = +15{\cdot}8°$ and $+5{\cdot}2°$ for $t = 3$ and 26, respectively) :

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=$ 0·053).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=$ 0·053).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=$ 0·053).
3	+2·75°	(2·75°)	7	2·00°	2·04°	13	1·44°	1·45°
4	2·51	2·54	8	1·94	1·91	20	1·05	1·13
5	2·39	2·35	9	1·80	1·79	26	0·90	(0·90)
6	2·20	2·18	11	1·59	1·60		(final value)	

The second fraction showed, however, a strong initial lævorotation and was *brucine* 1-*berylliobenzoylpyruvate* (Found : C, 66·7 ; H, 5·55 ; Be, 0·7. $C_{66}H_{66}O_{16}N_4Be$ requires C, 67·1 ; H, 5·6 ; Be, 0·8%).

Mutarotation of brucine *l*-berylliobenzoylpyruvate in chloroform : A solution of the anhydrous salt (0·6334 g.) in chloroform (20·70 g.)

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* The alcohol was first dried over lime, then over calcium, and finally distilled from a little silver nitrate to remove ammonia.

gave the following rotations ($l = 2$) ($[\alpha]^{20^\circ}_{5461} = -11{\cdot}8^\circ$ and $+5{\cdot}0^\circ$ for $t = 2$ and 25, respectively):

t (mins.).	$\alpha^{20^\circ}_{5461}$.	α calc. ($k =$ 0·076).	t (mins.).	$\alpha^{20^\circ}_{5461}$.	α calc. ($k =$ 0·076).	t (mins.).	$\alpha^{20^\circ}_{5461}$.	α calc. ($k =$ 0·076).
2	−1·04°	−(1·04°)	8	0·00°	−0·08°	20	+0·41°	+0·38°
2½	0·93	0·92	10	+0·16	+0·07	22	0·43	0·39
4	0·60	0·60	12	0·19	0·18	25	0·44	(0·42)
5	0·46	0·44	14	0·24	0·26			
7	0·32	0·18	17	0·35	0·33			

Optically Active Solutions of Dimethylammonium Berylliobenzoylpyruvate.—(1) *The dextrorotatory salt.* Dimethylamine hydrochloride (0·36 g.; 4 mols.), dried over phosphorus pentoxide, was dissolved in carefully purified alcohol (50 c.c.) in a silica flask at 20°. Finely-powdered anhydrous brucine *d*-berylliobenzoylpyruvate (1·97 g.) was added, and the mixture well shaken. Brucine hydrochloride began to separate after a few seconds and as soon as the precipitation was finished (usually in 60—90 seconds) the solution was forced by gentle air-pressure through a dry asbestos filter directly into a 2-dcm. silica polarimeter tube and observations were taken as rapidly as possible. The weight of crude brucine hydrochloride collected on the filter was 1·5 g. (calc., 1·44 g.).

With the above-mentioned quantities the following polarimetric observations were made:

t (mins.).	$\alpha^{20^\circ}_{5461}$.	α calc. ($k =$ 0·095).	t (mins.).	$\alpha^{20^\circ}_{5461}$.	α calc. ($k =$ 0·095).	t (mins.).	$\alpha^{20^\circ}_{5461}$.	α calc. ($k =$ 0·095).
2	+1·13°	+(1·11°)	7	0·29°	0·31°	13	+0·03°	+0·01°
3	0·83	0·87	8	0·23	0·23	14	0·00	−0·01
4	0·68	0·68	9	0·16	0·16	15	−0·08	−0·03
5	0·52	0·53	10	0·10	0·11	16	−0·10	—
6	0·40	0·40	11	0·10	0·07		(final value)	

After the completion of the polarimetric observations, the whole of the filtrate was allowed to evaporate. The crystalline residue was washed with a very little cold water to remove the excess of dimethylamine hydrochloride and then crystallised from dilute alcohol to remove the small amount of brucine hydrochloride which was left in the original solution and to which the final lævorotation was due. *Dimethylammonium berylliobenzoylpyruvate* was thus obtained as small, nearly colourless prisms, m. p. 95—96° (Found: N, 5·9; Be, 1·9. $C_{24}H_{23}O_8N_2Be$ requires N, 5·8; Be, 1·9%). The salt is moderately soluble in absolute, easily soluble in dilute alcohol. It is not hygroscopic, but is easily hydrolysed in presence of water with the formation of acetophenone.

(2) *The lævorotatory salt.* Brucine *l*-berylliobenzoylpyruvate (1 g.) was digested with a solution of dimethylamine hydrochloride

(0·24 g.) in carefully purified alcohol (31·5 c.c.). After the separation of the brucine hydrochloride was finished, the mixture was filtered and the following polarimetric observations were made on the filtrate ($l = 2$):

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=$ 0·164).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=$ 0·164).	t (mins.).	$\alpha^{20°}_{5461}$.	α calc. ($k=$ 0·164).
2	−0·63°	(0·63°)	5	0·30°	0·24°	9	0·10°	0·10°
3	0·42	0·45	7	0·15	0·15	10	−0·06	0·09
4	0·36	0·33	8	0·10	0·12		(final value)	

Strychnine Cupribenzoylpyruvate.—An alcoholic solution of strychnine benzoylpyruvate was prepared by dissolving finely-powdered strychnine (6·6 g.) in a solution of benzoylpyruvic acid (4·2 g.) in alcohol (50 c.c.). To this was added, drop by drop, a solution of cupric acetate (1·82 g.) in warm dilute alcohol (15 c.c.). A further quantity of strychnine (3—4 g.) was then added to take up part of the acetic acid liberated in the reaction. After long standing in the cold, the green, alcoholic solution deposited the *strychnine* salt of the cupri-derivative of the acid in small, dark green prisms containing 4 mols. of water of crystallisation, m. p. (decomp.) 97—98°. The salt is insoluble in water, benzene, or ether and sparingly soluble in aqueous alcohol or acetone. It can be recrystallised from warm dilute alcohol or acetone containing a trace of acetic acid to prevent the hydrolytic decomposition which otherwise takes place.

It was dehydrated by heating for 6—8 hours at 80°/80 mm. over phosphorus pentoxide. The anhydrous salt is readily soluble in chloroform. (Found for anhydrous salt: C, 66·6; H, 5·3; Cu, 5·6. $C_{62}H_{58}O_{12}N_4Cu$ requires C, 66·8; H, 5·2; Cu, 5·7%. Found for hydrated salt: H_2O, 5·6. Calc. for $4H_2O$: H_2O, 5·5%).

Mutarotation.—(1) A solution of the anhydrous salt (0·0826 g.) in chloroform (17·30 g.) showed the following rotations:

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. (k=0·067).	$[\alpha]^{20°}_{5461}$.
3	+0·39°	(0·39°)	+27·6°
7	0·23	0·24	—
14	0·13	0·12	—
30	0·06 (final value)	0·065	4·2

(2) A solution of the anhydrous salt (0·0877 g.) in chloroform (17·654 g.) showed the following rotations:

t (mins.).	$\alpha^{20°}_{5461}$.	α calc. (k=0·067).	$[\alpha]^{20°}_{5461}$.
5	+0·23°	(0·23°)	+15·6°
7	0·17	0·18	—
11	0·12	0·13	—
15	0·10	0·10	—
24	0·06 (final value)	0·06	4·1

Brucine Zincibenzoylpyruvate.—An aqueous alcoholic solution of brucine benzoylpyruvate, prepared from benzoylpyruvic acid (4·2 g.), brucine (9·2 g.), alcohol (50 c.c.), and water (10 c.c.) was boiled gently for 15 minutes with the equivalent quantity of moist freshly-precipitated basic zinc carbonate. The deep yellow liquid was filtered hot, and the filtrate was allowed to cool after the addition of a few drops of acetic acid. A pale yellow, gelatinous mass, in which a zinc salt as well as the brucine salt of zincibenzoylpyruvic acid was present, was precipitated. In order to obtain the latter compound the precipitate (10 g.) was collected, dried, and extracted with chloroform (50 c.c.) for ½ hour in a Soxhlet apparatus. The yellow solution, evaporated, left a gum (1·8 g.) which was dissolved in warm alcohol containing a little acetic acid. This solution, filtered and allowed to stand, deposited *brucine zincibenzoylpyruvate* as a mass of microscopic, yellow needles decomposing at 185°.

The salt dissolves readily in warm dilute alcohol but is easily hydrolysed with the formation of acetophenone (Found : Zn, 5·4. $C_{66}H_{66}O_{16}N_4Zn$ requires Zn, 5·3%).

Mutarotation.—The following polarimetric observations were made in a 2-dcm. tube on a solution prepared from the dehydrated salt (0·3167 g.) and chloroform (20·70 g.) :

t (mins.).	$\alpha_{5461}^{20^\circ}$.	α calc. (k=0·082).	$[\alpha]_{5461}^{20^\circ}$.
2	+0·90°	(0·90°)	+20·1°
4	0·74	0·67	—
6	0·52	0·52	—
10	0·33	0·34	—
15	+0·18 (final value)	0·24	+ 4·0

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

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