CXXX.—*The Influence of Various Substituents on the Optical Activity of Tartramide.*

By PERCY FARADAY FRANKLAND and ARTHUR SLATOR, M.Sc., Ph.D.

THIS research forms a part of the systematic investigation which is being carried out by one of us on the rotatory power of optically active amides and their substitution products (see P. F. Frankland, F. M. Wharton, and H. Aston, *Trans.*, 1901, **79**, 266).

In this part of the investigation, various substituted amides, $(\text{CH}\cdot\text{OH})_2(\text{CONHR})_2$ of tartaric acid have been prepared and their rotation observed in solution, the primary object being to ascertain the influence on optical rotation of the various radicles *R*. Some of these amides have been prepared before, but with the exception of the toluidides and anilide their rotations have not been determined.

P. A. Guye and A. Babel (*Arch. Sci. phys. nat.*, 1899, [iv], **7**, 34) have published determinations of the anilide and toluidides in pyridine solutions of 5 per cent. concentration, but the figures given differ considerably from those recorded in this paper, and these discrepancies are discussed later (p. 1352). The following is the general method of preparation: the amine (2 mols.) is heated with tartaric acid or methyl tartrate (1 mol.) either directly or in alcoholic solution. The yields are good, and the resulting amides are purified by crystallisation from a suitable solvent until the melting point is constant. In general, the amides are white, somewhat insoluble substances, usually crystallising in needles or flat plates; they melt at high temperatures, undergoing more or less decomposition.

The methyl ester was obtained by the method of preparation described by P. F. Frankland and F. W. Aston (*Trans.*, 1901, **79**, 517); when distilled *in vacuo* and crystallised from benzene and ligroin, it had a rotation $\alpha_D^{100} = +7.79^\circ$.

The aromatic amides, which were only slightly soluble in the commoner solvents at the ordinary temperature, dissolved fairly readily in cold pyridine. The amide and the hydrazide were the only two derivatives which were practically insoluble in pyridine, and their rotations were determined in aqueous solution.

The compounds were recrystallised until they were optically constant, and the rotations were then determined at various concentrations by means of a Laurent half-shadow polarimeter. The length of the tube was usually 100 mm. for strong solutions and 300 mm. for dilute solutions; the tube was surrounded by a water-jacket with an arrangement for obtaining a constant temperature, and the rotations, except where otherwise stated, were determined at 20° .

The pyridine used for the rotation was Kahlbaum's "gereinigt," which was dried with lime or caustic potash and distilled. This base is a remarkably good solvent for many organic substances and, as has been shown (W. R. Innes, Trans., 1901, 79, 261) by ebullioscopic observations, the compounds are not associated in solution. The molecular weight of tartaric *p*-toluidide as determined by the rise in boiling point of pyridine solutions was 331, 330, and 354 with concentrations of 1.23, 2.42, and 3.67 grams per 100 grams of the solvent, the normal molecular weight being 328.

Pyridine is a strongly dissociating solvent as compared with other organic liquids, and its effect on the specific rotation of optically active substances at various concentrations has not hitherto been determined. It will be seen that for low concentrations the specific rotation is in most cases constant. Ethyl tartrate in pyridine solution (now being examined by one of us) gives a specific rotation which is almost constant up to 10 per cent. This constant is about 8 times as large as the specific rotation of the pure ester, and also several times larger than that determined in any other solvent (alcohol, water, &c.), even at the highest dilution. In the case of the amides, again, it is noticeable that water and alcoholic solutions generally give lower rotations than pyridine solutions.

Most of the amides of *d*-tartaric acid have very high positive rotations, and the appended list (p. 1367) gives a comparison of their molecular rotations. Tartramide has a positive molecular rotation of nearly 160° in water solution and about 210° in methyl alcohol solution. With the exception of the phenylhydrazide, the substituted amides hitherto examined have a higher molecular rotation. Aromatic groups (such as toluidide, anilide, naphthylamide) raise the rotation very considerably, whereas the effect of the aliphatic radicles (such as ethylamide and methylamide) is smaller.

The dextro-influence of the anilide and toluidide groups is as follows: *p*-toluidide > *m*-toluidide > anilide > *o*-toluidide. The *o*-toluidide is considerably lower than the others. It is noticeable that in the substitution of hydroxy-groups by benzoyl and the three toluy groups it has been found that the dextro-influence is in the order *p*-toluyl > *m*-toluyl > *o*-toluyl, whilst the relative position of the benzoyl group varies in different substances (P. F. Frankland, Trans., 1899, 75, 345). The same order is noticed in the isomeric toluidides as given above, whilst the *m*-toluidide and anilide have almost identical molecular rotations.

The β -naphthylamide has a much higher rotation than the α -compound. There is a resemblance in constitution between an α - and an ortho-compound, and also between a β - and either a para- or a meta-compound, and this similarity is brought out in the rotation of these

amides. Thus the α -naphthylamide is more soluble, has a lower melting point, and a lower rotation than its β -isomeride, and, similarly, the *o*-toluidide is more soluble, has a lower melting point and a lower rotation than the para-compound.

The ethylamide and methylamide have almost identical molecular rotations in pyridine, but in water the former has a slightly higher rotation. The influence of these two groups is in the positive direction, but is not nearly so great as that of the aromatic groups previously discussed above.

Tartaric hydrazide has a slightly higher molecular rotation than tartramide; the phenylhydrazide, however, unexpectedly exhibits a much lower rotation than either of the former compounds, but, on the other hand, the hydrazones have extremely high rotations, thus :

		$[\text{M}]_D^{20^\circ}$.
Tartramide	$\text{---} \text{C} \text{---} \text{CO} \cdot \text{NH}_2$	+ 158°
Tartaric hydrazide	$\text{---} \text{C} \text{---} \text{CO} \cdot \text{NH} \cdot \text{NH}_2$	170
Tartaric phenylhydrazide	$\text{---} \text{C} \text{---} \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$...	< 80
Tartaric benzylidenehydrazone .	$\text{---} \text{C} \text{---} \text{CO} \cdot \text{NH} \cdot \text{N} \text{:} \text{CH} \cdot \text{C}_6\text{H}_5$.	554
Tartaric furfurylidenehydrazone	$\text{---} \text{C} \text{---} \text{CO} \cdot \text{NH} \cdot \text{N} \text{:} \text{CH} \cdot \text{C}_4\text{H}_3\text{O}$	736
Tartaric acetophenonehydrazone	$\text{---} \text{C} \text{---} \text{CO} \cdot \text{NH} \cdot \text{N} \text{:} \text{C} \begin{array}{l} \text{CH}_3 \\ \text{C}_6\text{H}_5 \end{array}$.	397

The great influence on the rotation brought about by the introduction of the benzylidene, furfurylidene, and acetophenone residues respectively is doubtless an example of the phenomenon which has recently been attracting much attention, namely, the powerful rotatory effect of a double linking, either between two carbon atoms or between an atom of carbon and an atom of nitrogen (Eykmán, *Ber.*, 1891, 24, 1278; Binz, *Zeit. physikal. Chem.*, 1893, 12, 723; Forster, *Trans.*, 1899, 75, 1149; Walden, *Zeit. physikal. Chem.*, 1896, 20, 569; Haller and Müller, *Compt. rend.*, 1899, 128, 1270; 129, 1005; Haller and Minguin, *Compt. rend.*, 1900, 130, 362; Rupe, *Annalen*, 1903, 327, 157; *Ber.*, 1903, 36, 2796; Haller, *Compt. rend.*, 136, 1222).

It is worthy of note that the tartaric hydrazones may be capable of existing in two (or even three) geometrically isomeric forms, and, as these isomerides would doubtless differ considerably in rotation, it is obvious that a strict comparison of the rotations observed is hardly warrantable until these compounds have been more fully investigated from this point of view.

In order to ascertain the influence of a benzene ring united through a side chain, the benzylamide of tartaric acid has been prepared. It is interesting to note that this amide ranks with the fatty amides and has a molecular rotation slightly higher than the methyl- and ethyl-amides, and not nearly so high as the aromatic amides, thus confirming the rule previously enunciated with respect to distance from the asymmetric carbon atom. This was also previously found to be the case in the substitution of hydroxyl radicles, in which the phenacetyl group ranks rather with the aliphatic radicles than with the aromatic ones. Thus we have a uniform resemblance between acetyl, phenacetyl, benzoyl, and toluyl groups, replacing the hydrogen of the hydroxyl group, and the ethylamide, benzylamide, anilide, toluidide, and other groups replacing the hydroxyls of the carboxyl groups.

As already mentioned, the rotations of the anilide and toluidides observed by Guye and Babel differed considerably from the values obtained in the present communication. Our results were verified by observations of the rotatory power of specimens of the anilide and toluidides prepared from the ester of tartaric acid and the corresponding aromatic amine. Fresh preparations of these amides, made by Miss M. B. Thomas, afforded a further confirmation of our results.

The following table gives a comparison of the different values* obtained:

Rotations in Pyridine Solutions.

Amide.	$[\alpha]_D^{20}$		$[\alpha]_D^{15^\circ}$	
	Slator.	Miss Thomas.	Miss Thomas.	Guye.
Anilide	246	246	249	259
<i>p</i> -Toluidide	242	241	243	240
<i>o</i> - „	199	203	205	239
<i>m</i> - „	224	226	228	233
„ „	218			

The first specimen of the *m*-toluidide was prepared from Kahlbaum's *m*-toluidine, the second from König's specially pure base. It is remarkable that the density of Guye and Babel's 5 per cent. solutions (about 0.966) is so considerably smaller than that determined by Miss Thomas and ourselves (about 0.994), and even smaller than that of pure pyridine itself (about 0.980).

By correcting for the manifestly erroneous density of the pyridine solutions given by Guye and Babel, their rotations for the anilide and *m*-toluidide become practically the same as ours, whereas their rota-

* These values are independent of the concentration of the solutions.

tions for the ortho-compound are materially higher, and for the para-isomeride lower, than our own observations for the corresponding compounds.

Besides the amides described, two of the imide compounds have been prepared, namely, tartranil and tartaric *p*-toluil. Estimations of the rotations have been taken in pyridine and methyl alcohol solutions. As we should expect, the toluil has a higher rotation than the anil, although they are not so high as the corresponding toluidide and anilide.

Ladenburg (*Ber.*, 1896, 29, 2710) describes two imides, namely methyl and ethyl tartrimide, which have respectively molecular rotations of $+281^\circ$ and $+261^\circ$ in 7.3 per cent. aqueous solution.

In these cases, the imide compound has a slightly higher molecular rotation than the corresponding amides in aqueous solution, but, inasmuch as the ethylimide has a lower molecular rotation than the methylimide, it suggests that with aromatic radicles the rotation should be still lower, as with tartranil in aqueous solution we have actually found to be the case.

Walden (*Zeit. physikal. Chem.*, 1895, 17, 248) similarly found malanil and malic β -naphthimide to have lower rotations than the amides. The comparatively low rotation of all these imides is remarkable in view of the fact that they contain a cyclic grouping, which is generally attended with a high rotation.

If only one series of compounds, the amides, for example, be prepared from tartaric acid, only the comparative rotatory influences of the various amide groups in the molecule will be obtained. Similarly, by preparing amides of acetyltartaric acid, another series is obtained, and it will be possible to judge whether the acetyl group has in any way a constant influence and whether the amide groups have the same comparative influences as in the foregoing series. So far, we have only one acetyl derivative, the rotatory power of which has been determined. Others have been prepared, but their rotations are as yet unknown. The *o*-toluidide of acetyltartaric acid, which has been prepared by acetylating the *o*-toluidide, gives a lower molecular rotation than any of the other compounds described in this paper excepting the phenylhydrazide.

The diminution in rotation which we have observed on acetylating tartaric *o*-toluidide is what would be anticipated from the known relationship between the rotations of the tartaric esters and their diacetyl derivatives.

Similarly, inasmuch as it has been shown by Purdie and Irvine (*Trans.*, 1901, 79, 957) that the dextro-rotation of the tartaric esters is enhanced by replacing the $>\text{CH}\cdot\text{OH}$ groups by $>\text{CH}\cdot\text{OMe}$, we should anticipate that the dextro-rotation of tartramide would be

exceeded by that of dimethoxysuccinamide, and this is actually found to be the case. A survey of these relations is conveniently obtained by means of the following data :

	$[M]_D^{20^\circ}$		$[M]_D^{20^\circ}$
Ethyl dimethoxysuccinate (liquid)	+ 210.6°	Ethyl diacetyl tartrate (liquid)	+ 9.9°
Dimethoxysuccinamide (aqueous solution)...	166.2	Tartaric <i>o</i> -toluidide (pyridine solution) ...	+ 667.0
Tartramide (aqueous solution).....	158.0	Diacetyltartarico-toluidide (pyridine solution) +	80.0
Ethyl tartrate (liquid)	15.8		

EXPERIMENTAL.

Tartramide.

This substance slowly crystallised in well-defined needles from a methyl alcoholic solution of methyl tartrate which had been saturated with dry ammonia at the temperature of a mixture of ice and salt, a further crop of crystals being obtained by removing ammonia from the mother liquor in a vacuum desiccator. The amide melted at 195° with decomposition.

0.1307 gave 21.3 c.c. moist nitrogen at 20.3° and 759.7 mm, $N = 18.63$.
 $C_4H_8O_4N_2$ requires $N = 18.92$ per cent.

Tartramide is insoluble in chloroform, benzene, ligroin, acetone, ether, and cold pyridine; it is slightly soluble in alcohol and dissolves more readily in water. At 12°, 100 grams of methyl, ethyl, and isobutyl alcohols dissolve respectively 0.1987, 0.0355, and 0.0152 gram of tartramide.

Rotations were taken in aqueous and in methyl alcohol solutions, but owing to the insolubility of the substance very dilute solutions had to be used. The rotation in aqueous solution remained unaltered after 31 days, and on heating the solution from 14—30° no variation in rotation was observed; $[\alpha]_D$ at 14°, 20°, and 30° was found to have the values +107°, 106°, 107°, respectively.

Rotations in Water.

Per cent. solution = <i>p</i> .	$\alpha_D^{20^\circ} (l=1)$.	Density <i>d</i> 20°/4°.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
1.305	+ 1.394°	1.0031	+ 106.5°	+ 158°
0.077	0.083	0.9984	108	160

Rotations in Methyl Alcohol.

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d\ 20^\circ/4^\circ$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
0.1797	0.207°	0.7997	+144°	213°
0.0807	0.090	0.7930	141	208

Tartranilide (Polikier, *Ber.*, 1891, 24, 2959).

This compound was prepared by slowly adding 1 part of dry tartaric acid to 5 parts by weight of boiling aniline.

A white mass (aniline hydrogen tartrate) at first separated, but soon redissolved, and when all the tartaric acid had been added the contents of the flask suddenly solidified to a mass of yellowish-white, pearly plates. These crystals, which were rendered colourless by washing successively with dilute hydrochloric acid and a small quantity of alcohol, were found to be insoluble in water, only very slightly soluble in benzene, ligroin, chloroform, glacial acetic acid, and nitrobenzene, but dissolving readily in cold pyridine; when recrystallised from methyl alcohol, they melted at 250° with decomposition.

- 0.2003 gave 16.7 c.c. moist nitrogen at 21° and 746.9 mm. $N = 9.32$.
 - 0.2012 „ 0.1001 H_2O and 0.4725 CO_2 . $C = 64.06$; $H = 5.53$.
 - 0.2002 „ 0.0994 H_2O „ 0.4691 CO_2 . $C = 63.90$; $H = 5.52$.
- $C_{16}H_{16}O_4N_2$ requires $N = 9.33$; $C = 64.00$; $H = 5.33$ per cent.

Rotations in Pyridine.

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d\ 20^\circ/4^\circ$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
5.421	+13.26°	0.9920	+246.5°	+740°
1.820	4.39	0.9825	245.6	737

This anilide was also prepared from methyl tartrate and aniline, and was purified by crystallisation from alcohol. This specimen gave the following data: $p = 3.100$; $\alpha_D^{20^\circ}(l=1) = +7.535^\circ$; $d\ 20^\circ/4^\circ = 0.9854$; $[\alpha]_D^{20^\circ} = +246.7^\circ$; $[M]_D^{20^\circ} = +740^\circ$.

These results were confirmed by rotations obtained from another specimen made from the acid.* Traces of water in the pyridine solution were found to affect the rotation appreciably (to 3 or 4 per cent.), and the following results were obtained from the specially dried solvent:

* This specimen was independently prepared and examined by Miss M. B. Thomas.

	Per cent. solution = p .	$\alpha_D(l=1)$.	Density $d_{20^\circ/4^\circ}$	$[\alpha]_D$.	$[M]_D$.
At 20°	2.289	+5.54°	0.9847	+245.9°	738°
	4.05	9.86	0.9877	246.4	739
			$d_{15^\circ/4^\circ}$.		
At 15°	4.05	10.03	0.9936	249.3	748

The rotation diminishes slightly with increase of temperature, as shown by the above numbers.

Rotation in Methyl Alcohol.— $p=0.0803$; $\alpha_D^{20^\circ}(l=1) = +0.127^\circ$; $d_{20^\circ/4^\circ} = 0.792$; $[\alpha]_D^{20^\circ} = +200^\circ$; $[M]_D^{20^\circ} = +600^\circ$.

Tartaric p-Toluidide, $(C_7H_7 \cdot NH \cdot CO)_2 \cdot (CH \cdot OH)_2$.

This substance can be prepared by heating *p*-toluidine hydrogen tartrate (1 mol.) with toluidine (1 mol.) (Bischoff, *Ber.*, 1890, 23, 2049), but is more readily obtained by heating *p*-toluidine (2 mols.) and tartaric acid (1 mol.) for about 10 hours in an oil-bath at 180 — 185° . The mixture of reagents did not fuse and the reaction was rather slow.

The *p*-toluidide, which remained after extracting the product successively with boiling water, dilute hydrochloric acid, and alcohol, was crystallised from a mixture of alcohol and pyridine and then melted at about 240° with decomposition. This substance is slightly soluble in ethyl and methyl alcohols, and still less so in chloroform, acetone, carbon disulphide, and water; it dissolves in hot aniline, hot nitrobenzene, strong sulphuric acid (without blackening), and also in pyridine.

0.2863 yielded 21.0 c.c. moist nitrogen at 14.6° and 751 mm. $N = 8.51$. $C_{18}H_{20}O_4N_2$ requires 8.56 per cent.

Rotations in Pyridine.

The first preparation, which had possibly slightly racemised, gave a constant rotation $[\alpha]_D^{20^\circ} = +238^\circ$ in solution of from 1/2 to 7 per cent. strength. With a later preparation, which was subsequently shown to be non-racemised, the following data were obtained: 4 per cent. solution, $\alpha_D^{20^\circ}(l=1) = +9.54^\circ$; $d_{20^\circ/4^\circ} = +0.9863$; $[\alpha]_D^{20^\circ} = +242^\circ$; $[M]_D^{20^\circ} = +793^\circ$.

A preparation made from methyl tartrate and *p*-toluidine and purified as before gave the following result: 3.885 per cent. solution, $\alpha_D^{20^\circ}(l=1) = +9.23^\circ$; $d_{20^\circ/4^\circ} = +0.986$; $[\alpha]_D^{20^\circ} = +241^\circ$; $[M]_D^{20^\circ} = +790^\circ$.

As a comparatively high temperature was used in the foregoing preparation from tartaric acid, it was considered necessary to prove more conclusively the absence of racemisation in the product. The specimen

of amide was, therefore, hydrolysed with hydrochloric acid at 120—125° for 5 hours, and the rotation of the resulting tartaric acid measured. The tartaric acid, which was separated in the form of its lead salt, was liberated from this substance by the action of hydrogen sulphide and finally obtained from the filtered solution by evaporation.

A blank experiment was performed by heating some tartaric acid in hydrochloric acid solution in a sealed tube under conditions similar to those employed in the hydrolysis tube.

The following rotations were obtained with 10 per cent. tartaric acid solutions ($l = 2.962$):

Pure tartaric acid (calculated)	+ 4°15'	1st hydrolysis	+ 3°59'
Pure tartaric acid (used in preparations).....	+ 4°12'	2nd „	+ 4° 3'
		„ „ (blank experiment)	+ 4° 2'

From these results, it is probable that the foregoing specimen of *p*-toluidide was not appreciably racemised, but that a slight racemisation took place during hydrolysis.

A later observation of the rotatory power of this amide gave the following results:

Temp.	Per cent. solution = p .	$\alpha_D(l=1)$.	Density.	$[\alpha]_D$	$[M]_D$
20°	4.502	+ 10.70°	0.987	+ 241°	+ 790
15	„	10.87	0.994	243	796

Tartaric o-Toluidide.

Tartaric acid (1 mol.) and *o*-toluidine (2 mols.) were heated together for about 8 hours in a flask placed in an oil-bath at 160°. The impure product was boiled with water to get rid of tartaric acid, and the residual di-*o*-toluidide, when crystallised from 70 per cent. alcohol, separated in acicular plates and melted at 184—185°; it was slightly soluble in hot benzene, carbon disulphide, and other common solvents, easily soluble in pyridine, and also in hot alcohol.

0.2694 gave 19.8 c.c. moist nitrogen at 15° and 739.5 mm. $N = 8.38$.

$C_{18}H_{20}O_4N_2$ requires $N = 8.56$ per cent.

Rotations in Pyridine.

This toluidide was also prepared from the methyl ester; it melted at 189°, and when the two specimens were dried the rotations of both

were found to agree, recently distilled pyridine being used as the solvent.

Temp.	Per cent. solution = p .	$\alpha_D(l=1)$.	Density.	$[\alpha]_D$.	$[M]_D$.
20°	3·012	+ 5·90°	0·9845	+ 199°	+ 653°
20	4·994	10·02	0·9868	203	667
15	4·994	10·18	0·9936	205	673

Tartaric m-Toluidide.

Tartaric acid (1 mol.) and Kahlbaum's purest *m*-toluidine (2 mols.) were heated in a flask placed in an oil-bath at 160° for about 8 hours. The whole became liquid and after a time resolidified owing to the separation of ditoluidide. The product, when purified by the method employed for its *o*- and *p*-isomerides, crystallised from alcohol in needles, and its solubility lay between those of the other two isomerides; it melted at 184°.

0·2309 gave 17·1 c.c. nitrogen at 16·5° and 750 mm. $N = 8·50$.

$C_{13}H_{20}O_4N_2$ requires $N = 8·56$ per cent.

Rotations in Pyridine.—The substance is very soluble in pyridine, and in a 2 per cent. solution it gave $[\alpha]_D = +224·0^\circ$, and $224·6^\circ$ after recrystallisation, this constancy indicating the purity of the specimen.

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
15·93	+ 36·03°	1·012°	+ 223·6°	+ 733°
0·9665	2·13	0·978	225·3	739

Specimen prepared from the methyl ester (m. p. 184°) gave :

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
2·009	+ 4·34°	0·9822	+ 220°	+ 722°

Specially purified *m*-toluidine from Messrs König (Leipzig) gave specimens of di-*m*-toluidide having the following rotatory power :

Prepared from Tartaric Acid (m. p. 182—183°).

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
2·121	+ 4·571°	0·9824	+ 219°	+ 720°
1·705	3·599	0·9822	215	705

Prepared from Methyl Tartrate (m. p. 182°).

Per cent. solution = <i>p</i> .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
2.153	+ 4.58°	0.9329	+ 217°	+ 710°
6.65	14.37	0.9934	218	713

Another specimen prepared from Kahlbaum's *m*-toluidine gave the following results :

Temp.	Per cent. solution = <i>p</i> .	$\alpha_D^{20^\circ}(l=1)$.	Density.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
20°	4.772	+ 10.64°	0.9875	+ 226°	+ 740°
15	4.772	10.80	0.994	228	747

Tartaric α -Naphthylamide, $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)_2$.

α -Naphthylamine (2 mols.) and powdered tartaric acid (1 mol.) were heated in an oil-bath at 170° for 5 hours. The brown product was extracted with boiling dilute hydrochloric acid, and the residue, when crystallised from a mixture of pyridine and alcohol, separated in fine needles, often in large clusters. When washed with alcohol and recrystallised from the above mixture, it melted at 213–214°. The α -naphthylamide is insoluble in the common solvents except pyridine and hot acetic acid, and dissolves to a less extent in alcohol.

0.1531 gave 9.4 c.c. moist nitrogen at 14° and 739.7 mm. $\text{N} = 7.03$.

$\text{C}_{24}\text{H}_{20}\text{O}_4\text{N}_2$ requires $\text{N} = 7.02$ per cent.

Rotations in Pyridine.

Per cent. solution = <i>p</i> .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
3.378	+ 3.28°	0.988	+ 98.3°	+ 393°
3.806 (recryst.)	3.71	0.991	98.4	394
6.560	6.56	0.997	100.3	401
1.303	1.25	0.983	97.6	390

Tartaric β -Naphthylamide, $(\text{CHOH})_2(\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)_2$.

β -Naphthylamine (2 mols.) and tartaric acid (1 mol.) were heated for about 6 hours at 160–170° in an oil-bath. The product was boiled with water and dilute hydrochloric acid, the residue being treated with warm alcohol to extract coloured matter and then crystallised from pyridine. The compound crystallises in plates melting at 279°; it is insoluble in the common solvents, with the exception of alcohol and pyridine; in the former of these, it is slightly soluble, and

dissolves readily in the latter. It differs from the α -compound in crystalline form, has a much higher rotation and melting point, and is much less soluble.

0.2362 gave 14.2 c.c. moist nitrogen at 14.2° and 742.6 mm. $N = 6.90$.

$C_{24}H_{20}O_4N_2$ requires $N = 7.02$ per cent.

Rotations in Pyridine.

First Specimen.

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
1.339	+ 3.83°	0.984	+ 291°	+ 1163°
2.129	5.96	0.984*	284	1138

* A different specimen of pyridine.

Second Specimen.

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
0.7373	+ 2.11°	0.9798	+ 292°	+ 1169°
1.185	3.359	0.982	289	1155

The β -naphthylamide was also prepared from methyl tartrate. After purification and recrystallising, the following rotations were obtained:

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
1.316	+ 3.764°	0.9808	+ 292°	+ 1167°
0.5505	1.566	0.9795	290	1162

Tartaric Methylamide, $(CH \cdot OH)_2(CO \cdot NH \cdot CH_3)_2$.

An attempt was made to prepare this compound by warming a mixture of methyl tartrate with a 33 per cent. solution of methylamine; the product, after crystallisation from alcohol and benzene, melted at 187—189°, and combustion pointed to its being the methylamine salt of a substituted tartramic acid,

0.1860 gave 23.1 c.c. moist nitrogen at 11.5° and 755 mm. $N = 14.68$.

0.2045 „ 25.1 c.c. „ „ 9.5° „ 754.6 mm. $N = 14.64$.

$C_6H_{14}O_5N_2$ requires $N = 14.43$ per cent.

This substance gives no precipitate with silver nitrate, but, on boiling the solution, silver is precipitated.

The diamide was obtained by distilling the gaseous amine (dried with lime) into a cooled solution of methyl tartrate in anhydrous methylated spirit. After a short time, the amide separated and was recrystallised from alcohol, the melting point being 189° ; it gave no precipitate of silver when boiled with silver nitrate solution. The amide is easily soluble in water and pyridine, insoluble in cold alcohol, benzene, ethyl acetate, and carbon disulphide.

0.1980 gave 26.6 c.c. moist nitrogen at 14° and 756 mm. $N = 15.72$.

$C_6H_{12}O_4N_2$ requires $N = 15.95$ per cent.

The compound gave a specific rotation in a 3 per cent. pyridine solution of $+158.0^{\circ}$, and $+158.6^{\circ}$ in the same solvent after recrystallisation from alcohol.

Rotations in Pyridine.

Per cent. solution = p .	$\alpha_D^{20^{\circ}}(l=1)$.	Density $d_{20^{\circ}/4^{\circ}}$.	$[\alpha]_D^{20^{\circ}}$.	$[M]_D^{20^{\circ}}$.
2.988	$+4.65^{\circ}$	0.985	$+158.0^{\circ}$	$+278^{\circ}$
2.932 (recryst.)	4.60	0.989*	158.6	279
7.679	12.16	1.000	158.3	279
1.433	2.21	0.981	157.2	277
0.684	1.045	0.980	155.9	274

* A different specimen of pyridine.

Rotations in Water.

Per cent. solution = p .	$\alpha_D^{20^{\circ}}(l=1)$.	Density $d_{20^{\circ}/4^{\circ}}$.	$[\alpha]_D^{20^{\circ}}$.	$[\alpha]_D^{20^{\circ}}$.
0.994	$+1.44^{\circ}$	1.001	$+144.7^{\circ}$	255°
2.325	3.334	1.005	142.7	251
3.041	4.235	1.006	138.5	244
(After boiling)*	4.245	1.006	138.8	244
7.475	10.31	1.018	135.5	239
7.774	10.84	1.020	136.7	241
10.35	14.59	1.027	137.3	242

* Part of the solution was tared, boiled, cooled, and made up to the original weight; the rotation of this boiled solution was practically identical with that of the original, showing that there is no birotation.

Tartaric Ethylamide, $(CH_3OH)_2(CO \cdot NH \cdot C_2H_5)_2$.

A mixture of ethylamine (2 mols.) and methyl tartrate (1 mol.) in anhydrous alcoholic solution slowly deposits the ethylamide on cooling. After distilling off the alcohol, more crystals were obtained, the total yield being 75–80 per cent. The amide, when recrystallised from ethyl acetate and a small quantity of alcohol, was obtained in white,

glistening, felted needles melting at $210-211^{\circ}$; it is easily soluble in water and pyridine, fairly soluble in alcohol, less so in ethyl acetate and benzene, and dissolves in acetic acid.

0.1958 gave 24.1 c.c. moist nitrogen at 15° and 735 mm. $N = 13.93$.

$C_8H_{16}O_4N_2$ requires $N = 13.76$ per cent.

The specimen obtained from the first crystallisation had a specific rotation of $+137.1^{\circ}$ and when recrystallised gave $+137.9^{\circ}$. The remaining rotations were determined with the latter specimen.

Rotations in Pyridine.

Per cent. solution = p .	$\alpha_D^{20^{\circ}}(l=1)$.	Density $d_{20^{\circ}/4^{\circ}}$.	$[\alpha]_D^{20^{\circ}}$.	$[M]_D^{20^{\circ}}$.
3.871	$+5.25^{\circ}$	0.989	$+137.1^{\circ}$	$+280^{\circ}$
3.761	5.125	0.988	137.9	281
5.030	6.83	0.9936	136.6	279
2.401	3.26	0.985	137.8	281
1.049	1.395	0.982	135.7	277

Rotations in Water.

Per cent. solution = p .	$\alpha_D^{20^{\circ}}(l=1)$.	Density $d_{20^{\circ}/4^{\circ}}$.	$[\alpha]_D^{20^{\circ}}$.	$[M]_D^{20^{\circ}}$.
1.390	$+1.790^{\circ}$	1.001	128.6°	$+262^{\circ}$
1.905	2.396	1.002	125.5	256
3.942	4.990	1.007	125.7	256
7.468	9.53	1.017	125.5	256

Tartaric Benzylamide, $(CH \cdot OH)_2(CO \cdot NH \cdot CH_2C_6H_5)_2$.

Methyl tartrate (1 mol.) and benzylamine (2 mols.) in alcoholic solution were allowed to react in the cold, when the benzylamide separated in white, glistening plates. On recrystallisation from hot alcohol, it separated either in plates or needles according to the conditions. The amide is easily soluble in pyridine and insoluble in water; it melts at 199° .

0.2767 gave 21.1 c.c. moist nitrogen at 14° and 731 mm. $N = 8.63$.

$C_{13}H_{20}O_4N_2$ requires $N = 8.56$ per cent.

Rotations in Pyridine Solution.

Per cent. solution = p .	$\alpha_D^{20^{\circ}}(l=1)$.	Density $d_{20^{\circ}/4^{\circ}}$.	$[\alpha]_D^{20^{\circ}}$.	$[M]_D^{20^{\circ}}$.
5.497	$+4.983^{\circ}$	0.9911	$+91.5^{\circ}$	$+300^{\circ}$
3.461	3.123	0.9861	91.5	300
1.022	0.932	0.9802	(93.0)	(305)

Tartaric Phenylhydrazide, $(\text{CH}\cdot\text{OH})_2\cdot(\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)_2$.

This compound has been prepared by heating methyl tartrate with phenylhydrazine, and was crystallised from alcohol or from glacial acetic acid (Bülow, *Annalen*, 1886, **236**, 195; Fischer and Passmore, *Ber.*, 1889, **22**, 2734). In alcoholic solution, tartaric acid and phenylhydrazine form diphenylhydrazine tartrate, in distinction to aniline and the toluidines, which form only the mono-salt. The phenylhydrazide can be prepared by heating either the above-mentioned salt or a mixture of phenylhydrazine with an alkyl tartrate or the free acid; when recrystallised from pyridine and water, it melted and decomposed at about 231°.

0.1877 gave 28.2 c.c. moist nitrogen at 13.7° and 744 mm. $N = 17.33$.

$\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_4$ requires $N = 17.02$ per cent.

The specific rotation $[\alpha]_D^{20}$ of different specimens varied considerably (from 16° to 24°). These inconsistencies are possibly due to traces of anilide, which would greatly affect the rotatory power. We can only conclude from these figures that the value of $[\text{M}]_D^{20}$ for the phenylhydrazide is many times smaller than that of the anilide or the toluidide, being probably $< 80^\circ$. We hope soon to be able to obtain more accurate information as to the rotatory power of this compound, which is being further examined by one of us.

Tartaric Hydrazide, $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$.

This compound was prepared as described by Von Rothenburg (*Ber.*, 1893, **26**, 2057). An alcoholic solution of hydrazine hydrate, prepared by the interaction of caustic potash and hydrazine hydrochloride dissolved in alcohol, when treated with methyl tartrate, slowly deposited the hydrazide, which was collected and dried. This compound was insoluble in pyridine, slightly soluble in alcohol, and readily dissolved in water, giving a neutral solution, from which it had a tendency to separate as an oil. The determinations of rotatory power were made on the substance so obtained without recrystallising. Like the amide, it is insoluble in the common solvents except water. It differs from the amide in being much more soluble in water, and the aqueous solution when shaken up with benzaldehyde, forms a benzylidine derivative.

Rotations in Water.

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
2.074	+2.206°	1.0058	+97.1°	+173°
3.264	3.146	1.0105	95.4	170
6.552	6.41	1.0257	95.4	170

Tartaric Benzylidenehydrazide, $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_5)_2$.

This substance, which is described by Von Rothenburg (*loc. cit.*), is obtained on shaking up an aqueous solution of the hydrazide with benzaldehyde; it is slightly soluble in alcohol and more so in pyridine. It was recrystallised from pyridine and gave white, lustrous plates melting at 230° with decomposition.

Rotations in Pyridine.

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
0.3826	+0.600°	0.9788	+160.2°	+567°
0.922	1.411	0.9802	156.1	553
1.834	2.826	0.9829	156.8	555

Tartaric Furfurylidenehydrazide, $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_4\text{H}_3\text{O})_2$.

On shaking up a cold, not too dilute, aqueous solution of the hydrazide of tartaric acid with freshly distilled furfuraldehyde, this compound was precipitated; this was filtered off, thoroughly washed with water, and recrystallised from pyridine and alcohol, when it crystallised in small, irregular plates, melting at about 204° , which tend to become brown.

0.1395 gave 20.4 c.c. moist nitrogen at 15.5° and 746.5 mm. $N = 16.77$.

$\text{C}_{14}\text{H}_{14}\text{O}_6\text{N}_4$ requires $N = 16.82$ per cent.

The rotations in pyridine solution were not very constant, owing, probably, to slight decomposition. After the first crystallisation, the following results were obtained:

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
0.8418	+1.82°	0.9802	+220.6°	+737°
3.054	6.64	0.9890	219.9°	735

Tartaric Hydrazone of Acetophenone,
 $(\text{CH}\cdot\text{OH})_2(\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{C}_6\text{H}_5)_2.$

Acetophenone reacts with tartaric hydrazide, forming a hydrazone having similar properties to the above-described aldehydic hydrazones.

The new hydrazone was recrystallised from a mixture of pyridine and alcohol and melted at about 232° .

0.1478 gave 18.9 c.c. of moist nitrogen at 18.5° and 750 mm. $N = 14.54$.

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{N}_4$ requires $N = 14.7$ per cent.

A 0.747 per cent. solution in pyridine gave the following data: $\alpha_D^{20} (l=1) = +0.760^\circ$; $d_{20}^{20/4} = 0.9814$; $[\alpha]_D^{20} = +104^\circ$; $[M]_D^{20} = +397^\circ$.

Tartranil, $(\text{CH}\cdot\text{OH})_2(\text{CO})_2\cdot\text{NC}_6\text{H}_5$.—One part of tartaric acid was heated for 4 hours at 180° with 2 parts of aniline in an open flask on the oil-bath. The mass was extracted with boiling water and the solution concentrated until crystallisation took place. The crystals were dissolved in methylated spirit and decolorised with animal charcoal; they somewhat resembled tartranilide in appearance and melted with decomposition at 225° .

The compound is soluble in water, alcohol, and pyridine, but only to a very slight extent in the other common solvents; 100 grams of water and methyl alcohol dissolve 1.3079 and 3.8315 grams of the tartranil respectively at 20° .

0.1994 gave 0.4223 CO_2 and 0.0790 H_2O . $C = 57.76$; $H = 4.40$.

0.2004 „ 0.4247 CO_2 „ 0.0791 H_2O . $C = 57.80$; $H = 4.39$.

$\text{C}_{10}\text{H}_9\text{O}_4\text{N}$ requires $C = 57.97$ and $H = 4.35$ per cent.

Rotations in (1) Water, (2) Methyl Alcohol, and (3) Pyridine.

	Per cent. solution= p .	$\alpha_D^{20} (l=1).$	Density $d_{20}^{20/4}$.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
1.	0.5964	$+0.68^\circ$	1.0003	$+114^\circ$	$+236^\circ$
	1.2346	1.29	1.0021	104	216
2.	1.3049	1.36	0.7980	131	270
	1.6393	1.70	0.8001	130	268
	3.2258	3.31	0.8077	127	263
3.	0.693	0.89	0.9827	131	271
	4.760	6.23	0.9950	132	272

Tartaric p-Toluil, $(\text{CH}\cdot\text{OH})_2(\text{CO})_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$.

The toluidine hydrogen salt was made by warming together *p*-toluidine (1 mol.) and tartaric acid (1 mol.) until they melt and resolidify, this salt being then heated for about 7 hours in an oil-bath at 200° . The toluil was extracted from the slightly charred mass with boiling water, and, after repeated crystallisation from water, melted at 235° with decomposition; it was soluble in alcohol and pyridine, insoluble in chloroform, benzene, and most of the other organic solvents.

0.2205 gave 12.6 c.c. of moist nitrogen at 14° and 737 mm. $\text{N} = 6.52$.

0.2254 gave 0.4943 CO_2 and 0.1008 H_2O . $\text{C} = 59.81$; $\text{H} = 4.97$.

$\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$ requires $\text{C} = 59.73$; $\text{H} = 4.98$; $\text{N} = 6.35$ per cent.

Rotations in (1) Methyl Alcohol, (2) Pyridine.

	Per cent. solution = <i>p</i> .	$\alpha_D^{20}(l=1)$.	Density $d_{20}^{20}/4^\circ$.	$[\alpha]_D^{20}$.	$[\text{M}]_D^{20}$.
1.	1.976	+1.87°	0.7996	+118.3°	+261°
	1.177	1.187	0.7963	126.7	280
	1.064	1.091	0.7962	128.7	284
2.	6.317	10.43	0.9971	165.6	366
	1.93	3.136	0.9838	165.2	365
	1.36	2.180	0.9818	163.3	361

Acetyltartaric o-Toluidide, $(\text{CH}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3)_2(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_7)_2$.

The *o*-toluidide of tartaric acid can be acetylated by acetic anhydride (Bischoff, *Ber.*, 1890, 23, 2050), but more easily by warming with acetyl chloride. When hydrochloric acid was evolved only very slowly, the excess of acetyl chloride was distilled off and the residue extracted with a small quantity of alcohol. The main part of the acetyl compound which remained in the residue was crystallised from glacial acetic acid; it separated in a colloidal form from the solvent and was slightly coloured. On washing with ether, the colour was removed, although on drying the substance it again became slightly yellow. The substance, which dried to a fine powder and melted at 229° , was fairly soluble in hot chloroform, alcohol, glacial acetic acid, but less so in benzene; it was easily soluble in pyridine, but insoluble in water.

0.2595 gave 15.5 c.c. of nitrogen at 12.5° and 750 mm. $\text{N} = 6.98$.

$\text{C}_{22}\text{H}_{24}\text{O}_6\text{N}_2$ requires $\text{N} = 6.81$ per cent.

Rotations in Pyridine.

Per cent. solution = p .	$\alpha_D^{20^\circ}(l=1)$.	Density $d_{20^\circ/4^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
5.237	+1.016°	0.9891	+19.61°	80.8
5.315 (recryst.)	1.036	0.9895	19.7	81.2
2.594	0.432	0.9830	16.94	69.8
4.492	0.844	0.9872	19.0	78.4

Summary of Rotations.

$[M]_D^{20^\circ}$. Solvent.				$[M]_D^{20^\circ}$. Solvent.			
Amide.	Pyridine.	Water.	Methyl alcohol.	Amide.	Pyridine.	Water.	Methyl alcohol.
Tartramide	—	+158°	+210°	Hydrazide.....	—	+170°	—
Anilide	+739°	—	600	Benzylidene			
<i>p</i> -Toluidide	793	—	—	hydrazide ...	+554°	—	—
<i>o</i> -Toluidide	667	—	—	Furfurylidene			
<i>m</i> -Toluidide	730	—	—	hydrazide	736	—	—
α -Naphthylamide	400	—	—	Hydrazone of			
β -Naphthylamide	1160	—	—	acetophenone	397	—	—
Methylamide ...	278	240	—	Tartranil	272	216	268°
Ethylamide	279	256	—	Tartaric <i>p</i> -Toluid	366	—	280
Benzylamide.....	300	—	—	Diacetyltartaric			
Phenylhydrazide (<80)	—	—	—	<i>o</i> -toluidide ...	80	—	—

THE UNIVERSITY,
BIRMINGHAM.