

LXXXVIII.—*The Influences Modifying the Specific Rotatory Power of Gallotannic Acid.*

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THE specific rotatory power of an optically active substance in solution for a given ray of light is by no means a definite and fixed number, but, in the majority of cases, depends to a greater or less extent on the following conditions.

1. The temperature of the solution. 2. The concentration of the solution. 3. The nature of the solvent. 4. The action of optically inactive substances (salts, &c.).

It appeared of interest to the authors to study the influences modifying the specific rotation of gallotannic acid, for various reasons, and, among others, in order, if possible, to obtain some explanation of the great differences in optical properties displayed by the various commercial 'pure' gallotannic acids described in the preceding paper. The gross percentage of impurity in these samples being insufficient to account for the very low rotations of some of the samples, it was, therefore, probable that they contained salts or other substances which *specifically* affected the rotatory power. It may be stated at once that the authors have not yet succeeded in identifying, as such, the substances which exercise this modifying influence; but it must be remembered that the percentage of mineral matter in the various substances is very small, and that the nature of the, no doubt chiefly organic, acids with which this mineral matter is originally combined is practically unknown. The object of the present paper was rather in the nature of a preliminary investigation of the various influences which may affect the specific rotatory power of gallotannic acid, and thus, eventually, to throw some light on the actual causes.

The authors have examined the changes produced in the specific rotatory power of gallotannic acid in regard to 2, 3, and 4 (see above), but have, for the sake of simplicity, eliminated the influence of temperature by conducting all the experiments at 15°. The material employed was the apparently homogeneous product of the constant specific rotation  $[\alpha]_D^{15} + 75 \cdot 2^\circ$  described in the preceding paper.

*Influence of Concentration.*

Biot (*Mém. de l'Acad.*, 15, 93) first showed the dependence of specific rotation on the concentration of the solution, in the case of aqueous solutions of tartaric acid. Since then, numerous\* investigations in this direction, with interesting results, have been carried out on a great number of substances.

*The Influence of Concentration on the Specific Rotatory Power of Gallotannic Acid.*—The authors have found that, in aqueous solutions containing up to 1 per cent., it appears that the rotation is constant at  $[\alpha]_D^{15^\circ} + 75 \cdot 2^\circ$ . By increasing the concentration beyond this figure, the optical activity is *decreased*, but the numbers obtained cannot be considered very accurate, on account of the rapid deepening of the yellow colour of the solution, which, in fact, makes readings above 10 per cent., even in a 100 mm. tube, quite impossible (compare Schiff, *Chem. Ru. Zeit.*, 1895, p. 1680). The subjoined table shows the actual influence of concentration as far as it has been capable of determination by the authors.†

TABLE I.—*Influence of Concentration on the Specific Rotatory Power of Gallotannic Acid in Aqueous Solution.*

Strength of solution per cent.	$[\alpha]_D^{15^\circ}$	Strength of solution per cent.	$[\alpha]_D^{15^\circ}$
10	+66·1 <sup>‡</sup>	1·0	+75·2°
5	+71·8 <sup>‡</sup>	0·5	+75·2
2·5	+75·0	0·25	+75·2

*Influence of the Solvent.*

Relatively complete investigations on the influence of the solvent on rotation generally are by no means so numerous as those on concentration, and are, broadly speaking, restricted to dextrotartaric acid (Landolt, *Ber.*, 1880, 13, 2332; Přibram, *Ber.*, 1889, 22, 6); three substituted ethereal salts of tartaric acid (Freundler, *Compt. rend.*, 1893, 117, 556; *Ann. chim. phys.*, 1895, [vii], 4, 244); camphor (H. Vogel, *Dissert. Berlin*, 1892); American turpentine (Landolt,

\* For a full account, see Landolt, "Das optische Drehungsvermögen," 1898, pp. 146—148.

† The instrument used in all our work was a half-shadow Schmidt and Haensch polarimeter, five readings being made in each case and the mean taken.

‡ In 100 mm. tube, the other readings in 200 mm. tube.

*Annalen*, 1877, 189, 311, &c.), and saccharose (Tollens, *Ber.*, 1880, 13, 2303).

The authors have examined the influence of various solvents on the rotatory power of gallotannic acid, and have found that the optical activity of this substance depends to a very marked extent on the nature of the solvent. Thus the original specific rotation  $[\alpha]_D^{15} + 75.2^\circ$  (for water) is actually reduced to  $\pm 0^\circ$  for a mixture of acetone and carbon tetrachloride, and acetone alone produces a remarkable fall. This is of considerable interest, as, so far as the authors are aware, there is only one other substance that is affected to anything like the same degree by this solvent, namely, dextrotartaric acid, the rotation of which is reduced from  $+14.40^\circ$  for water to  $\pm 0^\circ$  for a mixture of acetone and ether. It will be seen on referring to Table II that mixtures of acetone with ether, benzene, chloroform or ethylic acetate, as well as alcohol, ethylic acetate, and ethylic acetoacetate by themselves have a very powerful effect.

TABLE II.—*Influence of the Solvent on the Specific Rotation of Gallotannic Acid.*

(Strength of solution = 1 per cent.)

Solvent.	$[\alpha]_D^{15}$	Solvent.	$[\alpha]_D^{15}$
1. Water .....	+75.2°	6. 50 per cent. acetone + 50	
2. Alcohol .....	+15.0	per cent. benzene .....	+16.6°
3. Acetone .....	+11.6	7. 50 per cent. acetone + 50	
4. 50 per cent. acetone + 50		per cent. chloroform...	+14.3
per cent. ether .....	+11.6	8. Ethylic acetate .....	+8.3
5. 50 per cent. acetone + 50		9. Ethylic acetoacetate .....	+12.6
per cent. ethylic aceto-		10. 80 per cent. acetone + 20	
acetate .....	+12.3	per cent. CCl <sub>4</sub> .....	$\pm 0$

In reference to this section, it may be stated that, although none of the solvents examined produced a change of sign (as is the case, for instance, with dextrotartaric acid),\* yet the gross effect produced is greater with gallotannic acid than in the case of any other substance that has formed the subject of similar investigations.

*Action of Optically Inactive Substances.*

Experiments, chiefly with tartaric acid (Biot, *Mem. del' Acad.*, 1838, 16, 229; and *Ann chim. phys.*, 1844, [iii], 11, 82; Koch, *Dissert. Tubingen*,

\* From  $+14.4^\circ$  for water to  $-8.09^\circ$  for monochlorobenzene.

1869; Gernez, *Compt. rend.*, 1887, 104, 283, &c.); the tartrates (Long, *Sill. Americ. J.*, 1888, [iii], 36, 351; Schütt, *Ber.*, 1888, 21, 2586); malic acid (Gernez, *Compt. rend.*, 1889, 109, 151 and 769, &c.); and the sugars (E. v. Lippmann, *Die Chemie der Zuckerarten*, pp. 673—681; Farnsteiner, *Ber.*, 1890, 23, 3570, &c.), have shown that the addition of various inactive substances to a solution of an active compound exercises a more or less important influence on its rotatory power. Work in this direction has so far been practically confined to the substances mentioned above, a fact which appears at first sight somewhat remarkable considering the importance of the matter, both from a scientific and practical point of view. We have found in gallotannic acid a substance the optical properties of which are influenced to a remarkable degree by the presence of certain inactive compounds. For the sake of convenience we have classified these inactive substances into three groups, namely,

a. Acids;                      b. Bases;                      c. Salts.

a. There does not appear to be any detailed account, in literature, of the action of acids on rotation generally, but the addition of boric acid to tartaric acid solutions causes a very great rise (from  $[\alpha]_D + 12.88^\circ$  for a 16.63 per cent. solution to  $[\alpha]_D + 43.44^\circ$  for the same solution with 1 molecule of boric acid (Biot and Koch, *loc. cit.*).

The authors have found that mineral acids and boric acid have no influence on the specific rotation of gallotannic acid, but, on the contrary, restore the same to the normal if added to a solution, the optical properties of which have been previously depressed by the addition of alkalis or alkaline salts in small quantities. Thus the addition of concentrated hydrochloric acid up to 10 per cent., and of sulphuric acid to the point of precipitation, produced no effects whatever. Acetic acid exercises a depressing influence, but this is probably due to partial acetylation. A 10 per cent. aqueous solution of gallotannic acid (originally  $[\alpha]_D^{15} + 75.2^\circ$ ) containing 25 per cent. acetic acid has  $[\alpha]_D^{15} + 65.0^\circ$ . A similar solution containing 50 per cent. acetic acid shows  $[\alpha]_D^{15} + 36.6^\circ$ .

In view of the fact that gallic acid is one of the chief impurities in commercial gallotannic acid, it is of interest to note that this substance does not specifically affect the rotation of gallotannic acid, but only (as will be seen from the subjoined tables) reduces the same in direct proportion to the quantity present in any particular mixture.

*Influence of Gallic Acid on the Specific Rotation of Gallotannic Acid.*

*a. Specific Influence.*—To 1 c.c. of a 20 per cent. solution of gallotannic acid ( $[\alpha]_D^{15} + 75.2^\circ$ ) varying quantities of gallic acid were added, the whole made up at  $15^\circ$  to 20 c.c., and polarised in a 200 mm. tube.

TABLE IIIa.

Quantity of gallic acid.	Percentage of gallic acid in solution.	$[\alpha]_D^{15}$	Quantity of gallic acid.	Percentage of gallic acid in solution.	$[\alpha]_D^{15}$
0.019 gram.	0.05	$75.2^\circ$	0.2 gram.	1.0	$75.2^\circ$
0.05 "	0.25	"	0.4 "	2.0	"
0.1 "	0.5	"	2.0 "	10.0	"

TABLE IIIb.—*Influence of Decreasing Percentage of Gallotannic Acid in Solution.*

Quantities in 20 c.c. of solution.		Percentages in solution.		$[\alpha]_{D_{gt+g}}^{15}$	$[\alpha]_{D_{gt}}^{15}$
Gallotannic acid.	Gallic acid.	Gallotannic acid.	Gallic acid.		
0.18 gram.	0.02 gram.	90	10	$67.5^\circ$	$75.0^\circ$
0.16 "	0.04 "	80	20	$60.0$	"
0.10 "	0.10 "	50	50	$37.5$	"
0.08 "	0.12 "	40	60	$30.0$	"

NOTE.— $[\alpha]_{D_{gt+g}}^{15}$  = Specific rotation of mixture.  $[\alpha]_{D_{gt}}^{15}$  = Specific rotation of gallotannic acid alone, as calculated from  $gt + g$ .

*b.*—E. von Lippmann (*loc. cit.*) has described the influence of the alkalis and alkaline earths on cane-sugar, and found that they decrease the rotation. Apart from this, the description of the action of alkalis and bases generally on optically active substances, in literature, is very meagre. We have found that the behaviour of ammonia in relation to the specific rotation of gallotannic acid is in striking contrast to the inactivity of acids, in fact, it exercises a very powerful specific action. On adding 5 or 6 drops of ammonia to a 1 per cent. solution of gallotannic acid ( $[\alpha]_D^{15} + 75.2^\circ$ ), *total inactivity* is immediately pro-

duced. If more ammonia be added, the colour of the solution becomes a dark yellow, which makes further readings impossible. The action of the caustic alkalis could not be studied at all, owing to the fact that the addition of even very small quantities rendered the solutions so dark in colour as to be too opaque for polarimetric measurements.

*c. The Action of Salts.*—The influence of salts on specific rotation has been fairly exhaustively studied in the cases of tartaric acid, the tartrates, malic acid, and the sugar (see pp. 887—8). Speaking broadly, the influence is slight if we except the extraordinary action of the molybdates, tungstates, and uranium derivatives. For example, Gernez (*loc. cit.*) has shown that the addition of ammonium molybdate to a solution of tartaric acid, in the proportion of 1 mol. of the former to 18 of the latter, increases the rotation no less than 60-fold. Walden (*Ber.*, 1897, 29, 2889) has recently made similar observations in regard to the influence of an alkaline uranyl nitrate solution on the rotation of malic acid, the increase being upwards of 500-fold. The influence of borax on the members of the mannitol group is also considerable (Landolt, *loc. cit.*), but apart from these examples the action of salts generally is, as we have already stated, slight, relatively large quantities producing only small effects.

The authors have found, however, that salts generally exercise a very great influence on the specific rotation of gallotannic acid. In many cases, a very small proportion of the salt suffices to produce a very considerable effect, and it seems more than probable that the extremely low rotations of some of the commercial samples mentioned in the preceding paper are due to the presence of small quantities of inactive salts which exercise a powerful specific action.

All the salts examined by us have a *depressing* action, the rotation decreasing up to a certain point as the percentage of added salt increases. This point forms, in the majority of cases, a *minimum*, and the further addition of salt causes a rise. This minimum varies according to the nature of the salt in question, as also does the quantity of salt necessary to produce the same, and the character of the subsequent rise. There is, however, apparently, a connection between the molecular weight of the salt and this minimum of rotation; *that is to say, the molecular rotation of the mixture of salt and gallotannic acid remains (within reasonable limits) fairly constant, and approximately equal to the molecular rotation of gallotannic acid alone.*

Thus, if  $x$  = the molecular weight of gallotannic acid,  $y$  = the molecular weight of salt,  $z$  = the minimum of rotation, then  $\frac{(x+y)z}{100} = M$ .

Within limits,  $M$  is found (considering all the circumstances) to be

a fairly constant number, approaching closely to the molecular rotation of gallotannic acid.

The following table gives the values of  $M$  for the various salts examined.

TABLE IV.—Values of  $M = \frac{(x+y)z}{100}$

Salt.	$[\alpha]_D^{25}$ minimum.	$x+y$	$M$
1. $W_4O_{13}Na_2 + 10H_2O$ .....	12·9°	1470	189·6
2. $Na_2B_4O_7 + 10H_2O$ .....	25·6	704	180·2
3. $K_2B_4O_7 + 5H_2O$ .....	26·3	646	169·8
4. $(NH_4)_2B_4O_7 + 4H_2O$ .....	26·5	586	155·3
5. $Li_2B_4O_7$ .....	28·3	492	139·2
6. NaCl .....	68·0	380·5	258·7
7. KCl .....	70·6	396·5	279·9
8. $NH_4Cl$ .....	71·1	375·5	266·9
9. $LiCl + H_2O$ .....	70·0	382·5	267·7
10. $NaHCO_3$ .....	54·0	406	219·2
11. $KHCO_3$ .....	56·3*	422	[265·8]
12. $Zn(CH_3COO)_2 + 3H_2O$ .....	68·5*	559	[382·9]
Gallotannic acid.....	75·2	322	242·1

\* Doubtful *minima*, the series interrupted owing to precipitation on further addition of the salt.

In order to study the influence of varying proportions of the above salts on gallotannic acid, the methods described under sodium tungstate (which exercises a more powerful action than any other salt examined) were in general employed. Modification of the general procedure was dependent on the solubility of the salt in question. It is needless to say that the salts used were all highly purified. It must also be remembered that the quantity of added salt was, in each case, limited by the precipitation of the gallotannic acid when a certain concentration was reached.

1. *Sodium tungstate*,  $W_4O_{13}Na_2 + 10H_2O$ .

Solutions I. 4 grams of purified gallotannic acid ( $[\alpha]_D^{25} + 75·2^\circ$ ) were dissolved in water to 20 c.c. (1 c.c. = 0·2 g.).

II. 4 grams of sodium tungstate were dissolved in water to 40 c.c. (1 c.c. = 0·1 g.).

III. 5 c.c. of II diluted with water to 100 c.c. (1 c.c. = 0·05 g.).

To 1 c.c. of solution I, varying amounts of II and III were added, the whole made up to 20 c.c.\* at 15°, and polarised at that temperature. The solutions of tungstate and gallotannic acid were all of a lemon-yellow colour, which became too deep for readings in the 200 mm. tube above 1 per cent. Nos. 6 and 7 were therefore determined in a 100 mm. tube. Above 4—5 per cent., a precipitate commenced to form.

\* The final solution therefore contained 1 per cent. of gallotannic acid; this strength was kept constant throughout.

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TABLE V.—*The Influence of Sodium Tungstate on the Rotation of Gallo-tannic Acid.*

Quantities of III and II.	Weight of sodium tungstate in solution.	Percentage of sodium tungstate in solution.	$[\alpha]_D^{15}$
1. 0.5 c.c. III .....	0.0025 gram.	0.0125	69.2°
2. 2 c.c. III .....	0.01 ,,	0.05	62.2
3. 4 c.c. III .....	0.02 ,,	0.1	53.8
4. 1 c.c. II.....	0.1 ,,	0.5	24.6
5. 2 c.c. II.....	0.2 ,,	1.0	12.9
6. 4 c.c. II.....	0.4 ,,	2.0	13.5
7. 8 c.c. II.....	0.8 ,,	4.0	22.6

TABLE VI.

Percentage of salt dissolved.	Change of rotation for $[\alpha]_D^{15}$ .				
	$\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ .	$\text{K}_2\text{B}_4\text{O}_7 + 5\text{H}_2\text{O}$ .	$(\text{NH}_4)_2\text{B}_4\text{O}_7 + 4\text{H}_2\text{O}$ .	$\text{Li}_2\text{B}_4\text{O}_7$ .	$\text{NaHCO}_3$ .
0.01	73.5°	—	73.5°	74.5°*	72.6°
0.025	71.0	70.5°	70.9	—	—
0.05	66.8	68.8	68.0	64.6	66.3
0.1	61.3	60.1	64.6	64.5	62.1
0.25	56.5	—	57.0	—	—
0.5	45.3	49.3	50.0	49.3	58.0
1.0	26.0	40.0	41.6	28.3	54.0
2.0	25.6	26.3	26.5	29.8	54.2
3.0	27.6	—	—	—	—
4.0	28.6	—	26.5	—	54.2
5.0	—	26.3	26.5	—	—

\* The percentage in this case was 0.0125 and not 0.01.

Percentage of salt dissolved.	Change of rotation for $[\alpha]_D^{15}$ .					
	$\text{NaCl}$ .	$\text{KCl}$ .	$\text{NH}_4\text{Cl}$ .	$\text{LiCl} + \text{H}_2\text{O}$ .	$\text{KHCO}_3$ .	$\text{Zn}(\text{CH}_3\text{COO})_2 + 3\text{H}_2\text{O}$ .
0.01	73.6°	73.8°	72.8°	73.3°	73.0°	75.1°
0.05	71.1	72.2	71.8	72.1	68.6	73.5
0.1	68.0	70.6	71.5	70.1	64.8	68.5
0.2	70.5	72.2	71.1	70.0	—	—
0.5	72.0	73.1	72.8	72.6	56.3	—
1.0	—	73.3	73.3	72.8	—	—
2.5	72.6	—	—	—	—	—
5.0	73.5	75.5	74.5	73.1	—	—



The influence of ammonium molybdate and of uranium acetate was also examined, but owing to the deep coloration produced with the former and the precipitation caused by the latter, it was impossible to obtain readings.

#### NOTES TO TABLE VI.

It is interesting to note the marked influence of borax in contradistinction to boric acid, which has no effect. On neutralising carefully with mineral acids, the rotation was restored to the normal.

As is the case with other salts of an alkaline nature, the depression produced by sodium hydrogen carbonate is very considerable. It would be of interest to obtain readings for higher percentages of the salt, but this was found to be impracticable owing to the fact that above 4 per cent. the solutions become very dark coloured and reading difficult.

It was impossible to determine values for quantities of potassium hydrogen carbonate above 0.5 per cent., as on increasing the proportion of the salt precipitation of gallotannic acid occurred.

In the case of zinc acetate also, readings could not be obtained with more than 0.1 per cent. of the salt owing to precipitation of the metallic tannate, but it is clear that this acetate exercises considerable influence on the rotation.

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