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THE RELATION BETWEEN
NATURAL AND SYNTHETICAL
GLYCERYLPHOSPHORIC ACIDS

BY

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AND

FRANK TUTIN

(From the Transactions of the Chemical Society, 1905)



THE WELLCOME CHEMICAL RESEARCH LABORATORIES

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XXX.—*The Relation between Natural and Synthetical Glycerolphosphoric Acids.*

By FREDERICK BELDING POWER and FRANK TUTIN.

THE fact that glycerylphosphoric acid is a constituent of the molecular complex known as lecithin has led to the medicinal use of a number of salts of this acid and to their chemical study.

The first to prepare glycerylphosphoric acid synthetically was Pelouze (*Compt. rend.*, 1845, 21, 718, and *J. pr. Chem.*, 1845, 36, 257), who obtained it by the action of phosphoric oxide or of metaphosphoric acid on glycerol. The analyses recorded by Pelouze of its calcium, barium, and lead salts indicate that under the conditions employed by him a monoglyceryl ester, $C_3H_5(OH)_2 \cdot O \cdot PO(OH)_2$, was obtained, and his purpose in preparing this was to confirm the correctness of the formula previously assigned to glycerol. At about the same time, Gobley had obtained glycerylphosphoric acid from the yolk of egg, and it was stated by Pelouze (*loc. cit.*), solely from analytical comparisons, that not the slightest doubt could be entertained respecting the absolute identity of the glycerylphosphoric acid from this source with that obtained by the action of phosphoric acid on glycerol.

By the interaction of glycerol and phosphoric acid, there is the possibility that several esters may be formed, and the product would therefore contain one or more of these, according to the relative proportions of the interacting substances and to the varying conditions of time, temperature, and pressure to which the mixture is subjected. The only known products of this action, however, appear to be (1) the mono-ester, glycerylphosphoric acid, $C_3H_5(OH)_2 \cdot O \cdot PO(OH)_2$; (2) the so-called di-ester, $C_3H_5(OH) \langle \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ O \end{smallmatrix} \rangle PO \cdot OH$, and (3) the tri-ester or glyceryl phosphate, $C_3H_5:PO_4$.

The conditions under which these three esters respectively are formed, and the relative proportions in which they are contained in

the product of the reaction, have been determined by Carré (*Compt. rend.*, 1903, 137, 1070). He has also shown that by the method usually employed for the preparation of glycerylphosphoric acid it is associated with some of the above-mentioned di-ester, to which the

constitution $\text{PO} \begin{cases} \text{O} - \text{CH}_2 \\ \text{OH} \\ \text{O} - \text{CH}_2 \end{cases} \text{CH} \cdot \text{OH}$ has been assigned, and not with the diglycerylphosphoric acid, $[\text{C}_3\text{H}_5(\text{OH})_2\text{O}]_2\text{:PO} \cdot \text{OH}$, as had been assumed by Adrian and Trillat (*J. Pharm.*, 1898, 7, 226).

The discrepancies of statement respecting the composition and characters of the salts of glycerylphosphoric acid (compare Portes and Prunier, *J. Pharm.*, 1894, 29, 393, and Petit and Polonowsky, *ibid.*, 1894, 30, 193) are evidently due, as suggested by Carré (*loc. cit.*), to their contamination with the salts of the di-ester. It was therefore deemed of interest to ascertain the characters of the above-mentioned salts when prepared under such conditions as are known to exclude the formation of the di-ester.

In the course of our work, a paper has appeared by Willstätter and Lüdecke (*Ber.*, 1904, 37, 3753) on the subject of lecithin, in which the relation between the glycerylphosphoric acid obtained from the latter and that prepared synthetically is considered. They claim to have found essential differences between the barium and calcium salts of these two acids, not only with respect to solubility, but especially in the composition of the preparations when dried by heat. Although the salts of the natural acid are lævorotatory, from which they infer

that this must have the unsymmetrical formula $\begin{array}{c} \text{CH}_2 \cdot \text{O} \cdot \text{PO}_3\text{H}_2 \\ | \\ \text{CH} \cdot \text{OH} \\ | \\ \text{CH}_2 \cdot \text{OH} \end{array}$, they

think there is very little probability that the differences are simply those which usually exist between optically active compounds and the corresponding racemic ones, especially in consideration of the fact that the salts of the glycerylphosphoric acid obtained from lecithin, which served for the purpose of comparison, did not possess their full degree of optical activity, but in the course of preparation had become partially racemised. As an example of these differences, they note that the calcium salt of the partially racemised natural acid, dried at 130° , is anhydrous, whilst that of the synthetical acid prepared by them, on account of containing more than 2 per cent. less of calcium, appears to retain at that temperature $1\frac{1}{2}$ molecules of water. From these considerations, they were led to the conclusion that the glycerylphosphoric acid of Pelouze is different from that obtained from lecithin, although the question as to the cause of this difference and that of the constitution of the synthetical acid was left undecided.

In our investigation, it is shown that the above conclusion of Willstätter and Lüdecke is invalid, as it is evident that the conditions under which they prepared their synthetical glycerylphosphoric acid were such as are now known to afford some of the di-ester,

$C_3H_5(OH)\langle\begin{smallmatrix} O \\ \diagup \quad \diagdown \\ O \end{smallmatrix}\rangle PO\cdot OH$ (compare Carré, *loc. cit.*). The differences

observed by them in the percentages of metal contained in the salts of the natural acid and in those of their synthetical acid do not, therefore, justify their assumption that the latter retained water when heated to the specified temperatures.

Furthermore, the observation of Willstätter and Lüdecke that the glycerylphosphoric acid from lecithin possessed optical activity, although certainly proving the presence of the unsymmetrical acid in the preparation, does not necessarily exclude the possibility that some of the symmetrical acid was also present. Inasmuch as the natural acid has in no instance been prepared from a lecithin which was known to be a pure substance (compare Bergell, *Ber.*, 1900, 33, 2584), no proof can as yet be adduced that it is not a mixture of the unsymmetrical and the symmetrical isomerides. The same possibility naturally exists with respect to the homogeneity of the synthetical acid, which, however, doubtless consists chiefly of the unsymmetrical isomeride.

We shall endeavour to prepare both these isomerides in order to compare them, on the one hand with the completely racemised natural acid, and on the other hand with the acid obtained by the interaction of phosphoric acid and glycerol.

EXPERIMENTAL.

In order to determine and compare the characters of some of the salts of glycerylphosphoric acid, when prepared by definite methods, the following experiments were conducted.

I. Twenty-five grams of glycerol and 30 grams of phosphoric acid (sp. gr. 1.70) were mixed, and heated together for 24 hours (in three periods of 8 hours each), in an oil-bath at 105—110°. The mixture was then added to an excess of milk of lime, the liquid filtered when cold, and the precipitate thoroughly washed with water. The combined filtrate and washings, after being deprived of the excess of lime by means of carbon dioxide, were divided into two portions, (a) and (b), which were evaporated to a small bulk, when some of the salt separated.

(a) In one case, the calcium salt which had separated from the hot liquid was collected, and washed with a little hot water.

1.1031 of the salt, dried at 125°, gave 0.2940 CaO. Ca = 19.04 per cent.

(b) In the other case, the calcium salt was completely precipitated

by the addition of alcohol. This was collected and washed with alcohol.

1.0100 of the salt, dried at 125° , gave 0.2695 CaO. $\text{Ca} = 19.06$.

$\text{C}_3\text{H}_7\text{O}_6\text{PCa}$ requires $\text{Ca} = 19.04$ per cent.

II. A mixture of glycerol and phosphoric acid, in the above-mentioned proportions, was heated for the same length of time as in I, but at 120 — 125° . The calcium salt was obtained by complete precipitation with alcohol.

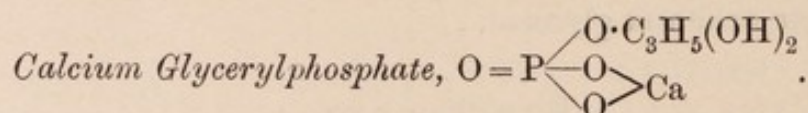
1.0245 of the salt, dried at 125° , gave 0.2464 CaO. $\text{Ca} = 17.2$ per cent.

III. A mixture of glycerol and phosphoric acid was heated in the same proportions and for the same length of time as in the preceding experiments, but at 135° . The calcium salt was obtained by complete precipitation with alcohol.

1.0512 of the salt, dried at 125° , gave 0.2466 CaO. $\text{Ca} = 16.7$ per cent.

It is evident from the above results that when glycerylphosphoric acid is prepared at temperatures above 110° it is associated with varying amounts of the di-ester, the calcium salt of which requires $\text{Ca} = 11.56$ per cent.

Having confirmed the conditions, ascertained by Carré (*loc. cit.*), under which only the mono-ester (I) is formed, a considerable quantity of it was prepared for the purpose of examining some of its salts more completely.



This salt forms tufts of crystalline leaflets when its cold, saturated solution is heated on a water-bath; it is soluble at 16° in 22.4 parts, at 25° in 25.2 parts, and, at 100° in 108.6 parts of water; it is insoluble in alcohol.

0.5696, previously dried in a vacuum, lost on heating at 125° 0.0044 or 0.77 per cent. This salt was therefore practically anhydrous, since half a molecule of water would require a loss of 4.1 per cent.

0.5652, dried at 125° gave 0.1523 CaO. $\text{Ca} = 19.25$.

$\text{C}_3\text{H}_7\text{O}_6\text{PCa}$ requires $\text{Ca} = 19.04$ per cent.

0.6954, dried at 125° , gave after ignition, solution in nitric acid, and precipitation by ammonium molybdate, 0.3649 $\text{Mg}_2\text{P}_2\text{O}_7$. $\text{P} = 14.75$.

$\text{C}_3\text{H}_7\text{O}_6\text{PCa}$ requires $\text{P} = 14.76$ per cent.

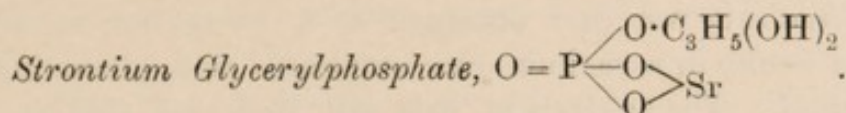
For further confirmation of the composition of this salt, its combustion with both copper oxide and lead chromate was attempted, but

owing to the difficulty of completely burning away the carbon, only the hydrogen was estimated.

0.3651, dried at 125° , gave 0.1129 H_2O . $\text{H} = 3.43$.

0.3907, " " " 0.1191 H_2O . $\text{H} = 3.38$.

$\text{C}_3\text{H}_7\text{O}_6\text{PCa}$ requires $\text{H} = 3.33$ per cent.

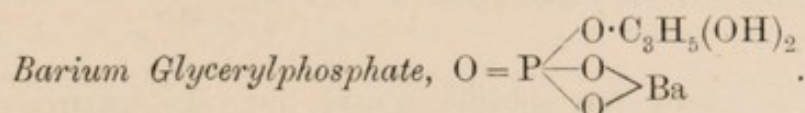


This salt, like that of calcium, is more sparingly soluble in hot than in cold water. On heating a cold, saturated solution of it on a water-bath, it separated as a white, granular powder.

0.4957, previously dried in a vacuum, lost, on heating at 125° , 0.0074 or 1.49 per cent. Half a molecule of water would require a loss of 3.37 per cent.

0.4883, dried at 125° , gave 0.3451 SrSO_4 . $\text{Sr} = 33.7$.

$\text{C}_3\text{H}_7\text{O}_6\text{PSr}$ requires $\text{Sr} = 34.0$ per cent.



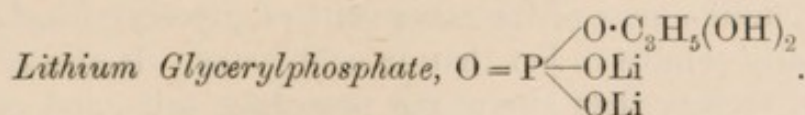
This is similar in its properties to the strontium salt.

0.4550, previously dried in a vacuum, lost, on heating at 125° , 0.0041 or 0.90 per cent. Half a molecule of water would require a loss of 2.84 per cent.

0.4401, dried at 125° , gave 0.3301 BaSO_4 . $\text{Ba} = 44.1$.

$\text{C}_3\text{H}_7\text{O}_6\text{PBa}$ requires $\text{Ba} = 44.7$ per cent.

The following salts were all prepared from a solution of the pure barium salt by exact precipitation with a solution of the sulphate of the respective metal, filtering, and concentrating the filtrate.



This salt is very readily soluble in cold, but only moderately so in hot water. On warming its cold, saturated solution, it is deposited in tufts of small leaflets.

0.2934 of the air-dried salt, heated at 125° , lost 0.0204 or 6.9 per cent.

This represents between one-half and one molecule of water, which would require respectively a loss of 4.6 and 8.9 per cent.

0.3842 of the anhydrous salt gave, on ignition, 0.2101 $\text{Li}_4\text{P}_2\text{O}_7$.
 $\text{Li}_4\text{P}_2\text{O}_7 = 54.6$.

$\text{C}_3\text{H}_7\text{O}_6\text{PLi}_2$ requires $\text{Li}_4\text{P}_2\text{O}_7 = 54.9$ per cent.

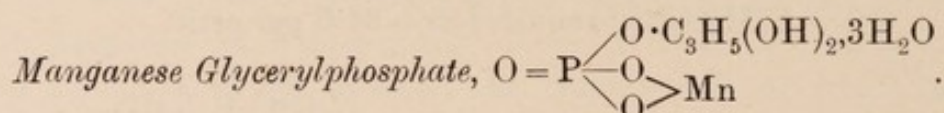
0.2703 of the anhydrous salt gave, after ignition and solution in water, 0.1634 $\text{Mg}_2\text{P}_2\text{O}_7$. $\text{P} = 16.8$.

$\text{C}_3\text{H}_7\text{O}_6\text{PLi}_2$ requires $\text{P} = 16.7$ per cent.

The *sodium* salt was first obtained as a syrup, but on remaining for several weeks in a vacuum over sulphuric acid, glistening leaflets slowly formed. The analysis of this salt indicated that it was not perfectly pure, and the amount was too small to admit of its recrystallisation.

The *potassium* salt was only obtained in the form of an uncrystallisable syrup.

The *ammonium* salt, on concentrating its solution, likewise formed a syrup, and, when this was allowed to remain in a vacuum over sulphuric acid, it gradually dissociated, with the loss of ammonia.



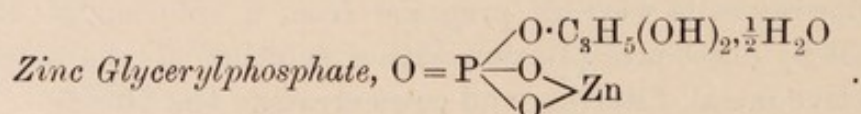
This salt is moderately soluble in cold, but very sparingly so in hot water. On warming its cold solution, it separates in tufts of small, well-defined needles of a light pink colour.

0.4617 of the air-dried salt, heated at 125° , lost 0.0873 H_2O .
 $\text{H}_2\text{O} = 18.9$.

$\text{C}_3\text{H}_7\text{O}_6\text{PMn}, 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 19.3$ per cent.

0.3744 of the anhydrous salt gave 0.1255 Mn_3O_4 . $\text{Mn} = 24.1$.

$\text{C}_3\text{H}_7\text{O}_6\text{PMn}$ requires $\text{Mn} = 24.4$ per cent.



This salt, unlike most of the other salts of glycerylphosphoric acid, is more readily soluble in hot than in cold water. It also crystallised with greater facility than any of the preceding salts, and on cooling its hot concentrated solution separated as a mass of colourless, glistening plates. On heating at 125° , it underwent some change, apparently becoming converted into a basic salt, which was insoluble in water.

0.3769 of the air-dried salt gave 0.1221 ZnO . $\text{Zn} = 26.0$.

$\text{C}_3\text{H}_7\text{O}_6\text{PZn}, \frac{1}{2}\text{H}_2\text{O}$ requires $\text{Zn} = 26.7$ per cent.

Examination of the Salts of Glycerolphosphoric Acid prepared by Willstätter and Lüdecke's Method.

In order to test the validity of the conclusions of Willstätter and Lüdecke (*Ber.*, 1904, 37, 3753) respecting the difference which they supposed to exist between the natural and synthetical glycerolphosphoric acids, we have also prepared some of the barium and calcium salts of the latter acid exactly in accordance with the method adopted by them. From the results of our initial experiments (II and III), it was to be expected that the salts obtained by the method of the above-mentioned investigators would not consist wholly of those of the mono-ester, but would contain varying amounts of the corresponding salts of the di-ester, a fact which they appear to have completely overlooked, and which is rendered evident by a consideration of the analytical data.

Molecular proportions of crystallised phosphoric acid and pure dry glycerol (53.2 grams of the former and 50 grams of the latter) were heated together in an oil-bath at 135—140° under 15 mm. pressure, and the water eliminated by the reaction absorbed by strong sulphuric acid contained in a flask adapted to the apparatus. After 6 hours, acrolein was given off, and the heating was then discontinued. The mixture was poured into an excess of baryta solution, and, when cold, the liquid was filtered, and the precipitate thoroughly washed with water. The combined filtrate and washings, after being freed from baryta by carbon dioxide, was again filtered, and concentrated on a water-bath to a small bulk. The salt was then completely precipitated by the addition of alcohol, collected on a filter, washed with alcohol, and dried in the air.

Barium Salt.—A portion of this salt was dissolved in water, the solution filtered, concentrated, precipitated by alcohol, and these operations repeated five times consecutively. This product was then dissolved in water and the salt which separated by heating the solution on a water-bath was collected and analysed.

0.4322, dried at 105° until of constant weight, gave 0.3176 BaSO₄.
Ba = 43.2 per cent.

Another portion of the barium salt was precipitated from its aqueous solution six times successively by alcohol, and was then analysed without subsequent treatment with water.

0.3040, dried at 105° until of constant weight, gave 0.2139 BaSO₄.
Ba = 41.4 per cent.

As a barium salt of the mono-ester requires Ba = 44.6 per cent., Willstätter and Lüdecke (*loc. cit.*), having found a somewhat lower

percentage of barium, calculate their results for a salt having the composition $C_3H_7O_6PBa, H_2O$, but without any direct evidence that it contained a molecule of water. They also consider it remarkable that the salt precipitated by alcohol contains relatively less barium than that obtained by heating the aqueous solution. As we have previously shown, however, the lower percentage of barium in these salts is not due in either case to the presence of water, but to a salt of the di-ester, and this is in relatively greater proportion when the salt is precipitated by alcohol than when separated by heating the aqueous solution.

Calcium Salt.—This was prepared from the original barium salt, obtained by the above-described method, by shaking its solution with freshly precipitated calcium sulphate until the liquid no longer gave a reaction for barium. The filtered liquid was then concentrated on a water-bath, and the salt which separated from the hot solution was collected. It was first dried in a vacuum over sulphuric acid until of constant weight, and then analysed.

0.6435, heated at $125-130^\circ$, lost 0.0262 H_2O . $H_2O = 4.07$.

0.6191, „ „ „ „ „ „ 0.1447 CaO . $Ca = 16.69$ per cent.

Willstätter and Lüdecke, in interpreting the results of their analysis of this salt, state that the loss of weight on heating at $125-130^\circ$ appears to correspond to $\frac{3}{4}$ molecule of water, and that when heated at this temperature it contains an amount of calcium (16.69 per cent.) agreeing best with the formula $C_3H_7O_6PCa, 1\frac{1}{2}H_2O$, which requires $Ca = 16.87$ per cent.

It should be considered, however, that as anhydrous calcium glycerylphosphate contains 19.04 per cent., and the corresponding salt of the di-ester 11.56 per cent. of calcium, a mixture of these two salts in the proportion of 69 per cent. of the former and 31 per cent. of the latter would contain 16.72 per cent. of calcium, or almost precisely the amount that was found in the salt assumed to contain $1\frac{1}{2}$ molecules of water. It has been found possible to decide which of these conditions obtains by estimating the total amount of hydrogen in the salt. This was accomplished by its combustion with copper oxide, as indicated in the case of the previously described calcium salt.

0.3715, previously heated at $125-130^\circ$, gave 0.1121 H_2O . $H = 3.35$.

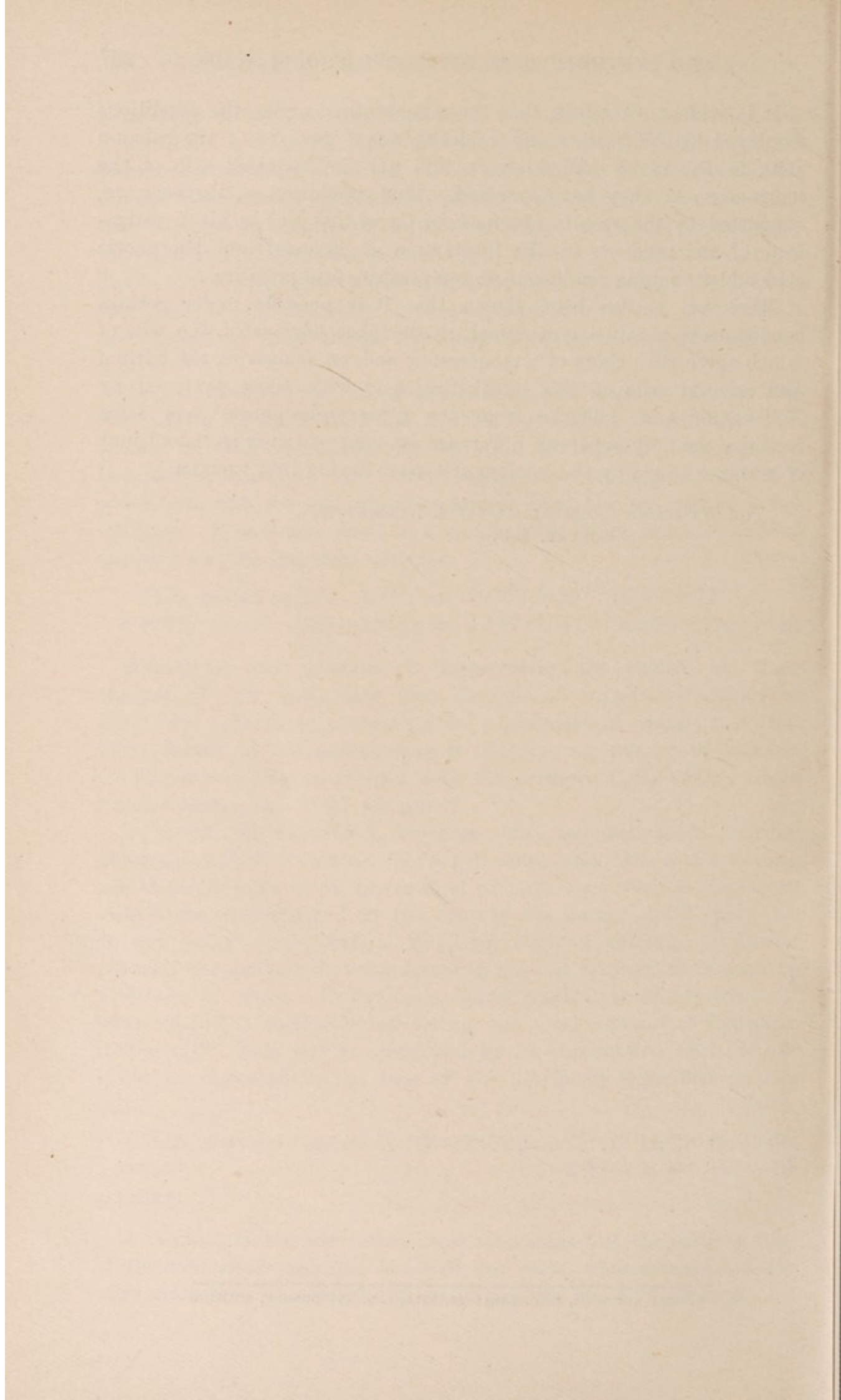
0.3742, „ „ „ „ „ „ 0.1167 H_2O . $H = 3.46$.
per cent.

A mixture, in the above-mentioned proportions, of the calcium salts of the two esters requires $H = 3.37$ per cent., whereas a salt of the mono-ester with $1\frac{1}{2}$ molecules of water requires $H = 4.22$ per cent.

It is evident, therefore, that the salt obtained under the conditions employed by Willstätter and Lüdecke was a mixture of the calcium salts of the mono- and di-esters, and not the hydrated salt of the mono-ester, as they have assumed. This conclusion is, furthermore, supported by the results obtained by Carré (*loc. cit.*) in his investigation of the products of the interaction of glycerol and phosphoric acid under varying conditions of temperature and pressure.

Moreover, it has been shown that it is possible under certain conditions to obtain a synthetic glycerylphosphoric acid, the salts of which agree with those of a mono-ester, and, on comparing the barium and calcium salts of this synthetic acid with those prepared by Willstätter and Lüdecke from the glycerylphosphoric acid from lecithin, the only apparent difference in composition is in the amount of water retained by the calcium salt after drying in a vacuum.

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