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XXVI. *Chemical Examination of the Fruit of* Menispermum Cocculus (*Semina Cocculi Indici*). *By* WILLIAM FRANCIS, *Ph. D.**

NOTWITHSTANDING the numerous investigations to which the grains of this plant have been submitted, much doubt still remains respecting the constitution, and even with regard to the existence of some of the many interesting bodies said to occur in them.

Boullay†, to whom we are indebted for the first examination, found in them a fatty oil, stearine, yellow extractive colouring matter, picrotoxine,—to which he ascribed the properties of an alkaloid,—menispermic acid, vegetable fibre, albumen, and several of the inorganic salts usually contained in plants. They were subsequently investigated by Casaseca‡, principally with regard to the menispermic acid; he showed that no such acid existed in them, a fact which has been confirmed by all later researches. The same chemist, in conjunction with Lecanu§, made the fatty bodies which occur in this fruit the subject of a distinct treatise, which I shall hereafter have occasion to notice more fully. Oppermann‖ and quite recently Regnault¶ have published analyses of picrotoxine.

The most complete memoir on these grains is one published by Peltier and Couerbe**. They describe in it two new alkaloids, menispermine and paramenispermine, which are said to occur in the shells, and a new acid, hypopicrotoxinic acid, and they ascribe to picrotoxine acid properties. The manner in

* Communicated by the Author.
† *Bulletin de Pharmacie*, vol. iv.
‡ Ibid. xii[ième] *Année*, *Fév.* 1826, p. 99.
§ Ibid. *Janv.* 1826, p. 55.
‖ *Mag. für Pharmacie*, xxxv. p. 233.
¶ *Ann. de Chimie et de Phys.*, lxviii. p. 157.
** *Ann. der Pharm.* B. x. p. 181.

which they arrived at their conclusions has not merely appeared satisfactory to few chemists, but seems rather to have created increased doubt with respect to the true constituents of these grains.

Under these circumstances I was induced to subject this fruit to an entirely fresh analysis: the results of my investigations I shall from time to time communicate, as soon as they are so far advanced as to be fit for publication; in the present memoir I shall treat of the fatty substances which occur so abundantly in the Cocculus grains.

I. *The Fatty Substances—Stearophanic Acid.*

The only paper with which I am acquainted in which these substances are made the subject of investigation, is the one above-mentioned by Casaseca and Lecanu. By treating the coarsely pounded grains with boiling water they obtained as extract a considerable quantity of a fatty matter, impregnated with a green colouring substance which reddened litmus paper: treated with strong boiling alcohol a green solution was obtained possessed of acid properties, and from which on cooling were deposited flocky masses of a neutral fat of a white colour. On evaporating this alcoholic solution they obtained a fat substance, which pressed between bibulous paper afforded a nearly colourless adherent nacreous mass, easily soluble in boiling alcohol, but sparingly in cold, and which melted at 59°. From these properties the authors regarded it as margaric acid.

The mass which had been imbibed by the blotting-paper was extracted with alcohol, which on evaporation left behind an oily substance of a deep green colour, which Casaseca and Lecanu considered to be oleic acid. They conclude therefore from their examination, that margaric and oleic acids occur in an uncombined state in the grains of Cocculus, and moreover a neutral fat, probably analogous to stearine.

From the following experiments, however, it will be seen that this acid, which it is true occurs in large quantity in a free state in these grains, is not margaric acid, but a new acid nearly related to the latter in its constitution, but widely differing from it in its properties; and further, that this acid likewise occurs combined with the oxide of glyceryle, and thus constitutes the neutral fat of Casaseca and Lecanu. For this acid I propose the name of *stearophanic acid*, (from στέαρ and φαίνομαι), on account of its beautiful lustre in the crystallized state, and for the neutral fat that of *stearophanine*.

When the coarsely pounded grains are digested with boiling alcohol (that commonly used for spirit-lamps is sufficiently

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strong) and the extract concentrated by distilling off the alcohol, on cooling, a cake floating on the surface is obtained, which consists of a deep green-coloured smeary fat matter. If the kernels after having been removed from the outer shells are submitted to a similar treatment, the same fat mass is obtained, only with this difference, that it is no longer green but of a yellowish colour, proving that the green colouring matter is only contained in the outer shells. The fat mass was separated from the remainder of the extract and boiled several times with distilled water, to remove all traces of picrotoxine and other soluble substances. It possessed an acid reaction, and was easily saponified by boiling with a dilute solution of caustic potash. The soap, which was separated by common salt, is hard, of a green colour, and affords after decomposition by an acid a green mass which solidifies on cooling. It is very easily soluble in weak boiling alcohol; on cooling, a portion, which however is still of a yellow colour, crystallizes, the solution remaining green. The solid acid thus prepared, although recrystallized ten or twelve times, could not be obtained white; it always preserved its yellow tint, which was especially evident on its being melted. The filtered alcoholic liquor afforded on evaporation a dark green acid oily liquid, which could not be obtained free either from colouring matter or from solid acid.

If after all the picrotoxine and colouring matter have been removed by treatment three or four times with boiling alcohol, the grains be now acted upon by æther employing the gentle heat of a sand-bath, and the filtered æthereal solution be placed in the cold, a shining white fat crystallizes slowly out of it in arborescent aggregations. It was obtained perfectly pure by dissolving it once or twice in absolute boiling alcohol, which takes up very little of it, and from which it separates on cooling in grains and flocks; it has then a dull white colour and a constant melting-point.

Stearophanic Acid.—The pure fat thus prepared was saponified by a solution of caustic potash until it formed a perfectly clear jelly, and then treated by salt, the solid soap dissolved in much water, and decomposed by hydrochloric acid. It collects on the surface as a colourless oil, which soon solidifies into a white crystalline mass. It was now boiled with distilled water till all the hydrochloric acid was removed, and dissolved in weak warm alcohol and filtered warm. On cooling, the acid separates in small needles, which having been dried by exposure to the air, or by pressing between bibulous paper, possess a strong lustre of mother-of-pearl. Its melting point is constant 68° C.; on cooling it crystallizes in

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stellate groups strongly resembling some kinds of Wavellite, and has a shining white colour. It may easily be reduced to a fine powder; it is very soluble in warm weak alcohol, from which nearly the whole quantity separates on cooling; the solution has strong acid properties.

The acid obtained in the above manner is the hydrate; the anhydrous acid has, according to the analyses of several of its compounds, the following composition:—

		Calculated for 100.
35 atoms Carbon	2654·89	78·57
68 ... Hydrogen	424·30	12·55
3 ... Oxygen	300·00	8·88
	3379·19	100·00

The composition of the hydrated acid in the state in which it is separated from the salts, and likewise occurs free in the kernels, was determined in the following ultimate analyses:—

I. 0·275 grm. of the hydrated acid gave 0·757 carbonic acid, and 0·312 water.

II. 0·294 grm. of the hydrated acid gave 0·8054 carbonic acid, and 0·337 water.

III. 0·224 grm. of the hydrated acid gave 0·613 carbonic acid, and 0·252 water.

IV. 0·331 grm. of the hydrated acid gave 0·913 carbonic acid, and 0·357 water.

V. 0·242 grm. of the hydrated acid gave 0·667 carbonic acid, and 0·272 water.

In No. I. the combustion was effected by chromate of lead, in the remainder oxide of copper was employed. No. V. is an analysis of the hydrated acid as it occurs uncombined in the grains; it was still coloured somewhat yellow, but was quite crystalline, and had the same melting-point as the perfectly white hydrate.

The above numbers afford in 100 parts, —

	I.	II.	III.	IV.	V.
Carbon	75·71	75·32	75·24	75·84	75·79
Hydrogen...	12·60	12·73	12·50	11·98	12·49
Oxygen.....	11·69	11·95	12·26	12·18	11·72
	100·00	100·00	100·00	100·00	100·00

These closely approach the formula $C^{35}\,H^{70}\,O^{4}$.

		In 100 parts.
35 atoms Carbon.....	2654·89	76·04
70 ... Hydrogen ...	436·78	12·51
4 ... Oxygen	400·00	11·75
	3491·67	100·00

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The acid therefore contains in the state of hydrate 1 atom of water, which is replaced in the salts by one equivalent of base.

Stearophanate of Soda.—This salt was prepared by digesting the pure acid with an excess of carbonate of soda. On exposing it to a gentle heat the carbonic acid is expelled with violent ebullition, and a perfectly clear solution formed, which was evaporated to dryness in the water-bath. The finely powdered mixture was then digested with absolute alcohol, which leaves the excess of carbonate of soda undissolved: a perfectly clear solution is obtained, which however soon solidifies into a gelatinous mass, which, transferred to a filter and dried by exposure to the air or between folds of bibulous paper, leaves behind a crystalline tissue consisting of long prisms, with a strong nacreous lustre.

This compound, when treated with a small quantity of water, forms a stiff jelly; it is decomposed on the addition of much water into an acid crystalline salt, which settles slowly, and imparts to the liquid an opake appearance.

Several stearophanates may be prepared from this salt by double decomposition.

Stearophanate of Silver.—This compound was prepared by decomposing a weak alcoholic solution of the preceding salt by a perfectly neutral solution of the nitrate of silver. The precipitate is very bulky, but it soon settles. The white colour which it at first possesses is only of momentary duration; it acquires a slight tint of brown. Well washed and dried, it can be exposed to light without undergoing apparently any further decomposition. It dissolves easily in a solution of caustic ammonia.

I. 1·134 grm. of the salt, well dried at 100°, left after ignition 0·317 metallic silver, corresponding to 0·3404 oxide of silver.

II. 0·379 grain of the salt gave 0·105 silver, corresponding to 0·1127 of the oxide.

This gives in 100 parts,—

	Calculated.		Obtained.	
			I.	II.
1 atom Oxide of silver. .	1451·61	30·05	30·01	29·73
1 ... of Stearophanic acid	3379·19	69·95	69·99	70·27
	4830·80	100·00	100·00	100·00

On burning with oxide of copper,—

I. 0·543 grm. of the silver salt gave 1·0695 carbonic acid, and 0·433 water.

II. 0·4925 grm. of the salt gave 0·9763 carbonic acid, and 0·393 water.

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III. 0·259 grm. of the salt gave 0·205 water, which reduced to 100 parts, gives

	According to theory.	I.	II.	III.
35 at. Carbon.	54·94	54·15	54·51	
68 ... Hydrogen	8·78	8·83	8·86	8·79
3 ... Oxygen	6·23	7·15	6·76	
1 ... Oxide of silver. .	30·05	29·87	29·87	
	100·00	100·00	100·00	

Stearophanate of the Oxide of Æthyle.—This salt is a solid, brownish-white, semi-transparent mass. It was formed by passing a stream of dried muriatic gas for several hours into a warm saturated alcoholic solution of the acid. After some time the æther collects upon the surface as a colourless oily fluid, which solidifies on cooling. A portion still remaining in solution is obtained on the addition of water. To free it from acid it was boiled several times with a dilute solution of the carbonate of soda, and afterwards with water. It melts at 32° C., is very fragile, void of smell in the cold, but on being warmed acquires a slight fruity odour. It melts easily on the tongue, imparting to it a sensation of cold, and has a buttery taste: it is very volatile, but is partially decomposed on distillation. It is decomposed by potash into the stearophanate of potash and alcohol.

The composition was ascertained in the following ultimate analyses:—

I. 0·381 grm. of the æther gave 1·0668 carbonic acid, and 0·436 water.

II. 0·247 grm. gave 0·6925 carbonic acid, and 0·286 water.

No. I. analysis was made with oxide of copper. For No. II. I am indebted to the kindness of Dr. Lawrence Smith; it was made with oxide of copper and chlorate of potash.

	I.	II.
Carbon . .	77·01	77·09
Hydrogen.	12·69	12·85
Oxygen . .	10·30	10·06

which agree with the formula $C^4 H^{10} O + C^{35} H^{68} O^3$.

39 Carbon . .	2958·40	77·11
78 Hydrogen.	491·70	12·51
4 Oxygen . .	400·00	10·38
	3850·10	

Stearophanine.—The mode of preparation has been described above. When the fat is extracted by pressing the grains between hot plates, or by means of boiling water, it is always contaminated by the free acids, colouring matter, &c., from which it separates with great difficulty. If, on the contrary, the

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grains are first digested several times with moderately strong alcohol, all the substances which would otherwise be taken up by the æther are removed, and the fat alone remains. In warm æther it is very easily soluble, from which it crystallizes on cooling in dendritic aggregations. It does not crystallize from alcohol, in which it is but sparingly soluble, but separates as a white powder. When perfectly pure it melts at from 35° to 36° C., does not crystallize on cooling, but shrinks together, forming a wave-like rough surface; it cannot be reduced to a powder, and strongly resembles wax. It does not saponify easily on being boiled with dilute solution of potash, but immediately when melted with potash and a small quantity of water. It then affords, when boiled with water, a clear solution, from which acids separate the stearophanic acid.

When subjected to dry distillation it afforded acroleine, a solid fat acid body, and a liquid product, but no sebacic acid; it therefore contains glycerine, but is free from oleine.

Before burning it with oxide of copper it was kept for some time in the water-bath, to free it from adhering traces of alcohol. The following numbers were obtained:—

I. 0·329 grm. of stearophanine gave 0·919 carbonic acid, and 0·361 water.

II. 0·231 grm. gave 0·645 carbonic acid, and 0·257 water.

III. 0·213 grm. gave 0·236 water.

In 100 we have

	I.	II.	III.
Carbon . .	76·81	76·69	
Hydrogen.	12·19	12·36	12·30
Oxygen . .	11·10	10·95	

which agrees with the formula $C^{38}\ H^{72}\ O^4$.

38 atoms Carbon. . .	2882·45	77·24
72 ... Hydrogen .	449·25	12·04
4 ... Oxygen. . .	400·00	10·72

In the present case the same formula must be admitted for the constitution of glycerine as was proposed by Mr. Stenhouse in his memoir on Palmitine*, and which has likewise been adopted by M. Marsson for that occurring in combination with Laurostearic acid in the bay berries†. According to the above analyses, stearophanine consists of

1 atom of Stearophanic acid	=	$C^{35}\ H^{68}\ O^3$
1 ... Glycerine.	=	$C^3\ H^4\ O$
1 ... Stearophanine . .	=	$\overline{C^{38}\ H^{72}\ O^4}$

However similar the constitution of stearophanic acid may appear to that of margaric acid, there cannot be the least doubt

* Philosophical Magazine, S. 3. vol. xviii. p. 190.

† *Annalen der Chem. und Pharm.*, vol. xli. p. 329; see also the present Number, pp. 237, 238.

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as to their distinctness: margaric acid melts at 60° C., the margarate of the oxide of æthyle at 22°; stearophanic acid, on the other hand, has its melting-point at 68° C., and its compound with æther at 32°. But this is more effectually proved by the splendid crystallization of the acid and of its soda salt. When compared with the very numerous preparations of fats and their salts in the collections of the Giessen laboratory, they surpassed all in lustre and beauty, and by the well-defined form of the crystals of the soda salt.

As above stated, the acid occurs in a free state in the grains, but only in small quantity, the greater part consists of the oily acid; it probably varies according to the time the grains have been preserved, as is the case with palmitic acid. On the whole the fatty substances may probably constitute 15 per cent. of the grains, of which about a third would consist of the neutral fat. Wittstock obtained 11·2 per cent. of oily matter by pressing the grains between hot plates.

A portion of the oily mass was subjected to dry distillation, and the products boiled with water, from which on cooling a large quantity of sebacic acid was deposited in beautiful needles with a nacrous lustre, and at the same time another fat acid separated on the surface, which was probably margaric acid. This experiment proved the oily fat and oily acid which occur together with that above described in the fruit of *Menispermum Cocculus*, to be oleine and oleic acid, since, according to Redtenbacher, these alone afford sebacic acid on dry distillation.

The colouring matter which is peculiar to the shells could not be obtained in a state fit for analysis.

XXVII. *Contributions to the Minute Anatomy of Animals.* By George Gulliver, *F.R.S., &c. &c.*—No. III*.

On the Pus-like Globules of the Blood.

IN the Philosophical Magazine for September 1838, (S. 3, vol. xiii., p. 193) I have described the frequent occurrence of globules of pus in the blood of persons affected with various severe inflammatory and suppurative diseases, and have since shown how the pale globules of the blood of healthy mammalia and birds differ from the lymph-globules of the same animals (Gerber's Anatomy, p. 83 and 84; Appendix to the same, p. 19; and Philosophical Magazine for June, 1842). In the present communication the globules first mentioned will be compared with the pale globules now so well known as belonging to healthy blood.

* Communicated by the Author. No. II. will be found in our last Number, p. 107.

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