FII. On the Resin of Ficus rubiginosa, and a new Homologue of Benzylic Alcohol. By Warren De la Rue, Ph.D., F.R.S., Treasurer of the Chemical Society, Secretary of the Royal Astronomical Society, &c., and Hugo Müller, Ph.D., F.C.S.

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Among the interesting collection of natural products contributed to the Paris Universal Exhibition of 1855 by the British Colonies, was a gum presenting some remarkable qualities. This substance was stated by the exhibitor to be a new species of gutta percha, in consequence of its becoming plastic when masticated, and on this account it attracted considerable attention. It had been contributed by Dr. Stephenson, of Manning River, N.S.W., who had obtained it from a species of *Ficus*, known as *F. rubiginosa*. The zealous Commissioner for New South Wales, Mr. (now Sir William) McArthur, brought this gum under our notice with the view of obtaining some information respecting its chemical properties.

A few preliminary experiments, which were made in Paris, at once showed us that this substance had very little in common with gutta percha, and, moreover, its chemical properties were found to be entirely different from those of that gum. Although our experiments did not allow us to hold out hopes to Mr. McArthur of the gum becoming a valuable article of exportation from the colony, they offered some inducement to us to make a more rigorous investigation of it on purely scientific grounds. On communicating this view to Mr. McArthur, he liberally placed at our disposal the remainder of the specimen exhibited.

In pursuing subsequently the study of this subject, we discovered one of the proximate constituents to be a Natural Acetic Ether of a new radical homologous to benzyl (C₁₄ H₇). The peculiar interest which attaches to this class of compounds, induces us to bring under the notice of the Society the results of our investigation.

As the resin under consideration has not, so far as we know, been described, it will not be out of place to commence with an account of its physical characters; we shall next proceed to state the results of our investigation in respect of the chemical characters, first of the gum, then of its constituents. On account of the greater importance of the new Acetic Ether, we shall reserve a description of it until the concluding part of our paper, in order that we may place in immediate juxtaposition an account of the derivatives by which we have been enabled to establish its formula and chemical relations.

This gum or resin exhibits, on the first glance, great similarity in its general appearance to "Gum Euphorbium," occurring, like that substance, in irregular pieces, generally

pierced with holes; some specimens also exhibiting a stalactitic formation. The holes in the fragments of this resin are produced by a small beetle of the tribe "Curculio," which apparently feeds upon, and lives in this resin, as it oozes in a semifluid state from the branch of the tree. We had no means of ascertaining whether or not this insect causes the secretion of the resin by puncturing the branches of the tree, in the same manner as the *Coccus ficus* does for the purpose of depositing its ova. The colour of the gum varies from a dirty yellow or red, almost to white. It is solid and brittle, but some of the larger pieces exhibit, especially in the interior, a degree of toughness which renders it difficult to powder. It is opake, the fracture being dull and wax-like.

At a temperature of about 30° C. (86° Fahr.) this resin becomes soft, when it resembles gutta percha, being plastic without becoming sticky, provided it has been previously wetted with water. In its natural condition this resin possesses neither taste nor odour; but when heated it evolves a wax-like odour, and on being masticated evinces a characteristic taste.

In hot or cold water it is perfectly insoluble, but warm alcohol, ether, oil of turpentine, and other solvents of resinous substances dissolve it with facility. Solutions of caustic alkalies have no effect on it, even when aided by heat.

When left for some time with cold alcohol of ordinary strength, the greater part of the resin is dissolved, whilst a white flocculent substance remains undissolved. By employing this solvent, we succeeded in separating several distinct classes of substances from the Ficus resin. The constituent, readily soluble in cold alcohol, formed an amorphous resinous substance, when separated from the solvent by means of distillation or precipitation with water. The white insoluble part, when further treated with boiling alcohol, is in part dissolved, particles of bark, sand, and other accidental impurities remaining undissolved. The alcoholic solution of the white substance deposits, on cooling, a white crystalline mass, which by repeated crystallization may be obtained in beautiful scaly crystals. From the residue, insoluble in boiling alcohol, bisulphide of carbon or chloroform extract a small quantity of caoutchouc.

A quantitative experiment by the above method yielded the following approximate per-centage result:—

Resinous substance, readily soluble in cold alcohol					
White crystalline substances, insoluble in cold alcohol, but					
soluble in warm alcohol	14				
Caoutchouc, fragments of bark, sand, and loss	13				

The resinous substance, readily soluble in cold alcohol, which forms, according to this analysis, by far the principal constituent of our resin, offered but little inducement for chemical investigation. However, a number of experiments were made, which, although unproductive in their results, may serve to characterize this substance, which possesses peculiarities distinguishing it from other bodies of like origin. In order to identify it hereafter, we propose to call this resin Sycoretin. At the same time we must state that

we were not successful, for reasons hereinafter mentioned, in obtaining this substance perfectly pure.

Sycoretin.

Cold alcohol of moderate strength dissolves the principal part of the original resin, forming a light brown solution, which on precipitation with water, or the separation of the alcohol by means of distillation, furnishes the sycoretin. The alcoholic solution of this resin is perfectly neutral, and scarcely any precipitate is caused in it on the addition of an alcoholic solution of acetate of lead or acetate of copper. This behaviour indicated at once that no acid compounds were present, and that this resin is perfectly The minute precipitate which formed we ascertained to be tannate of lead, the source of the tannic acid being probably the bark which contaminated the resin. This resin was purified by redissolving it in alcohol, and in order to remove the small amount of colour the solution was treated with animal charcoal, but this had no effect. No better result was obtained when a small quantity of acetate of lead was introduced in the solution, and a basic lead salt thrown down with ammonia. We afterwards found that the colour could be gradually removed by repeated precipitation of the resin from its alcoholic solution by means of water.

The decolorized resin was now redissolved in a just-sufficient quantity of alcohol, and the solution left for some time in a cool place, when a small amount of crystalline substance was deposited, which was filtered off. By the addition of a little water a small quantity of sycoretin was then thrown down, in order to carry down the last traces of the less soluble crystalline compound, in case any were still present. After this treatment the solution was again allowed to stand for some time, but no further precipitate was formed. The clear solution was now partly precipitated with water, and the precipitate removed after it had subsided, heat being used to facilitate the subsidence of the sycoretin by causing the precipitate to agglutinate into one mass. That part of the resin remaining in solution was afterwards thrown down with water and collected separately.

The two different lots of resin thus obtained had the same appearance; both were brittle, but only the last became sticky when masticated, and tasted like the original resin. Both products were powdered and kept for some time *in vacuo* over sulphuric acid, in order to remove all traces of any adhering water or alcohol.

The analysis of the first precipitated part (A) gave the following numbers:—

0.2055 grm. of substance gave 0.5625 grm. carbonic acid, and 0.1870 grm. water.

The analysis of the portion last thrown down (B) gave the following:—

0·1733 grm. of substance gave 0·4950 grm. carbonic acid, and 0·1550 grm. water.

The foregoing results give the following per-centages:—

				$\mathbf{A}.$	В.
Carbon .			•	74.65	77.89
Hydrogen		•		10.11	9.94

MDCCCLX.

It will be observed from the preceding numbers, that the resin, which has the property of agglutinating on being masticated, is richer in carbon than that first thrown down by water from their alcoholic solution. The peculiar characters of these substances did not, however, permit of any formulæ being determined for them.

Sycoretin is almost white; it is very brittle. It melts in boiling water to a thick liquid, floating on the surface, and when powdered it becomes so electric that it flies out of the mortar. In water, dilute acids, alkaline solutions, or ammonia, it is insoluble; but it is readily soluble in alcohol, ether, chloroform, oil of turpentine, &c.

In order to ascertain whether sycoretin was allied to that class of bodies called glucosides (for example, jalapine), the following experiments were made:—

Action of Sulphuric Acid on Sycoretin.

A portion of the sycoretin, prepared as stated above by fractional precipitation, was added to concentrated sulphuric acid; it was readily dissolved, forming a fine deep red solution, which gave off only a faint odour of sulphurous acid when kept for several days. By exposure to the air, or on addition of water, a brownish precipitate deposited, which differed from the original solution by its lesser solubility; the aqueous liquid contained a trace of a sulpho-copulate acid, but no saccharine substance could be discovered. Treated with a concentrated solution of potash, analogous results were obtained. These experiments show that sycoretin cannot be classed with the glucosides; moreover, all attempts to place this substance in connexion with some of the classified organic compounds were unsuccessful, and we are therefore constrained to leave it for the present among the so-called resins, under which term are comprised all sorts of bodies, acid and neutral, which have nothing in common except some physical resemblance.

Action of Nitric Acid on Sycoretin.

It appears that the only products of the action of concentrated nitric acid are a peculiar nitro-compound and a small quantity of oxalic acid, no picric acid being formed.

On submitting sycoretin to the action of nitric acid, the powdered resin was introduced in small quantities into the acid at the ordinary temperature, and when the action had somewhat subsided, the acid was boiled for some time, when every particle of resin disappeared. The resulting yellow liquid was mixed with water, when a copious precipitate of a pale yellow colour was formed. The precipitate was filtered off, and washed with water. The filtrate, when freed from nitric acid by evaporation, gave an additional precipitate of the nitro-compound on admixture with water. The nitro-compound has slightly acid properties, and is readily soluble in solutions of potash and ammonia. Carbonate of potash also dissolves it, but there is no evolution of carbonic acid, even when the solution is warmed. All the solutions in alkalies are dark yellowish brown, and leave on evaporation an amorphous residue. Lead and other metallic salts give coloured precipitates with its solution, but, as might be expected, no definite compounds

could be procured in this way. The compound with potash, when heated on the platinum-foil, melts, takes fire, puffs up, and burns with the vivacity of other nitro-compounds.

Action of Heat on Sycoretin.

When heated in a retort, sycoretin melts below 100° C. (212° Fahr.), and, at a temperature a few degrees higher, froths considerably, giving off water which retains the peculiar odour perceptible on heating the original resin. On raising the temperature much higher it becomes quiet, and begins to decompose, giving off at first a mobile liquid, and towards the end a dark yellow tar-like substance, leaving only a small quantity of charcoal behind. The distillate so obtained has a disagreeable smell, somewhat like burnt india-rubber; acetic acid being also present in considerable quantity.

Treated with a solution of carbonate of sodium the acetic acid is removed, a dark brown oily liquid remaining, which possesses now a less disagreeable odour. This oily liquid, submitted to a new distillation, gives at first a very fluid liquid, possessing in every respect the properties of caoutchin, and then a thick oily liquid, which soon becomes dark brown when exposed to the air.

Acetate of Sycoceryl.

We assign this name, for reasons hereafter to be mentioned, to the crystallizable substance, which, as already mentioned, is obtained when the residue, left after the treatment of the original resin with cold alcohol, is dissolved in boiling alcohol, and the solution allowed to cool.

For the preparation of this substance the original resin is coarsely powdered and extracted with cold alcohol, in order to remove, as far as possible, the sycoretin. The undissolved residue is then exhausted with boiling alcohol. The several solutions thus obtained are filtered and allowed to cool, when a white deposit is formed, which generally shows but little indication of crystallization. This white deposit is again dissolved in a large quantity of boiling alcohol, and left in a quiet place to cool slowly, when a more perfect crystallization is obtained.

Towards the latter period of the crystallization a substance is deposited of different appearance, being of a more flocculent nature, and altogether different from the crystals first deposited. This substance is present only in a very small quantity, and its separation from the other crystallizable constituents of the resin is attended with great difficulties. In order to effect this separation, the alcoholic solution is allowed to cool to about 40° C. (104° Fahr.), and then the crystals which may have formed are separated by straining off the liquor as quickly as possible through a piece of gauze. The mother-liquor, on further cooling, will now deposit the flocculent substance, contaminated however with the first substance. By repeating this operation a perfect separation of this second substance may be effected.

The crystalline substance (acetate of sycoceryl), by repeated solution in and recrystallization from hot alcohol, was obtained perfectly white and transparent and apparently pure. An examination with the microscope, however, proved that another foreign body had deposited in smaller crystals on the faces of the supposed pure substance. This new body proved to be much less soluble in different vehicles than our acetate of sycoceryl, but being present only in a very small quantity, its separation caused us at first very great perplexity, but finally we found the following method perfectly efficacious for that purpose.

The dry crystals were placed in a flask, and a quantity of ether insufficient to dissolve the whole substance was introduced, the temperature being maintained at about 30° C. (86° Fahr.); more ether was cautiously added from time to time until the larger crystals had just disappeared, leaving the smaller ones of the new substance undissolved. The separation of the two substances is not, however, perfect in a single operation; for when the flask is allowed to cool, a small part of this parasitical body deposits. After distilling the filtered etheric solution, the acetate of sycoceryl is obtained in a perfect state of purity; and by recrystallization from alcohol, ether or chloroform, it may be procured in beautiful crystals.

Acetate of sycoceryl so obtained is perfectly colourless, and crystallizes from ether in flat prisms, which generally appear as six-sided plates. When crystallized from alcohol the crystals are thin and scaly like mica, and have the greatest resemblance to cholesterin.

Acetate of sycoceryl is brittle, yet difficult to powder, on account of its becoming so very electric when triturated. It melts at 118°—120° C. (244°·4—248° Fahr.), and is still fluid when cooled down to 80° C. (176° Fahr.). It solidifies at first to a transparent mass, which, however, after a short time becomes opake and crystalline, especially if scratched with a hard body. Heated considerably above its melting-point, it boils and distils, almost without decomposition. The distillate is at first liquid, but solidifies after some time, and becomes gradually crystalline. When not perfectly pure, or if the heat is applied too rapidly, it gives out a rancid odour, in which that of acetic acid is recognizable. Hot alcohol, ether, chloroform, benzol, acetone, oil of turpentine, and concentrated acetic acid dissolve the acetate of sycoceryl with great facility. The alcoholic solution is perfectly neutral, and gives no precipitate with alcoholic solutions of the acetates of lead or copper.

Sulphuric acid dissolves it readily, forming a viscid colourless solution, which gets gradually brown, and then gives off traces of sulphurous and acetic acids. When the sulphuric solution is mixed with water, a substance is thrown down which is perfectly hard at common temperatures, but melts below 100° C. (212° FAHR.), and is very difficultly soluble in alcohol, but readily so in chloroform and benzol.

Nitric acid when diluted has no effect, at ordinary temperatures, on acetate of sycoceryl; but if warm, it evolves nitrous fumes, and produces a yellow resinous compound. Fuming nitrous acid, however, dissolves it readily at ordinary temperatures, giving a yellow solution from which water throws down a flocculent amorphous yellow nitrocompound.

Muriatic acid has no effect on acetate of sycoceryl.

Chlorine, bromine, and iodine in contact with this substance act upon it with violence,

especially the two first-named reagents; the products, however, procured in this manner are only resin-like compounds not adapted for analysis.

If, however, a warm alcoholic solution of the acetate of sycoceryl is employed, and the bromine or iodine also added in solution, and in small quantities at a time, the colour of these two reagents disappears, and after cooling a new bromo- or iodo-compound, as the case may be, is deposited in small crystals. The iodine compound is yellow, the bromine compound colourless. The purification of these two promising compounds, and their separation from the unaltered original substances, and another resinous body formed at the same time, was unfortunately not possible with the limited quantity of material which could be devoted to their preparation.

Solution of potash, even when boiled for a long time with the substance under consideration, does not act upon it. If hydrate of potash, however, is melted with it a decomposition takes place, and if the temperature is raised some hydrogen is given off. The product of this reaction, treated with water, leaves behind a colourless amorphous body, which could not be got in a crystalline state, or sufficiently pure for analysis. The alkaline mother-liquor saturated with diluted sulphuric acid became slightly turbid, and the presence of acetic acid was then perceptible. Soda-tartrate of copper gave no reaction indicating the presence of sugar in the solution.

Thus far we did not succeed in producing any derivative which would throw light upon the theoretical composition of our substance, and furnish us with the means of ascertaining its rational formula.

A combustion gave the following numbers:—

- I. 0.2745 grm. of substance gave 0.7962 grm. carbonic acid, and 0.2527 grm. water.
- II. 0.2649 grm. of substance gave 0.7681 grm. carbonic acid, and 0.2645 grm. water.

These numbers correspond to the following per-centages:—

		I.	II.
Carbon .		79.11	79.08
Hydrogen		10.23	10.34

which agree with the empirical formula C_{20} H_{16} O_2 , our substance being accordingly isomeric with camphor, to which, however, it has no further resemblance.

This composition varies also widely from that of the crystalline substances procured from analogous sources, and which have a great resemblance to our substance; for instance, the crystalline resins on the one hand, Chinese wax and waxes generally on the other.

We have mentioned above, in speaking of the action of various reagents on our new substance, the occurrence of acetic acid under two different circumstances; we did not attach much importance to this fact at the time, because this acid occurs so frequently among the products resulting from the breaking up of organic substances; we nevertheless repeated subsequently these experiments on a somewhat larger scale, with the view, however, chiefly of studying the other products of decomposition which are formed. In order to eliminate as much as possible the effect of temperature, we made use of that

powerful reagent, the so-called "sodium-alcohol," which is obtained by dissolving sodium in absolute alcohol. Sodium-alcohol and potassium-alcohol are at ordinary temperatures generally equivalent in their reactions to the hydrates of those alkalies when in a state of fusion, and hence present the advantage of effecting decompositions in a more simple manner, the effect of a high temperature not interfering with the final result, as is sometimes the case when the fusing hydrated alkalies are employed.

Some experiments of this kind, performed with great care, convinced us that the occurrence of acetic acid could not be attributed to the effect of empyreumatic decomposition, but that it actually existed as an integral proximate constituent of our crystallizable substance. This led us at once to suspect that our substance was in reality an ether-like compound. This supposition was confirmed by the separation of a body which might be considered as the hydrated oxide of a radical; moreover, we were ultimately enabled to give the fullest confirmation to this theoretical speculation, by actually reforming the original substance in a manner suggested by this view.

It should be stated that sodium-alcohol dissolves our substance with the greatest facility, and even at a temperature of 30° C. (86° Fahr.) decomposition takes place, the reaction being unaccompanied by the evolution of gas. On cooling, the solution continues liquid, although a large quantity of the substance may have been employed; but on addition of water, a white flocculent substance separates from the colourless alkaline mother-liquor.

The flocculent substance is insoluble in water, but readily soluble in even cold alcohol. When dissolved in a quantity of boiling alcohol, just sufficient to take it up, the solution on cooling completely solidifies to a mass of beautiful silky crystals, quite different from those of the original substance: this new derivative proved to be the new alcohol which we propose to call Sycocerylic Alcohol.

The aqueous liquor from which the flocculent precipitate was separated remains almost perfectly clear on saturation with a mineral acid; on examination no other product besides a volatile organic acid could be found in it. The existence of a volatile acid with the odour of acetic acid, was rendered evident by saturating the alkaline mother-liquor with phosphoric acid and distilling; the distillate was saturated with carbonate of barium and evaporated to the crystallization point, when prismatic crystals, of the characteristic form of acetate of barium, were obtained. A barium determination gave the following result:—

2·1525 grms. of substance, dried first over sulphuric acid, then at 200° C. (392° FAHR.), gave 1·9593 sulphate of barium, corresponding to 53·52 per cent. barium.

The formula, C₄ H₃ BaO₄, of anhydrous acetate of barium requires 53.73 per cent. of barium.

Alcohol of Sycoceryl.

The preparation of this substance has been already detailed. In order to render it pure, it is only necessary, after it has been precipitated from the solution of sodium alcohol, to wash it well with water in order to remove all traces of fixed alkali; then to crystallize it a few times from warm alcohol. The crystals usually occur aggregated in

spherical masses, like the mineral Wavellite; they are very thin, and have a great resemblance to caffeine.

In several instances during the earlier stages of its purification, or when dilute alcohol is employed for its solution, it was noticed that the substance did not deposit in crystals, but the transparent liquid congealed to a jelly. This jelly, however, after some time became crystalline, the crystallization commencing in several points of the mass, and extending gradually throughout the whole; ultimately a crystallization was obtained of the same appearance as occurs under other circumstances.

In the determination of the rational formula of this substance, we took cognizance of the fact, that, besides acetic acid, it was the only other product obtained in the decomposition of the original compound which we have denominated acetate of sycoceryl, and the analysis of which led to the empirical formula C_{20} H_{16} O_2 .

From the nature of this compound, we inferred that it contained the radical of acetic acid in a similar state as acetic ether does; that in fact we had to deal with a compound containing acetic acid minus one atom of hydrogen and a radical. According to this view the empirical formula C_{20} H_{16} O_2 would have to be doubled, whereby we obtain

and if we now deduct the elements of acetic acid minus hydrogen
$$= \frac{C_{40} H_{32} O_4}{C_{26} H_{29}}$$
 we have

for the radical of our new alcohol, whose formula would consequently be $C_{36} H_{30} O_2$.

The analysis of the supposed alcohol obtained from acetate of sycoceryl gave the following results:—

- I. 0·1678 grm. of preparation A gave 0·5103 grm. carbonic acid, and 0·1747 grm. water.
- II. 0.2547 grm. of preparation B gave 0.7644 grm. carbonic acid, and 0.2568 grm. water.

These numbers correspond to the following per-centages:—

		Ana	$\mathbf{Mean}.$	
		I.	II.	
$C_{36} = 216$	82.44	82.94	81.85	82.39
$H_{30} = 30$	11.45	11.57	11.20	11.38
$O_2 = 16$	6.11			
$\overline{262}$	$\overline{100.00}$			

According to this formula our new alcohol would be homologous with benzylic alcohol obtained from "oil of bitter almonds."

Alcohol of sycoceryl is perfectly insoluble in water, the fixed alkalies, and ammonia; but alcohol, especially when warm, also ether, benzol, chloroform, and naphtha, are good solvents for it.

At a temperature of about 90°C. (194°FAHR.), sycocerylic alcohol melts to a liquid heavier than water, and solidifies on cooling to a crystalline mass, especially if any

fragments of crystals have remained unfused, because they become the foci of a new crystallization. When, however, the heat is increased only a little beyond the fusion-point, it remains perfectly transparent and amorphous. By contact with alcohol, this glassy condition is changed to the normal crystalline structure. Heated considerably above its melting-point, a portion distils unchanged, and there remains a brownish residue in the retort.

Potassium brought in contact with this substance when in a state of fusion disengages hydrogen, and becomes covered with a white crust; but when heat is applied in order to fuse the so-formed potassium-compound of the sycocerylic alcohol, the reaction becomes so violent that the mass blackens and even catches fire.

Heated with hydrate of potash above the melting-point of the latter, it evolves hydrogen and becomes decomposed; it appears that this reaction does not stop with the probable formation of an acid which unites with the potash, but goes further, for in the product of this reaction we did not find the expected acid; but it is our intention to pursue this subject if ever we are so fortunate as to procure a larger supply of material.

Concentrated sulphuric acid dissolves readily sycocerylic alcohol with evolution of heat, forming a brown liquid which remains unaltered for some time. The liquid yields, on addition of water, a resinous viscid substance which melts at the temperature of boiling water, and is but very sparingly soluble in alcohol. Ether and chloroform dissolve it with facility, and, on evaporating, merely leave the resinous product in its original amorphous state. The aqueous liquor, saturated with carbonate of barium, gave no indications of the presence of a conjugated sulphuric acid.

Chlorine, bromine, and iodine act readily on sycocerylic alcohol: if solutions of these reagents are used, crystalline compounds are formed. The iodine compound is of a yellow colour.

In one experiment we obtained, on acting with sodium-alcohol on acetate of sycoceryl, a substance which resembled the alcohol just described, and which gave, on burning, the following numbers:—

- I. 0.2873 grm. of substance gave 0.8885 grm. carbonic acid, and 0.3042 grm. water.
- II. 0·1887 grm. of substance gave 0·5843 grm. carbonic acid, and 0·2017 grm. water.

The per-centage derived from these results agrees nearly with the composition of the ether of sycoceryl, C_{72} H_{58} O_4 , which might be formed under favourable conditions. This formula would require the following numbers:—

		Analysis.		
		I.	II.	
$C_{72} = 432$	$85 \cdot 376$	84.81	84.5	
$H_{58} = 58$	11.462	11.76	11.87	
$O_4 = 16$	3.162			
$\overline{506}$	$\overline{100.000}$			

Action of Chloride of Phosphorus on Sycocerylic Alcohol.

For the purpose of preparing the chloride of sycoceryl, we employed pentachloride of phosphorus and a solution of sycocerylic alcohol in benzol. At common temperatures no reaction took place, but when the temperature was elevated to about 60° C. (140° Fahr.), hydrochloric acid was given off, and the pentachloride gradually disap-After the disengagement of hydrochloric acid had ceased, the liquid was removed from the remaining pentachloride and washed with water, and afterwards with After the benzol had been got rid of by keeping the liquid for an alkaline solution. some time in a warm place, a viscid residue was obtained, which was soluble with great difficulty in alcohol, but easily soluble in ether or chloroform. These solutions, after evaporation, deposited this substance again in its original sticky state. experiments, which were carried out only on a very small scale, a crystalline substance was formed besides the amorphous greenish compound. This crystalline substance differed in its properties from the original alcohol. It therefore seems probable that a slight excess of pentachloride (or the phosphoric acid formed during the reaction) destroys to a great extent the chloride of sycoceryl formed during the reaction; or at all events, phosphate of sycoceryl, which is produced simultaneously and predominates, cannot be separated from the chloride. We are therefore at present unable to give a description of the chloride of sycoceryl in its pure state.

Benzoate of Sycoceryl.

Chloride of benzoyl dissolves with the greatest facility a large quantity of sycocerylic alcohol at common temperatures, but no hydrochloric acid is disengaged; probably, therefore, no reaction takes place at ordinary temperatures, but if heat is applied the liquid soon commences to give off hydrochloric acid. When the evolution of hydrochloric acid has ceased, the mixture is allowed to cool, when it solidifies to a fibrous Any excess of chloride of benzoyl is removed after the reaction by crystalline mass. throwing the mixture into a solution of bicarbonate of potassium, whereby a resinous The whole being kept warm for several hours, all the chloride of During this process a slight smell, somewhat like benzoate of benzovl is decomposed. The resinous mass, after removal from the saline liquors, is ethyl, is perceptible. washed several times with warm water; it is now free from benzoic acid and chloride of benzoyl. On boiling the resinous mass with absolute alcohol, a trace of a yellowish secondary product dissolves, leaving the principal quantity undissolved, which then appears as a white crystalline mass.

The product thus obtained, on being boiled with a large quantity of ether, and the solution allowed to cool, is procured in small crystals, which are soluble with difficulty in ether. Absolute alcohol dissolves only a trace of this substance, and when boiled with it deposits the dissolved part on cooling in minute spherical aggregations of crystals, which under the microscope are seen to be prismatic.

MDCCCLX.

The best solvent for this compound is benzol, it being soluble in all proportions in this liquid. On evaporating the solution, the substance is left behind in fine prismatic crystals. Chloroform behaves like benzol; but the crystals obtained from this solvent are much finer, and can be obtained of considerable size.

In order to ascertain the nature of the compound produced by the action of chloride of benzoyl on sycocerylic alcohol, we decomposed it by means of sodium-alcohol, which we found to be preferable to any other form of caustic alkali. Even with this reagent the decomposition is effected only with difficulty; possibly on account of the new substance being only sparingly soluble, and also on account of the benzoate of sodium which results not being much more soluble in the alcohol. However, after boiling for some time, the benzoate of sycoceryl disappears. On addition of water a voluminous substance was separated, which proved to be the regenerated alcohol of sycoceryl.

The aqueous liquid saturated with an acid soon formed a crystalline precipitate, which, on removal with ether, proved to be benzoic acid.

The foregoing experiments bear conclusive evidence that the alcohol of sycoceryl behaves toward chloride of benzoyl in a manner perfectly analogous with that of other members of the alcoholic group, that is to say, a benzoate of the ether radical being formed.

After having shown that the substance separated by sodium-alcohol may be regarded as the alcohol of the new radical sycoceryl, it became desirable to have a synthetic proof of this theory; and it occurred to us that if we could succeed in combining the sycocerylic alcohol again with the radical of othyl (acetyl), and thus reproduce the original substance, which we have called acetate of sycoceryl, it would be the best possible confirmation of our views. In order to test this, we accordingly brought chloride of othyl (acetyl) in contact with sycocerylic alcohol. At ordinary temperatures no action took place; but when a little heat was applied the alcohol was dissolved, and the liquid commenced to boil, giving off copious fumes of hydrochloric acid. After the reaction had ceased heat was again applied, and the whole subjected to the boiling temperature for some time, in order to get rid of the excess of othyl. After cooling, the resulting product was boiled with water, when a heavy oily body separated. The boiling with water was continued for some time, until at last the oily liquid became perfectly solid and beautifully crystalline; indicating at once that a substance had been formed differing from the original alcohol, which, it will be remembered, is fluid at the temperature of boiling water.

This white crystalline substance was now dissolved in boiling alcohol, of which it required a considerable quantity, and subsequently allowed to cool. When almost the whole had dissolved a small quantity of a compound was left behind, which at last melted, being evidently a new substance, the probable product of the action of a small quantity of oxychloride of phosphorus which contaminated the chloride of othyl.

On cooling, the filtered liquid commenced to crystallize, yielding beautiful iridescent flat prismatic crystals, which sparkled with the colours of the rainbow in the solution,

like chlorate of potash does in the act of crystallizing. The crystallized substance produced in this experiment proved to be in every respect identical with the natural acetate of sycoceryl, and thus gave the most direct confirmation to our theoretical views.

Having thus established the nature of the sycocerylic alcohol, it became desirable to produce also the acid which would be homologous with benzoic acid, and would stand in regard to this acid in such a relation as palmitic acid does to the lower members of the series to which it belongs. A small quantity of the alcohol was therefore boiled for about six hours with dilute nitric acid. A feeble reaction was indicated by the slight evolution of nitrous fumes, and after some time the sycocerylic alcohol became of a dark yellow colour, and presented a resinous aspect. After digesting for six hours, the resinous product was removed, washed with water, and dried. This substance was readily soluble in warm alcohol, and on cooling a white crystalline substance was deposited.

This crystalline substance had all the characters of an acid; it was perfectly soluble in an aqueous solution of potash or ammonia, and gave with an alcoholic solution of acetate of lead a copious precipitate. Although this reaction showed that we had obtained an acid which possesses all the properties that might be anticipated of an acid corresponding to our alcohol, we could not, with the very small quantity of substance at our disposal, get enough of it in a pure state for analysis, on account of the yellow nitrocompound (apparently the nitro-acid of the new acid) adhering with great obstinacy to it, and accompanying it in all its compounds and solutions. In order to exclude the formation of this secondary product, we tried the action of chromic acid on sycocerylic alcohol; a small quantity of the alcohol was boiled with a moderately concentrated solution of chromic acid for about eight hours. The product so obtained was washed and boiled with a dilute solution of potash, but after saturating this alkaline solution with an acid, no precipitate was formed, and it was altogether impossible to detect any acid; therefore we must conclude that this acid was not formed by this treatment.

On one occasion, on repeating this experiment, we accidentally observed, among the products of the action of chromic acid on sycocerylic alcohol, a crystalline body; on treating the mass with dilute alcohol, this product was procured in large flat prisms, resembling somewhat in appearance acetate of sycoceryl, but differing in its melting-point, and was perfectly neutral. From the mode of formation, it might be inferred that we had obtained the aldehyde ($C_{36}H_{28}O_2$) corresponding to our alcohol, but the minuteness of the quantity procured rendered it impossible to decide this point.

For the present we must content ourselves with the foregoing account of the compounds of the radical sycoceryl, the very small amount of the substance at our disposal being barely sufficient for the performance of those experiments which we have described.

The great interest which naturally attaches to this new homologue of the benzylalcohol series will be a sufficient inducement for us to take up this subject again, for the purpose of studying its derivatives, should we be so fortunate as to obtain a further supply of raw material. On reviewing the members of which benzylic alcohol of CANNIZZARO is the type, and with which our new alcohol must be classed, it will be perceived that there are still many gaps to be filled up in their series.

On comparing the properties of our sycocerylic alcohol with those of benzylic alcohol, very little resemblance will at first be traceable between them; but when it is remembered that there are not fewer than ten steps between benzylic and sycocerylic alcohol, this difference of properties is easily accounted for; more particularly if we take into consideration a similar case in another homologous series, the links of which are more fully known. The change in the properties of the acetic acid series, for example, by each increment of increase of C_2H_2 , is quite as remarkable; and when we compare acetic acid on the one hand with palmitic acid on the other, the dissimilarity is not less remarkable than if we compare sycocerylic alcohol, $C_{36}H_{30}O_2$, with benzylic alcohol, $C_{14}H_8O_2$.

In conclusion, we may mention that benzylic alcohol, and consequently also cuminylic alcohol, are generally considered to be homologues of phenyl-alcohol (carbolic acid); kresyl-alcohol would be isomeric with benzyl-alcohol, and carvacrol and thymol with cuminylic alcohol. On comparing these substances we find that this view is not tenable, and that there exist in reality at least two distinct series of isomeric compounds, the types of which are benzylic alcohol on the one hand and phenylic alcohol on the other.

The crystalline substance which adhered to the acetate of sycoceryl, and which it will be recollected was left in part undissolved when the acetate was dissolved out with ether, can be obtained in only very small crystals. It is perfectly neutral, and we did not succeed in obtaining any derivative from it calculated to throw light on its true nature. The quantity was indeed extremely small, and we therefore content ourselves with giving the ultimate analysis of it.

^{0·1806} grm. substance gave 0·5070 grm. carbonic acid, and 0·2000 water. These numbers give the following per-centage:—carbon 76·56, hydrogen 12·30.