LXXVIII.—*The Resins of Ficus rubiginosa and Ficus macrophylla.*
(Preliminary Notice.)

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IN the year 1859, De la Rue and Müller communicated a paper to the Royal Society (*Phil. Trans.*, 1860, 43), in which they described the results of an examination of the resin of *Ficus rubiginosa*. A sample of this resin, which had been sent to the Paris Exhibition of 1855, was brought under their notice by Sir Wm. McArthur. They separated from it:—(1) a resinous portion readily soluble in cold alcohol (73 per cent.); (2) a white, crystalline portion, readily soluble in warm alcohol (14 per cent.); and (3) caoutchouc, &c. (13 per cent.). The resinous portion soluble in cold alcohol was but little investigated, owing to difficulties met with in attempts to purify it. The crystalline material yielded two substances, one in very small quantity (too small for detailed examination), and a second in comparatively large quantity, which was found to contain

Carbon	79·11 and 79·08 per cent.
Hydrogen	10·23 „ 10·34 „

The formula $C_{20}H_{16}O_2$ (old notation) was therefore ascribed to it, and it was named sycoceryl acetate, because on hydrolysis it yielded acetic acid and an alcohol to which the name sycoceryl alcohol was given. In order to obtain the acetate pure, De la Rue and Müller first repeatedly crystallised their material from hot alcohol, then they partially dissolved it in ether at 30° , and, having allowed the ethereal solution to cool, filtered off a small quantity of flocculent matter (the other crystalline substance above referred to as present in small quantity). On distilling off the ether, crystals were obtained which were apparently pure. These crystals were very similar to those of cholesterol, and melted at from 118° to 120° . On hydrolysis, the substance yielded acetic acid, and an alcohol which was purified simply by recrystallisation from warm alcohol. It is described as melting at about 90° , and as crystallising in spherical masses resembling wavelite. The numbers obtained on combustion were as follows:—

Carbon	82.94 and 81.85 per cent.
Hydrogen	11.57 „ 11.20 „

De la Rue and Müller state, however, that on one occasion they obtained on hydrolysis a substance closely resembling that just described, but giving on combustion

Carbon	84.81 and 84.50 per cent.
Hydrogen	11.76 „ 11.87 „

and they suggest that this may be the ether corresponding to the alcohol.

It has been thought necessary to give this brief *résumé* of the work of De la Rue and Müller for the sake of comparison with the results obtained by us in the examination of very similar products.

Some three years ago, through the kindness of Mr. J. H. Maiden, Curator of the Technological Museum in Sydney, one of us received a small quantity of the liquid which exudes from *Ficus rubiginosa* when the tree is punctured or wounded. After evaporation on the water-bath, an excessively sticky mass remained, which looked very unpromising. It yielded some soluble matter to alcohol, and was finally extracted thoroughly with boiling alcohol, leaving a residue resembling caoutchouc, which was not further examined. The alcoholic extract did not deposit any crystalline matter on cooling, but, on dilution or evaporation, a nearly white substance was obtained, from which, so far as the experiments went, no crystalline substance could be separated. It was therefore boiled with alcoholic potash; on dilution, a white substance separated, which, to all outward appearance, was the same as the original, and showed no signs of crystallisation. The alkali solution, however, was found to yield,

on acidification, a small quantity of *cinnamic acid*, which was identified by its actions and melting point. An ethereal extract of the *alkaline* solution, after boiling off the alcohol, and subsequent evaporation, left a residue with a distinct smell of hyacinths. Possibly, therefore, traces of cinnamic alcohol had been formed during hydrolysis, but if so there was not sufficient for identification. The juice obtained from *Ficus rubiginosa*, therefore, if it contain the crystalline substances above described, does not readily yield them in a crystalline form. Possibly a more careful examination would give more satisfactory results, but as a quantity of the *dried* resin came to hand and promised much better results, our attention was directed to it.

We are indebted to Mr. Maiden also for a supply of the dried resin both of *Ficus rubiginosa* and *Ficus macrophylla*. We first directed our attention to the former. A preliminary experiment having convinced us that crystalline substances were present, the resin was extracted with boiling strong alcohol till nothing more could be dissolved. The residue consisted of a substance resembling caoutchouc (not further examined), fragments of bark, &c. The alcoholic extracts, on cooling, deposited impure crystals, which were then repeatedly crystallised from boiling alcohol. The second crystalline substance described by De la Rue and Müller as obstinately adhering to the sycoceryl acetate was not observed by us, nor, on dissolving in ether at 30° as recommended by them, did any flocculent substance separate as the ether cooled. In fact, by repeated crystallisation from boiling alcohol, a substance was obtained which appeared homogeneous under the microscope, and the melting point of which seemed to be constant after further crystallisation. In order to determine the melting point, the purified crystals were crystallised twice more from boiling alcohol (nearly absolute). They then melted at 120—121°. After a third crystallisation from the same medium, the melting point remained the same. The substance thus obtained exhibited the closest external resemblance to the sycoceryl acetate described by De la Rue and Müller, except that the melting point found by us was slightly higher than that given by them. It formed shining plates, often six-sided, and much resembled cholesterol in appearance.

An examination of the resin from *F. macrophylla* gave precisely similar results in so far as this crystalline substance was concerned, but no comparison has yet been made between the two samples of resin to ascertain whether or not there are other differences. The crystalline substance obtained from *F. macrophylla* was shown to be identical with that from *F. rubiginosa*, by its appearance, melting point, reactions, and analysis.

On submitting it to combustion, however, numbers were obtained

which differed very considerably from those obtained by De la Rue and Müller. Our numbers lead to the formula $C_{34}H_{56}O_2$, a result which is confirmed by experiments to be presently described.

	Theory for		From <i>F. rubiginosa</i> .	
	$C_{34}H_{56}O_2$.	$C_{34}H_{54}O_2$.	I.	II.
Carbon*	82·26	82·59	82·04	81·64
Hydrogen	11·29	10·93	11·63	11·45
Oxygen	6·45	6·48	—	—
	100·00	100·00		

	From <i>F. macrophylla</i> .				
	III.	IV.	V.	VI.	VII.
Carbon*	81·85	81·81	82·24	82·15	82·02
Hydrogen	11·54	lost	11·20	11·25	11·50
Oxygen	—	—	—	—	—

It will be seen that the figures for carbon are about 3 per cent., and those for hydrogen about 1 per cent. higher than those obtained by De la Rue and Müller for the substance they examined. Of course, the numbers do not definitely decide between the alternative formulæ given by us, but as far as they go they favour the formula $C_{34}H_{56}O_2$, and this formula is further confirmed by the results of the combustions of the alcohol obtained by hydrolysis.

On warming with alcoholic potash or soda, the compound was readily hydrolysed, and the liquid, on cooling, deposited another substance, which crystallised in spherical masses of needles, just as described by De la Rue and Müller, acetic acid being formed at the same time. The crystalline mass was filtered off and recrystallised several times from very strong alcohol; in fact, till the melting point was not altered by further crystallisation. It then melted at 114° , a temperature considerably higher than that given for the substance obtained by De la Rue and Müller (about 90°). On combustion, it gave results differing considerably from those first obtained by the authors just named, but agreeing fairly well with those given by a substance which they obtained on one occasion by hydrolysis (*vide supra*). The following are the numbers:—

* It is usual to give the actual analytical figures in these cases, but in the present instance the paper was written during a holiday at a distance from Adelaide, and in the notes hastily written down for the purpose from the note-books, it happened that only the results were transcribed. The same remark applies to the combustion of sycocerylic alcohol given further on in the paper.—E. H. R.

	Theory for		I.	II.	III.
	$C_{32}H_{54}O$.	$C_{32}H_{52}O$.			
Carbon	84.58	84.95	84.67	84.45	84.20
Hydrogen	11.89	11.50	12.11	12.03	11.98
Oxygen	3.53	3.55	—	—	—
	100.00	100.00			

These figures favour the formula $C_{32}H_{54}O$ rather than the other, and therefore so far confirm the formula $C_{34}H_{56}O_2$ for the acetate.

In order to ascertain whether acetic acid was formed during hydrolysis, a portion of the original substance was warmed with alcoholic soda, the alcohol distilled off, the residual liquor filtered, and the filtrate acidified with pure sulphuric acid and distilled. The distillate, on neutralisation with barium carbonate, yielded a soluble barium salt which behaved as barium acetate, and was analysed with the following result:—

0.5045 gram of substance gave 0.4645 gram $BaSO_4 = 0.27312$ gram of barium = 54.13 per cent.

Theory for $Ba(C_2H_3O_2)_2$ 53.72 per cent.

A weighed portion of the acetate was then taken and hydrolysed as above, but the crystalline substance was carefully extracted (after distilling off the alcohol) by ether, the ethereal solution put into a weighed flask, and the ether distilled off. The residue was first dried as far as possible at 100° , then just melted, air being gently blown into the flask till it no longer lost weight. The following are the figures:—

3.8844 grams of the acetate gave 3.6045 grams of the product of hydrolysis = 92.8 per cent.

The equation

requires 91.53 per cent., a very fair result, considering the difficulties of the operation. A similar equation for substances having the compositions of those examined by De la Rue and Müller would require 86.18 per cent.

Molecular weight determinations of the product of hydrolysis were then made by Raoult's freezing point method. The following are the details, acetic acid being used as the solvent:—

I. Weight of substance taken .. 0.1725 gram.
 „ solvent „ .. 24.033 grams.

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Freezing point of solvent (arbitrary scale)	1.443°
" " solution "	1.377°
Actual depression of freezing point	0.063°

Therefore, using the constant 3860 given by Ostwald for acetic acid—

$$\text{Molecular weight} = \frac{3860 \times 0.1725}{0.063 \times 24.033} = 439.$$

II. Weight of substance taken ..	0.175 gram.
" solvent " ..	23.595 grams.

Freezing point of solvent (arbitrary scale)	2.660°
" " solution "	2.592°
Actual depression of freezing point	0.068°

Therefore, as above, molecular weight

$$= \frac{3860 \times 0.175}{0.068 \times 23.595} = 421.$$

These figures come very fairly near that calculated for the formula $C_{32}H_{54}O$, namely 454, considering that a difference of 0.01° would make a difference of about 70 in the molecular weight. The formula for the substance described by De la Rue and Müller, $C_{16}H_{30}O$, would require a molecular weight of 262.

We propose to submit these substances to a closer examination, and to study their oxidation products. Experiments are now in progress having these objects in view.

The mother liquors from the earlier crystallisations of the acetate deposited on standing an apparently amorphous substance, also some long needles. These substances have not yet been examined.