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LXVII.—*Chemical Examination of the Oleo-resin of Dacryodes Hexandra.*

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The specimen of oleo-resin examined was obtained from trees growing on Pond Mountain, in the island of Montserrat, W.I. The resin was accompanied by some leaves of the tree from which it had been extracted, and these were submitted to the Director of Kew Gardens for identification. The plant was pronounced to be the 'mountain gommier,' or incense tree, *Dacryodes hexandra*, and it appears to be abundant throughout the West Indies. The oleo-resin is collected from the living trees, and is largely used for lacquer (see *Kew Bulletin*, 1891, 149).

The crude oleo-resin was a very sticky, white solid with a strong aromatic odour, and contained a few fragments of leaves and woody matter. It was first submitted to steam distillation, to separate the essential oil, and during the process, the resin melted sufficiently to form a layer above the water, but it was never very fluid. After all the oil had distilled over, the soft residual mass was removed from the flask and on cooling it solidified. The water which remained with the resin was evaporated to a small bulk, but nothing was left except a few tarry drops and a slight sticky residue.

The oil separated from the distillate amounted to 16 c.c. for every 100 grams of the oleo-resin employed, and I am indebted to Professor Tilden for its examination. After shaking with a saturated solution of sodium hydrogen sulphite, 60 c.c. of the oil were not reduced in volume, although the aqueous solution contained a trace of an aldehyde which reduced silver. The oil, washed with water, dried and distilled, gave a series of fractions from 156° to 180°, and a viscid, brown residue of higher boiling point which was too small in amount for further examination. Phenols were practically absent from the various fractions. The fractions of low boiling point, 156—163°, contained a large proportion of *lævorotatory pinene*, which was identified by its odour, boiling point, and by the preparation of the familiar monohydrochloride melting at 128°.

The fraction boiling at 173—176° was saturated with dry hydrogen chloride; it gave a purple colour at first, which faded, and on cooling to about −10° the whole solidified, forming a nearly white, crystalline mass. After crystallisation from ether, this hydrochloride formed long, flat prisms melting at 71°, and by its odour and melting point served to establish the presence of *sylvestrene*. The fraction of hydrocarbon from which this was obtained was strongly lævorotatory, and

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it would have been interesting, if possible, to separate the pure hydrocarbon for comparison with Atterberg's sylvestrene, which is dextrorotatory (*Ber.*, 1878, ii, 1206); the quantity of material was, however, far too small for this purpose.

Limonene was probably present in small quantity, but phellandrene, terpinene, and cineol could not be detected.

The estimated proportions of constituents of the oil were:

Pinene (lævorotatory).....	64 per cent.
Sylvestrene (lævorotatory).....	17 ,,
Other liquids, undetermined	6—7 ,,
Resin and loss.....	12—13 ,,

The resinous mass left after steam distillation was reduced to coarse powder, and alcohol was added until the bulk was about doubled. After a few hours, the dark yellow liquid was drained off with the help of the suction pump, and a mass of very small, nearly white needles, mixed with particles of vegetable tissue, remained on the filter, the crude product from 500 grams weighing 109 grams. The solid was crystallised several times from boiling 80 per cent. alcohol (methylated spirit) until the melting point was constant.

The dark yellow filtrate, containing the part soluble in cold alcohol, left a soft varnish on evaporation. This substance has not been fully investigated, but it does not contain any appreciable quantity of ordinary resin acids.

The crystalline compound is deposited from all solvents in tufts of white needles and melts at 166—167°; 100 grams of absolute alcohol dissolve 5·935 grams, and 100 grams of benzene dissolve 7·810 grams at 16°; it is quite insoluble in water.

On combustion, the following percentages were obtained:

	I.	II.	III.	Mean.	Calculated for $C_{22}H_{36}O$.	Calculated for $C_{25}H_{44}O$.
C	83·61	83·58	83·10	83·43	83·52	83·33
H	11·49	11·69	11·32	11·50	11·42	12·22
O (by difference)				5·07	5·06	4·44

The molecular weight of the substance was determined by the cryoscopic method with a Beckmann apparatus, the results being checked by determinations with pure naphthalene. Using benzene as the solvent, the values for the molecular weight were 366, 366, and 372, but with acetic acid as solvent the results were lower, namely, 312, 314, and 358, the mean being 368 in benzene and 328 in acetic acid. The value for $C_{22}H_{36}O$ is 316. It appears probable therefore that the molecular weight is greater than this, and the formula $C_{25}H_{44}O$, corresponding to the molecular weight 360, seems to be more nearly in conformity with experimental results.

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The substance is slightly soluble in concentrated sulphuric acid, and is reprecipitated on the addition of water. Bromine, dissolved in petroleum, and added to a petroleum solution of the compound, is very slowly decolorised, colourless, solid globules being deposited; these probably consist of a brominated derivative, but the substance changes in a short time to a purplish mass, and is unsuitable for analysis. It could not be crystallised from any solvent, and the corresponding chlorine derivative, which is also uncrystallisable, could not be obtained pure. It is insoluble in aqueous potash, and showed no sign of hydrolysis when boiled with strong alcoholic potash for 8 hours, the original substance being recovered unchanged. Fusion with potash also produced no change until the temperature was raised above the melting point, when charring occurred.

Concentrated nitric acid, added to an acetic acid solution, gives a yellow colour; such a solution was heated for 12 hours with fuming nitric acid to complete the reaction, and, on the addition of water, a soft yellow, uncrystallisable substance was precipitated, which was not changed by further heating with the acid. The yellow substance contained nitrogen varying in amount between 10·23—11·10 per cent.; this corresponds nearly to the formula $C_{25}H_{40}O(NO_2)_4$, which requires N = 10·3 per cent.

The substance being soluble in glacial acetic acid, an attempt was made to oxidise it by means of chromic acid. A yellowish precipitate was obtained, which was dissolved in dilute caustic soda solution, filtered, and reprecipitated with hydrochloric acid. The product was soluble in alcohol, benzene, petroleum, and chloroform, but was uncrystallisable; it began to melt at about 149°. It became very strongly electrified when powdered. The oxidation product seemed to possess feeble acid properties, as it dissolved in caustic alkalis, and gave precipitates with lead and barium salts, but the molecular weights deduced from analyses of these salts were not concordant, and the cryoscopic method was therefore used. Benzene being the solvent, a depression of the freezing point was observed corresponding to 812 for the molecular weight. On combustion, the following percentages of carbon and hydrogen were obtained:

C = 72·91 and 72·01; H = 8·65 and 8·90.

$C_{50}H_{72}O_{10}$ requires C = 72·11; H = 8·65 per cent.

The molecular weight for $C_{50}H_{72}O_{10}$ is 832, and these results seem to indicate that, in the process of oxidation, two molecules of the substance are condensed into one.

An attempt was made to reduce the compound by heating in sealed tubes with phosphorus and concentrated hydriodic acid, but the product was a varnish-like substance which contained iodine. After treatment with zinc dust in acetic acid and removal of the iodine, it

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was still of the consistence of vaseline, which it closely resembled. Distillation with zinc dust gave a paraffin-like product, very similar to that which was obtained by reduction with hydriodic acid. The solid part of the distillate had a strong, greenish fluorescence, resembling that of commercial "petroleum jellies."

The remarkable indifference to the action of alkali and oxidising agents led at first to the idea that this compound must have the constitution of an ether, and not that of an ester or an alcohol. It was found, however, that on heating with acetic anhydride, a substance was produced which was evidently an acetyl derivative; this crystallises, not, like the original substance, in needles, but in small, lustrous scales, and melts at 199°. The percentage of acetyl was determined by boiling with alcoholic potash for half an hour, diluting with water, distilling off the alcohol, filtering, acidifying with sulphuric acid, and distilling off the acetic acid. The distillate was treated with excess of well-washed barium carbonate, and the barium acetate dried at 130°, the result being checked by conversion of the acetate into barium sulphate. On analysis:

0·9942 gave 0·2834 $Ba(C_2H_3O_2)_2$ and 0·2590 $BaSO_4$.

This corresponds to acetyl = 9·61; theory requires 10·69 per cent.

As the acetylation seemed incomplete, the process was repeated, the boiling being continued for $2\frac{1}{2}$ hours with excess of acetic anhydride; the product then melted at 200°, and contained 9·49 per cent. of acetyl. It was then heated in a sealed tube with acetyl chloride for 4 hours at 100°; there was no pressure in the tube after cooling, and the product, which melted at 199·5°, contained 9·27 per cent. of acetyl.

There can be little doubt, therefore, that the substance under investigation is a monohydric alcohol, $C_{25}H_{43}\cdot OH$, and that it is a saturated compound.

A substance obtained from birdlime has been described by Personne (*Compt. rend.*, 1884, **98**, 1586) under the name ilicic alcohol, which in properties approaches very nearly to the compound described in this paper, and is probably identical with it. As the mean of five analyses, it was found to contain carbon = 83·36, hydrogen = 12·20 per cent., and the formula assigned to it was $C_{25}H_{44}O$, which has also been adopted for the substance described in this paper. The melting point of the acetyl derivative is given by Personne as 204—206°.

Divers and Kawakita (Trans., 1888, **53**, 274) have also isolated a similar alcohol from birdlime, but although in melting point and composition their compound agreed very closely with Personne's ilicic alcohol, they failed to obtain an acetate by treating it with acetic anhydride.

Cork is known to yield a crystalline compound, to which the name

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cerin has been given. A specimen of cerin, prepared many years ago by Professor Tilden, was found to melt at 251°. It was unaltered by boiling with acetic anhydride, and was so slightly soluble in cold benzene that an attempt to determine its molecular weight by the freezing point method was only imperfectly successful. The number 355 was obtained, and this approximates to the value 374, calculated for the formula $C_{26}H_{46}O$, attributed by Divers and Kawakita (*loc. cit.*) to mochylic alcohol, which is also present in Japanese birdlime. Mochylic alcohol melts at 234°, and, like cerin, does not give an acetate. Combustion of this specimen of cerin, however, gave the following numbers, which show that it is not a substance of the same character:—

C = 79·32 and 79·22; H = 10·98 and 11·01 per cent.

Cerin was but slightly soluble in boiling alcohol, even with the addition of potash, by which it was unaffected; no acids could be detected in the solution, and the substance was recovered unchanged. Notwithstanding the large proportion of oxygen it contains, this specimen of cerin is therefore apparently neither an acid nor an ester.

This investigation has been carried out under the direction of Professor Tilden, whom I wish to thank for his valuable advice and assistance.

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