ERRATA.

The following species were admitted into the previous paper in error, and the names should therefore be deleted from the list.

Cyathea Cunninghamii Hook. f.

The plant from Cooper's Knobs is no doubt *Hemitelia.* However, I have reintroduced the species for a plant from Peraki Reserve, on the authority of Dr. Holloway. This has the complete indusium of *Cyathea.* —R. M. L.

Festuca multinodis Petrie.

No form of *Festuca* in this neighbourhood is anything like Petrie's plant, which is very distinct. Very few individuals of *F. novae-zelandiae* have even three nodes.—A. W.

Scirpus antarcticus Linn.

Is recorded in error for *S. aucklandicus* Boeck, by which it should be replaced.

Carex flava Linn. var. *cataractae* R. Br.

I have recorded this from Castle Rock; but I find on examining my herbarium again that there is possibly a mistake in the locality. The species should therefore be removed from the list, pending confirmation of the locality.—R. M. L.

Libertia grandiflora Sweet.

This is probably only a form, though a distinct form, of *L. ixioides.*

Plantago spathulata Hook. f.

This is an erroneous identification of *P. Raoulii* Decaisne.

A Chemical Investigation of Pintsch Oil.

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It is well known that the cracking of saturated oils leads to very complex products, which are generally highly unsaturated and very volatile. The gases obtained are of high illuminating-power, and have long been used by various railway companies for this purpose. In New Zealand, kerosene (density 0·860), on cracking, yields such a gas, which is known as Pintsch gas, and at the same time a quantity of tarry matter, and the gas itself on compression into the storing-cylinders deposits a surprisingly large amount of water and a considerable amount of a crude light oil which may be appropriately designated Pintsch oil. At present the only commercially important product of this cracking is the illuminating-gas, the only use to which the Pintsch oil is put being in carburetting gases of low illuminating-power, and to a slight extent in preventing napthalene from crystallizing in gas-pipes. Apart from this it is practically wasted, and, as about 15,000 gallons are produced annually, it becomes a matter of commercial importance to find some use for it.

The oil at present is unfit for commercial use because of its stench, its extreme volatility and inflammability, and especially its property of depositing a gummy layer on all vessels in which it is kept. If it were not for this last objection the oil would make an excellent motor-spirit.

Armstrong and Miller have published a paper (*J.C.S.*, 1886, vol. 49, T., 74) on "The Pyrogenesis of Hydrocarbons," in which an oil similar to Pintsch oil is described. In their oil they showed the presence of paraffins, naphthenes, olefines, pseudacetylenes, and aromatic hydrocarbons, ethylene, butadiene, and benzene being the chief constituents.

The Pintsch oil itself is light-yellowish and very mobile, possessing a nauseous, persistent smell, similar to crude acetylene. It contains large amounts of dissolved gases which are expelled on warming, the liquid beginning to boil at 35° C. and distilling irregularly up to about 112° C., at least half of the oil being benzene, and another quarter toluene. All the fractions, more especially the lower ones, are highly unsaturated. Above 112° C. the residue rapidly darkens, and decomposes spontaneously with evolution of pungent-smelling white fumes.

Oxidation with permanganate of a fraction boiling between 60° and 90° C. yielded formic and probably butyric acids, thus indicating the presence of *n*-amylene in the original oil, in agreement with Armstrong and Miller's conclusions.

As it was thought that the "gumming" of the oil would probably be due to polymerization of the unsaturated hydrocarbons present, experiments were carried out with a view to increasing the speed and amount of the action. The action of sodium wire at 60° C., in a sealed tube, was tried on the original oil, and on a fraction consisting mostly of butadiene (obtained by condensing Pintsch-oil vapour by means of a freezing mixture). There was no perceptible action with the oil itself, but the low boiling-fraction gave a considerable quantity of a soft rubber-like mass, differing in its solubilities from true rubber. It was probably a polymer which had not reached the rubber stage.

Most of the work done on the chemistry of the oil was performed on bromides obtained from the various fractions. To obtain these without excessive decomposition it is essential that the addition of bromine should be cautious and slow (liquid bromine is too vigorous; dropping bromine through a layer of bromine water was tried, but the best results were obtained by the gradual mixing of the vapours from Pintsch oil and bromine), and the reaction-flask be constantly cooled by a stream of water. The method adopted was to pass the vapour obtained by warming a large quantity of Pintsch oil into ammoniacal silver-nitrate solution, then into the absorption-flask (containing a layer of liquid Br_2), then through another small quantity of Br_2 to catch any escaping unsaturated gas, then through a bubbler of NaOH solution, and finally into a cylinder where the residual paraffinoid gas was collected by downward displacement. Even with all precautions to guard against overheating, each shaking of the absorption-flask caused a torrent of HBr fumes to rush over (the reason for the formation of this substance is not apparent); the bromides in the absorption-flask, though at first clear, gradually turned dark brown, and much decomposition occurred. The chlorides and iodides, which were also prepared in small amount, showed the usual gradation of properties, the order of decreasing stability being chloride, bromide, iodide. The iodides decomposed at once, producing a carbonaceous residue and methyl iodide.

When the absorption-flask became quite cold the contents practically solidified. The liquid bromides were slowly filtered off, using a Buchner funnel, and the solid bromide, after recrystallization twice from alcohol, was obtained as a pure-white, powdery mass, appearing under the microscope as very irregular tables with a few short and thin prisms (M.P. 113° C.; Br percentage, by Stepanow's method, 85·9). This is in good agreement with the data obtained by Armstrong and Miller for their solid butadiene tetrabromide, so that the more volatile parts of Pintsch oil consist largely of butadiene. This solid bromide is extremely stable to most reagents. Alcoholic potash, zinc-copper couple in boiling alcohol, and boiling concentrated nitric acid have alike very little action on it. The vapours of both the liquid and solid bromides have an extremely irritating effect on the eyes.

Large quantities of the liquid bromides were prepared and fractionally distilled at atmospheric and at reduced pressure. Purification proved difficult, but repeated distillations at length yielded 40 c.c. of a clear colourless fraction (B.P. 58–66° at 23 mm.; density, 1·825 at 13° C.) which remained stable on keeping. The substance was very refractory in combustion, the values finally obtained being—C, 21·1 per cent.; H, 3·5 per cent. Analysis* (Carius method) gave 75·9 per cent. bromine, so that the fraction was probably a slightly impure specimen of butylene dibromide. (Calculated percentages—C, 22·2 per cent.; H, 3·7 per cent.: Br, 74 per cent.) Thus butylene is present in considerable amount in the lower boiling fractions of Pintsch oil, so that the liquid dibromides that Armstrong and Miller lost by fire would probably have yielded them butylene on treatment with zinc-copper couple, thus completing their list of olefines present. The question as to which of the butylene isomers this substance is was not definitely settled, but probability points to the normal olefine.

The liquid bromide, also, is very unreactive, KOH (alcoholic and 30 per cent. aqueous), HNO_3, and KCN having very little effect. Zinc-dust or zinc-copper couple in alcohol reduces it, $SbCl_5$ liberates bromine, PCl_5 dissolves without action. Anhydrous $AlCl_3$ has a rather peculiar action, which is the same with the pure bromide or its benzene solution. Clouds of HBr are given off, and a dark-brown oil,† insoluble in benzene, is formed.

Further fractions of the Pintsch oil were brominated, and one boiling between 55° and 65° gave evidence of the presence of amylene and hexylene, in agreement with the results found by Armstrong and Miller, who used an oxidation method.

In the preparation of the bromides by the method already detailed it was found that the ammoniacal silver-nitrate solution, through which the vapour from the Pintsch oil was passed, rapidly turned black, while a copious precipitate formed. This is in direct opposition to the results recorded by Armstrong and Miller, and indicates that true acetylenes are present in at least the lower fractions of Pintsch oil. The gas that passed

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* The Stepanow method, which was previously tried, gave results which, though consistent, were always about 14 per cent. low, so that the method is not always reliable. Later experiments showed that correct results could be obtained only by using double the quantity of sodium recommended by Bacon, and prolonging the time of adding the sodium and of the subsequent refluxing.

† This oil is decomposed by water, yielding a light-yellow oil with fragrant odour, strongly fluorescent in ether, alcohol, or acetone solution. The violet fluorescence of the pure oil disappears on heating, but returns in the cold. It contains no bromide or aluminium. This action is very remarkable, simulating as it does the Friedel and Craft reaction, which, however, is supposed to be restricted to aromatic substances.

through all the absorption-solutions and finally collected in the storing-cylinder was very small in amount, and consisted mostly of air driven out of the apparatus, indicating that paraffins or other saturated constituents are present in the volatile fractions in only very slight amount.

A considerable amount of work was done to determine the possibility of a commercial use for the oil, but in the following brief summary all details are omitted, and only the main results indicated. The chief objections to the oil are its smell, and its tendency to form a gum on standing, and so clog the engine-valves; both these effects are possibly due to the higher unsaturated fractions. Distillation of the dry oil up to 100° C. gave a 60 per cent. fraction which apparently did not gum after standing for some months, but which still made a poor motor-fuel (as tried in a motor-cycle). The best effects were obtained with equal parts of petrol and Pintsch oil, but extensive trials are needed in this direction.

The effect of various catalysts and other reagents in reducing the unsaturation (and therefore, presumably, the gumming, &c.) was tried, but with discouraging results: boiling under reflux condenser with alcoholic sulphuric acid, and subjecting to the catalytic action of freshly reduced iron and nickel at various temperatures up to 340° C., producing little effect. Aluminium chloride, a reagent that has frequently been used for treating unsaturated oils, had a decided action (increasing with the boiling-point of the fraction used), producing a viscid, pitch-like polymerization product, soluble in organic solvents, containing no aluminium, and with no taste. In spite of this action, however, the distillate of volatile oil was still highly unsaturated, and its bad properties had not been markedly reduced.

Since benzene forms the largest constituent of the oil, it was thought that immersion of the oil in a freezing mixture might induce separation of crude benzene crystals. No such effect was, however, observed, nor could solid benzene be obtained even by similarly treating fractions in the neighbourhood of 80° C., though crystals of pure benzene were repeatedly introduced while the temperature was —20° C.; in fact, the crystals readily dissolved up. If the oil is previously treated with concentrated sulphuric acid to absorb the unsaturated constituents, fractions in the neighbourhood of 80° C. readily yield solid benzene on freezing, but there is apparently no hope of obtaining it easily from the original oil.

In conclusion, the writer wishes to thank Dr. Inglis for his help and advice during the investigation.
