III.—ON THE COMPOSITION OF JAPANESE BIRD-LIME.*

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No results worthy of publication seem to have been obtained in the examination of bird-lime until the year 1884, when J. Personne (*Compt. rend.*, **98**, 1585), made known those obtained by his father and himself. When that paper appeared, we ourselves had been for some time occupied with the investigation of Japanese bird-lime, and had already obtained results which proved to be in general agreement with those of Personne, and yet sufficiently unlike them, and, in some respects, in advance of them, to lead us to continue our work, although he had promised further attention to the subject. Up to the present date, however, nothing more from him has appeared, and we now offer this paper as an extension and partial confirmation of his observations.

Bird-lime, or *tori-mochi*, is prepared in Japan, just as it is in Northern Europe, from a species of holly, by macerating and pounding its inner bark in water, and afterwards picking out the fragments of crushed tissue from the viscid mass. Bird-lime exists ready formed in the bark in great abundance, and is not apparently modified in any way by fermentative action during its preparation. In Europe it is prepared from the common or prickly-leaved holly (*Ilex aquifolium*), but in Japan it is obtained from *Mochi-no-ki*, the *I. integra* of Thunberg (*Prinus integra*, H. and A.). We are not familiar with bird-lime as prepared in Europe, but judging from descriptions, Japanese bird-lime is like it, except perhaps in not having a greenish hue, although of that even we are not certain, since the Japanese product may well have it sometimes when quite freshly prepared. Bird-lime is extensively used in Japan, as in Europe, for catching birds and insects, and with the usually attendant cruelty.

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In manuals of economic botany, we find enumerated as peculiar constituents of the holly, a bitter principle named *ilicine*, an aromatic resin, and bird-lime itself. In the account of bird-lime given in Ure's *Dictionary*, the true substance is not well distinguished from the viscid matter of mistletoe (*Viscum album*), examined by Reinsch, from which it appears to be entirely different.

Some Properties of Japanese Bird-lime.

The bird-lime is pale-greyish, nearly opaque, of faint, peculiar odour, almost tasteless, soft, elastic, tenacious, and adhesive to dry surfaces, and slightly lighter than water. It can be preserved in water for an indefinite time without change, except on its upper surface. Exposed to air, it very slowly turns brown outside, and becomes coated with a thin brittle skin. If heated moderately, it gives off water, and above 100° froths from disengagement of steam. By the loss of its moisture, it becomes transparent, brown, and while hot of the consistency of cold oil. If now allowed to cool, it remains transparent, and forms a soft, solid mass, elastic, tenacious, and sticky as before, somewhat resembling Canada balsam in appearance. Ether, carbon bisulphide, chloroform, light petroleum, and benzene dissolve bird-lime, leaving a residue which although of not inconsiderable volume, is of little weight. Cold alcohol scarcely dissolves it at all, and even hot alcohol, which has some solvent action at first, attacks merely the surface-portion of the mass. The alcoholic solution as it cools deposits a nearly colourless, transparent, adhesive matter, differing but little from the purified bird-lime itself. Ether is much to be preferred to other solvents, because it yields a clear solution, whereas carbon bisulphide and the rest give milky liquids, owing to the presence of water. The ether solution mixed with alcohol becomes turbid and deposits a tenacious mass. Freed from water and particles of woody fibre, bird-lime undergoes scarcely any change when heated up to temperatures below 350°, merely becoming slightly fluorescent, and a little darker in colour, and acquiring a feeble,

waxy odour. About the melting point of zinc, however, it undergoes destructive distillation, in which most of it comes over as fatty acids and fluorescent hydrocarbons of waxy and mild empyreumatic odour and buttery consistence; very little permanent gas is formed, and only a small carbonaceous residue is left. Bird-lime burns in the air with a bright, smoky flame.

It is not very sensitive to reagents. *Sulphuric acid* dissolves it slowly, forming a red liquid, which blackens only when heated, and which, when poured into water, gives a viscid precipitate, like bird-lime, but dark-coloured. Boiling *nitric acid* slowly dissolves it with partial oxidation, this solution also yields a precipitate with water. The sulphuric acid solution poured into concentrated nitric acid, and then diluted with water, yields a precipitate of a mixture of feebly nitrated compounds. Aqueous solutions of *potassium hydroxide* only slowly and slightly emulsify bird-lime; fusion with the hydroxide is attended with much darkening in colour, and leaves a mass which emulsifies in water. Potassium hydroxide in strong spirit slowly dissolves the greater part of purified bird-lime, producing a dark-coloured solution. In this way,—that is by continued boiling with strong alcoholic potash—bird-lime has been attacked by both Personne and ourselves, in order to determine its composition.

The Constituents of Bird-lime.

Personne has found bird-lime, prepared from *I. aquifolium*, to contain water 27, and vegetable debris and calcareous salts, 23 parts per cent., the remaining and essential part being some caoutchouc, the compound ether or ethers of a new alcohol, and other matters undetermined. The acids, or acid, forming the ethers were also not investigated by him. He isolated the caoutchouc by saponifying the ethers with alcoholic potash, which left the caoutchouc undissolved.

Japanese bird-lime is much cleaner than that described by Personne, containing only 2 per cent. of dry-bark fragments, and no separate lime salts. Its water content, however, is larger (probably

because it is kept in stock under water), the percentage lost at 110—120° being 38. Caoutchouc forms about 6 per cent., leaving 54 per cent. as the proportion of compound ethers and allied matters.

The Bark, &c.—Of the 23 parts per cent. found in French bird-lime by Personne, some 13 parts consisted of *calcium oxalate*. On boiling out the bark fragments from Japanese bird-lime with sodium carbonate, some oxalate was dissolved out, but only in small quantity. The bark burnt to ashes gave as much as 6·3 per cent. of ash, principally calcareous and largely phosphate, but of course with some carbonate; but as the whole ash was only one-eighth per cent. of the entire bird-lime, and as only a little of the calcium salts was oxalate, Japanese differs in this respect remarkably from French bird-lime.

The Caoutchouc.—As we have stated, the caoutchouc can be separated by boiling out the purified bird-lime with alcoholic potash, and this is the best way of proceeding. It is, however, difficult to get it quite free from potash, and to this end needs to be repeatedly dissolved in ether, and reprecipitated by alcohol. The caoutchouc can also be separated by dissolving the bird-lime in ether, and precipitating the solution with 95 per cent. spirit, but then only very imperfectly, because the main constituent of the bird-lime is also precipitated in part. The caoutchouc of bird-lime is pale-yellow and transparent, highly elastic, and when heated evolves the well-known penetrating odour. A combustion gave carbon 86·56 and hydrogen 11·31 per cent., so that oxygen to the extent of 2 per cent. was present. Before weighing it out, it had been kept for some time at 120—130°. It left a trace of ash when burnt.

Other and Principal Constituents of Bird-lime.—We have not fully isolated these by proximate analytical methods, but their general properties appear to be those of the partially purified bird-lime; for when a boiling alcoholic solution of bird-lime is evaporated and cooled, or, again, when an ethereal solution of bird-lime is mixed with a little alcohol to separate the caoutchouc, and then evaporated, in either case the solid matter obtained is like the partially purified

bird-lime, except in being colourless when deposited from the alcoholic solution.

Products of the Saponification of Bird-lime, and their Isolation.—Saponification with alcoholic potash yields besides the residual caoutchouc, firstly, the potassium salt of *palmitic acid*, and a very little of that of a *semi-solid acid* which we have been unable to purify or identify; secondly, *two crystalline alcohols*; and thirdly, a small quantity of a *resinoid substance*. The separation of these may be carried out in somewhat different ways, and is unavoidably tedious. The purified bird-lime is boiled for two hours with potash and 95 per cent. spirit, in a flask fitted with a reflux condenser; and the alkaline solution, decanted from the caoutchouc, is poured into dilute spirit, by which a voluminous, gelatinous precipitate is produced, consisting of the alcohols, with some of the resinoid body and potassium palmitate. The precipitate is well broken up by stirring, collected on a cloth filter, pressed, and washed with dilute spirit.

Three ways of proceeding from this point have been employed by us. In one, the precipitate is diffused through dilute spirit, stirred well and warmed with calcium chloride solution. The now much less voluminous precipitate is repeatedly washed with water, dried, and extracted with ether, which leaves the calcium palmitate undissolved. Spirit of 95 per cent. may be used in place of ether, but as it dissolves out a little calcium salt, its use is less satisfactory. On evaporating the ether (or spirit), the alcohols and resinoid body are obtained. A second way of proceeding is to warm the precipitate with water and hydrochloric acid until it has shrunk to a small volume, wash repeatedly with water, press moderately, and extract with light petroleum, which dissolves out the palmitic acid and some of the resinoid substance, and leaves behind all the alcohols and the rest of the resinoid substance. After treatment by either method, the resinoid compound is separated by repeated extractions with warm 80 per cent. spirit. A small quantity of the alcohols at the same time dissolves, and may be partly recovered by precipitation with a very little water, and extracting the precipitate with 80 per

cent. spirit. The third way of proceeding, which is simpler in execution than the others, but much less effective, is to use 70—80 per cent. spirit in place of the light petroleum in the second way of working. This dissolves out the resinoïd substance, as well as palmitic acid.

Personne's method of procedure is to pour the product of saponification into water, to wash the precipitate with much water, treat it with acetic acid to neutral reaction, again wash, dry, dissolve in hot 90 per cent. spirit, cool, and crystallise out the bird-lime alcohol from the solution. We have not found this method to work well, on account of the great difficulty in washing properly the voluminous gelatinous precipitate, and in just neutralising it with acetic acid. This precipitate contains, besides the alcohols and resinoïd substance, much acid potassium palmitate, to which indeed its bulky nature is partly due, and we have found it far preferable to convert the potassium palmitate either into the calcium salt or into free acid, as above described. Personne seems not to have recognised the presence of any fatty salt in the precipitate containing the alcohols.

Separation of the Alcohols from each other, and their Purification.—The crude solid alcohols can only be fully separated from each other by fractional extraction with strong spirit, repeated until the products obtained are of constant melting point. The alcohols, already treated as described with 80 per cent. spirit to remove the resinoïd substance, are warmed with successive portions of spirit, increasing in strength from about 85 per cent. to over 90 per cent., each portion of the solvent depositing crystals of the alcohols as it cools and each mother-liquor by successive evaporations yielding a series of other crystalline deposits, all similar in appearance. When the last mother-liquors are too small in quantity and too impure to yield a satisfactory product by further evaporation, they are rejected or worked up for the little resinoïd substance they contain. The portions of the alcohols least soluble in spirit consist principally of the one alcohol, and those most soluble of the other alcohol. By a repetition of the treatment with spirit, the intermediate portions yield other series of

deposits of higher and lower degrees of solubility, the extremes of which contain the two alcohols. The portions of the less soluble alcohol are submitted to further fractionation until the part undissolved by hot 90 per cent. spirit, and that dissolved and deposited by it on cooling have the same melting point. It is then finally dissolved in hot 95 per cent. spirit, crystallised out and again tested as to its melting point. The most soluble crystalline deposit, consisting principally of the more soluble alcohol, requires much further fractionation, in order to separate the less soluble alcohol on the one side, and the resinoid substance on the other, so that the ultimate yield of the pure alcohol becomes very small. In fractionating out this alcohol, spirit of 85 per cent. is used, but finally this alcohol, like the other, should be crystallised out from 95 per cent. spirit, in order to get good crystals.

Personne observed the comparative insolubility of the solid alcohol in 80 per cent. spirit, but making no use of this fact, he purified the cake of crude solid alcohol by repeated crystallisations from boiling 90 per cent. spirit. During the purification, he met with a substance of peculiar form, visible under the microscope, and less soluble in spirit than the solid alcohol, and this he found to be gradually removed by repeated crystallisation. We have met with no such substance in Japanese bird-lime.

Purification of the Resinoid Compound.—This is found mainly in the 80 per cent. spirit used to wash the crude alcohols after they have been separated from palmitic acid. When this separation has been effected in the second way, the spirit contains some fatty acids also. The light petroleum used to dissolve out palmitic acid also contains some of the resinoid substance. In order, therefore, to separate palmitic acid, the residue, after evaporating the petroleum spirit, is dissolved in alcoholic potash, the palmitic acid precipitated by calcium chloride, water added, and the precipitate washed, dried, and extracted with ether. On evaporating the ether, the resinoid substance is left, still mixed with some of the alcohols, but free from any fatty acid. The impure product is dissolved in strong spirit,

and left to evaporate slowly. The alcohols separate as indistinctly crystalline, opaque matter, while the resin separates on the bottom and sides of the vessel as a translucent, gummy deposit, still containing spirit; the resin is then redissolved in spirit and the solution left to evaporate for some hours. On repeating these operations several times, it is obtained in a condition in which it has no longer any tendency to deposit crystalline matter.

Separation and Purification of the Fatty Acids.—By far the greater part of the fatty salts remain dissolved when the saponified bird-lime solution is poured into dilute spirit. The filtrate and washings from the gelatinous precipitate of alcohols are diluted with water, mixed with hydrochloric acid, and warmed, in order to separate the fatty acids. By similar and well-known methods, the portions of these acids thrown down along with the bird-lime alcohols can be recovered, after separating them as calcium salts from the alcohols and resinoid substance, and added to the main quantity. The crude fatty acids, which when cold form a soft, brown, solid mass, are dissolved in alcoholic potash and precipitated again with calcium chloride; the calcium precipitate is washed with spirit which removes chlorides and some colouring matter, as well as some of the calcium salt of the soft fatty acid; the precipitate is then washed with ether, as this dissolves out most of the remaining colouring matter and calcium salt of the soft fatty acid more easily than spirit does; lastly, it is heated with hydrochloric acid and water in order to get the crude palmitic acid. On repeating these operations once or twice, and finally crystallising the product from spirit, the palmitic acid is obtained in a pure state. By appropriate treatment, the spirit and ether washings of the calcium precipitate yield the semi-liquid acid although in an impure condition.

Palmitic acid can also be prepared from bird-lime by destructive distillation. Its purification from hydrocarbons, by means of saponification, presents no great difficulty, and need not be described.

The Alcohols of Bird-lime.

To one of the two alcohols of bird-lime we give the same *mochylic alcohol*, formed from the Japanese word, *mochi*, for (bird-)lime or glutinous matter; and to the other we attach the name *ilicylic alcohol*, essentially the same as *ilicic alcohol*, given by Personne to the single alcohol described by him, but framed more in accordance with the accepted nomenclature for alcohols. Our ilicylic alcohol differs but little from Personne's ilicic alcohol. Both the alcohols of bird-lime are obtained in tufts of small, slender, lustrous prisms, and are distinguishable from each other only in solubility, in melting point, and in composition.

Mochylic alcohol occurs much more abundantly than ilicylic alcohol. It dissolves well in 95—98 per cent. spirit, but is almost insoluble in 80 per cent. spirit. It is very little soluble in light petroleum in the cold, is readily soluble in ether, and dissolves also in concentrated sulphuric acid to which, like bird-lime itself, it imparts a red colour. It melts at 234°, and under atmospheric pressure decomposes at a little below the melting point of zinc, the principal product being a viscid matter, apparently the hydrocarbon to be described among the products of the destructive distillation of bird-lime. In a vacuum, it sublimes slightly at a little above 160°, and freely and entirely near and above its melting point, without decomposing or changing in melting point. Heated with palmitic acid in a sealed tube at 150—160°, it yields a substance indistinguishable from bird-lime in essential properties, a sticky transparent matter, readily soluble in ether, but nearly insoluble in the strongest spirit. Our attempts to obtain mochyl acetate by the action of acetic oxide or chloride have been unsuccessful.

Ilicylic alcohol differs from mochylic alcohol in melting at 172°, and in being moderately soluble in 85—90 per cent., although almost insoluble in 80 per cent. spirit. It begins to volatilise in a vacuum below 150°, and sublimes freely near its melting point in beautiful tufts of needles still melting at 172°. Heated with palmitic acid, it

also forms a substance like bird-lime. It fails apparently to yield an acetate, even after long heating at 150—170° with acetic oxide, in which when hot it, as also mochylic alcohol, readily dissolves, partly crystallising out again unchanged on cooling, and partly becoming a dark viscid matter, not the acetate. Personne found that his ilicic alcohol when treated with acetic oxide yielded a crystalline acetate melting at 204—206°. The melting point of Personne's ilicic alcohol was 170°, and its boiling point above 350°, but under a reduced pressure of 100 mm. it began to sublime at 115°. In appearance and in behaviour to spirit of different strengths, it was like our ilicylic alcohol. Both mochylic and ilicylic alcohols dissolve in a mixture of sulphuric and nitric acids, and from the solution water separates a gelatinous matter, readily soluble in spirit, and deflagrating only slightly when dried and heated.

Chemical Composition of the Two Alcohols.—Combustion of the two alcohols has given us the following results:—

Mochylic Alcohol, m. p. 234°.

	I.	II.	III.	$C_{26}H_{46}O$
Carbon.....	83·37	83·39	83·28	83·42
Hydrogen...	12·29	12·16	12·38	12·30
Oxygen.....	—	—	—	4·28
				<hr/> 100·00

Ilicylic Alcohol, m. p. 172°.

	I.	II.	$C_{22}H_{38}O$
Carbon.....	83·09	82·98	83·02
Hydrogen.....	11·93	11·92	11·95
Oxygen.....	—	—	5·03
			<hr/> 100·00

Ilicic Alcohol, m. p. 175° (Personne's Analyses).

	I.	II.	III.	IV.	V.	Mean.	$C_{25}H_{44}O$.
Carbon..	83·25	83·64	83·48	83·07	83·40	83·36	83·33
Hydrogen	12·18	12·44	12·17	12·24	11·98	12·20	12·22
Oxygen..	—	—	—	—	—	—	4·45
							<hr/> 100·00

It will be seen that Personne's numbers vary rather widely, but fall for the most part between those obtained by us for our two alcohols. It will also be seen that the formula he has proposed, as agreeing best with the mean of his analysis, is that of a homologue of our alcohols, the general expression being $C_nH_{2n-6}O$. As he worked on bird-lime from a species of *Ilex* different from that which yields Japanese bird-lime, it cannot for the present be decided whether ilicic alcohol is distinct from the alcohols here described.

The Resinoid Component of Bird-lime.

The resinoid substance is obtained in pale-yellow fragments, which are brittle, and not sticky like bird-lime. It melts at 110°, and does not volatilise when heated to 220° in a vacuum. Above 360° it darkens, boils, and distils without much apparent change. It is very soluble in spirit, even of 80 per cent. strength, also in ether. When its alcoholic solution is sufficiently evaporated by heat, it separates from its solvent as a viscid liquid, still containing spirit, but this evaporates on further heating below 100°. Its solubility in spirit is not increased by the presence of potassium hydroxide. Heated with the solid hydroxide barely to the melting point, it slowly combines with it, probably at the same time absorbing oxygen. The cooled mass wholly dissolves in water, from which hydrochloric acid precipitates a gelatinous substance, very brittle when dried. We have not further examined it for want of material.

When bird-lime is kept for a long time, a thin brittle skin forms on its surface which is readily soluble in spirit. This skin consists

probably of the resinoid substance. If it does not, then we have no evidence as to whether the resinoid substance is produced during the saponification of the bird-lime, or exists in it ready formed as the result of slow atmospheric oxidation.

In composition, the resinoid substance differs from mochylic alcohol only in having two atoms less of hydrogen, as the following analyses and calculation show :—

	I.	II.	$C_{26}H_{44}O$.
Carbon.....	83.79	83.66	83.87
Hydrogen.....	11.80	11.92	11.83
Oxygen.....	—	—	4.30
			<hr/> 100.00

The Fatty Acids of Bird-lime.

The fatty acids of bird-lime are two, as already stated, *palmitic acid*, and, in small quantity only, a semi-liquid acid, the calcium salt of which is soluble in spirit and in ether. This acid has not been further examined. The other shows all the characters of palmitic acid. Melting point, 61.5° . Analysis of (I) acid prepared by saponification, and (II) acid obtained by destructive distillation of purified bird-lime :—

	I.	II.	Palmitic acid.
Carbon.....	74.98	74.86	75.00
Hydrogen.....	12.67	12.55	12.50
Oxygen.....	—	—	12.50
			<hr/> 100.00

The potassium salt yielded 13.3 per cent. of potassium.

Products of Destructive Distillation.

These have been already enumerated, so far as their nature is known to us, and the result of analysis of the palmitic acid has just

been tabulated. The principal hydrocarbon, distilling next after the palmitic acid, was prepared from the middle portion of the distillate by treating it with hot spirit so as to leave about half of it undissolved. This was then washed with cold spirit. The hydrocarbon thus left was a thick oil, slightly yellow but not fluorescent. On analysis it gave numbers agreeing with the formula $C_{26}H_{44}$:—

	Found	Calculated.
Carbon.....	87.59	87.64
Hydrogen.....	12.49	12.36
	<hr/> 100.08	<hr/> 100.00

Apparently the same compound is obtained by distilling mochylic alcohol under the ordinary atmospheric pressure. The decomposition of the main constituent of bird-lime by heat may therefore be thus represented :—

Mochyl palmitate, $C_{42}H_{76}O_2 = C_{26}H_{44} + C_{16}H_{32}O_2$,
and the decomposition of mochylic alcohol by—

The last fractions of the distillate consisted of hydrocarbons yielding nearly 91 per cent. of carbon. No attempt was made to isolate the caoutchouc-hydrocarbons no doubt present in the mixture.

Constitution of Bird-lime.

Bird-lime is closely allied to the waxes, and consists principally of *mochyl* and *ilicyl palmitates*, $C_{42}H_{76}O_2$ and $C_{38}H_{68}O_2$.