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XXIV.—*Educts from Baphia Nitida (Barwood).*

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THE wood, after having been torn to a fine dust, is placed in a digesting apparatus, and exhausted thoroughly with anhydrous "methylated" ether free from alcohol. The liquid which traverses the wood gradually diminishes in colour as the extraction proceeds, until, from having been strongly red, it becomes almost (though never quite) colourless. This liquid is heated in the water-bath, so as to drive off the greater part of the ether. The residue is left to itself for a short time in a cool place; it may deposit a small quantity of *baphic acid*, in the form of platy crystals. These are separated from the mother-liquid, in which they are quite insoluble; the latter is evaporated so as to drive off the greater part of the ether, and then mixed with alcohol. After an interval varying from one to several days, a crystalline magma forms; this consists of *baphiin*, contaminated with a solid red colouring matter, and containing besides some dark and viscous tinctorial substance which has not been examined.

After thoroughly drying off the ether from the wood used in the experiment referred to in the preceding paragraph, exhaustion with alcohol may be commenced. The alcoholic fluid is distilled to nearly dryness, and left to itself. It solidifies after long standing, to a semi-crystalline mass, containing (as in the case of the ethereal extract) a viscous colouring matter of a deep red colour. The mass, on exposure to air, dries up, with fission, into a granular powder. Its crystalline constituent has not been examined.

The use of other solvents than those above mentioned is not satisfactory. Benzol and carbonic sulphide have both been employed at about 100° C. They have the advantage of dissolving scarcely a trace of the colouring matters, but, on the other hand, the disadvantage of extracting a very trifling quantity of the colourless ingredient existing in the wood, to which the term baphiin has been applied. But should there be any baphic acid present, this is removed by the hot benzol with tolerable facility.

Baphiin

Is obtained, as mentioned above, from the ethereal extract of the wood. In order to free it from colouring matter, it is repeatedly crystallised from strong spirit, whereby it is at length obtained perfectly pure. Baphiin is a colourless substance; it crystallises from

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alcohol in plates of considerable lustre,—from ether, by rapid evaporation, in tufts of needles. It is only very sparingly soluble in benzol or carbonic sulphide; in water it is insoluble. When allowed to crystallise from its solution in alcohol on a finely divided surface in presence of air, it rapidly oxidises, producing colours which vary from yellowish-red to light purple. It has an odour of orris root. When submitted to the action of heat, baphiin fuses, but only in part, below 200°; in part at a higher temperature. This is an obvious sign of decomposition. At 100° it remains unchanged. Dried at the latter temperature it yielded on analysis the following results:—

	Subs.	Carb. dioxide.	Water.	Carbon.	Hydrogen.	$C_{12}H_{10}O_4$.
(1.)	·5340 gram.	1·2974	·2278	66·26	4·74	
(2.)	·3251 gram.	·7887	·1427	66·16	4·88	
(3.)	·3733 gram.*	·9142	·1780	66·79	5·29	
			Mean.....	66·40	4·97	66·05 : 4·59

which agree with the formula $nC_{12}H_{10}O_4$.

When an alcoholic solution of baphiin is mixed with acetate of lead (also in alcoholic solution), a white precipitate is thrown down, insoluble in alcohol. It is washed thoroughly with alcohol, and dried over sulphuric acid. While drying it turns brown, perhaps in consequence of oxidation. It probably consists of plumbic baphate. The alcoholic filtrate from this precipitate, when mixed with water, yields a crystalline precipitate of *baphinitin*. When baphiin is boiled with aqueous potash, the same reaction takes place as with alcoholic plumbic acetate; if the potash-solution be not dilute, other bodies are produced. The potassic baphate, in presence of excess of potash and acid, rapidly colours, so that it requires immediate filtration into hydrochloric acid to prevent further decomposition.

Baphic Acid.

When the alcoholic solutions of acetate of lead and baphiin are mixed, a white precipitate falls, which is probably plumbic baphate. The acid itself is obtained by boiling baphiin with aqueous potash, filtering, and adding hydrochloric acid to the filtrate. It then falls out as a yellowish-white powder, to be purified by placing on the filter (without washing), drying in the air, extracting with anhydrous ether, and evaporating the ethereal solution. Purified still further by repeated crystallisation, it presents itself in the form of white nacreous scales, very readily soluble in alcohol, and especially in ether (even in the cold), insoluble in water. Its ammoniacal solution instantaneously

* New preparation.

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precipitates metallic silver from the nitrate. An attempt to prepare a barium salt met with no success. The following analyses were made:—

	Subs.	Carb. dioxide.	Water.	Carbon.	Hydrogen.	$C_{24}H_{22}O_{10}$.	$C_{24}H_{22}O_9$.
(1.)	·1268 gram.	·2850	·0528	61·29	4·63		
(2.)	·2999 „	·6940	·1144	63·11	4·24		
(3.)	·2779 „	·6520	·1059	63·99	4·23		
(4.)	·5385 „	1·2203	·2444	61·80	5·04		
(5.)	·3105 „	·7047	·1410	61·87	5·05		
(6.)	·5275 „	1·1872	·2371	61·38	4·99	(61·28 : 4·67)	(63·43 : 4·85)

Lead salt.—Prepared by adding the acid, or an alcoholic solution of baphiin, to an alcoholic solution of plumbic acetate, and washing with alcohol. It is at first white, but dries up to a brown mass over sulphuric acid. The results of the analysis of different preparations are unsatisfactory.

	Subs.	Carbon dioxide.	Water.	Plumbic oxide.	Carbon.	Hydrogen.	Lead.
(1.)	·6414 gram.	—	—	·2908	—	—	42·09
(2.)	·5065 „	—	—	·2432	—	—	44·57
(3.)	·6992 „	·8589	·1564	—	33·50	2·48	—

An example of the splitting up of an organic compound into an acid and an indifferent substance like baphinitin is to be found in the case of athamantin (*Ann. Chem. Pharm.*, li, 315), which, on boiling with potash, gives valeric acid and oreoselone—

$$C_{24}H_{30}O_7 = 2C_5H_{10}O_2 + C_{14}H_{10}O_3.$$

Baphinitin.

This is the insoluble product, and the chief one, when baphiin is boiled with aqueous potash: it is found in the alcoholic mother-liquid when baphiin and plumbic acetate are brought in contact in alcohol. It is white, having the odour of the original baphiin still more strongly developed; it dissolves with moderate freedom in alcohol and ether, and crystallises in needles. It is insoluble in water. On analysis it gave results leading to the formula nC_4H_4O.

	Subs.	Carb. dioxide.	Water.	Carbon.	Hydrogen.	nC_4H_4O.
(1.)	·3175	·8186	·1670	70·32	5·85	
(2.)*	·2613	·6667	·1376	69·59	5·85	
(3.)†	·3174	·8228	·1738	70·69	6·09	(70·59 : 5·88)

Treated with strong sulphuric acid, and afterwards with water and carbonate of barium, it yields a solution from which sulphuric acid

* New preparation. † Burned with chromate.

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precipitates sulphate of barium, and which yields on evaporation a deliquescent barium salt.

Baphinitone.

When baphiin is boiled with strong aqueous potash, air being excluded as much as possible during the operation, there is left undissolved a mixture of three substances;—(1) baphinitin, which dissolves in alcohol and ether with moderate ease; (2) baphinitone, which is very easily soluble in these liquids; and (3) a small quantity of an unexamined body, fusing at 164·1° (corr.), very sparingly soluble in alcohol, even when hot, and separating therefrom in granular crystals. Baphinitone is prepared by treating the part of baphiin which is insoluble in aqueous potash with cold alcohol, which readily dissolves the baphinitone, and but little baphinitin. The solution is evaporated and the treatment repeated, till the crystals thus obtained, after drying over sulphuric acid, fuse at or near 88° C. Baphinitone crystallises from alcohol in hemispherical masses, composed of radiating crystals, beautifully white and lustrous. It is insoluble in water. On analysis it gave the following numbers:—

	Subs.	Carb. dioxide.	Water.	Carbon.	Hydrogen.	$C_{26}H_{26}O_6$.
(1.)	·2910	·7648	·1666	71·68	6·36	
(2.)	·1961	·5130	·1035	70·93	5·29	(71·89 : 5·99)

When an ethereal solution of baphinitone is treated with an ethereal solution of bromine, the latter is decolorised: and on evaporating off the ether, a white substance remains, which, after washing with alcohol or ether (in both of which it is almost insoluble), is pure tribromobaphinitone.

Tribromobaphinitone separates from a hot ethereal solution in small granules. As first prepared, it appears to consist of a compact mass of very small, snow-white needles. It fuses, with sudden blackening, at 180·2° (corr.). It yielded on analysis numbers which agree very well with the formula, $C_{26}H_{23}Br_3O_6$.

Sub.	Carb. dioxide.	Water.	Carbon.	Hydrogen.	$C_{26}H_{23}Br_3O_6$.
·5409	·9191	·1741	·46·34	3·58	(46·49 : 3·43)

Baphiin, baphinitone, and the substance least soluble in alcohol which occurs with the latter, are all coloured orange-yellow by sulphuric acid; with nitric acid an orange-red is obtained, changing to green.

The molecular formulæ of the above bodies are somewhat complex, and there do not appear to be ready means of determining them with precision. Taking, however, that of baphinitone to be precisely deter-

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mined, we may fairly assume a C_{20+n} formula for all these bodies. We shall then have the following series:—

Baphiin	$C_{24}H_{20}O_8$
Baphic acid	$C_{24}H_{22}O_{10}$ [O_9?]
Baphinitin	$C_{24}H_{24}O_6$
Baphinitone	$C_{26}H_{26}O_6$

Colouring Matters.

Barwood contains at least three colouring matters. Ether dissolves out two of these: one (A) which is less soluble, and obstinately adheres to the baphiin, and another more soluble (B), which is easily got rid of. After the extraction with ether is complete, alcohol dissolves a third (C). All are insoluble in benzol; all give purple lakes with plumbic acetate, and purple colorations with alkalis.

(A.) The solubility of this body in ether diminishes after exposure to air. It may be purified from baphiin by boiling with benzol, in which the latter dissolves. It is a bright red powder.

(B.) Crystalline; dissolves easily in boiling alcohol. A strong solution cuts off the blue, and nearly all the green of the spectrum—the blue first. The same solution, mixed with hydrochloric acid, becomes darker, transmits the blue faintly, and very much obscures the green; the yellow and red are transmitted. The solution, after the addition of the acid, on mixing with ammonia or potash, becomes deep pink; the green and blue are much obscured, while the red is left, and the yellow is cut off, and replaced by a black band.

(C.) The green is more absorbed by this colour in alcoholic solution than by (A). When the solution is moderately strong, a black band appears in the yellow. When hydrochloric acid is added, the green is more obscured, and the yellow is still decidedly effaced, notwithstanding the dilution; the blue is nearly removed; the red remains. When ammonia is added to the solution after the action of hydrochloric acid, the colour becomes intensely purple; the red ray is transmitted, the yellow is effaced, the green scarcely visible. C acts on the green and yellow more than A.

N.B.—It has been stated that the "colouring matter" of barwood is identical with santonin. The above renders this very improbable.