

XCIV.—*Some Derivatives of Maclurin.*

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SOME years ago, during some experiments with old fustic (*Morus tinctoria*), it was found by one of us that when an aqueous extract of this dye-stuff is treated with diazobenzene sulphate or other analogous substance, a new colouring matter is produced. As this was recognised to be of commercial value, the process was patented (C. S. Bedford, Eng. Pat. No. 12667, 1887), and the manufactured product is now known under the name of "Fustin."

The principal constituents of old fustic are, as is well known, morin, $C_{15}H_{10}O_7$, and maclurin, $C_{13}H_{10}O_6$, both of which are colouring matters, and investigation soon revealed the fact that the latter only is useful for this purpose. As the constitution of maclurin has lately been the subject of numerous investigations, and, moreover, as it is not generally known which of the constituents of old fustic form the basis of these new dye-stuffs, it appeared desirable to submit the subject to examination.

Benzeneazomaclurin.

To a slightly alkaline aqueous solution of maclurin, a solution containing diazobenzene sulphate (2 mols.) was added, causing the formation of a bright red precipitate. After standing a short time this was collected, washed with water, dried, and purified by crystallisation from nitrobenzene.

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0.1056 gave 0.2460 CO₂ and 0.0393 H₂O. C = 63.52; H = 4.13.
 0.1344 „ 0.3126 „ 0.0415 „ C = 63.43; H = 3.84.
 0.1467 „ 16 c.c. N; *t* = 25°; bar., 745 mm. N = 11.97.
 C₁₃H₈O₆(N:N·C₆H₅)₂ requires C = 63.82; H = 3.82; N = 11.91 per cent.

It was therefore a compound of maclurin with 2 mols. of diazobenzene. When crystallised from nitrobenzene, it appears as a salmon-red mass of slender, hair-like needles, when from acetic acid, in the form of small needles, somewhat resembling alizarin in appearance. By the addition of alcohol to a boiling solution of this substance in a mixture of acetic acid and nitrobenzene, it is deposited on long standing as a beautiful, glistening mass of prismatic needles. It is very sparingly soluble in acetic acid, more readily in nitrobenzene, almost insoluble in alcohol and benzene. Dilute alkalis dissolve it with a bright, orange-red colour, and if these solutions are treated with zinc dust, reduction rapidly ensues with production of a pale yellow liquid. The barium salt produced by double decomposition forms orange-red flocks almost insoluble in water. The colouring matter dissolves in sulphuric acid with an orange-red colour. Attempts to produce a compound of maclurin with 1 mol. of diazobenzene were unsuccessful, in all cases the substance above described was produced, and the presence of free maclurin could be detected in the filtrate.

Orthotolueneazomaclurin was prepared from orthotoluidine and maclurin in a similar manner to the preceding compound. It was purified by crystallisation from nitrobenzene. On analysis,

0.1150 gave 0.2742 CO₂ and 0.0467 H₂O. C = 65.02; H = 4.51.
 0.1345 „ 13.4 c.c. N; *t* = 23; bar., 745 mm. N = 11.00.
 C₁₃H₈O₆(N₂·C₆H₄·CH₃)₂ requires C = 65.06; H = 4.41; N = 11.25 per cent.

It was obtained as slender, hair-like needles, closely resembling the diazobenzene compound.

Paratolueneazomaclurin crystallised similarly. On analysis

0.1430 gave 14.6 c.c. nitrogen at 22°, and 762 mm. N = 11.59.
 C₁₃H₈O₆(N:N·C₆H₄·CH₃)₂ requires N = 11.25 per cent.

Paranitrobenzeneazomaclurin, from paranitraniline and maclurin was obtained as a chocolate coloured mass, which crystallised from a mixture of nitrobenzene and acetic acid in spongy masses of very minute needles.

0.1155 gave 15.4 c.c. nitrogen at 23° and 745 mm. N = 14.72.
 C₁₃H₈O₆(N:N·C₆H₄·NO₂)₂ requires N = 15 per cent.

Maclurinazobenzeneparasulphonate of sodium.—To maclurin, dis-

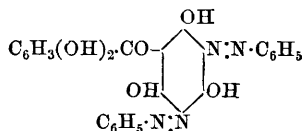
solved in dilute alkali, a solution containing 2 mols. of diazobenzene-parasulphonic acid was added, causing the formation of an orange-red liquid. As this solution gave no precipitate when neutralised and saturated with common salt, it was, in the acid condition, treated with a large excess of this substance; an orange-red, tarry, resinous mass then separated. This product, when dissolved in a little hot water and treated with a small quantity of sodium carbonate solution, deposited an orange-red, crystalline precipitate, which was washed with a little water, followed by dilute alcohol, and recrystallised from water.

It formed an orange-red mass, seen under the microscope to consist of minute crystals. These were moderately soluble in water, almost insoluble in alcohol, and, when dry, possessed a beetle-green lustre. Analysis indicated that this substance consisted of the acid sodium salt, $C_{13}H_8O_6(N:N \cdot C_6H_4 \cdot SO_3Na)_2$, but contaminated with a trace of a more alkaline salt. Owing to the somewhat poor yield obtainable of this substance, it was not found possible to isolate it in an absolutely pure condition without the use of considerably larger quantities of raw material than were at our disposal. By double decomposition it yields a barium salt in the form of an orange-red, amorphous precipitate, slightly soluble in water.

Maclurin, as is to be expected, yields colouring matters with diazoxylenes, tetra-azodiphenyl, and allied substances. The former closely resemble the diazobenzene derivative, and the latter is obtained as a chocolate-brown powder of a very insoluble nature.

Maclurin has been shown by König and Kostanecki (*Ber.*, 1893, **27**, 1994) to yield a pentabenzoyl derivative, $C_{13}H_5O(C_7H_5O)_5$, and, moreover, as it yields phloroglucin and protocatechuic acid by reduction or digestion with strong alkali, it appears to be an hydroxyketone, which may be represented thus, $C_6H_3(OH)_2 \cdot CO \cdot C_6H_2(OH)_3$.

Experiments showed that protocatechuic acid does not combine with diazobenzene, whereas from phloroglucin, Weselsky and Benedikt (*Ber.*, 1879, **12**, 226) have obtained benzeneazophloroglucin $(OH)_3C_6H(N:N \cdot C_6H_5)_2$. It is, therefore, most probable that in benzeneazomaclurin, both diazobenzene molecules are united with the phloroglucin nucleus, the formula of the substance being consequently



It is interesting to note that catechin yields a compound with diazobenzene, $C_{18}H_{16}O_8(N_2 \cdot C_6H_5)_2$ (Etti, *Monatsh.*, 1881, **2**, 252), and

that the substance termed cyanomaclurin which is present with morin in jack wood gives a similar substance, $C_{15}H_{10}O_6(N_2 \cdot C_6H_5)_2$ (Perkin and Cope, this vol., p. 942). Our experiments have shown also that aqueous extracts of some tannin substances yield new compounds in this way, and it is known that these contain substances allied most probably to maclurin and catechin. Experiments with quercetin, fisetin, and morin, showed that they behave towards diazobenzene somewhat differently, though, like maclurin and catechin, all yield phloroglucin as one of the products of their decomposition with alkali. When treated in alkaline solution with diazobenzene sulphate, they yield deep *brown* precipitates, though with some difficulty, and these possess little tinctorial value. It is possible that these reactions are characteristic of the above two classes of natural products, the *red* coloured easily formed dye-stuffs being produced from derivatives of the benzophenone class, whereas the brown indicate the presence of the xanthone or phenylated γ -pyron group.

Dyeing Properties.

As is to be expected from their constitution, benzeneazomaclurin and its homologues, dye wool and silk, both alone and with the aid of mordants. By the former method, using a slightly acidified bath, shades are obtained which vary from a light orange to a brown colour according to the strength of the solution. On striped mordanted calico there is obtained with aluminium mordant, orange-red, and, with iron mordant, pale olive to deep brown shades, and closely similar results are obtainable with wool and silk in the same manner. With chromium mordant upon wool and silk, the results resemble those obtained with unmordanted fabrics, the colours, however, being deeper and of greater utility. The benzeneazo-, ortho-, and para-tolueneazo-, xyleneazo-, and paranitrobenzeneazo-derivatives of maclurin yield very similar colours; the shades become, however, redder in tone in the order in which they are here placed. By the action of soap the colours obtained are at first slightly impoverished, but further treatment has but little action.

The acid sodium salt of maclurinazobenzeneparasulphonic acid dyes unmordanted wool and silk orange-yellow to orange coloured shades.

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