[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NORTH CAROLINA]

# The Constitution of Natural Tannins. VII. Coloring Matters Derived from β-Naphthol Aldehyde

BY ALFRED RUSSELL AND JOHN C. SPECK

With the exception of members derived from the more inaccessible hydroxy-phenyl aldehydes and ketones, nearly all the available coloring matters of the chalcone and 2-phenylbenzopyran series have been prepared synthetically. Many of these are identical with natural plant products, but it is probable that the synthetic members outnumber the natural ones. Although natural products containing condensed benzene nuclei are not uncommon, there have not thus far been identified, among natural coloring matters, any members containing such nuclei analogous to the parent chalcones, flavanones or anthocyanidins. In spite of this it seems desirable to extend appropriate synthetic work to these other possible series.

All of these compounds bear a close resemblance to the known members of the 2-phenylbenzopyran series, with this exception: all give a yellow color in acid solution while their ammoniacal solutions are pink. Their solutions in sulfuric acid have varying degrees of a green fluorescence that tends to become less as substitution increases. Unlike those of the parent compound and the methyl ethers, the decomposition points of the members containing free hydroxyl groups could be determined only as lying approximately in the neighborhood of 200°, because they did not liquefy upon decomposition and their deep colors made it impossible to see color changes with any degree of accuracy.

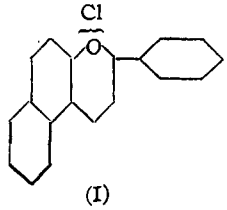
TABLE I

| Compound | Physical appearance[b] | Decompn. point, °C. | Yield, % | Formula | Cl analysis, % Calcd. | Found |
|---|---|---|---|---|---|---|
| 2-Phenyl-1-α-naphthopyrylium chloride | Fine, orange | 118 | 44 | $C_{19}H_{13}OCl$ | 12.2 | 12.1 |
| 4′-Hydroxy- | Dark-red | *Ca.* 200 | 63 | $C_{19}H_{13}O_2Cl$ | 11.5 | 11.75 |
| 2′-Methoxy- | Light-orange micro | 110 | 31.5 | $C_{20}H_{15}O_2Cl$ | 11.0 | 10.65 |
| 2′,4′-Dimethoxy- | Red | 132 | 58.5 | $C_{21}H_{17}O_3Cl$ | 10.05 | 10.2 |
| 2′,3′,4′-Trimethoxy- | Light-red | 121 | 81 | $C_{22}H_{19}O_4Cl$ | 9.28 | 9.1 |
| 2′,3′,4′-Trihydroxy- | Dark-red micro | *Ca.* 200 | 46 | $C_{19}H_{13}O_4Cl$ | 9.32 | 9.1 |
| 2′-Hydroxy- | Dark-red | *Ca.* 200 | 58[a] | $C_{19}H_{13}O_2Cl$ | 11.5 | 11.3 |
| 2′,4′-Dihydroxy- | Dark-red | *Ca.* 200 | 67[a] | $C_{19}H_{13}O_3Cl$ | 9.7 | 9.62 |

[a] Based on the benzoate. [b] Needles unless stated otherwise.

There is now described the preparation of a number of analogs of the 2-phenylbenzopyrylium salts, derived from β-napthol aldehyde and various substituted acetophenones. The reaction is the familiar one employed by Sir Robert Robinson and others, which involves the condensation of an *o*-hydroxy aromatic aldehyde and a methyl aryl ketone with hydrochloric acid.

A suggested name for the compound (I), which may be regarded as the parent of this series, is 2-phenyl-1-α-naphthopyrylium chloride. Substituents on the 2-phenyl group will be designated by conventional prime numbers.




(I)

The general procedure for the preparation of the anthocyanidin benzoates and methyl ethers, as well as the parent compound (I), consisted of dissolving equimolecular quantities of β-naphthol-aldehyde and the properly substituted acetophenone in glacial acetic acid, excepting as noted.[1] The solution was then kept saturated with hydrogen chloride at room temperature until the precipitation of the product or the viscosity of the solution indicated the reaction approached completion. This usually required one to two days. The product remaining in solution was then precipitated with ether, and recrystallization effected from dilute alcoholic hydrochloric acid.[2]

The free hydroxy compounds (VII) and (VIII) were obtained by hydrolysis of the corresponding benzoates, the preparation of which is described above. This was accomplished by dissolving 4–5 g. of the benzoate in 100 cc. of alcohol acidified with 75 cc. of concentrated hydrochloric acid, and heating for twenty-four hours on the steam-bath; these products crystallized on cooling.

(VI) was prepared by demethylating (V) as follows:

(1) III was prepared in anhydrous ether.

(2) The benzoates precipitated as dark-green, amorphous solids which could not be recrystallized and were, hence, incapable of analysis; they are not mentioned in the table.

4.6 g. of the methoxy compound was heated at reflux for one-half hour with 10 g. of anhydrous aluminum chloride in 60 cc. of chlorobenzene. The mixture was then acidified with hydrochloric acid and the chlorobenzene removed by steam distillation; the excess water was distilled off and the residue allowed to cool, whereupon the anthocyanidin separated from solution. It was recrystallized from dilute alcoholic hydrochloric acid.

## Summary

1. The familiar reactions involved in the preparation of 2-phenyl benzopyrylium salts can be extended to include compounds having condensed benzene nuclei.

2. A series of 2-phenylnaphthopyrylium chlorides is described. As might be anticipated the members are very similar to those of the analogous 2-phenylbenzopyrylium series but their colors are much darker.

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# Ethylenediamine. IV.[1] Monoalkyl Derivatives

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Examples of every type of alkyl ethylenediamine (*viz.*, $RNHCH_2CH_2NH_2$, $RNHCH_2CH_2NHR$, $R_2NCH_2CH_2NH_2$, $R_2NCH_2CH_2NHR$, $R_2NCH_2CH_2NR_2$) are to be found in the literature, but in some cases the syntheses are laborious and give poor yields or ill-defined products. It was thought the amines represented by $RNHCH_2CH_2NH_2$, which are secondary amines having the $\beta$-amino ethyl group in common, might be interesting in themselves or as starting materials for synthetic work. Several representatives of this type are known and have been characterized as derivatives, but the data on the free amines are in many cases lacking or contradictory, presumably because the syntheses yielded very small amounts of impure products.

Since direct alkylation of ethylenediamine is reported[2] to yield only the bis-diquaternary ammonium salt, several indirect methods of controlled monoalkylation have been tried. (1) Johnson and Bailey[3] discuss several reactions which might be expected to yield monoalkylated ethylenediamines, but which in fact fail to do so. They obtained monomethylethylenediamine by the following series of reactions

$$o\text{-}C_6H_4(CO)_2NCH_2CH_2Br \xrightarrow{KNHSO_2CH_2C_6H_5} o\text{-}C_6H_4(CO)_2NCH_2CH_2NHSO_2CH_2C_6H_5 \xrightarrow[CH_3ONa]{CH_3I} o\text{-}C_6H_4(CO)_2NCH_2CH_2N(CH_3)SO_2CH_2C_6H_5 \xrightarrow{HCl} CH_3NHCH_2CH_2NH_2$$

The method is worthless for general synthetic work since only 2 g. of the sulfonamide could be alkylated at one time. (2) Winans and Adkins[4] describe the catalytic hydrogenation of $CH_2{=}NCH_2CN$ to monomethylethylenediamine, but the boiling point reported by them is not the same as that found by others. (3) Von Braun[5] and co-workers produced monomethylethylenediamine by the nitrous acid dephenylation of the acetyl derivative of $C_6H_5(CH_3)NCH_2CH_2NH_2$ (obtained from $C_6H_5(CH_3)NCH_2CH_2Br$ and liquid ammonia), but the yield is only a few per cent. of the theoretical. (4) Schotte[6] and co-workers describe the preparation of monoalkyl ethylenediamines in unspecified yields by the hydrochloric acid fission of $\beta$-guanido ethanols. $NH_2C(NH)N(R)CH_2CH_2OH \xrightarrow{HCl} RNHCH_2CH_2NH_2$. (5) Bleier[7] reports that monobenzylethylenediamine is a by-product from the hydrochloric acid fission of *sym*-dibenzenesulfonyldibenzylethylenediamine together with the expected dibenzylethylenediamine. (6) Van Alphen[8] states that monobenzylethylenediamine is produced in small amounts when the mixture resulting from the interaction of benzaldehyde and excess ethylenediamine is reduced with sodium and alcohol.

The present investigation has resulted in a synthesis for molecules of the type $RNHCH_2CH_2NH_2$ in pure condition and reasonable yields using well known reactions with cheap reagents.

$$NH_2CH_2CH_2NH_2 \xrightarrow{CH_3COOC_2H_5}$$

(1) For the third paper of this series see THIS JOURNAL, **62**, 1202 (1940).

(2) Schneider, *Ber.*, **28**, 3073 (1895).

(3) Johnson and Bailey, THIS JOURNAL, **38**, 2135 (1916).

(4) Winans and Adkins, *ibid.*, **55**, 4167 (1933).

(5) Von Braun, *Ber.*, **70**, 979 (1937).

(6) Schotte, *Z. physiol. Chem.*, **174**, 119 (1928); German Patent 446,547.

(7) Bleier, *Ber.*, **32**, 1829 (1899).

(8) Van Alphen, *Rec. trav. chim.*, **54**, 594 (1935).