The Synthesis of Some Food Azo Dyes

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The present paper describes the synthesis of some bis-azo dyes which can be used as food dyes. They were obtained by the diazotization of a monoazo component of the 4-mono-azobenzene type followed by coupling with: β-naphtol, Schäffer acid, salt R and acid γ. The monoazo components resulted from the diazotization of the sulphanilic acid and the coupling with: aniline, cresidine and ortho-toluidine. All the synthesized dyes were later analysed via chromatography, IR and UV-Vis spectrometry and food analysis.

Keywords: food azo dyes, FT-IR and UV-VIS spectra

The food dyes are used for food products only for organoleptic reasons, usually in order to restore the color which faded during the processing, to reinforce the natural colour, or to give the product colourings that it never had, which are however directly related to its flavour, taste, composition and aspect [1].

There are many food dyes in use today and their erratic use may cause irritation reactions to tissues. In 1956, FAO-OMG initiated the use of the defined daily dose (DDD), i.e. the dye dose which can be daily ingested for long periods of time (even throughout the entire life), without causing any harmful health effects.

The dye water solubility as a salt must be 15% and the stability to heat must be of 20 min at 120°C, $pH=7$ without adding any preservatives. The majority of the synthesis food dyes are azo [2-4].

We can exemplify with the first food bis-azo dye, structure 1, obtained from two molecules of diazotized naphtionic acid and coupled with 2,4-dihydroxy-benzene alcohol having the structure 1 (fig. 1):

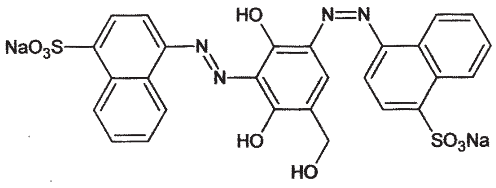

Fig. 1.

The food azo dyes contained in each sequence resulted from at least one sulphonic group, so that their reductive splitting in the body should lead to harmless aminoacids, not toxic amines.

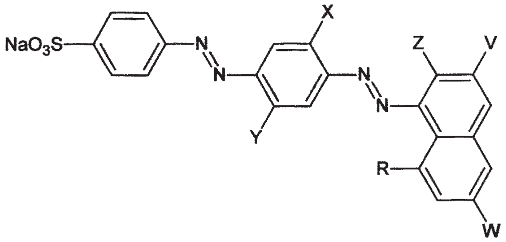

Fig. 2. Structure of synthesized bis-azoic compounds (2a-2l)
2a: $X=H$, $Z=OH$, $V=W=H$, $R=H$
2b: $X=Y=H$, $Z=OH$, $V=H$, $W=SO_3Na$, $R=H$
2c: $X=Y=H$, $Z=OH$, $V=W=SO\text{--}_3Na$, $R=H$
2d: $X=Y=H$, $Z=OH$, $V=H$, $W=SO_3Na$, $R=H$
2e: $X=OCH_3$, $Y=CH_3$, $Z=OH$, $V=H$, $W=SO_3Na$, $R=H$
2f: $X=OCH_3$, $Y=CH_3$, $Z= OH$, $V=W=SO_3Na$, $R=H$
2g: $X=OCH_3$, $Y=CH_3$, $Z=OH$, $V=SO_3Na$, $W=H$, $R=NH_2$
2h: $X=CH_3$, $Y=H$, $Z=OH$, $V=H$, $W=SO_3Na$, $R=H$
2i: X=CH3, $Z=OH$, $V=H$, $W=SO_3Na$, $R=NH_2$
2l: $X=CH_3$, $Y=H$, $Z=OH$, $V=H$, $W=SO_3Na$, $R=H$

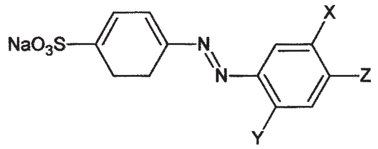

Fig 3. Structure of monoazo dyes (3a-3c)
3a: $X=Y=H$, $Z=NH_2$
3b: $X=OCH_3$, $Y=CH_3$, $Z=NH_2$
3c: $X=CH_3$, $Y=H$, $Z=NH_2$

Experimental part

The paper presents the synthesis and the description of ten synthesized bis-azo dyes with the structure presented in figure 2.

The synthesis of the following monoazo intermediates with the structure 3a-3c was necessary for the preparation of these dyes (fig. 3a-3c).

The 3a-3c intermediated were obtained from the diazotization of the sulphanilic acid and the coupling of the resulted diazonium salt with aniline, cresidine and ortho-toluidine.

For the synthesis of 3a, 0.1 moles (17.3g) sulphanilic acid is dissolved into a solution of 0.05 moles (5.3g) sodium carbonate into 200 mL water, to which 0.1 moles (6.9g) sodium nitrite 30% are added. This solution is further poured slowly, upon continuous stirring, over a mixture of 0.255 moles (2.64 g) hydrochloric acid 30% and 100g ice. The presence of a fine, white precipitate in an orange solution can be noticed. It is stirred for 50 min at 10-15°C. The excess of nitrous acid is removed with sulphamic acid. Then, 0.14 moles (4.2g) acid sodium carbonate solution 39% are mixed with 0.1187 moles (3.9g) formaldehyde, stirring for 30 min. It is heated at 60°C for 30 min and in the next 1-1.5 h, 0.0984 (8.8 g) aniline is added in drops, while stirring it. The stirring continues until a clear solution is obtained [7].

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Table 1
MONOAZOIC
INTERMEDIATES

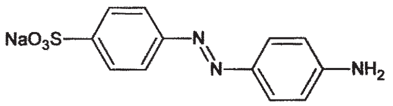
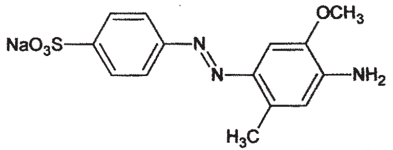
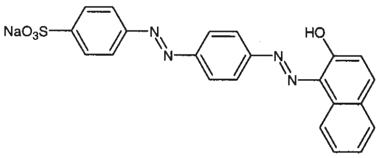
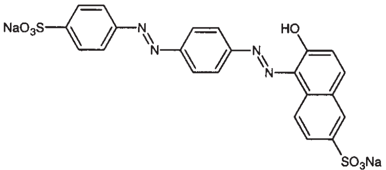
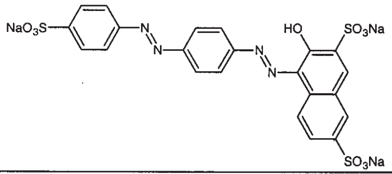
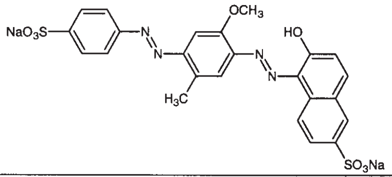
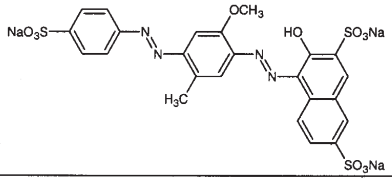
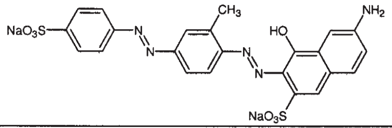
Dye	Diazo-coupling Molar ratio	pH	Reaction temperature (°C)	Reaction time (hours)	Yield(%)	Color
3a 	1:1.01	5-6	5	9	92.13	yellow
3b 	1:1.05	6-7	15-20	7	96.45	orange

Table 2
REACTION CONDITIONS
AND THE RESULTS
OBTAINED FOR 2a-2l DYES

Dye	Diazo-coupling Molar ratio	pH	Reaction temperature (°C)	Reaction time (hours)	Yield(%)	Color
2a 	1:1.02	8-9	10-15	2	93.27	red
2b 	1:1.10	8-9	15-20	2	91,80	red
2c 	1:1.10	8-9	15-20	3	92.38	red
2h 	1:1,50	8-9	10-20	3	95.31	black
2i 	1:1,10	8-9	15-20	2	96.18	black
2l 	1:1,20	8-9	15-20	3	93.22	black

The aniline is cooled at 5°C, then 0.1321 moles (6g) acid sodium carbonate are added to it. The diazo derivative solution which was prepared previously is slowly poured with continuous stirring for 6 h. 115g sodium chloride are added to it, stirring the mixture for an hour and then filtering it.

The moist cake is mixed with 0.52 moles (16.64g) sodium hydroxide solution 7% and it is heated for 3 h to the boil while stirring it. The mixture is then cooled to 20°C, salified, filtered and washed on filter with sodium chloride solution 5%. The moist cake is dried, the result being 23g 4-aminobenzene-4'-sulphonic acid sodium salt (η = 82.1%)

In order to prepare intermediate 3b, 0.1 moles (6.5g) cresidine are dissolved into 0.26 moles (12 mL) glacial acetic acid. 0.5 mL (32g) NF_8 (dispersing agent) are added to it. Next, 0.1 moles (6.6 mL) anhydrous sodium acetate and 0.16 moles (10.5g) sodium carbonate are dissolved into 100 mL water, to which 0.5 mL (32g) NF_8 are added. Solution I is poured over solution II in 1/2-1 hour, while stirring continuously.

The diazonium salt which was kept at 10-15°C is now added over the couplant at 20-25°C, while stirring permanently. The reaction mass is kept at 30°C for 1 h and at 45-50°C for 1 more hour, to finalize the reaction.

Table 3
UV -Vis ANALYSIS

Nr	2a	2b	2c	2d	2e	2f	2g	2h	2i	2l	3a	3b	3c
R_f	0,90	0,97	0,95	0,97	0,95	0,95	0,94	0,95	0,97	0,90	0,83	0,80	0,82
Color	Red	Red	Orange	Orange	Orange	Red	Red	Red	Red	Red	Orange	Orange	Orange

The mixture is filtered and the resulted moist cake is dried at 50-60°, 27g of product being obtained (η=96.4%)

For the synthesis of intermediate 3c, the diazonium salt is prepared in a similar manner to 3b (table 1).

The coupling component is prepared by dissolving 0.1107 moles (6.8g) o-toluidine into a solution which was made by mixing 0.08 moles (0.48g) hydrochloric acid with 0.0267 moles (1.188g) glacial acetic acid.

The mixture is then cooled to 20°C and ice is added to it. The coupling component solution is poured over the diazonium salt and a solution of ammonia 25% is dripped (below the level of the liquid) until a positive reaction is obtained on Litmus paper (*p*H=8). The precipitate is then filtered and washed with cold water. The resulted moist cake is mixed with 1 mole (68g) *orto*-toluidine and 0.05 moles (3.4g) *orto*-toluidine hydrochloride are added to it.

The mixture is heated for 3 h and 30-40°C, then the temperature is raised to 50°C where it is maintained for 12 h. The mixture is drained into a solution which was formed from 0.77 moles (4.8g) hydrochloric acid and 100 mL water. It is then filtered, washed on filter with hydrochloric acid solution 3%, the result being 28g product 3c (η=87.2%).

Dye 2a is prepared by mixing 0.07 moles intermediate 3a (3 mL) with 80 mL water and ice, then adding 0.105 moles (2 mL) hydrochloric acid and 0.084 moles (2.8g) sodium nitrite 30% solution while stirring for 1 hour at 5-10°C.

The nitrous acid excess is removed with sulphamic acid.

0.072 moles (2.08 g) β-naphtol are dissolved into a hot solution (80°C) which was prepared from 0.073 moles (2.33g) sodium hydroxide. The mixture is cooled at 15°C by external temperature.

The diazoderivative solution is now poured over the coupling component. The reaction mass is maintained at 10-15°C with stirring.

Sodium carbonate is added until *p*H=8.5-9.

The mixture continues to be stirred for 1.5 h to complete the reaction. From time to time the *p*H level is checked and sodium carbonate is added if necessary. It is salified and filtered. A red dye is obtained at an yield of 93.2%.

Dyes 2b-2l are similarly obtained. Table 1 and 2 presents the reaction conditions and the obtained results.

In order to verify the purity of the intermediates and of the dyes a thin layer cromatography was performed. The new products were purified [5]. The intermediates were also purified by repeated recrystallizations from ethyl alcohol.

Dyes 2a-2c were purified like the acid azo dyes [6]. The sodium salts of the dyes are dissolved in water, then they are filtered to remove insoluble substances, afterwards the free acid dye is precipitated with hydrochloric acid solution 32%. The acid dye is then neutralized in hot aqueous suspension with sodium hydroxide (*p*H=7).

The sodium salt solution which is obtained in this manner is evaporated completely and the precipitate is dried.

The bis-azo dyes 2a-2i were purified by washing them on the filter with methanol. The methanolic solution was evaporated on a water bath and the spectra for the aqueous solution of the residue which was left after washing with methanol and of the fraction extracted with methanol were drawn.

In the case of dye 2i, approximately 97% of the water soluble fraction was extracted out of methanol.

Dye 2l was extracted 98% from the initial amount.

All the fractions which were recovered from methanol were purified again by washing on the filter with a methyl chloride: methyl alcohol mixture in a 3:1 ratio. The same procedures were applied for dyes 2a-2h.

The cromatographic analysis and the IR spectra which were recorded for dyes 2a-2l show that all the dyes are pure.

The fractions which were estimated to be pure were solubilized in ethyl alcohol and then were analysed via thin layer cromatography on G silicagel, using two elution systems:

- propyl carbinol: ethyl alcohol: aqueous ammonia = 4:3:3 (v/v);
- ethyl alcohol: water = 95:5 (v/v).

The analysis of chromatograms shows that there are unitary coloured spots in both systems, which proves the purity of these products. For intermediates 3a-3c, IR spectra in KBr pill were recorded [8] (table 4).

The IR spectra were recorded with a JASCO FT-IR 410 spectrometer. The UV-VIs spectra (table 3)were made with a SPECORD 75R Carl Zeiss Jena apparatus.

Results and discussions

The bis-azo dyes 2a-2l were analyzed by verifying their purity and the purity of their intermediates 3a-3c. Besides chromatography, IR and UV-Vis spectra were also recorded. The Vis absorption spectra demonstrate that the resulted compounds are impure.

The intermediates purity could not be proven spectrophotometrically because of their low water solubility. A thin layer cromatograme on G silicagel on plastic leaf plate, using as mobile phase n-propyl carbinol: ethyl alcohol: ammonia in a 4:3:3 ratio (v/v) pr ethyl alcohol: water in a 95:5 ratio (v/v).

Table 4
IR SPECTRA

Dye	ν[cm^{-1}]	3a	3b	3c	2a	2b	2c	2d	2e	2f	2g	2h	2i	2l
Aromatic cycle	ν_{CH}	3019	3020	3018	3020	3021	3017	3019	3020	3021	3019	3020	3018	3020
Aromatic Cycle	ν_{CH}	1800	1805	1806	1805	1805	1806	1805	1806	1806	1806	1806	1807	1808
Aromatic cycle	$\nu_{C=C}$	1578	1580	1579	1580	1580	1579	1582	1580	1580	1587	1580	1587	1580
Aromatic cycle	ν_{CH}	1220	1220	1221	1222	1218	1220	1221	1220	1219	1222	1220	1221	1220
CH_3O	ν_{CH3O}	-	2848	2850	2844	2852	2851	2849	2850	2852	2850	2850	2849	2850
CH_3O C aromatic	ν_{C-O-C} as.	-	1251	1252	1250	1250	1249	1251	1252	1249	1253	1250	1251	1249

CH_3 C arom.	ν_{C-O-C} as.	-	1049	1050	1051	1049	1050	1051	1052	1053	1049	1050	1048	1052
CH_3 C arom.	ν_{CH3} as.	-	1460	1460	1461	1462	1461	1460	1459	1460	1461	1462	1460	1461
CH_3 C arom.	ν_{CH3} sim	-	2869	2870	2869	2870	2872	2871	2869	2870	2870	2871	2872	2871
CH_3 C arom.	ν_{CH3} as.	-	1460	1461	1462	1460	1460	1461	1461	1462	1461	1460	1462	1460
NH_2-Ar	ν_{NH2} as	3500	3500	3510	-	-	-	-	-	-	3500	-	3495	-
NH_2-Ar	ν_{NH2} sim.	3400	3400	3390	-	-	-	-	-	-	3400	-	3450	-
Ar-NH-	ν_{NH}	3450	3450	3439	-	-	-	-	-	-	3450	-	3450	-
SO_3H	ν_{SO2} as	1350	1350	1350	-	1350	1350	1351	1382	1350	1351	1350	1351	1352
SO_3H	ν_{SO2} sim	1160	1160	1158	1160	1160	1160	1160	1160	1160	1160	1160	1160	1160
SO_3H	ν_{S-O}	700	702	701	700	700	700	700	700	700	700	700	700	700

Table 5

UV-VIs SPECTRA

Dye	Formula	Molar mass	λ_{max} (nm)	Molar conc.	ε	log ε
monoazoic 3a	$C_{12}H_{10}N_3SNaO_3$	299	396	$3.35*10^{-5}$	7164.81	3.85
bisazoic 2a	$C_{22}H_{13}N_4SNaO_4$	452	508	$2.19*10^{-5}$	10502.37	4.02
bisazoic 2b	$C_{22}H_{14}N_4S_2Na_2O7$	556	505	$1.94*10^{-5}$	38144.37	4.52
bisazoic 2c	$C_{22}H_{13}N_4S_2Na_2O_7$	555	507	$1.67*10^{-5}$	16766.51	4.28
monoazoic 3b	$C_{12}H_{14}N_3SNaO_3$	303	393	$2.91*10^{-5-}$	26460.48	4.42
bisazoic 2d	$C_{22}H_{13}N_4SNaO_3$	436	420	$1.78*10^{-5}$	24710.03	4.39
bisazoic 2e	$C_{22}H_{18}N_4S_2Na_2O_8$	576	422	$1.47*10^{-5}$	13605.4	4.13
bisazoic 2f	$C_{24}H_{17}N_4S_2Na_2O_8$	599	420	$1.66*10^{-5}$	3975.09	4.59
monoazoic 3c	$C_{12}H_{12}N_3SNaO_3$	301	-	$3.19*10^{-5}$	-	-
bisazoic 2g	$C_{24}H_{18}N_4S_2Na_2O_8$	600	502	$1.82*10^{-5}$	27322.97	4.43
bisazoic 2h	$C_{23}H_{16}N_4S_2Na_2O_7$	586	500	$1.74*10^{-5}$	54022.45	4.73
bisazoic 2i	$C_{23}H_{16}N_4S_2Na_2O_7$	586	498	$1.52*10^{-5}$	12500	4.0
bisazoic 2l	$C_{23}H_{13}N_4S_2Na_2O_7$	583	497	$1.51*10^{-5}$	12501	4.01

Opaque images were obtained in the IR spectra in KBr pill and the spectra could not be recorded. For those reasons, the IR determinations for the dyes were done in trichloromethane solution.

As a resuslt of the IR spectra analysis, both for the monoazo components and for the bis-azo dyes, the main functional groups from their structure were identified, as it appears in table 4.

Conclusions

It has been noticed that barium is absent and arsenium is of max. 5 p.p.m. The latter comes from the raw materials which were available. Selenium is also absent. As far as heavy metals with a content of max. 50 p.p.m. are concerned, the samples exceeded the standard limit, their source being the raw materials which were used [8-10].

The solubility of the synthesized products in ahydrous ethyl ether of 100 p.p.m at 15% concentration is the right one in all samples.

In the case of the water solubility of min. 0.1%, 3a intermediate and dyes 2d, 2g, 2h did not meet the requirements, as they are water soluble below the imposed limits.

The norms require a spectrophotometric exam a thin layer cromatography of FIPO norms on food analysis (solubility, thermic stability, heavy metals content) [11].

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