On Derivatives of α-Thujaplicin. III.[1] *Azo Dyes of α-Thujaplicin (o Isopropyl tropolone)*[2]

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T. Nozoe and his coworkers[3,4,5] carried out the detailed study about the azo dyes of hinokitiol (*m*-isopropyltropolone) but only *p*-tolyl-azo-dye of α-thujaplicin was reported.[6,7]

Fourteen kinds of azo dyes of α-thujaplicin are described in this paper. The alkali salt of α-thujaplicin was coupled with diazonium salts of aromatic amines in cold aqueous solution to yield orange yellow to reddish brown azo dyes easily and in good yield. The application of an excess diazonium salt gave only a mono-azo compound. The azo dyes obtained are given in Table I.

TABLE I
AZO DYES OF α-THUJAPLICIN OBTAINED

Aromatic amines used.	Color and form	m.p.	Solvents (for recrystallization)
Aniline	red prisms	132.8–134°	alcohol
o-Toluidine	red prisms	120–121°	cyclohexane
p-Toluidine	orange red prisms	130–131°	benzene
p-Anisidine	orange fine needles	107–108°	alcohol
p-Chloroaniline	yellowish brown fine crystal	123–124°	cyclohexane
p-Bromoaniline	reddish brown needles	123–124°	alcohol
m-Nitroaniline	reddish brown fine crystal	144–145.3°	benzene
p-Nitroaniline	reddish brown fine crystal	166–167°	benzene
Sulfanilic acid	orange brown fine crystal	275°<(dec.)	water
p-Sulfanilamide	yellow fine needles	227–228°	acetic acid
p-Aminobenzoic acid	yellow fine crystal	267–268° (dec.)	water (K-salt)
α-Naphthylamine	brownish red plates	135–136°	acetic acid
β-Naphthylamine	red prisms	136–137°	pet.-ether
Benzidine	dark brown fine crystal	249–250° (dec.)	benzene

Most of the azo dyes are soluble in benzene, alcohol, petroleum ether, cyclohexane and glacial acetic acid, but some derived from sulfanilic acid, *p*-sulfanilamide and *p*-aminobenzoic acid are slightly soluble in these solvents. The azo dyes dissolve in a caustic alkali solution to give an orange red or deep red solution, and precipitate with acid. The azo dyes show a red coloration by ferric chloride, characteristic to tropolone nucleus.

p-Tolyl-azo-α-thujaplicin absorbed two molar equivalents of hydrogen when hydrogenated in ethyl acetate with Adams' PtO_2 catalyst, giving amino-α-thujaplicin m.p. 172–173° and *p*-toluidine. Methylation of *p*-anisyl-azo-α-thujaplicin with diazomethane in ether gave *p*-anisyl-azo-α-thujaplicin methyl-ether m.p.

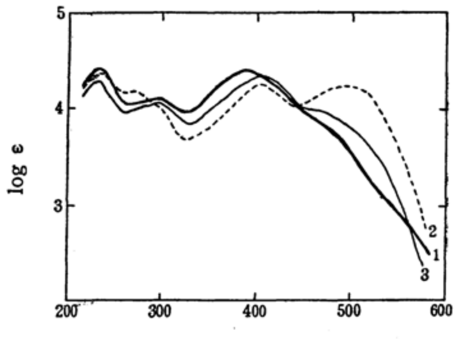

Fig. 1. Ultraviolet absorption spectra of phenyl-azo-α-thujaplicin (Curve 1), *m*-nitro-phenyl-azo-α-thujaplicin (Curve 2), *p*-sulfo-phenyl-azo-α-thujaplicin (Curve 3).

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[1] II. K. Yamane and S. Morosawa, This Bulletin, **27**, 18, (1954).

[2] This work was presented at the Hiroshima District Meeting of the Chemical Society of Japan, Nov. 15 (1953).

[3] T. Nozoe, E. Sebe and S. Ebine, *Proc. Japan. Acad.*, **26**, (8) 24 (1950).

[4] T. Nozoe, S. Ebine, S. Ito and I. Takasu, Ibid., **27**, 197 (1951).

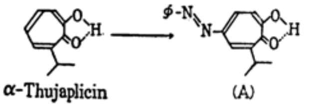
[5] T. Nozoe, E. Sebe, Y. Kitahara and H. Fujii, *Sci. Rep. of Tohoku Univ.*, Ser. I., **33**, 166 (1952).

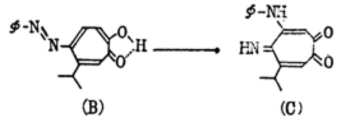
[6] T. Nozoe, A. Yasue and K. Yamane, *Proc. Japan Acad.*, **27**, 15 (1951).

[7] T. Nozoe, Y. Kitahara, K. Yamane and T. Ikemi, Ibid., **27**, 193 (1951).

99–100°. Ultraviolet absorption spectra of some azo dyes are given in Fig. 1. Absorption maximum of about 400 mμ is characteristic to tropolone nucleus.

T. Nozoe et al.[4,5] have reported that the azo dyes of hinokitiol (B) rearranged when heated with alcohol or acetic acid containing one drop of hydrochloric acid, giving dark reddish purple crystals, that is "hinopurpurins", which have a tropoquinonoid structure (C). It is interesting, however, that all the azo dyes of α-thujaplicin do not undergo rearrangement by the same procedure.





T. Nozoe and E. Sebe[5] have reported that the position of the azo group in azohinokitiols was at the para (5) position in spite of steric interference of the isopropyl group. In the case of azo-α-thujaplicin, the position of the azo group must be either at the para (5) or the ortho (7) position of the cycloheptatrienolone ring.

Amino-α-thujaplicin m. p. 172–173° obtained by the catalytic reduction of *p*-tolyl-azo-α-thujaplicin as described above, is the same substance prepared from the catalytic reduction of nitroso-α-thujaplicin[7] and mononitro-α-thujaplicin m. p. 112–113°.[1]

T. Nozoe et al.[8] have reported that the electrophilic substitution takes place predominantly at the *p*-position in the nitration and the nitrosation of tropolones. From these facts, therefore, the azo coupling of α-thujaplicin may take place at the *p*-position as in (A).

A trial to obtain azoxy-compound by the oxidation of phenyl-azo-α-thujaplicin with 30 per cent hydrogen peroxide solution in glacial acetic acid failed, yielding a syrupy matter which gave no red coloration with ferric chloride.

Beside the crystals of m. p. 131° of *p*-tolyl-azo-α-thujaplicin, the author obtained yellow prisms of m. p. 124° in small amount, but no detailed study has yet been made.

Experimental

Phenyl-azo-α-thujaplicin [(A)*: ϕ =C_6H_5–]:—To a solution of 0.11 g. aniline dissolved in 3.3 cc. of 0.93 N-hydrochloric acid, a solution of 0.1 g. of sodium nitrite in 1.5 cc. of water was dropped in, and the resultant cold diazonium solution was added dropwise to the cold solution of 0.2 g. of α-thujaplicin in a mixture of 1.5 cc. of 1.7 N-potassium hydroxide solution and 15 cc. of water. After the completion of the addition, the mixture was stirred for ten minutes and 1 cc. of 2 N-hydrochloric acid was added. The mixture was stirred for a further 30 minutes in the cold, and the crystals were collected by filtration. 0.34 g. of azo dye was obtained. The recrystallization from alcohol yielded red prisms, m. p. 133–134°. Found: C, 71.32; H, 5.87; N, 10.39, Calculated for $C_{16}H_{16}O_2N_2$: C, 71.62; H, 6.01; N, 10.44%.

Azo-α-thujaplicins derived from *o*- and *p*-toluidine, *p*-anisidine, *p*-chloroaniline, *p*-bromoaniline, *m*- and *p*-nitroaniline, sulfanilic acid, *p*-sulfanilamide, *p*-aminobenzoic acid, α- and β-naphthylamine and benzidine were prepared in a manner like the above (ordinary method). The color, crystalline form and melting point of these azo dyes are shown in Table I. [(A): ϕ=*o*-$CH_3 \cdot C_6H_4$-]. Found: N, 10.04, Calculated for $C_{17}H_{18}O_2N_2$: N, 9.92%. [(A): ϕ=*p*-$CH_3 \cdot C_6H_4$-]. Found: N, 9.39, Calculated for $C_{17}H_{18}O_2N_2$: N, 9.92%. [(A): ϕ=*p*-$CH_3O \cdot C_6H_4$-]. Found: N, 9.16, Calculated for $C_{17}H_{18}O_3N_2$: N, 9.39%. [(A): ϕ=*p*-$Cl \cdot C_6H_4$-]. Found: N, 9.20, Calculated for $C_{16}H_{15}O_2N_2Cl$: N, 9.25%. [(A): ϕ=*p*-$Br \cdot C_6H_4$-]. Found: N, 7.99, Calculated for $C_{16}H_{15}O_2N_2Br$: N, 8.07%. [(A): ϕ=*m*-$NO_2 \cdot C_6H_4$-]. Found: N, 13.63, Calculated for $C_{16}H_{15}O_4N_3$: N, 13.41%. [(A): ϕ=*p*-$NO_2 \cdot C_6H_4$-]. Found: N, 13.63, Calculated for $C_{16}H_{15}O_4N_3$: N, 13.41%. [(A): ϕ=*p*-$HO_3S \cdot C_6H_4$-]. Found: N, 7.87, Calculated for $C_{16}H_{16}O_5N_2S$: N, 8.04%. [(A): ϕ=*p*-$H_2NO_2S \cdot C_6H_4$-]. Found: N, 12.20, Calculated for $C_{16}H_{17}O_4N_2S$: N, 12.09%. [(A): ϕ=*p*-$HOOC \cdot C_6H_4$-]. Found: N, 9.04, Calculated $C_{17}H_{16}O_4N_2$: N, 8.97%. [(A): ϕ=α-$C_{10}H_9$-]. Found: N, 8.82, Calculated for $C_{20}H_{18}O_2N_2$: N, 8.80%. [(A): ϕ=β-$C_{10}H_9$-]. Found: N, 8.32, Calculated for $C_{20}H_{18}O_2N_2$: N, 8.80%. *p*, *p*′-Diphenyl-bisazo-α-thujaplicin: Found: N, 10.60, Calculated for $C_{32}H_{30}O_4N_4$: N, 10.48%.

Catalytic reduction of *p*-tolyl-azo-α-thujaplicin:—A solution of 5.22 g. of *p*-tolyl-azo-α-thujaplicin in 150 cc. of ethyl acetate was catalytically reduced with 0.21 g. Adams' PtO_2 at ordinary temperature and pressure, by which 1050 cc. of hydrogen was absorbed. The removal of the solvent and the catalyst gave a solid residue, crude amino-α-thujaplicin. The recrystallization from benzene yielded yellow prisms m. p. 172–173°. Found: C, 67.20; H, 7.26; N, 7.59, Calculated for $C_{10}H_{13}O_2N$: C, 67.04: H, 7.26; N, 7.80%.

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[8] (a) T. Nozoe, *Science of Drugs*, **3**, 174 (1949): *Sci. Rep. of Tohoku Univ.*, I, **34**, 199 (1950). (b) T. Nozoe et al., *Proc. Japan. Acad.*, **26**, 33 (1950). (c) T. Nozoe et al, Ibid., **27**, 190 (1950). (d) T. Nozoe and E. Sebe, Ibid., **26**., 45 (1950). (e) T. Nozoe et al., Ibid., **27**, 565 (1951). (f) T. Nozoe et al., Ibid., **28**, 488 (1952).

* Formula of azo-dyes of α-thujaplicin

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