The Synthesis of 3-Carboxyalkyl-salicylaldehyde Derivatives and Application of Their Chelate Forming Properties to the Analysis of Copper and Nickel[1]

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(Received March 7, 1968)

In connection with the previous report on the ethylenediamine conjugate of bis-*O*-carboxymethyl-salicylaldehyde-alkylenediimine-copper,[2] Reimer-Tiemann synthesis of the following three 3-carboxy-alkylsalicylaldehydes IIa, b, c and the synthesis of their derivatives were made with hydroxyacid Ia, b, c as the starting material.

Ia (mp 151°C, Found: C, 41.62; H, 3.19%. Calcd for $C_8H_7O_8Br$: C, 42.01; H, 3.05%) was prepared by the bromination of 2-hydroxyphenyl-acetic acid[3] in carbon disulfide solution. IIIa, b, c were obtained by the reaction of two moles of IIa,b,c, with one mole of ethylenediamine in ethanolic solutions and IVa, b were obtained by the reduction of IIIa, b with sodium borohydride in methanolic solutions.[4] The results are summarised in Table 1.

TABLE 1

Starting material	React. prod.	Yield %	Mp °C	Found (Calcd) C	H	N
Ia	IIa PY	12.30	204	42.01 (41.72)	3.00 (2.72)	
Ib	IIb PY	0.65	95	63.71 (63.45)	5.84 (5.81)	
Ic	IIc Y	6.30	118	52.70 (52.53)	4.02 (3.97)	
IIa	IIIa Y	92.23	242	44.69 (44.30)	3.16 (3.35)	4.94 (5.17)
IIb	IIIb Y	83.63	195	64.19 (65.44)	6.46 (6.41)	7.09 (6.36)
IIc	IIIc Y	46.98	204	54.89 (54.74)	4.61 (5.03)	5.82 (5.55)
IIIa	IVa G	50.32	300*	43.37 (43.98)	4.32 (4.06)	5.41 (5.13)
IIIb	IVb·$2H_2O$ W	51.53	285	59.54 (59.98)	7.23 (7.55)	5.99 (5.83)

P=pale, Y=yellow, G=gray, W=white; * decomposition

Disodium salt of IVb works as a hexadentate ligand and forms a green copper(II) chelate but does not form any stable nickel chelate in aqueous solutions of pH 10 (it does not reveal any purple color of Murexide when added into an aqueous solution of nickel-Murexide complex), and was satisfactorily used in the spectrophotometric determination of copper(II) ions out of the mixed solutions of copper(II) and nickel(II) ions as illustrated in Fig. 2 and Table 2.

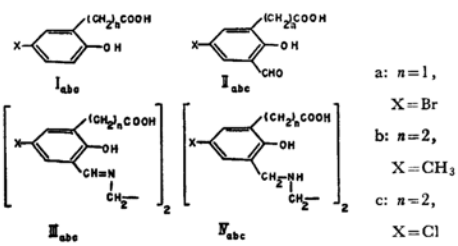

Fig. 1.

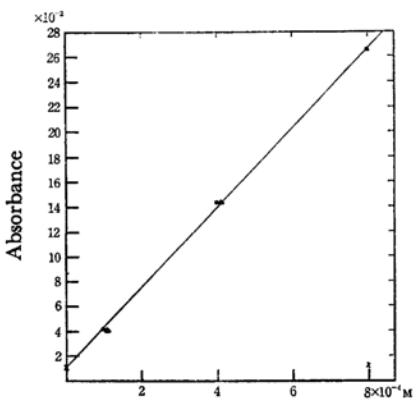

Fig. 2. Measurements were made of 5 m*l* of aqueous solutions containing 0.5 m*l* of 1/100 mol solution of disodium salt of IVb, 0.1 m*l* of pH 10 buffer solution[6] and; ○, moles of copper (II) acetate; ×, moles of nickel acetate; △, each moles of copper (II) acetate and nickel acetate, respectively. Cell depth 1 cm and pure water as reference.

TABLE 2

Sample	Found (as Cu)		Sample	Found (as Cu)
Cu 0.798 mg	0.798 mg		Cu 0.399 mg	0.411 mg
Ni 0.780 mg	0.001 mg		Cu 0.099 mg	0.094 mg
Cu {0.399 mg} Ni {0.390 mg}	0.411 mg		Cu {0.099 mg} Ni {0.097 mg}	0.091 mg

In aqueous solutions of pH 10 containing Murexide indicator, IVa (Ni taken 1.76 mg, found 1.87 mg) and IVb (Cu taken 0.636 mg, found 0.699 mg) can be used as the reagent of chelatometric titration of nickel and copper respectively in place of EDTA.[5]

1) Part IX of "Some Addition Compounds of Salicylaldehyde-ethylenediimine-copper."
2) T. Tanaka, This Bulletin, **39**, 2558 (1966).
3) J. Levine, T. E. Eble and H. Fischbach, *J. Am. Chem. Soc.*, **60**, 1930 (1948).
4) I. L. Finar and K. Utling, *J. Chem. Soc.*, **1959**, 4015.
5) H. A. Flaschka, "EDTA Titrations," Pergamon Press., New York (1964), p. 82.
6) H. A. Flaschka, *ibid.*, p. 72.