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Spectroscopic Determination of Salicylhydroxamic and 5-Bromosalicylhydroxamic Acids

by

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Summary. Salicylhydroxamic and 5-bromosalicylhydroxamic acids can be distinguished from salicylic and 5-bromosalicylic acids or salicylamide and 5-bromosalicylamide, respectively, by their electronic spectra of their vanadium V^V complexes manifested by a wide maximum at 410–790 nm and analytical λ_{max}=620 nm.

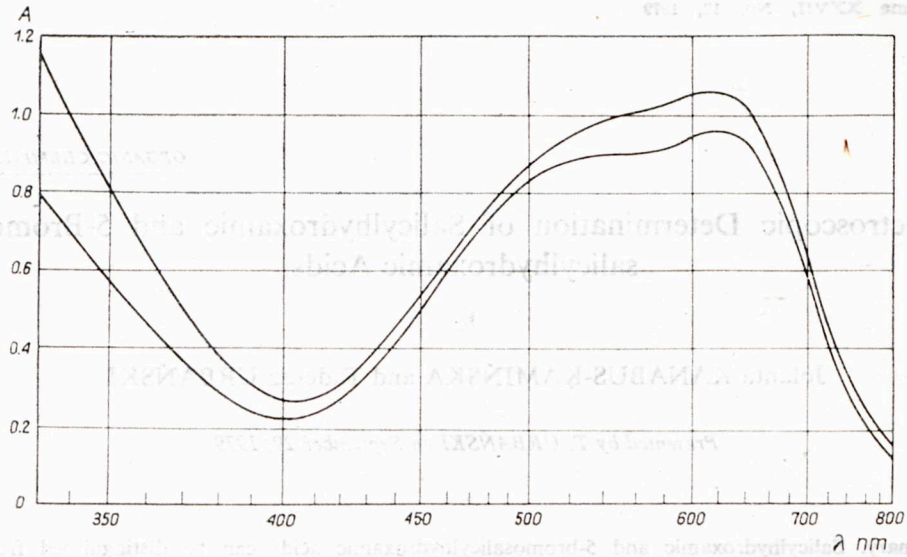
The recent discovery of aromatic hydroxamic acids, particularly salicylhydroxamic acid (SH), being potential drugs against *Trypanosomiasis* [1] has necessitated finding an analytical method of determining SH in physiological fluids, particularly in view of the earlier finding of biological activity of hydroxamic acids [2, 3]. Also it seemed advisable to examine 5-bromosalicylhydroxamic acid (BSH) which was in use for some time as an antitubercular agent [4].

Salicylhydroxamic acid and its derivatives form complexes with vanadium $V^{(V)}$ used in the form of ammonium vanadate at pH=ca.2. The complexes are formed by ammonium vanadate and salicylhydroxamic acid and its derivatives used in the molar proportion 1:1. The complexes are readily detectable thanks to a deep purple colour due to the absorption stretching from 410 to 790 nm in aqueous ethanol solution. It is composed of two submaxima: near 500–510 nm and near 620 nm. The absorption at 620 nm was taken for quantitative analysis. For salicylhydroxamic and 5-bromosalicylhydroxamic acids the extinction λ_{620} was found to be $2.40 \cdot 10^6$ and $2.65 \cdot 10^6$ cm²/mol, respectively (Figure).

The method is suitable for determining the concentration of the above acids as low as $5 \cdot 10^{-5}$ mol/l.

The total amount of an acid should not be lower than 10^{-7} mol. By extraction a smaller quantity of the acid can be detected.

Salicylic acid, salicylamide and their derivatives do not form coloured complexes with vanadium ion.



Electronic absorption spectra of salicylhydroxamic acid (*1*) and 5-bromosalicylhydroxamic acid (*2*) complexes with ammonium vanadate

Experimental

Salicylhydroxamic acid and 5-bromosalicylhydroxamic acid were prepared according to [5] and [6], respectively.

Salicylic acid, salicylamide and their bromoderivatives were of commercial grade.

All these substances were purified by crystallization.

Ammonium vanadate (Reachim, USSR) was of the analytical grade. It was used in the form of an aqueous solution of the concentration of $2 \cdot 10^{-2}$ mol/l. It was prepared by dissolving 0.117 g ammonium *meta*-vanadate in 100 ml water and acidified with 0.01 ml nitric acid (*d* 1.40).

Solutions of salicylhydroxamic and bromosalicylhydroxamic acids, salicylic and bromosalicylic acid, salicylamide and bromosalicylamide were made by dissolving the substances in ethanol (96 %) to the concentration of $1 \cdot 10^{-2}$ mol/l.

Spectroscopic measurements were made in recording spectrometer: Specord UV/VIS (Zeiss, Jena, GDR).

2 ml of each: the solution of a hydroxamic acid, of ammonium *meta*-vanadate and of the buffer solution of pH=2 were mixed in a measuring flask and completed with ethanol/water 50/50 solution to 25 ml. The solution originally gray-green gradually changed its colour to deep purple. The measurements were made of the layer of 1 cm thickness in a quartz cuvette 2–3 h after mixing the solutions.

Salicylic acid and salicylamide and their derivatives give the same absorption as the solvent.

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REFERENCES

[1] D. A. Evans, R. C. Brown, J. Protozoology, **20**, 157 (1973); Trans. Roy. Soc. Trop. Medicine and Hygiene, **67**, 258 (1973); D. A. Evans, C. A. J. Brightman, M. F. Holland, Lancet, 769, II (1977); D. A. Evans, M. F. Holland, Trans. Roy. Soc. Trop. Medicine and Hy-

giene, **72**, 303 (1978); F. R. Opperdoes, P. N. Aarsen, C. van der Meer, P. Borst, Exp. Parasitology, **40**, 198 (1976); F. R. Opperdoes, P. Borst, K. Fonk, TEBS Letters, **62**, 169 (1976); A. H. Fairlamb, F. R. Opperdoes, P. Borst, Nature, **265**, 270 (1977); A. B. Clarkson, F. H. Brohn, Science, **194**, 204 (1976); F. H. Brohn, A. B. Clarkson, Acta Tropica, **35**, 23 (1978).

[2] T. Urbański, Nature, **166**, 267 (1950); J. Alkiewicz, Z. Eckstein, H. Halveg, P. Krakówka, T. Urbański, ibid., **180**, 1204 (1957); T. Chęciński, R. Dąbkowski, Lancet, 1352, I (1961).

[3] Z. Eckstein, T. Urbański, Bull. Acad. Polon. Sci., Cl. III, **4**, 617 (1956).

[4] A. Czyżyk, A. Ostaszyński, H. Plenkiewicz, Z. Szczepanik, T. Urbański, Arzneimittel-Forschung, **22**, 465 (1972) [and references therein].

[5] A. Jeanrenaud, Chem. Ber., **22**, 1270 (1889).

[6] T. Urbański, W. Lewenstein, Roczn. Chem., **26**, 565 (1952); Z. Eckstein, Z. Dominiak, ibid., **28**, 139 (1954); Przemysł Chem., **9**, 536 (1953).

Ё. Канабус-Каминьска, Т. Урбаньски, **Спектроскопное определение салицилгидроксамовой и 5-бромсалицилгидроксамовой кислот**

Содержание. Салицилгидроксамовая и 5-бвомсалицилгидроксамовая кислота отличаются от салициловой и 5-бромсалициловой кислот (или соответственоо, от амида салицилового и амида 5-бромсалицилового) электронными спектрами своих комплексов ванадия V^V, что проявляется широким максимумом при 410—790 *нм* и аналитическим $\lambda_{макс}=620$ *нм*.