Acetic acid, run on a column under the identical conditions, had the same threshold volume as the acid in the second zone. This acid was positively identified as acetic by Duclaux numbers; known acetic acid—6.45, 7.1, 7.2; acetic acid from wilforgine—6.5, 7.1, 7.3.

The water layer of the first zone was evaporated to a small volume and then acidified with a drop of concentrated hydrochloric acid, but there separated only a few small crystals which either melted or sublimed at 112° (hot stage). The ultraviolet spectrum of the remaining mother liquor was identical with that of 3-furoic acid (Fig. 5).

In a subsequent experiment 0.2984 g. of wilforgine was saponified. Its saponification equivalent was 107.6 (7.97 equivalents of acid per mole). After repetition of the procedure described above 10.8 mg. of pure 3-furoic acid was isolated from the first zone by repeated recrystallizations from water. An additional 13.6 mg. of less pure material was recovered from the mother liquors. The isolated acid and the authentic sample melted at 120–120.5° (in sealed tube to prevent sublimation), and the mixed melting point showed no depression. The ultraviolet spectrum in water was identical with that of the authentic sample (Fig. 5). The ultraviolet spectra of the sodium salts, formed by the addition of the theoretical quantity of alkali, were also identical (Fig. 5). After drying for several days over phosphorus pentoxide, the acid was analyzed.

Anal. Calcd. for $C_5H_4O_3$: C, 53.57; H, 3.60; neut. equiv., 112. Found: C, 53.40; H, 3.97; neut. equiv., 109.

Saponification of Wilfortrine.—32.50 mg. of wilfortrine was saponified as above. The saponification equivalent was determined to be 108.9 (8.02 equivalents of acid per mole). After acidification to congo red with sulfuric acid, the solution was steam distilled exhaustively. The distillate required 1.785 ml. of 0.1242 *N* sodium hydroxide (5.96 equivalents of steam volatile acid per mole). By difference there were 2.06 equivalents of steam non-volatile acid per mole.

Identification of Volatile Acids in Wilfortrine.—The titrated volatile acids were separated and analyzed as described above for wilforgine. The first zone required 0.735 ml. of 0.0512 *N* alkali (1.01 equivalents of acid per mole). The second zone required 3.505 ml. of 0.0512 *N* alkali (4.82 equivalents of acid per mole). The acid in the second zone was identified as acetic in the same manner as described above; Duclaux numbers—6.6, 7.1, 7.3.

On another lot of 0.1545 g. of wilfortrine the saponification equivalent was determined to be 108.7 (8.04 equivalents of acid per mole). From this lot 12.2 mg. of crude 3-furoic acid was isolated, which was purified and identified as above.

BELTSVILLE, MD. RECEIVED OCTOBER 29, 1951

NOTES

Acetylenic Compounds from Fungi

BY MARJORIE ANCHEL

During the past few years, there have been isolated in this Laboratory, from culture liquids of different species of *Basidiomycetes*, several antibiotic substances which have in common an ultraviolet absorption spectrum of striking and unusual form. The spectra show a series of five to seven sharp maxima in the region of 205 to 360 mμ, giving a characteristic "finger" effect when plotted.

The first compounds of this type isolated and studied spectrophotometrically were obtained from the culture liquids of three different species of *Basidiomycetes: Poria tenuis, P. corticola* and an unidentified species.[1,2] These compounds are remarkable not only because of their striking absorption spectra, but also because of their extreme instability.[3] At that time the only naturally occurring compounds described in the literature as having both similar spectra and similar behavior were the polyene fatty acids.[5]

In 1950,[6] a most interesting series of papers from the laboratory of N. A. Sörensen appeared, in which the isolation of polyacetylenic compounds from several genera of *Compositae* was reported, and their ultraviolet absorption spectra presented.[8] The spectra of these compounds resemble closely those of the compounds isolated from *Basidiomycetes*. In correspondence with Dr. Sörensen, we mentioned this similarity and sent him data on the ultraviolet spectra of our compounds. From these spectra, Dr. Sörensen identified our compounds as polyacetylenes. He pointed out to us that according to the rule of Hausser, Kuhn and Seitz[9] concerning the frequency differences of absorption maxima of polyenes and polyacetylenes (about 44 and about 63 f., respectively), our compounds must belong to the latter class. He further made detailed comparisons of the maxima of our compounds with those of acetylenic compounds isolated in his laboratory, as well as some synthesized in the laboratory of E. R. H. Jones,[10] in Manchester. From the near-identity of these, Dr. Sörensen has suggested the presence in our compounds of several specific groupings to which the spectra might be attributed.

In the following tables, the wave lengths of the maxima of the compounds from the *Basidiomycetes* are compared with those of the acetylenic compounds from the laboratories of Dr. Sörensen and Dr. Jones, and the responsible groupings suggested

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(1) M. Anchel, J. Polatnick and F. Kavanagh, *Arch. Biochem.*, **25**, 208 (1950).

(2) F. Kavanagh, A. Hervey and W. J. Robbins, *Proc. Nat. Acad. Sci.*, **36**, 1, 102 (1950).

(3) Biformin[4] also, in view of its behavior (instability and silver salt formation) and of the ultraviolet absorption spectrum[11] of a crude preparation, probably belongs to this class of compounds.

(4) W. J. Robbins, F. Kavanagh and A. Hervey, *Proc. Nat. Acad. Sci.*, **33**, 176 (1947).

(5) K. S. Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N. Y., Chapter 5.

(6) The first paper in this series was published in 1941.[7] It described the isolation of a highly unsaturated ester to which an acetylenic structure was assigned, tentatively. Due to lack of facilities, spectrophotometric studies were not made.

(7) N. A. Sörensen and J. Stene, *Ann.*, **549**, 80 (1941).

(8) (a) R. T. Holman and N. A. Sörensen, *Acta Chem. Scand.*, **4**, 416 (1950); (b) T. Bruun, C. M. Haug and N. A. Sörensen, *ibid.*, **4**, 850 (1950); (c) N. A. Sörensen and K. Stavholt, *ibid.*, **4**, 1080 (1950); (d) K. Stavholt and N. A. Sörensen, *ibid.*, **4**, 1567 (1950); (e) N. A. Sörensen and K. Stavholt, *ibid.*, **4**, 1575 (1950).

(9) K. W. Hausser, R. Kuhn and G. Seitz, *Z. physik. Chem.*, **29B**, 391 (1935).

(10) E. R. H. Jones, unpublished data.

TABLE I

Compound	Maxima, mμ					Solvent	Ref.
cis-α,β-Dihydromatricaria acid (CH_3—CH=CH—C≡C—C≡C—CH_2CH_2—COOH)	215	239	251.5	265.5	282.2	Hexane	[a]
trans-α,β-Dihydromatricaria acid	215	239	252.0	265.5	282.0	Hexane	[a]
CH_2=CH—C≡C—C≡CH	...	236	248	262	277	95% EtOH	[b]
CH_3—CH=CH—C≡C—C≡CH	...	238	251	264	280	95% EtOH	[b]
Nemotin (—C=C—C≡C—C≡C—)[d]	207	236	248	262	276	Water	[c]
Nemotinic acid	208	237	249	263	277	Water	[c]
Nemotin (ν of maxima)		1271.2	1209.7	1145.0	1087.0	f.	
(Δν)			61.5	64.7	58	f.	
Nemotinic acid (ν of max.)		1265.8	1204.8	1140.7	1081.1	f.	
(Δν)			61.0	64.1	59.6	f.	

[a] Laboratory of Sörensen.[11] [b] Laboratory of E. R. H. Jones.[10] [c] New York Botanical Garden.[1,2] [d] Grouping suggested by Dr. Sörensen.

TABLE II

Compound	Maxima mμ							Solvent	Ref.
Compound $C_{12}H_{10}O$ from *Artemisia vulgaris* (probably an ene-triyne)	231.0	242.5	257.7	272.5	289.0	308.1	328.6	Hexane	[a]
Nemotin A (alkali conversion product of Nemotin) (—C≡C—C≡C—C≡C—C=C—)[d]	231	242	257.8 (shoulder)	272	289	307	328	Phosphate buffer (*p*H 7)	[b]
Compound from *Clitocybe diatreta* (not analyzed)[e] (—C≡C—C≡C—C≡C—C=C—)[d]	230	240	...	270	285	303	323	95% ethanol	[c]
Nemotin A (ν of maxima)	1298.7	1239.7		1102.9	1038.1	977.2	914.6	f.	
(Δν)		59			64.8	60.9	62.6	f.	
Compound from *Clitocybe diatreta* (ν of maxima)	1304.3	1250.0		1111.1	1052.6	990.1	928.2	f.	
(Δν)		54.3			58.5	69	61.9	f.	

[a] Laboratory of Sörensen.[8a] [b] New York Botanical Garden.[1,2] [c] New York Botanical Garden.[12] [d] Grouping suggested by Dr. Sörensen. [e] This compound was obtained in amounts insufficient for satisfactory purification. In different preparations the positions of the maxima above 300 mμ varied by 2 or 3 mμ.

TABLE III

Compound	Maxima, mμ					Solvent	Ref.
cis-Lachnophyllum ester (CH_3—CH_2—CH_2—C≡C—C≡C—CH=CH—$COOCH_3$)	224.0	Inflexion	277.0	291.1	308.8	Hexane	[a]
trans-Lachnophyllum ester	223.5	256.8	271.0	287.2	305.3	Hexane	[b]
Compound from *Clitocybe diatreta* (tentative formula, $C_{17}H_{12}N_2O_6$) (—C≡C—C≡C—C=C—COOR)[d]	225	260	275	291	310	95% Ethanol	[c]
Compound from *Clitocybe diatreta* (ν of maxima)	1333.3	1153.8	1090.9	1030.9	967.7	f.	
(Δν)			63.1	60.0	63.2	f.	

[a] Laboratory of Sörensen.[8b,e] [b] Laboratory of Sörensen.[8b] [c] New York Botanical Garden.[12] [d] Grouping suggested by Dr. Sörensen.

TABLE IV

Compound	Maxima, mμ						Solvent	Ref.
R—C≡C—C≡C—C≡C—COOH	....	....	272	288	307	328	95% Ethanol	[a]
Agrocybin (—C≡C—C≡C—C≡C—COOR)[c]	216	224	269	286	304	325	95% Ethanol	[b]
Agrocybin (ν of maxima)	1388.9	1339.3	1115.2	1048.9	986.8	923.1	f.	
(Δν)		49.6		66.3	62.1	63.7	f.	

[a] Laboratory of E. R. H. Jones.[10] [b] New York Botanical Garden.[12] [c] Grouping suggested by Dr. Sörensen.

by Dr. Sörensen as probably common to both are indicated.

At least two other compounds with this characteristic absorption spectrum have been found in culture liquids of *Basidiomycetes*. These are being studied.

Besides the compounds already referred to, other examples of naturally occurring di- or polyacetylenes so far reported are described in the Annals of the Ministry of Agriculture of the Dutch East Indies in 1907, one by Wiljams, Smirnow and Goljmov[13] in 1935, and one by Castille[14] in 1939. The first two of these were obtained from plants of Compositae, the third from boleko nuts. It is of interest that these highly unstable compounds occur both in higher plants and in fungi.

Acknowledgment.—The author wishes to express

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(11) P. K. Christeusen, unpublished data.

(12) M. Auchel, unpublished data.

(13) W. W. Wiljams, V. S. Smirnow and V. P. Goljmov, *J. Gen. Chem.* (*U. S. S. R.*), **5**, 1195 (1935).

(14) A. Castille, *Ann.*, **543**, 104 (1940).

her gratitude to Dr. Jones and Dr. Sörensen for reading the manuscript, and for making available their unpublished data.

THE NEW YORK BOTANICAL GARDEN
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Non-exchange of Radiocyanide and Radiosulfide Ions with Aqueous Thiocyanate Ion[1]

BY ARTHUR W. ADAMSON AND PHILLIP S. MAGEE

The exchange reactions of $C^{14}N^-$ and $S^{35=}$ ions with thiocyanate ion have been investigated with essentially negative results.

Experimental

The $KC^{14}N$ solution was prepared from $BaC^{14}O_3$ by the method of Adamson,[2] and that of Na_2S^{35} by the addition of sulfate-free BaS^{35}.[3] The exchange experiments were carried out by mixing the appropriate solutions in small centrifuge tubes which were then sealed. Those containing sulfate were sealed in a nitrogen atmosphere.

After the elapse of the desired time, the separation of radiocyanide and thiocyanate ions was carried out by the precipitation of zinc cyanide. The zinc cyanide was purified by reprecipitation and then treated by the distillation and sample preparation method previously reported.[4] The separation of radiosulfide and thiocyanate ions was accomplished by precipitation of cadmium sulfide. The cadmium sulfide was subjected to a fairly elaborate purification before being counted, in order to remove coprecipitated thiocyanate ion. The samples of zinc cyanide or of cadmium sulfide were counted with a mica end window counter (2 mg./cm.^{2} window) and with an atmospheric pressure flow counter, respectively.

Approximate corrections for self absorption were made.

TABLE I

EXCHANGE OF RADIOCYANIDE WITH THIOCYANATE IN AQUEOUS SOLUTION

$(KSCN) = 0.19 f$; $(KC^{14}N) = 0.59 f$

*p*H	Temp., °C.	Exchange time, hr.	Exchange,[a] %
11.10	24	140	0.80
12.70	24	334	.61
12.70	60	170	.26
14.0	24	187	.65
14.0	60	163	.10
0.5	24	160	2.26

[a] Defined as in reference 5.

The data given in Table I are representative of the rather larger total amount of results obtained, and indicates no measurable exchange, with the possible exception of the system at *p*H 0.5. The results with radiosulfide agree with those reported in this issue by Heisig and Holt[5] in that no exchange was found in solutions 0.3 *f* in KSCN and 0.05 *f* in Na_2S at room temperature, after 204 hours at *p*H 12.6, and after 554 hours at *p*H 13.4.

These findings of negligible exchange are in accord with the difficulties of formulating potential mechanisms. Thus, the fact that the free energy for the primary dissociation of thiocyanate into sulfur and cyanide ion is positive by 16 kcal.[6] is in agreement with the fact that this path does not lead to exchange.

An alternative mechanism, in the case of the cyanide-thiocyanate system, might be considered to be an exchange of sulfur through the intermediate $NCSCN^{-2}$, but one is confronted with the impossibility of writing a structure for this species without exceeding the octet on carbon or invoking an improbable imide formulation for the cyanide group. It is noteworthy, however, that the analogous intermediate $O_3SSSO_3^{-4}$ has been proposed for the measurable exchange between sulfite and thiosulfate.[7] Here, however, structures of some *a priori* plausibility can be written since it is not unreasonable to exceed the octet on sulfur. Somewhat similar considerations serve to rationalize the lack of exchange of sulfide and thiocyanate, in contrast to the measurable exchange of sulfide with thiosulfate.[7]

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[1] (1) These investigations were carried out under contract N6onr23809 between the University of Southern California and the Office of Naval Research.

[2] (2) A. W. Adamson, THIS JOURNAL, **69**, 2564 (1947).

[3] (3) The tracers were obtained from the Atomic Energy Commission.

[4] (4) A. W. Adamson, J. P. Walker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

[5] (5) G. E. Heisig and R. Holt, *ibid.*, **74**, 1597 (1952).

[6] (6) W. M. Latimer, "The Oxidation States of the Elements," Prentice-Hall, Inc., New York, N. Y., 1938, p. 128.

[7] (7) D. P. Ames and J. E. Willard, THIS JOURNAL, **73**, 164 (1951).

DEPARTMENT OF CHEMISTRY
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The Kinetics of the Thermal Decomposition of Aluminum Borohydride[1]

BY RICHARD S. BROKAW AND ROBERT N. PEASE

Schlesinger, Sanderson and Burg[2] have observed that as the temperature is raised aluminum borohydride ($Al(BH_4)_3$) decomposes yielding hydrogen and solid products. This research was undertaken in order to obtain more detailed information as to the nature of the pyrolysis. Preliminary observations[3] of pressure–time curves at temperatures of 150° and higher showed the initial slopes of such curves to be proportional to the initial aluminum borohydride pressure, suggesting that the decomposition is essentially a first order process. Products were hydrogen and inhomogeneous solid products containing varying amounts of hydrogen.

Since both aluminum borohydride and the solid products yield hydrogen on heating it is not possible to calculate the aluminum borohydride pressure as a function of time from the total pressure. Instead, borohydride was run into a thermostated reaction bulb[4] to the desired pressure, and the clock started. After a predetermined time the thermostat was removed and the reaction bulb rapidly cooled to room temperature. A pressure reading was made, and then the hydrogen evolved was pumped off at liquid nitrogen temperature. On warming again to room temperature the pressure of undecomposed borohydride was measured, and from this the pressure at the reaction temperature was calculated. From a series of such runs for different time intervals the disappearance of aluminum borohydride as a function of time was determined. That the condensible residue was in fact undecomposed aluminum borohydride was established by observing (a) on exhaustive decomposition at 450–600° (by heating in the luminous flame of a torch) about 5.6–5.9 volumes of hydrogen are obtained both with the condensible gaseous residue and with aluminum borohydride and (b) if the residues from several runs are returned to the re-

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[1] (1) (a) Taken from a thesis submitted by Richard S. Brokaw in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University. (b) The work described in this paper was done in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, and Contract N6-ori-105 with the Office of Naval Research and Office of Air Research as coördinated by Project Squid, Princeton University. (c) We wish to acknowledge the assistance of Dean H. S. Taylor, who has general supervision of this project. (d) Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] (2) H. T. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **62**, 3421 (1940).

[3] (3) E. J. Badin and P. C. Hunter, unpublished work.

[4] (4) The apparatus was the one used in studying the reaction of aluminum borohydride with olefins: see Brokaw and Pease, THIS JOURNAL, **72**, 3237 (1950).