Es ist somit festzustellen, dass das durch H. Schmid und P. Karrer beschriebene „Sulforaphen" mit dem schon früher durch den einen von uns in Gemeinschaft mit St. Horváth isoliertem „Raphanin" identisch ist. Wir danken Herrn Prof. V. Bruckner auch an dieser Stelle für seine wertvollen Ratschläge.

Zusammenfassung.

Es wurde auf Grunde chemisch-analytischer, präparatiewer und biologischer Befunde festgestellt, dass die aus Rettichsamen zweierlei Art isolierten antibiotischen Substanzen „Raphanin" und „Sulforaphen" identisch sind.

Szeged, (Ungarn), Febr. 1949.

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Absorption Spectra of Diastereoisomeric Alkanolamine Derivatives.

Preliminary Communication.

By JÓZSEF KISS and LÁSZLÓ LÁNG.

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In preceding investigations one of us established, cooperating with Fodor that the acyl derivatives or aryl-proponol-amines of psi-ephedrine configuration undergo acyl-migration, whereas in the case of corresponding ephedrine derivatives, under similar experimental conditions, this reaction does not take place.

Fodor and Kiss (1) therefore came to the conclusion that in the case of ephedrine derivatives the substituted amino resp. methyl-amino group and the secondary alcoholic hydroxyl take up a spacially distant position — independently from the relative position of the other radicals attached to the asymmetric carbon atoms — consequently we must suppose that the corresponding groups of psi-ephedrine derivatives take up a specially near position.

The correctnes of this statement seems to be supported by the fact that some N-benzoyl-nor-psi-ephedrine derivatives gave with thionyl chloride at low temperature on oxazoline derivative whereas

the corresponding norephedrine analogue was not able to undergo, under the given mild conditions, a similar ring closure. As many important compounds can be found among diastereoisomeric amino alcohols, and the literature proved to be incomplete and erroneous concerning the correct interpretation of the steric structure of some of these compounds, it deemed of interest to examine the ultraviolet absorption spectra of some aryl-alkanolamine-derivatives.

Investigators have already dealt occasionally with the ultraviolet absorption spectrum of ephedrine and psi-ephedrine.

Graubner (2) has established that the optically active l-ephedrine and racemic dl-ephedrine deliver an identical ultraviolet absorbption curve with maxima at 317 and 257 m$^\mu$ wave lengths.

Marchlewski and Skarzinski (3) have studied the ultraviolet absorption curve of ephedrine and psi-ephedrine hydrochlorides. In aqueous solution dl-ephedrine hydrochloride shows 3 absorption bands, its maxima can be found at 2628, 2564 and 2504 Å, l-ephedrinehydrocloride, as well as d-psi-ephedrine hydrocloride, gave the same absorptiom maxima.

Wolfes (4) referring to other experiments reports the ultraviolet absorption spectrum of a 1 percent aqueous solution of d-norpsi-ephedrine hydrochloride. According to him the absorption maximum is betweem 250—260 m. Abildgaard and Baggesgaard-Rasmussen (5) investigated the absorption spectrum of 0.02 and 0.002 mole solution of ephedrine and psi-ephedrine hydrochloride establishing that l-ephedrine and different recamie ephedrines deliver an *idcntical* absorption curve. The maximum of the d-psi-ephedrines is at 2575 Å slightly below the one of l-ephedrine, otherwise they are nearly of the same type.

Fodor and Csokán (6) studying spectroscopically the structure of the nitrones, also examined the ultraviolet absorption spectra of different-alkoxy-phenyl-β-benzylamino-propanol-amiens. Their investigations were strictly confined to the steric modification of one of the diastereoisomeric pairs synthesized from psi-nitrosites and corresponding to the psi-ephedrine configuration. The absorption maxima were found at 230, 236, 228 resp. 239, 286 and 277 m$^\mu$.

In connection with their investigations on the interaction of several chromophores in the same molecule, Kiss, Fodor and Lózsa (7) examined the ultraviolet absorption spectra of some acylated propanolamines. In their study they only discuss acylamines of psi-ephedrin series.

The cited literary data seem to evidence that diastereoisomer alkanolamine pairs were not submitted to systematic and comparative spectroscopic examinations. As in the course of the above mentioned acylmigration experiments a well defined significant difference was found between the derivatives of ephedrine and psiephedrine and as this difference could of course only be established among the acylized derivatives, the suggestion was put forward as to whether one can observe a systematic difference in their ultraviolet absorption spectra, as well as in that of the substituted alkanolamines and their derivatives. For this purpose the following diastereoisomeric alkanolamine pairs were submitted to a very thorough examination.

The alkanolamines of ephedrine configuration, needed for our investigations were obtained by catalytic reduction of the oximino-ketones, whereas the diastereoisomers corresponding to the steric structure configuration of psi-ephedrine were prepared by synthe-sizing them from psi-nitrosites, further by isomerisation of the the resp. ephedrine derivatives with hydrochloric acid. The diaste-reoisomeric pairs obtained in this manner was a form separated by means of acyl migration.

The experimental results are summarized in the following table:

No.	Name of compound	Formula-type	Absorptions maxima in mμ	Log e	Curve
1.	dl-Ephedrine	I. R = H	251, 258, 263	2.03, 2.13, 2.14	I. a.
2.	dl-psi-Ephedrine	II. R = H	251, 258, 265	1.96	I. b.
3.	N-Benzoyl-dl-ephedrine	I. R = C_6H_5 — CO —	Ascending branch		I. c.
4.	N-Benzoyl-dl-psi-ephedrine	II. R = C_6H_5 — CO —	Ascending branch		I. d.
5.	N-Benzoyl-dl-nor-ephedrine	III. R = C_6H_5 — CO — R' = H	Ascending branch		II. a.
6.	N-Benzozl-dl-nor-psi-ephedrine	IV. R = C_6H_5 — CO — R' = H	Ascending branch		II. b.
7.	N-Benzozl-O-acetyl-dl-nor-ephedrine	IV. R = C_6H_5 — CO — R' = CH_3 — CO —	Ascending branch		II. c.
8.	N-Benzoyl-O-acetyl-dl-nor-psi-ephedrine	IV. R = C_6H_5 — CO — R' = CH_3 — CO —	Ascending branch		II. d.
9.	N-acetyl-3 : 4-di-ethoxy-dl-nor-ephedrine	V. R = CH_3 — CO — R' = H; R'' = C_2H_5 —	280, 230	3.58, 4.09	III. a.
10.	N-acetyl-3 : 4-di-ethoxy-dl-nor-psi-ephedrine	VI. R = CH_3 — CO — R' = H; R'' = C_2H_5 —	280, 230	3.57, 4.09	III. b.
11.	N,O-diacetyl-3 : 4-diethoxy-dl-nor-ephedrine	V. R,R' = CH_3 — CO — R'' = C_2H_5 —	280, 234	3.59, 4.07	III. c.
12.	N,O-diacetyl-3 : 4-diethoxy-dl-nor-psi-ephedrine	VI. R,R' = CH_3 - CO — R'' = C_2H_5 —	280, 233	4.49, 3.98	III. d.
13.	N-acetyl-diphenyl-ethanolamine	VII. R = CH_3 — CO —	251, 258, 265	2.47, 2.51, 2.59	IV. a.
14.	N-acetyl-diphenyl-psi-ethanolamine	VIII. R = CH_3 — CO —	252, 258, 265	2.56, 2.66, 2.68	IV. b.
15.	N-benzoyl-diphenyl-ethanolamine	VII. R = C_6H_5 — CO —	Ascending branch		IV. c.
16.	N-benzoyl-diphenyl-psi-ethanolamine	VIII. R = C_6H_5 — CO —	Ascending branch		IV. d.

The interpretation of the Absorption Curves.

The light absorption of compounds number 1 and 2 is deter-mined by the phenyl radical capable of causing a mesomeric effect. The saturated side-chain is unable to give a mesomeric effect and absorption is only appreciable around 200 mμ, thus only increasing the extinction of the compounds in the ascending branch. The cur-ves of the compounds are benzol spectra, influenced by an induc-tive effect. The feebleness of the inductive effect is proved by the fact that the spectra of the compounds are only slightly shifted to-

I. II. III. IV. V. VI. VII. VIII.
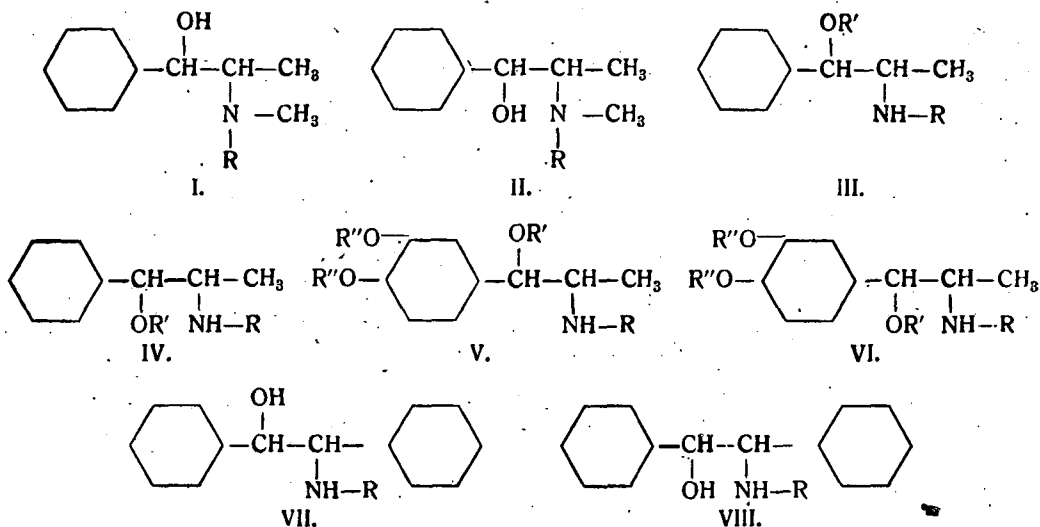
wards longer wave lengths — in comparison to the benzene spectrum — and that the extinction has hardly increased. The difference in intensity of the curves of compounds number 1—2 indicates that the diastereoisomerism is demostrated by the curves. In
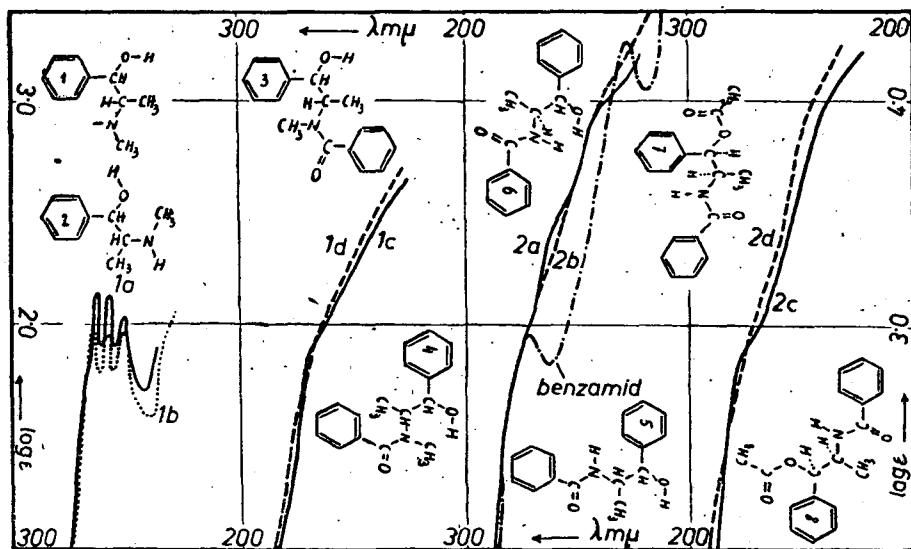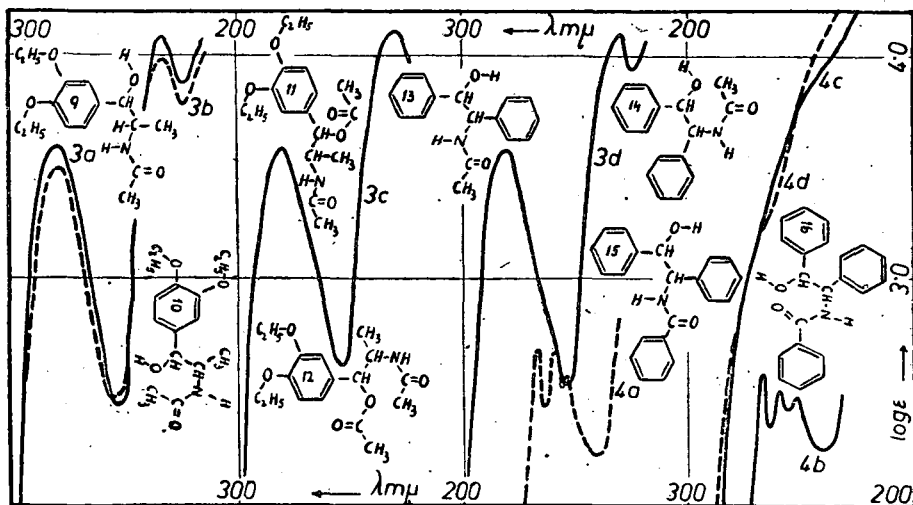

the case of compounds number 13—14 the 2 phenyl radicals being separated by the non-absorbant side-chain possess independent mesomeric systems. The extinction of the compounds is determined by the phenyl radicals A and B.

The side-chain is also idependent with its chromofore carbonamide- imino-hydrine tautomerism. Its extinction exerts its influence in the ascending branch. The absorption curves of the compounds running wich log 0.7 units higher than those of compounds number

1—2, are benzene spectra influenced by an inductive effect with is not very comprehensive, as namely if the extinction values of the 2 phenyl radicals would be added, the curve of compounds number 14 like that of number 2 runs higher. The difference caused by diastereoisomerism is also expressed here. The enhanced extinction of the compounds points to the fact that the side-chain does not inhibit the 2 phenyl radicals from assuming their position in the same plane.

The light absorption of compounds number 9—10 is dominated by the extinction of the diethoxy-phenyl radical. The latter and the side-chain have independent mesomeric systems. The mesomeric effect of the 3 oxygen atoms is inhibited by etherification. The course of the curves of the compounds are almost similar to those of the corresponding dimethoxy-derivatives photographed by Lózsa (7), showing that the mesomeric effect of the oxygen atoms is equally influenced by the methyl, resp. ethyl radicals. The extinctin of the side-chain exerts its influence in the ascending branch. In the light absorption of the diastereoisomers, probably owing to the extinction, there is already no significant difference.

In the case of compounds number 11 and 12 the diethoxy-phenyl radical and the side-chains are independent chromophores. The absorption curve of the 2 compounds is also determined by the axtinction of the diethoxy-phenyl radical. The effect of the side-chains only influences the ascending branch. Thus the curves of the compounds are very similar to those of compounds number 9 and 12. The sharply defined bands of the absorption curves of the 4 compounds indicate that the chromophore radicals do not distrub one anothers extinction.

In the case of compounds 5 and 6, A and B phenyl radicals, owing to the isolating effect of the radicals connecting them, constitute an independent chromophore system. The mesomeric effect of radical A is identical with the phenyl radical of compound number 1 and that of radical B with the one of benzamide.

. The light absorption of the compounds is dominated by the extinction radical B. Beside this the absorption of radical A, owing to its feeble extinction, cannot exert any influence. Therefore, the curves of the compounds ought to resemble that of benzamide and truly the position of the curves is identical with that of benzamide. The difference lies in the faintness of the benzamide bands. This cannot even be explained satisfactorily by the fact of the 2 phenyl radicals, owing to steric reasons, not beeng able to take up a position in the same plane. The structureless curve renders the investigation of the diastereoisomeric effect more difficult.

In the case of compounds number 3 and 4, resp. 7 and 8 the conditions are essentially identical, so that their detailed treatment is superfluous.

In the case of compounds number 15 and 16 all — A, B, C — benzene rings have, owing to the isolating effect of their connecting radicals, independent mesomeric systems. Rings A and B may be in the same plane, ring C, however, deviates from this plane. The light absorption of these compounds is also dominated by the extinction of ring B, beside which that of rings A and C can hardly exert any influence. Thus the curves of these compounds are also benzamide curves with an only faintly distinguishable structure. If owing to steric reasons all of the 3 benzene rings would occupy a different plane, this would not influence the course of the curves esentially, in consequence of the feeble extinction of radicals A and B.

Compounds 3—8, furthermore 15—16 are structures with faint bands. If steric models would confirm that already in the case of compounds 3—8, owing to steric reasons, ring A and B enter different planes we could interprete this in the following manner:

If ring B takes up a vertical position in the plane against the light it gives the band structured spectrum of benzamide with a maximally intense absorption. If ring A takes up a vertical position against light, it absorbs with maximal intensity, whereas ring B taking up an angle position, absorbs less intensively and with a shift towards the short wave lengths. The additivity of the extinction of radical B in 2 situations can extinguish the band structure of the benzamide spectrum. To decide the correctness of the explanation one would have to photograph the absorption curve of such a benzamide derivative, in which one of the hydrogen atoms of one of the NH_2-radicals is substituted by an alkyl radical.

Our investigations give evidence of a significant difference betveen ultraviolet absorption spectra of the diastereoisomeric alkalonamines and that of their derivatives. Further examinations are in progress involving similar investigations of still more of such types of diastereoisomeric pairs and careful studies of the ultraviolet absorption spectra of other types of diastereoisomers.

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Zur Lichtabsorption der Komplexe von Aminobenzolsulfosäuren.

Von Á. Kiss und J. Faredin.

1. *Einleitung.*

Den Komplexen von Aminobenzolsulfosäuren schreibt Pfeiffer (1) eine betainartige Struktur zu (Vgl. Abb. 2, Form. a und Abb. 5, Form. c) U. E. wird diese Behauptung bei den Komplexen von Metanil- und Sulfanilsäure aus sterischen Gründen zutreffen. Die Metalle mit unaufgefüllten äusseren Elektronenschalen werden aber mit Orthanilsäure innerkomplexe Salze bilden. (Abb. 2, Form. b). Um dies zu beantworten wurden die Extinktionskurven der Komplexe von Orthanil- und Sulfanilsäure im Wasser bei Zimmertemperatur ausgemessen (2).

Bezüglich der experimentellen Einrichtung und der Messmethode verweisen wir auf früheren Arbeiten (3). Die Komplexe wurden nach Literaturangaben (4) hergestellt. Da auch die neuen Verbindungen ähnlicher Weise leicht zu erhalten sind, sehen wir von der Wiedergabe der Darstellungsvorschriften ab. Die Reinheit der Komplexe, bzw. die Konzentration der Lösungen wurden analytisch kontrolliert.

2. *Zur Konstitution der Komplexe.*

Bei den Alkali- und Erdalkali-Verbindungen findet eine elektrostatische Bindung zwischen Sulfogruppe und Metallion statt. So dissoziieren diese Komplexe im Wasser elektrolytisch. (1). Bei den komplexbildenden Metallen, mit unaufgefüllten äusseren Elektronenschalen, von der o-, bzw. p-Stellung der Amino- und Sulfogruppen abhängend u. E. entstehen innerkomplexe Salze (Abb. 2, Form. b, bzw. Abb. 5, Form. c). Demgegenüber schreibt Pfeiffer (1) beiden Verbindungsreihen betainartige Struktur zu. Bei den Komplexen der Orthanilsäure findet eine semipolare Bindung zwischen dem