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FURTHER INVESTIGATIONS ON THE VALIDITY OF STEPANOV'S RELATION IN VISCOUS LUMINESCENT SOLUTIONS

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STEPANOV's relation appears to be fulfilled both for rhodamine B in aqueous-glycerol solutions quenched by KI, as well as of glycerol-ethanol solutions of trypaflavine, rhodulin orange and eosine of different viscosity and excited at different wavelengths. As the temperature T^*, which should be interpreted as the temperature in the vicinity of the fluorescent particle, depends on the concentration of quencher, the wavelength of the exciting light and the viscosity of the solution, it can be concluded that, in the system of solutions investigated, part of the excess energy of excitation is not dissipated during the mean life time of the excited state and may cause a local heat which persists even during the emission process, in accordance with some earlier assumptions.

1. Introduction

In the last years it became increasingly important to know the further way of the energy which appears as excess energy in the case of optical excitation of complicated molecules excited with frequencies greater than those of the pure electron transition 0—0 and is degraded by radiationless processes.

JABŁOŃSKI suggested [1] that in fluorescent solutions the above-mentioned energy should appear as an excess of the vibrational energy according to the Franck-Condon principle. This energy should increase the probability of rotation of the excited particle and thus cause the dependence of the "depolarization by initial shock" of the emitted fluorescence, on the mean life time and the frequency of the exciting light. Such an effect has been demonstrated by LISICKI [2]; the degree of polarization in the different alcoholic and alcohol-glycerol solutions of trypaflavine and acriflavine was found to increase considerably with excitation near to the 0—0 transition frequency. Later JABŁOŃSKI suggested [3] the possibility of the degradation of the excess-energy both by a quick and a slow mechanism. In case of the quick mechanism, the energy of the "initial shock" should be comparatively quickly dissipated (in $\sim 10^{-12}$ sec) from the vicinity of the excited particle in the form of elastic waves, while in case of the slow mechanism, thermal energy should persist in the environment of the excited particle causing local heat, which is dissipated comparatively slowly in a greater space pressumably according to the laws of heat conduction.

The appearence of the excess of the electron exciting energy in solids as lcalo heat was considered by NORMAN and PORTER [4] to cause the translational diffuonsi of the products of photodissociation. ALBRECHT and SIMPSON [5] postulated the appearance of similar local heat as a cause of rotational diffusion in condensed systems. ALBRECHT [6] supposed the possibility of a similar mechanism in connection with the "photo-orientation" of molecules excited by polarized light in solutions. The excess exciting energy in form of local heat should increase the probability of the dissolved particles to get oriented in a mechanical sense. Since such an effect could not be demonstrate experimentally as yet, ALBRECHT [7] suggested the local heat to be dissipated very quickly.

The above problems are closely connected with the results obtained by the investigation of STEPANOV's relation concerning the connection of absorption and emission spectra. According to STEPANOV [8], the following relation between the absorption spectrum $\varepsilon(\nu)$ and the emission spectrum $f_e(\nu)$ should exist

$$f_e(\nu)/\varepsilon(\nu) = d\nu^3 \exp(-h\nu/kT), \tag{1}$$

where d is a constant independent of frequency (ν), T the temperature of the solution, h and k are PLANCK's and BOLTZMANN's constants, respectively. It has been shown by KETSKEMÉTY and co-workers [9] that the formula

$$f_e(\nu)/\varepsilon(\nu) = d\nu^3\eta^*(\nu)n^2(\nu) \exp(-h\nu/kT) \tag{2}$$

is more generally valid. Here $\eta^*(\nu)$ and $n(\nu)$ are the relative yield and the refractive index of the solution, both depending on frequency (ν). The validity of equation (1) [respectively (2)] has been studied by several authors. In the papers of ALENCEV [10], ALENCEV and PAHOMITCHEVA [11], KRAVCOV and RUBINOV [12], HEVESI and KOZMA [13], RAZANOVA and coworkers [14], BORISSEVICH and GRUSINSKI [15], as well as KETSKEMÉTY and co-workers [9] STEPANOV's relation was found to be valid both in case of vapours, solutions and solids, but the slope of the straight found by plotting

$$F(\nu) \equiv 3 \ln \nu - \ln f_e(\nu) + \ln \varepsilon(\nu) = -h\nu/kT$$

versus ν gives, in the majority of cases, a temperature T^* higher than the temperature T of the solution. According to [10] this higher temperature appears because of the transformation of part of the absorbed energy into vibrational energy, which is not transmitted to the surroundings within the mean life of the excited state. In vapours this phenomenon may take place with a great probability and makes possible to determine the vibrational specific heat experimentally (see [15] and [16]).

It could be expected, however, that in liquid and solid systems the vibrational energy should be dissipated before the act of emission as a result of the very close interaction between the dissolved particles and those of the solvent, consequently a local heat should not appear. Therefore in [11] it is suggested that in the case of $T^* > T$ the solution should consist of more than two components slightly differing in optical characteristics and this causes a temperature $T^* > T$. According to their opinion, however, the distribution of the excited molecules among the vibrational levels always corresponds to the real temperature T. In other terms, the emission spectra should be independent of the exciting frequency. Yet, according to some recent publications (see *e. g.* KAWSKI [17]), though such a dependence may appear, it can not be reliably stated in most cases. Thus KAWSKI came to the conclusion that the process of energy transition between the fluorescent "centre" and its surroundings takes place very quickly both in solutions of high and low viscosity.

The aim of the present paper is to investigate how equation (1) is fulfilled as a function of quenching, viscosity of the solution and exciting frequency in solutions of some organic dyestuffs and to draw some conclusions concerning the local heat in solutions.

2. *Experimental method and solutions investigated*

According to our program, the dependence of temperature T^* on quenching and on the frequency of exciting light calculated with equation (1) was investigated in solutions of four dyestuffs. The most important data of the solutions and the conditions of the investigations are given in Table I. As it can be seen from Table I, the dependence of T^* on quenching with constant glycerol concentration was investigated in rhodamine B solutions, while in trypaflavine, rhodulin orange and eosine solutions our aim was to investigate the dependence on glycerol concentration and wavelength of the exciting light. These dyestuffs had been chosen, because according to former results (see *e. g.* KOZMA [19]) T* appeared to be relatively high compared with T; thus it was to be expected that the possible dependence of T^* on viscosity and wavelength of exciting light could be more easily demonstrated.

An Optica Milano grating spectro-photometer (Type CF—4) was used to measure the absorption spectra. As it is very important to measure the absorption spectra very precisely, the layer thickness was varied from 0,05 to 5 cm, to keep the extinction between 0,2 and 0,8, in which region the error of measurements is minimal. The smallest values of extinction in the long-wave region could not be plotted, though they are very important for the calculations.

For the measurement of emission spectra a method given in [18] was used, taking great care to fulfil the condition $k(\lambda)_{\max} \cdot l < 0{,}1$ by appropriate choosing of the layer thickness l. In this case the emission spectrum obtained experimentally agrees with that corrected to secondary luminescence within 0,5 per cent. (The values of $k(\lambda)_{\max}$ are given in Tables III—V.). The emission spectra were obtained with a high-pressure Hg-lamp (Hg 500) and the corresponding interference filter, or a Xenon-lamp (XBO 500) using a double monochromator (denoted by DM). (In the latter case the exciting band width was of 5—10mμ).

The dyestuffs were purified by repeated recrystallization, the criterion of purity was that the absorption spectrum should not change during two subsequent recrystallizations. The glycerol used for the varying of the viscosity was purified by repeated vacuum-destillation. Ethanol, water, glycerol and their mixtures in suitable proportions were used as solvents. In order to shift the proportion of the dyestuff ions in the solution to the corresponding luminescent ionic form, HCl or NaOH were given to the solution.

The investigations were carried out at a temperature of $T = 298 \pm 2$ °K. Values of T^* in the Tables were calculated with an accuracy of 0,1 degree, though this high accuracy should not be expected to be reliable.

3. *Results and discussion*

a) In a former paper [13] the dependence of the temperature difference $T^* - T = \Delta T$ on quenching and viscosity of the solution has been studied.

To investigate the dependence of ΔT on quenching further measurements were carried out on solutions in which the concentration of the quencher (KI) was varied between the limits given in Table I, the concentration of the dyestuff (rhodamine B), NaOH and glycerol being held constant. To illustrate the dependence, in Fig. 1 only the absorption and emission spectra belonging to quencher concentration zero (solid line) and 1 mol/l (dotted line) and the respective STEPANOV's straights are given. As it can be seen, the quencher concentration does not essentially influence the spectra and STEPANOV's relation is well fulfilled. The relative yield η/η_0 obtained by measurements, and determined with the method given in [20] and the values of T^* calculated from STEPANOV's straights are given in Table II. Absorption and

Table I

Dyestuff	Concentration mole/l	Composition of solvent	Additive agent	Layer thickness for emission spectra (cm)	Light source, filter, monochromator
Rhodamine B	$1 \cdot 10^{-4}$	H_2O glycerol (*per cent*) (60)	NaOH (3 *per cent*) KI (0 – 1 mole/l)	0,01	HBO 500 SIF 547
Trypaflavine	$2 \cdot 10^{-4}$	C_2H_5OH glycerol (*per cent*) (0, 40, 90)	CH_3COOH (2 *per cent*)	0,01	HBO 200 SIF 436 XBO 500 DM
Rhodulin-orange	$5 \cdot 10^{-5}$	C_2H_5OH glycerol (*per cent*) (0, 40, 90)	HCl ($5 \cdot 10^{-3}$ mole/l)	0,05	XBO 500 DM
Eosine	$5 \cdot 10^{-5}$	C_2H_5OH glycerol (*per cent*) (0, 40, 90)	NaOH ($5 \cdot 10^{-3}$ mole/l)	0,02 0,05	HBO 200 SIF 480 XBO 500 DM

emission maxima of the solutions were found at 555 mμ and 580 mμ respectively. The maximal value of the absorption coefficient was $k(\lambda)_{\max} = 23{,}13\ \mathrm{cm}^{-1}$.

In Fig. 2 the measured values of relative yield η/η_0 (●) and of T^* calculated from STEPANOV's straights (○) are plotted *versus* the logarithm of quencher concentration. It is to see that T^* increases with the increase of quenching (*i. e.* decrease of the mean life time of excited state). This increase can be interpreted by supposing

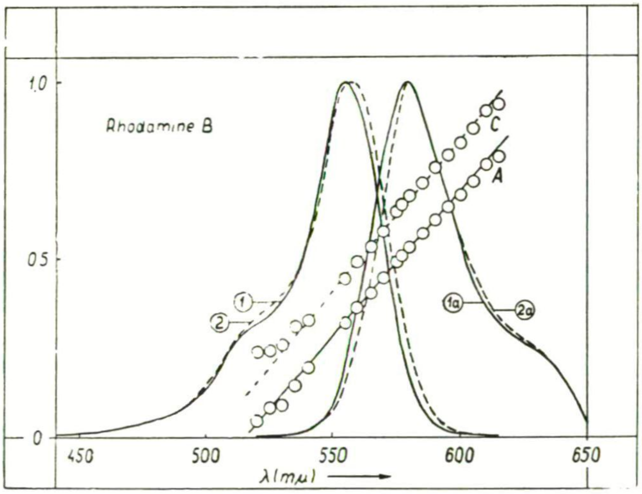

Fig. 1

that with decreasing decay time the possibility of the dissipation of the excess exciting energy decreases and therefore the local heat increases (for the case of quenched fluorescein solution see [13]).

b) As it had been referred to in [13] it could be inferred from the results given in [9] that the calculated values of T^* may depend on the wavelength of the exciting light. Such a dependence of T^* had been observed in several cases in vapours ([15], [16]).

Table II

c_{KI} (mole/l)	T^* (°K)	η/η_0
0	332,6	1,000
$5{,}62 \cdot 10^{-2}$	334,3	0,949
$1 \cdot 10^{-1}$	336,1	0,896
$1{,}78 \cdot 10^{-1}$	338,0	0,804
$3{,}16 \cdot 10^{-1}$	339,8	0,693
$5{,}62 \cdot 10^{-1}$	341,6	0,584
1	343,5	0,473

The dependence of T^* on the wavelength of exciting light and the glycerol concentration was investigated in the solutions listed in Table I with the method mentioned above. The values of T^*, the wavelengths of the maxima of absorption and emission spectra ($\lambda_{a,\max}$ and $\lambda_{e,\max}$) and the maxima of the absorption coefficients $(k(\lambda)_{\max})$ for different glycerol concentrations are given in the Tables III—V. It can be seen that the values of T^* depend on the frequency of exciting light and on the glycerol concentration. The results show that the difference $T^* - T = \Delta T$ increases with the increase of the difference between the absorbed and emitted energies $(h\nu_g - h\bar{\nu}_e)$. Similarly ΔT incresaes with increasing glycerol concentration in the cases investigated.

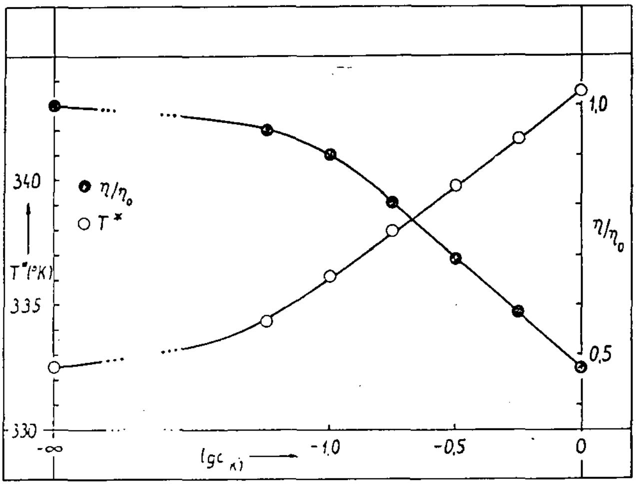

Fig. 2

The absorption and emission spectra belonging to the values T^* listed in Tables III—V and the calculated straights are plotted in figures 3—5. Fig. 3—5 give these curves for the solutions of trypaflavine, rhoduline orange and eosine, respectively. In these figures curve **1** and **2** represent the absorption spectrum of the dyestuff dissolved in pure ethanol, and in a 1:9 v/v mixture of ethanol and glycerol, while

1*a* and **2*a*** denote the respective emission spectra excited by the shortest wavelengths; curve **1*b*** is the emission spectrum for ethanol solution excited by the longest waves. *A*, *B*, *C* are STEPANOV's straights calculated from emission spectra **1*a***, **1*b***, **2*a*** and the corresponding absorption spectra using equation (1).

Table III

$c_{\text{glyc.}}$ (*per cent*)	T^* (°K)			$\lambda_{a,\max}$ (mμ)	$\lambda_{e,\max}$ (mμ)	$k(\lambda)_{\max}$ (cm^{-1})
	wavelength of exciting light					
	436 (mμ)	455 (mμ)	475 (mμ)			
0	325,6	319,0	314,1	460	495	23,03
40	330,8	325,6	319,0	461	497	22,36
90	361,4	347,3	336,1	462	500	20,10

Table IV

$c_{\text{glyc.}}$ (*per cent*)	T^* (°K)			$\lambda_{a,\max}$ (mμ)	$\lambda_{e,\max}$ (mμ)	$k(\lambda)_{\max}$ (cm^{-1})
	wavelength of exciting light					
	460 (mμ)	480 (mμ)	510 (mμ)			
0	339,8	319,0	302,0	492	521	3,23
40	343,5	322,3	309,5	494	524	3,19
90	365,6	357,3	332,6	497	528	3,21

Table V

$c_{\text{glyc.}}$ (*per cent*)	T^* (°K)			$\lambda_{a,\max}$ (mμ)	$\lambda_{e,\max}$ (mμ)	$k(\lambda)_{\max}$ (cm^{-1})
	wavelength of exciting light					
	460 (mμ)	520 (mμ)	555 (mμ)			
0	339,8	325,6	314,2	522	540	11,36
40	345,4	330,8	322,3	522,5	543	11,36
90	363,5	347,3	334,3	523	545	10,35

The figures show that in each of these solutions there exists a slight dependence of the emission spectrum on the exciting wavelength appearing in Tables III—V, as a corresponding dependence of T^*. This connection, already pointed out in several papers (see *e. g.* [21]—[25] and [17]), is interpreted by some authors with the supposition of more than one kind of luminescent molecules with somewhat different optical characteristics. This supposition is not sufficiently supported by the present investigations because of the results of chromatographical analysis of the dyestuffs. Rhodamine B in a mixture of ethanol, butanol and water in presence of ammonium hydroxide on silicagel as adsorbent appeared to consist of a single component. Eosine behaved similarly in the same system. Yet the respective values of T^* were greater than those of T, especially in case of eosine. On the other hand trypaflavine in the same system was separated in the presence of ammonium hydroxide as well as of acetic acid into two components acriflavine and proflavine (according to Walerys [26]). The behaviour of acriflavine purified chromatographically [2] points decidedly to the existence of local heat though it represents a single kind of luminescent particle in the solution. Rhodulin orange also appears to consist of two components in the mentioned chromatographical system. In case of fluorescein earlier investigations ([9], [11] and [13]) showed to have $T^* \approx T$ in unquenched and not viscous fluorescein solutions, with two different exciting wavelengths, though the dyestuff

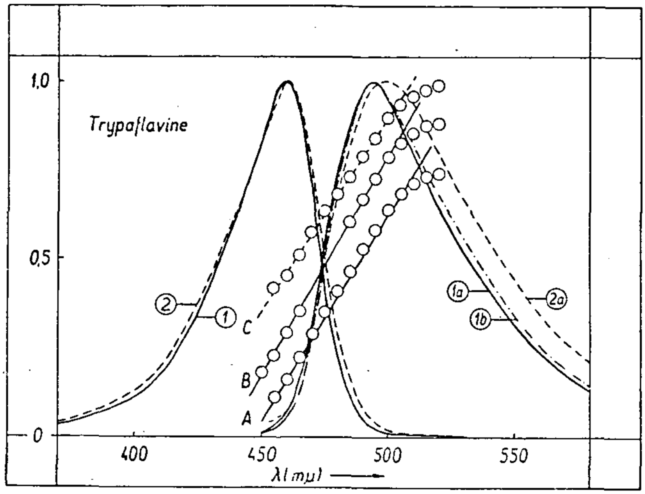

Fig. 3

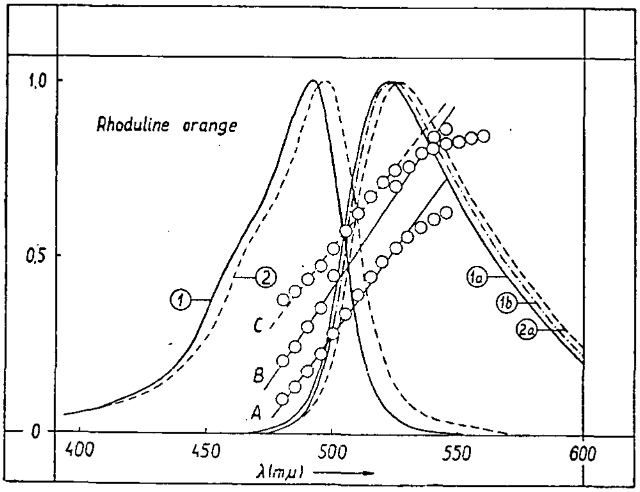

Fig. 4

used contained two kinds of impurities, however, in very little concentrations according to recent chromatographical analysis. Consequently the emission spectrum may be really independent of the exciting wavelength in some cases while it seems to depend on the exciting wavelength not only in solutions with more luminescent components, but also in case of a single luminescent component. In other terms the local temperature $T^* > T$ should be considered as physically existent in some solutions in agreement with Jabłoński's supposition [3] and Lisicki's investigations [2]. This seems further supported by measurements of Kozma [19] according to which T^* increases with the molecular weight in dyestuffs of a similar structure (the molecular weights of fluorescein, rhodamine B, eosine and rose bengale are 376; 479; 692; 949; and the corresponding values of T^* in the solutions 314; 328; 350; 395 °K respectively). This regularity may be understood if we consider that the energy carried away in form of elastic waves by the "initial shock" must decrease with increasing molecular weight.

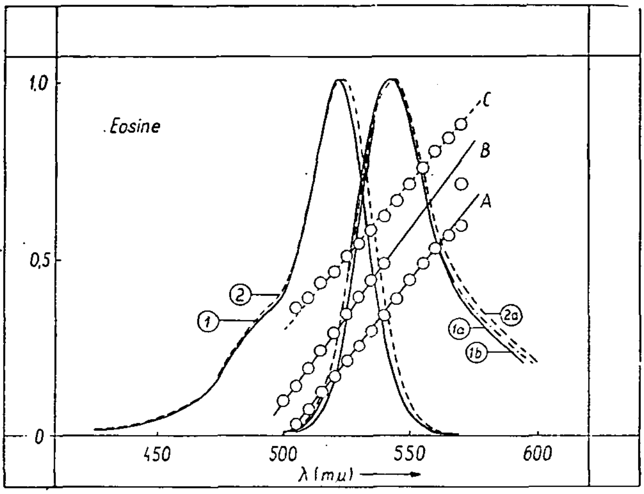

Fig. 5

It may be assumed that the dependence of T^* on viscosity is to be ascribed to two kinds of causes: *α)* the absorption and emission spectra may shift with the change of viscosity and thus the difference of absorbed and emitted energy may be altered (as supposed in [13]); *β)* with increasing viscosity the quick process ("initial shock") may carry away less and less energy from the surroundings of the excited particle (see [1]—[3]) and thus the local heat may increase. A similar role of the change of viscosity has been supposed earlier (see [4] and [6]) and this supposition was confirmed by experimental data obtained for solid solutions [14].

The above connections are also fulfilled in case of the spectra not plotted in the figures. It is to mention that, according to Ketskeméty and co-workers [9] the change in the slope the Stepanov's straights in the long wave region of the spectra is to be ascribed to the decrease of quantum yield in this region.

c) As an attempted thermodynamical interpretation of these phenomena let us consider the system of the excited molecules as a sub-system of temperature T^* to be in a thermal interaction with the sub-system of the solvent molecules of temperature $T \leqq T^*$. Since the number of the excited molecules is negligible against the number of the solvent molecules, the solvent may be treated as an infinitely large heat reservoir of temperature $T = constant$. Applying de GROOT's considerations [27] to this system we have

$$\frac{d(T^* - T)}{dt} = -\frac{1}{\tau'}(T^* - T), \tag{3}$$

where τ' is the relaxation time of the interaction process. From Eq. (3)

$$T^* - T = (T^* - T)_0 \exp\left(-\frac{\tau}{\tau'}\right), \tag{4}$$

where $(T^* - T)_0$ and $(T^* - T)$ denote the temperature difference of the sub-systems in time $t = 0$ (*i. e.* at the end of excitation) and in time $t = \tau$ (*i. e.* at the moment of emission), respectively.

According to Eq. (4) the temperature difference $T^* - T$ should increase if: α) the exciting frequency is increased (because of the respective increase of $(T^* - T)_0$); *β)* the mean life time of the excited state, τ, is decreased; *γ)* the viscosity is increased (because of the respective increase of τ' provided the interaction between the sub-systems is influenced by viscosity). Our experiments described above prove a fulfilment of these three conclusions.

As for a quantitative examination of the validity of Eq. (4), in lack of experimental data of $(T^* - T)_0$, τ and τ' we are restricted to estimations. We obtain an estimate for $(T^* - T)_0$ if we assume that the whole excess of the exciting energy as a value of $h(\nu_g - \nu_{e,\max})$ is converted into heat. In this case

$$(T^* - T)_0 \approx \frac{k' h(\nu_g - \nu_{e,\max}) \cdot N}{Mc}, \tag{5}$$

where $N = 6{,}02 \cdot 10^{23}$, $k' = 2{,}4 \cdot 10^{-8}$ cal/erg, h, M and c denote Planck's constant, molar weight and oscillation specific heat of the solute „gas", respectively. In case of fluorescein dissolved in a glycerol-water mixture and quenched by KI (see [13]) $\nu_g = 6{,}89 \cdot 10^{14}$ s^{-1}, $\nu_{e,\max} = 5{,}75 \cdot 10^{14}$ s^{-1} and $M = 332$ g. Taking a value of $c = 0{,}30$ cal/degree. g, Eq. (5) yields $(T^* - T)_0 \approx 100$ centigrade. With this value and the fluorometrically measured values of τ [28] (ranging from $2{,}3 \cdot 10^{-9}$ s to $5{,}05 \cdot 10^{-9}$ s) Eq. (4) gives $\tau' \approx 5{,}6 \cdot 10^{-9}$ s. In case of rhodamine B quenched by KI $\nu_g = 5{,}48 \cdot 10^{14}$ s^{-1}, $\nu_{e,\max} = 5{,}17 \cdot 10^{14}$ s^{-1} and $M = 479$ g. Taking a value of $c = 0{,}10$ cal/degree·g, from equation (5) we obtain $(T^* - T)_0 \approx 70$ centigrade. With this value and with $\tau' = 5{,}6 \cdot 10^{-9}$ s equation (4) yields $\tau \approx 3{,}1 \cdot 10^{-9}$ s for the unquenched solution. For the sake of comparison it should be mentioned that $\tau = 4{,}2 \cdot 10^{-9}$ s is given in [29] for unquenched solution of rhodamine B in pure glycerol and an extrapolated value of the dielectric relaxation time of $\tau' \approx 10^{-9}$ s may be estimated from [30] for the glycerol-water mixture applied in our case. According to [31], $c = 0{,}16 - 0{,}50$ cal/degree·g is given for 3—6-tetratmethyl-diamino-phtalimide, 3-aminophtalimide, β-naphtilamine, perylene and anthracene in vapour phase.

The similar order of magnitude of the dielectric relaxation time and the relaxation time introduced in Eq. (3) is to be expected, since both processes are governed by the weak thermal interaction.

Let us assume after JABŁOŃSKI [3] that the thermal interaction is realized as a heat conduction and consider the relaxation time in form of

$$\tau' = \frac{q\varrho c}{\lambda}, \tag{6}$$

where q is a surface through which the heat is transferred during the mean life time, ϱ, c and λ denote the density, the specific heat and the heat conductivity of the solvent. With the values $\tau' = 5 \cdot 10^{-9}$ s, $\varrho = 1$ gcm^{-3}, $\lambda = 5 \cdot 10^{-3}$ cal cm^{-1} s^{-1} degree^{-1} and $c = 0{,}8$ cal g^{-1} degree^{-1}, from Eq. (6) we obtain $q \approx 3 \cdot 10^{-11}$ cm^2. A sphere of radius $r \approx 1{,}5 \cdot 10^{-5}$ cm would belong to this surface. This should mean that the local heat might be present in a sphere around the excited particles, the order of magnitude of its radius being 10^{-5} cm. Though we are aware of the oversimplified character of the above considerations we hope they may contribute to an explanation of the appearence of the local heat to some extent.

From a thermodynamical point of view it would be very interesting to treat the system of excited molecules in case of higher concentrations when the interaction between neighbouring solute particles is not to be neglected.

For a more precise investigation of the validity of Eq. (3) we ought to know the dependence of τ and τ' on the composition of solution and the exciting wavelength.

* * *

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К ПРИМЕНИМОСТИ СООТНОЩЕНИЯ СТЕПАНОВА В СЛУЧАЕ ВЯЗКИХ, ФЛУОРЕСЦЕНЦИРУЮЩИХ РАСВОРОВ

Л. Козма, Л. Салаи и Я. Хевеши

Для спектров поглощение и испускание глицеринно-водных растворов родамина Б, потушенных *KJ*, а также для спектров поглощения и спектров испускания полученных разными возбуждающими длинными волнами, разных вязких глицеринно-этанольных растворов трипафлавина, родулина оранжа и эозина, формула Степанова оказывается действительной. Для температуры T^*, полученной из формулы и которую можно считать температурой в окружении флуоресценцирующих частиц, в зависимости от концентрации тушителя, длины волн возбуждения и вязкости, можно сделать вывод, что в системе исследованных растворов часть избытка энергии возбуждения во время возбуждения не рассеивается, а в согласии с более ранными предложениями, до момента излучение, эта не полностью рассеянная энергия вызывает локальное нагревание.

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ZUR FRAGE DER FLUORESZENZAUSBEUTE VON LÖSUNGEN

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Die Abhängigkeit der Lumineszenzausbeute von der Wellenlänge des Erregungslichtes wurde an Lösungen von fünf lumineszierenden Stoffen experimentell untersucht und die erhaltenen Ergebnisse mit der auf Grund der modifizierten STEPANOWschen Relation berechneten Quantenausbeute $\eta(\lambda)$ verglichen. Nach den Ergebnissen sind feinere Abweichungen vom WAWILOWschen Gesetz auch bei den untersuchten Systemen zu finden. Die experimentell und rechnerisch bestimmten Funktionen $\eta(\lambda)$ zeigen — mit Ausnahme eines Stoffes — eine gute Übereinstimmung.

1. §. Neuere Versuchsergebnisse zeigen, daß das WAWILOWsche Gesetz [1], das die Abhängigkeit der Quantenausbeute η lumineszierender Lösungen von der Wellenlänge λ des Erregungslichtes beschreibt, nicht genau gültig ist. ALENZEW [2] sowie KETSKEMÉTY u. A. [3] haben gezeigt, daß die Ausbeute η bei STOKESscher Erregung bemerkbar von der Erregungswellenlänge abhängt, während sie im anti-stokesschen Gebiet mit zunehmender Wellenlänge stark abnimmt. Dagegen fand BORISEWITSCH [4], [5] — auf Grund von Versuchen mit einigen sehr reinen Stoffen —, daß diese Abnahme im anti-stokesschen Gebiet nicht auftritt. Die Abnahme von η in diesem Gebiet ist nach seiner Ansicht der ungenügenden Reinheit der untersuchten Stoffe zuzuschreiben.

Die angeführten Erfahrungen können sowohl unsere Vorstellungen von den Lumineszenz-Prozessen (z. B. inaktive Absorption), als auch die auf der Gültigkeit des WAWILOWschen Gesetzes beruhenden theoretischen Erwägungen [6]—[8] beeinflussen (s. z.B. [9]).

Das Ziel der Untersuchungen war, die auf das WAWILOWsche Gesetz bezüglichen Probleme mit einer von uns bereits früher ausgearbeiteten Methode von relativ hoher Genauigkeit [3] an weiteren Stoffen zu untersuchen, sowie die gemessenen Ausbeutefunktionen $\eta(\lambda)$ mit den auf Grund des modifizierten STEPANOWschen Zusammenhanges

$$\frac{f_e(\nu)}{\varepsilon(\nu)} = d'\nu^3\eta(\nu)e^{-h\nu/kT} \tag{1}$$

berechneten zu vergleichen ($f_e(\nu)$ bedeutet das Emissionsenergiespektrum, $\varepsilon(\nu)$ das Absorptionsspektrum, d' eine von λ unabhängige Konstante, $\eta(\lambda)$ die Quantenausbeute, h bzw. k die Plancksche bzw. Boltzmannsche Konstante, und T die Temperatur der Lösung).

2. §. Die Untersuchungen wurden an wäßrigen Lösungen von Fluoreszein, sowie an in Äthylalkohol gelösten Al-Morin, Trypaflavin, Rhodulinorange und

Rhodamin B durchgeführt. Es wurden auch die Ausbeutefunktionen von mit KJ teilweise gelöschten Lösungen von Fluoreszein in Wasser und Glyzerin untersucht. Im letzteren Falle betrug die Konzentration des Löschstoffes (KJ) 0 bis 1 Mol/l.

Die bei den Untersuchungen benützten lumineszierenden Stoffe wurden durch wiederholtes Umkristallisieren gereinigt, bis ein konstantes Absorptionsspektrum der Lösung erreicht war. Die Reinigung der Lösungsmittel und der Zusätze erfolgte mit den Üblichen chemischen Methoden. Im Falle des Rhodulinorange, Fluoreszein und Rhodamin B überzeugten wir uns auch chromatographisch, daß die Lösungen nur eine Art von Farbstoffmolekülen enthielten.

Unsere Meßeinrichtung wich von der in [3] beschriebenen insofern ab, daß statt des SEV Typ RCA 1P21 der im langwelligen Gebiet empfindlichere Typ EMI 9558 A verwendet wurde. Infolgedessen konnte vor dem zur Messung der Lumineszenzintensität verwendeten SEV ein Filter angebracht werden, der nur die langwelligen Komponenten des Fluoreszenzlichtes durchließ und so die Korrektion auf Reabsorption überflüssig machte.

Die Quantenausbeutefunktion $\eta(\lambda)$ wurde aus den durch das Lumineszenzlicht und durch das Erregungslicht hervorgerufenen Photoströmen $I_2(\lambda)$ bzw. $I_1(\lambda)$ und der Empfindlichkeit $Q(\lambda)$ des zur Messung des letzteren angewendeten SEV (dem der Einheit des Photostromes entsprechenden Quantenstrom) nach folgender Formel berechnet:

$$\eta(\lambda) = C \frac{I_2(\lambda)}{I_1(\lambda) Q(\lambda) (1 - e^{-k(\lambda) l}) (1 + \varkappa)}. \tag{2}$$

Hierin bezeichnet C eine von der Wellenlänge λ unabhängige Konstante, $k(\lambda)$ den der Erregungswellenlänge λ entsprechenden Absorptionskoeffizienten, l die Schichtdicke der untersuchten Lösung und $\varkappa$ den Quotienten der in der Lösung in der Zeiteinheit entstehenden sekundären und primären Lumineszenzquanten (ausführlicher s. z. B. [10]). Die Absorptionsspektren der Lösungen wurden mittels eines Gitter-Spektrophotometers Optica Milano Typ CF-4 aufgenommen. Die erhaltenen Absorptionsspektren $k(\lambda)$, sowie die mit den in [11] angegebenen Methoden bestimmten Lumineszenzspektren $f_q(\lambda)$ zeigten eine gute Übereinstimmung mit den in unserem Institute früher ausgemessenen. Mit Benützung dieser Daten wurde die Ausbeutefunktion auf Grund der Formel

$$\eta(\lambda) = d \frac{f_q(\lambda)}{k(\lambda) \lambda^{-4} \exp[-hc/kT\lambda]} \tag{3}$$

berechnet, die dem Ausdrucke (1) äquivalent ist.

Die Untersuchungen wurden bei einer Temperatur $T = 298 \pm 2\,°\mathrm{K}$ durchgeführt. Ausführlichere Daten über Zusammensetzung der untersuchten Lösungen und Versuchsbedingungen (Beobachtung des Lumineszenzlichtes) enthält Tabelle I.

3. §. In Fig. 1 sind die auf Grund der Emissionspektren nach (3) berechneten Ausbeutefunktionen (ausgezogene Kurve), sowie die aus den Ergebnissen der Intensitätsmessungen mit (2) erhaltenen Werte (mit kleinen Kreisen bezeichnet) dargestellt. Aus der Figur ist folgendes ersichtlich:

a) Die Quantenausbeutefunktionen $\eta(\lambda)$ der untersuchten Lösungen zeigen im kurzwelligen Teile des Spektrums eine Abweichung vom WAWILOWschen Gesetz. Die einzige Ausnahme bildet Rhodulinorange, bei dem $\eta(\lambda)$ mit abnehmender Erregungswellenlänge in einem weitem Spektralbereich von λ unabhängig wird.

Bei diesem Stoff folgt dem Abschnitt mit $\eta(\lambda) = \text{Konst.}$ ein in der Nähe des Absorptionsmaximums steigender Abschnitt, und erst bei weiter zunehmender Wellenlänge beginnt die Abnahme der Ausbeutefunktion.

Tabelle I

Nr.	Art und Konzentration (Mol/l) der Farbstoffe	Lösungsmittel, Art und Konzentration der Zusatzstoffe	Typ des Filters
1.	Al-Morin $1 \cdot 10^{-3}$	C_2H_5OH; 2% CH_3COOH	Schott OG1
2.	Trypaflavin $1 \cdot 10^{-4}$	C_2H_5OH; $3 \cdot 10^{-3}$ Mol/l HCl	SIF 500 SIF 518 Schott OG2+OG3
3.	Fluoreszein $1 \cdot 10^{-3}$	H_2O; 3% NaOH	Schott RG1 OG3 RG2
4.	Fluoreszein $1 \cdot 10^{-4}$	40% H_2O, 60% Glyzerin; 3% NaOH KJ	SIF 621
5.	Rhodulinorange $1 \cdot 10^{-3}$	C_2H_5OH; $5 \cdot 10^{-3}$ Mol/l HCl	SIF 554, SIF 517 SIF 621 Schott RG1
6.	Rhodamin B $1 \cdot 10^{-3}$	C_2H_5OH; $3 \cdot 10^{-3}$ Mol/l HCl	SIF 570 SIF 621

b) Das in [4] und [5] mitgeteilte Ergebnis, daß die Quantenausbeute sehr reiner Stoffe von der Erregungswellenlänge unabhängig ist, wird durch den steilen Abfall der Ausbeutefunktion chromatographisch reiner lumineszierender Stoffe im anti-stokesschen Gebiet nicht bekräftigt. Übrigens kann auch aus den in [8] gegebenen theoretischen Erwägungen gefolgert werden, daß $\eta(\lambda)$ im anti-stokesschen Gebiet mit wachsendem λ von einer gewissen Wellenlänge an abfällt.

c) Bei gelöschten Fluoreszeinlösungen von höherer Viskosität ändert sich der Verlauf von $\eta(\lambda)$ mit zunehmender Löschung nicht bedeutend, deshalb sind die berechnete und die gemessene Funktion $\eta(\lambda)$ nur für eine Konzentration des Löschstoffes angegeben. Infolgedessen kann angenommen werden, daß die von der Löschung abhängige Änderung der aus der STEPANOWschen Relation berechneten „effektiven Temperatur" T^* (s. [12], [13]) dem Lumineszenzspektrum, und nicht der Änderung der Quantenausbeute zuzuschreiben ist.

d) Wie aus der Figur ersichtlich, zeigen die berechneten Ausbeutefunktionen — mit Ausnahme von Rhodamin B — eine gute Übereinstimmung mit den gemessenen Werten. Die Abweichung bei Rhodamin B wird wahrscheinlich dadurch verursacht, daß in diesem Falle irgendeine der zur Gültigkeit von (3) nötigen, in [6] angegebenen Bedingungen nicht erfüllt ist. Das anomale Verhalten des Rhodamin B erfordert weitere experimentelle Untersuchungen und Überlegungen zur weiteren Entwicklung der Theorie.

4. §. Wird die ursprünglich von Stepanow [12] erhaltene Formel

$$\frac{f_q(\lambda)}{k(\lambda)} = d\lambda^{-4}\exp[-hc/kT\lambda] \tag{4}$$

in eine der Gl. (3) entsprechende Gestalt gebracht, so steht an der linken Seite des erhaltenen Zusammenhanges eine von der Wellenlänge λ unabhängige Konstante. Dies wird aber durch die Versuchsergebnisse nicht unterstützt. Deshalb erscheint es angezeigt, die mit den Versuchsergebnissen übereinstimmende Formel (3) als allgemeinen gültig zu betrachten. Dementsprechend ist auch im Falle der annähernden Gültigkeit der ursprünglichen Stepanowschen Formel (4) die „effektive

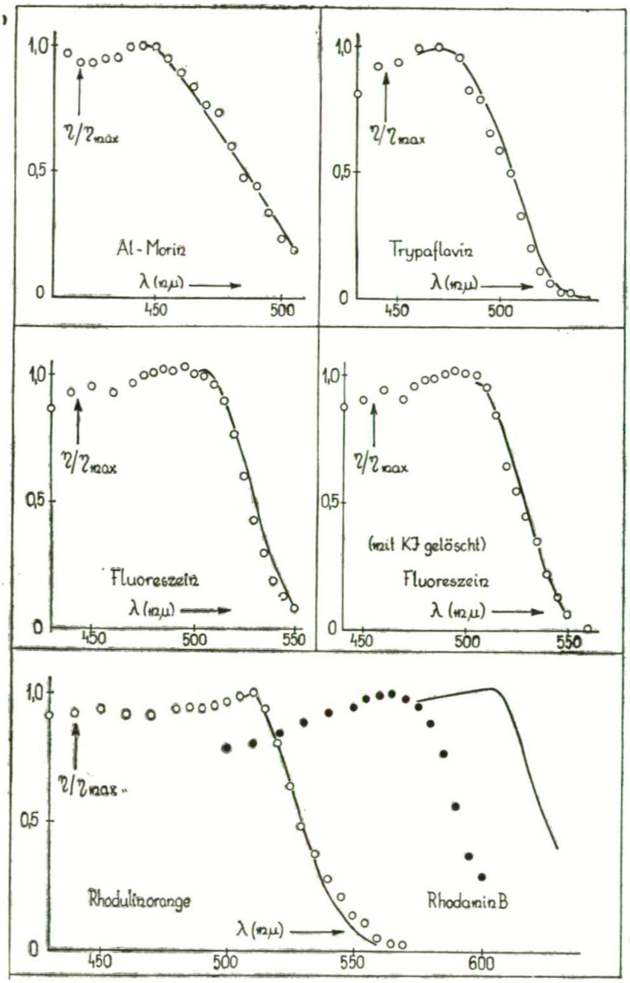

Fig. 1

Temperatur“ T^* der Lösungen nicht mit dem aus dieser Formel erhaltenen logarithmischen Zusammenhang

$$F_1(\bar{\nu}) \equiv \lg f_e(\bar{\nu}) - \lg \varepsilon(\bar{\nu}) - 3 \lg \bar{\nu} = \frac{h\bar{\nu}c}{2{,}3026\, kT^*} + C_1 \tag{5}$$

sondern mit der aus (3) folgenden Formel

$$F(\bar{\nu}) \equiv \lg f_e(\bar{\nu}) - \lg \varepsilon(\bar{\nu}) - 3 \lg \bar{\nu} - \lg \eta(\bar{\nu}) = \frac{h\bar{\nu}c}{2{,}3026\, kT^*} + C \tag{6}$$

zu berechnen ($\bar{\nu} = 1/\lambda$ die Wellenzahl).

In Fig. 2 sind die im Falle von Al-Morin, Trypaflavin, Fluoreszein und Rhodulinorange erhaltenen Funktionen $F_1(\bar{\nu})$ (kleine Kreise) sowie $F(\bar{\nu})$ (Punkte) dargestellt. Es ist ersichtlich, daß während im kurzwelligen Gebiete der Verlauf der beiden Kurven auf eine längere Strecke als nahezu gleich anzusehen ist, der Verlauf der auf Grund von (5) berechneten Kurve von der Umgebung des Maximums des Absorptionsspektrums eine wesentliche Abweichung von der auf Grund von (6) berechneten zeigt. Dies bedeutet, daß solange zur Bestimmung der „effektiven Temperatur“ T^* nur die nahezu gleichen Kurvenabschnitte gebraucht werden, auch die ursprüngliche STEPANOWsche Formel mit guter Annäherung benützt werden

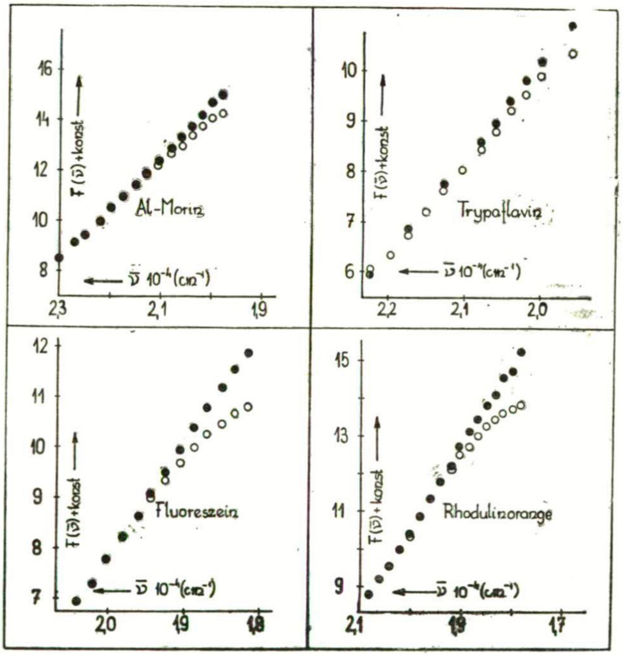

Fig. 2

kann; die Verhältnisse werden aber durch auch die Ausbeutefunktion enthaltende abgeänderte Relation richtiger beschrieben.

* * *

Die Verfasser sind Herrn Professor Dr. A. Budó, Direktor des Institutes für Experimentalphysik, sowie Herrn Dozenten Dr. I. Ketskeméty für ihr ständiges Interesse an der Arbeit und für ihre wertvollen Ratschläge zu aufrichtigem Danke verpflichtet.

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К ВОПРОСАМ ВЫХОДА ЛЮМИНЕСЦЕНЦИРУЮЩИХ РАСТВОРОВ

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Экспериментально исследовалось квантовый выход люминесценции в зависимости от длина волны возбуждения в случае 5 люминесценцирующих растворов. Полученные результаты сровнивались квантовыми выходами $\eta(\lambda)$, вычисленные из модифицированного соотношения Степанова. Результаты показывают отклонение от закона Вавилова. Рассчитанные и измеренные функции $\eta(\lambda)$ совпадают кроме одного вещества.

DIE EINWIRKUNG DER ELEKTRISCHEN FORMIERUNG AUF KADMIUMSELENID-SELEN-SPERRSCHICHTEN VERSCHIEDENER DICKE

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Es wurden die Veränderungen der mittels Aufdampfen hergestellten Kadmiumselenid-Selen-Sperrschichten als Funktion der Dauer der elektrischen Formierung untersucht. Nach den Versuchen wächst die Dicke der durch Aufdampfen von Kadmium hergestellten Kadmiumselenidschichten durch die Einwirkung der elektrischen Formierung und erreicht in etwa einer Stunde einen konstanten Wert, was praktisch die Beendingung der Formierung bedeutet.

Einleitung

Die Anwendung der SCHOTTKYschen Raumladungstheorie [1, 2] der Metall-Halbleiter-Kontakte auf die Selengleichrichter ermöglicht es, die Abhängigkeit der Kapazität C von der Spannung und der Störstellendichte n_{A^-} des Selens als Funktion der Spannung in Sperrichtung zu erhalten, falls wir den Selengleichrichter als einen Plattenkondensator betrachten. Nach den Untersuchungen von POGANSKI [3] und HOFFMANN und ROSE [4] bildet sich der bei der Herstellung von Selengleichrichtern zwischen dem Selen und der kadmiumhaltigen Deckelektrode eine dünne Kadmiumselenidschicht und die Gleichrichtereigenschaften werden durch den $p-n$ Übergang zwischen dem p-leitenden Selen und dem n-leitenden Kadmiumselenid bestimmt. SCHOTTKYS Überlegungen wurden durch DOLEGA [5] auf Halbleiter-Halbleiter-Kontakte angewendet. Er betrachtete die Raumladungsschichten im Kadmiumselenid und dem Selen gegenüber Wechselströmen als zwei in Reihe geschaltete Kapazitäten. Ist die Abhängigkeit der resultierenden Kapazität C bzw. des Wertes $1/C^2$ von der Spannung in Sperrichtung bekannt, so können folgende charakteristische Daten der Sperrschicht erhalten werden: die Schichtdicke L des Kadmiumselenids, die Dicke l_2 der Raumladungsschicht im Selen, die Störstellendichte n_{A^-} und n_{D^+} im Selen bzw. im Kadmiumselenid. Diese aus der Auswertung der Kapazitätsmessungen erhaltenen Ergebnisse sind bei dem Registrieren der Änderungen im Verhalten der Kadmiumselenid-Sperrschicht gegen verschiedene äußere Einwirkungen gut zu verwerten.

Wie bekannt, übt die elektrische Formierung einen wesentlichen Einfluß auf die Eigenschaften der technischen Selengleichrichtern aus. Die Erklärung des Formierungsprozesses wurde einerseits in der Änderung der Störstellenzahl, anderseits in der Diffusion der Störstellen gesucht; weiters wurde eine geringe Zunahme der Dicke der Sperrschicht während des Formierungprozesses nachgewiesen [6, 7, 8].

Gegenwärtige Arbeit bezweckt, die Wirkung der elektrischen Formierung auf die charakteristischen Eiegenschaften der durch Aufdampfen von Kadmiumschichten verschiedener Dicke auf eine Selenschicht hergestellten Kadmiumselenid-Selen-Sperrschichten mit der von DOLEGA für die Auswertung von Kapazitätsmessungen angegebenen Methode zu untersuchen.

Experimentelles

Die Untersuchungen wurden an folgenderweise hergestellten Selengleichrichter-Proben durchgeführt. Auf mittels Sandgebläse gereinigte quadratische Aluminiumplatten von 43 mm Kantenlänge wurde in Vakuum von der Größenordnung 10^{-3} Torr eine etwa 1μ dicke Wismutschicht aufgedampft. (Die Dicke der aufgedampften Schicht wurde, wie auch im weiteren, aus der Gewichtzunahme berechnet, unter der Voraussetzung, daß die Dichte der aufgedampften Schicht mit der makroskopischen Dichte übereinstimmt.) Das Aufdampfen der $40-50\mu$ dicken, eine entsprechende Bromzugabe enthaltenden Selenschicht erfolgte in einem Vakuum von derselben Größenordnung. Um eine entsprechende Homogenität der Selensicht zu erreichen, wurde die Temperatur während des Aufdampfens der Selenschicht auf die mit der Wismutschicht versehene Grundplatte auf einer Höhe von etwa 100 °C gehalten. Dann wurde die amorphe Selenschicht durch Temperieren in hexagonales Selen übergeführt. Die Herstellung der Kadmiumselenidschicht geschah durch Aufdampfen des thalliumhaltigen Kadmiums auf die Selenschicht bei einer Temperatur von 100 °C und einem Vakuum von etwa $5 \cdot 10^{-5}$ Torr. Bei der Bestimmung der Dicke der Kadmiumschicht wurde die Gewichtabnahme des Selens während des Temperierens im Vakuum berücksichtigt. Auf die Kadmiumschicht wurde dann eine aus einer Kadmium-Zinn-Legierung bestehende Deckelektrode aufgetragen. Während der mit einer Wechselspannung von 70—100 V erfolgten elektrischen Formierung waren die Proben paarweise gegeneinander geschaltet. 15, 30, 60 und 180 Minuten nach Beginn der Formierung wurden Kapazitätmessungen durchgeführt. Bei der Herstellung der Proben diente als Ausgangsmaterial Reinstselen und Reinstkadmium. Die Spektralanalyse zeigte beim Selen geringe Spuren von Cd, Ca, Si, Mg, Cu, Fe, As und Te, beim Kadmium von Fe, Zn, Pb, Cu und Tl. Die Zugabe des Broms zum Selen und des Thalliums zum Kadmium erfolgte in der bereits in einer früheren Arbeit [9] beschriebenen Weise. Zur Bestimmung der Spannungsabhängigkeit der Kapazität wurde die von LEHOVEC [10] und HOFFMANN [11] ausgearbeitete Methode benützt, die auf der Phasenverschiebung zwischen dem Verlauf der Stromstärke und der Spannung eines superponierten Wechselstromes beruht. Bei den untersuchten Gleichrichtern wurde die Frequenz des auf die in Sperrichtung angebrachten Gleichspannung superponierten Wechselspannung zu 1000 Hz gewählt.

Meßergebnisse und ihre Deutung

Bekanntlich werden die elektrischen Eigenschaften der Selengleichrichter durch den Bromgehalt des Selens und den Thalliumgehalt der Deckelektrode bzw. der aufgedampften Kadmiumschicht bedeutend beeinflußt. Auf Grund von Vorversuchen wurden für die Untersuchungen mit Selen von 0,05 Gew.-% Bromgehalt und mit Kadmium von 0,1 Gew.-% Thalliumgehalt hergestellte Gleichter-Proben benützt.

Fig. 1 zeigt die Abhängigkeit der Kapazität des Selengleichrichters von der Sperrspannung (U_{sp}) und der Dauer der Formierung bei zwei Proben, deren eine die dünnste, die andere die dickste aufgedampfte Kadmiumschicht besaß. Aus der Figur ist ersichtlich, daß einerseits die Kapazitätswerte der Probe mit der dünneren Kadmiumschicht kleiner sind, anderseits daß die Kapazität auf Einwirkung der

Formierung in beiden Fällen eine geringe Abnahme zeigt. Fig. 2 enthält die zur Berechnung der charakteristischen Werte der Sperrschicht benützte Kurven $1/C^2 = f(U)$ für dieselben Proben wie Fig. 1. Wie ersichtlich, bestehen die $1/C^2$ als Funktion der Spannung darstellenden Kurven aus je zwei, durch einen wohldefinierten Knickpunkt getrennten linearen Abschnitten von verschiedener Steigung. Die zur Berechnung der Störstellendichte und der Dicke der Raumladungsschichten dienenden Steigungen wurden aus den $1/C^2$-Kurven mit der Methode der kleinsten Quadrate berechnet.

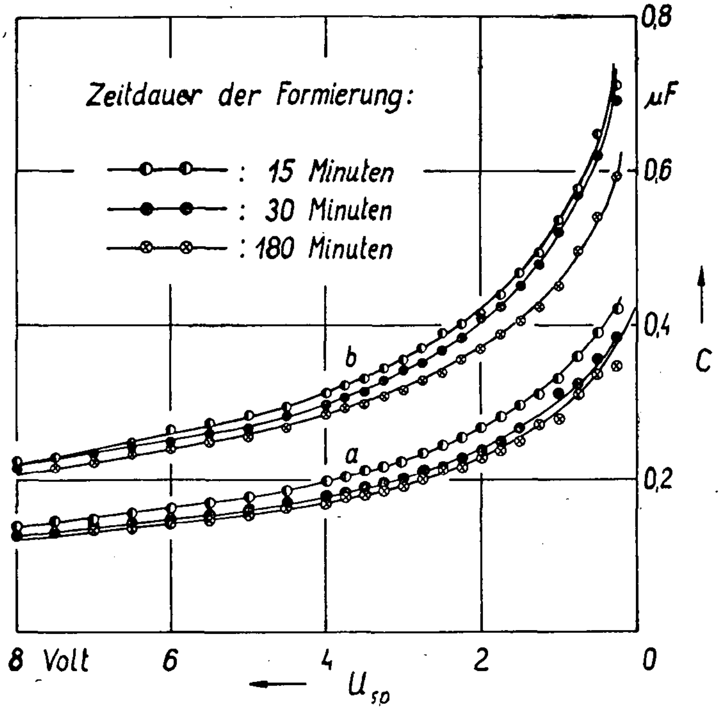

Fig. 1. Abhängigkeit der Kapazität von der Sperrspannung (U_{sp}) bei Selengleichrichtern mit verschiedener Cd-Schichtdicke (Kurven *a*: $8{,}19 \cdot 10^{-5}$ cm, Kurven *b*: $1{,}29 \cdot 10^{-5}$ cm) und verschiedenen Zeitdauern der Formierung

Die Ergebnisse der Berechnungen sind in Tabelle I bzw. Fig. 3 enthalten. Nach den Daten der Tabelle sind sowohl n_{A^-} als n_{D^+} von der Dicke der aufgedampften Kadmiumschicht stark abhängig, und zwar gehören zu den dickeren Schichten größere Störstellendichten. Bezüglich der Abhängigkeit der Störstellendichte von der Dauer des Formierungsprozesses geht aus der Tabelle hervor, das entgegen der kaum wachsenden Tendenz von n_{A^-}, n_{D^+} eine sehr stark abnehmende Tendenz aufweist, so daß nach 180 Minuten n_{A^-} nazehu gleich n_{D^+} wird.

Fig. 3 zeigt die Abhängigkeit der Dicke L der Kadmiumselenidschicht von der Formierungsdauer bei Proben mit verschiedener Kadmiumschichtdicke. Aus der Figur ist ersichtlich, daß die Schichtdicken L des Kadmiumselenids der Dicke der aufgedampften Kadmiumschicht umgekehrt proportional sind. Dieser Umstand kann dadurch erklärt werden, daß die verschiedenen Kadmiummengen in derselben Zeit auf die Selenschicht aufgetragen wurden; die verhältnismäßig langsamer auftragene Kadmiummenge wandelte sich fast vollständig in Kadmiumselenid um,

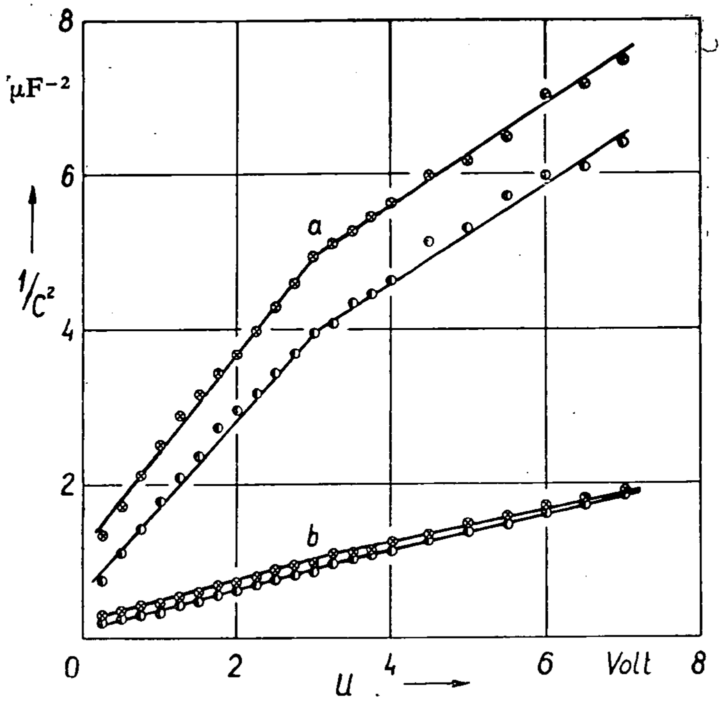

Fig. 2. Kurven $1/C^2=f(U)$ für dieselben Proben. Bezeichnungen wie in Fig. 1

Tabelle I

Probe	Zeitdauer der Formierung Min.	n_A- 10^{16} cm^{-3}	n_D+ 10^{16} cm^{-3}	L 10^{-6} cm	$L+l_2$ 10^{-5} cm	l 10^{-5} cm
654/A	15	1,12	2,78	14,28	4,96	5,01
654/C		3,92	100;2	9,34	2,59	2,61
654/D		3,7	100,4	0,95	2,66	2,67
654/A	30	1,42	3,03	16,79	5,25	5,26
654/C		4,17	50,12	10,70	2,66	2,65
654/D		4,17	50,7	2,04	2,63	2,64
654/A	60	1,18	2,08	19,2	5,29	5,31
654/C		4,76	25,0	4,4	2,78	2,80
654/D		4,76	25,6	4,04	2,52	2,54
654/A	180	1,42	1,82	25,7	5,86	5,88
654/C		7,41	6,67	14,36	2,73	2,74
654/D		9,52	7,14	14,2	2,49	2,50

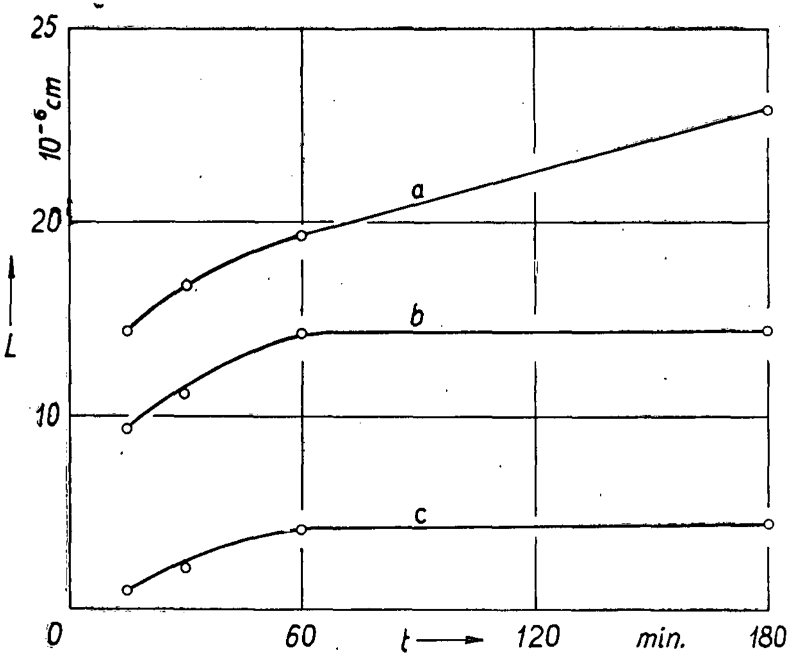

Fig. 3. Abhängigkeit der CdSe-Schichtdicke *L* von der Zeitdauer der Formierung bei Proben mit einer Cd-Schichtdicke von $1{,}29 \cdot 10^{-5}$ cm (Kurve *a*), $7{,}26 \cdot 10^{-5}$ cm (Kurve *b*) und $8{,}19 \cdot 10^{-5}$ cm (Kurve *c*)

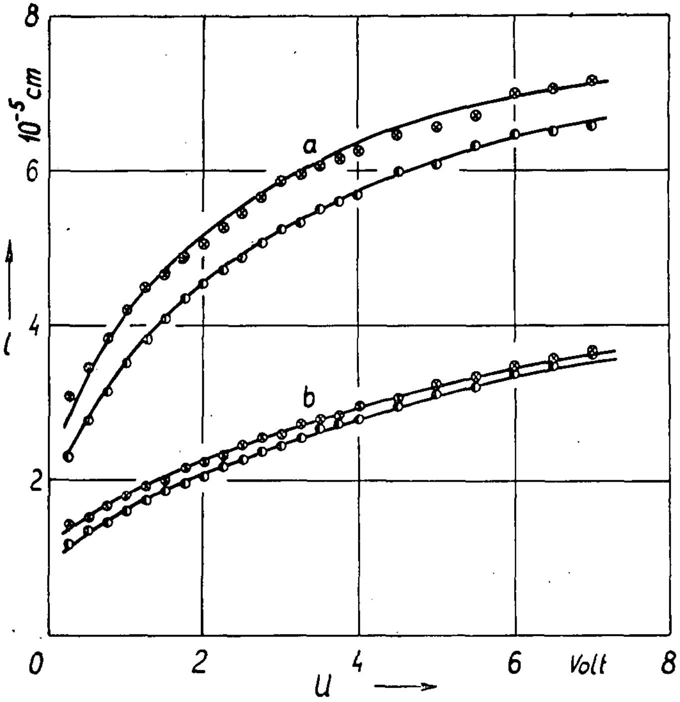

Fig. 4. Abhängigkeit der Dicke *l* der Raumladungsschicht von der Sperrspannung für dieselben Proben wie in Fig. 1 und 2

während bei der verhältnismäßig schneller aufgetragenen größeren Kadmiummenge sich nur ein Bruchteil in Kadmiumselenid umwandeln konnte. Die Dicke L der bereits während des Aufdampfens gebildeten Kadmiumselenidschicht wächst durch die Formierung weiter und nähert sich nach etwa 60 Minuten einem konstanten Wert. Das bedeutet praktisch die Beendigung des elektrischen Formierens. Die hierzu nötige Zeitdauer stimmt mit der üblichen Formierungsdauer der mit diesem Verfahren hergestellten Selengleichrichter überein. Wie zu erwarten war, stellte sich der konstante Wert bei der Probe 654 A mit einer dickeren Kadmiumselenidschicht später ein.

Wird die Abhängigkeit der Dicke l der Raumladungsschicht von der Sperrspannung aus dem Zusammenhange $1/C = l/\varepsilon\varepsilon_0 F$ der SCHOTTKYschen Raumladungstheorie [2] berechnet (Fig. 4), so ist der Verlauf der Kurve derjenigen der Kurve $1/C^2$ ähnlich, doch erscheint der Knickpunkt etwas weniger deutlich. Tabelle I enthält auch die zu diesen Knickpunkten gehörigen Werte l für die untersuchten Proben. Ein Vergleich dieser Werte mit der Summe von L und l_2 ergibt eine gute Übereinstimmung.

* * *

Die Verfasser sind Herrn Professor A. BUDÓ, Direktor des Intituts, für sein förderndes Interesse zu aufrichtigem Dank verpflichtet. Ferner wünschen sie der Gleichrichterfabrik „KONVERTA" ihren Dank für die Unterstützung der Arbeit auszudrücken.

ВЛИЯНИЕ ЭЛЕКТРИЧЕСКОЙ ФОРМИРОВКИ НА ЗАПИРАЮЩИЙ СЛОЙ СЕЛЕНИДА КАДМИЯ-СЕЛЕНА РАЗЛИЧНОЙ ТОЛЩИНЫ

Й. Кишпетэр, Я. Ланг и Л. Гомбаи

Были исследованы изменения запирающего слоя между селенидом кадмия-селеном, полученным выпариванием кадмия при селеновых выпрямителях в зависимости от электрической формировки. По экспериментам под влиянием электрической формировки толщина слоя селенида кадмия, образовавшегося при выпарывании кадмия, возрастает и приблизительно через час принимает постоянное значение, что означает практически заканчивание формировки.

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TUMOR-GROWTH INHIBITING SUBSTANCES OF PLANT ORIGIN.
I. Isolation of the Active Principle of Arctium Lappa

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(Received May 5, 1964)

A tumor-growth inhibiting substance was isolated by us from dichloro-methane and ethanolic extracts of the root of *Arctium lappa.* This has been performed by means of solvent precipitation and completed by chromatography.

The four most widely spread [1] species of the wildly growing burdock were used for the isolation. These are the following ones: *Arctium maius Bernh., A. minus (Hill.) Bernh., A. tomentosum Mill.* and *A. nemorosum Lej. et Court.* According to the data of the literature all four species contain the same principles but in a different concentration [2]. Oily extracts of the burdock root have been applied formerly for cosmetic purposes [3, 4]. Its various extracts contain etheric oils, palmitinic acid, fats, phytosterine [5], aromatic and mucinous substances [6], glycosides and a lot of inulin as well.

Experimental

The roots to be extracted were collected in October and no distinction was made with respect to the four species mentioned above.

After several approaches, having learnt the behaviour of the active principle, further extraction was achived by the aid of dichloromethane, according to the following procedure (Fig. 1.).

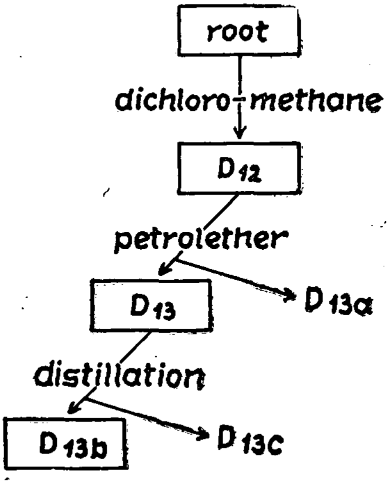

Fig. 1. Main pathways of the isolation

Dichloro-methane Extraction Procedure

5000 g of the finely ground dry root were extracted with 30 l. dichloromethane until no more coloured material was eluted. The solvent was distilled away first under atmospheric and later under reduced pressure. Thereafter a brownish-yellow oil (D_{12}) of a characteristic smell is left behind (32 g). After the addition of 2 l. petrolether a heavily filterable precipitate is formed (D_{13c}) which can be removed by centrifugation. The residue remaining after evaporation of the solvent was distilled at 0,1 mm Hg which yielded 4.7 g of a yellowish oil hardened on standing. Its boiling point was undeterminable as it distilled out very slowly from the system. The distillation residue is a brown viscous oil, not investigated in detail yet.

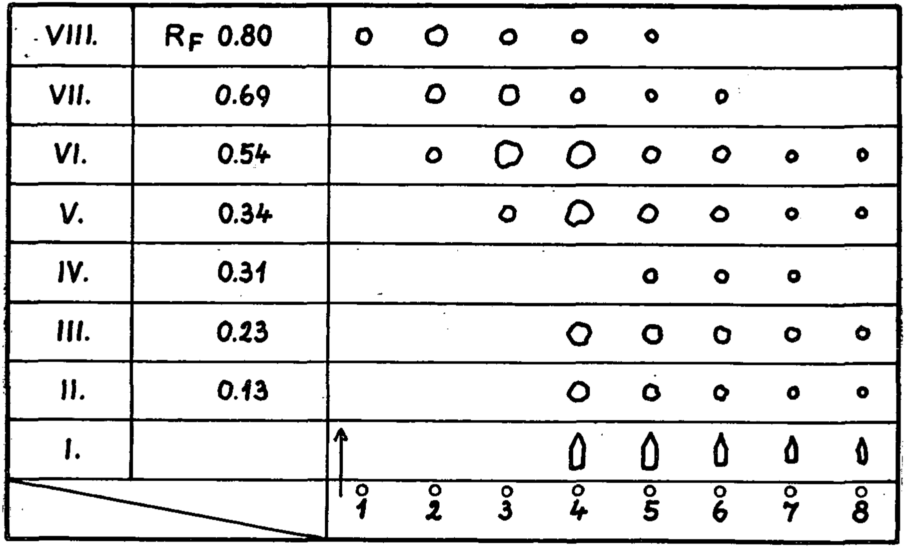

Fig. 2. Thin-layer chromatography of fractions obtained from silica gel column chromatography of D_{13} oil. Carrier: Kiesel Gel (Merck, Darmstadt), solvent: benzene-ether (10:1 by vol.) Serial numbers on the bottom refer to respective fractions represented in Table I.

Table I

Fractions	ml	mg yielded	Consistency
1	88	130	oil
2	110	640	greasy
3	128	660	,,
4	140	720	,,
5	144	770	,,
6	144	600	,,
7	164	550	,,
8	164	400	,,
9	158	600	,,
10	180		
11	226		
12	290		
13	290		

Column and Thin-layer Chromatography

6 g of the D_{13} oil were chromatographed in a 570 mm silica gel column of 4 cm internal diameter. The solvent mixture was benzene-ether (10:1 by vol.). The collection of fractions begun when the ultraviolet fluorescent part reached the bottom of the column. Results are contained in Table I.

Thereafter, respective fractions were separated on Kieselgel G plates (0.25 mm) using the same solvent. Visualization was effected at 366 mμ and the development in iodine vapor (Fig. 2). Serial numbers on the bottom of Fig. 2. are identical with respective fractions represented in Table 1. Fractions 9 through 13, not representedin Fig. 2., contain substances identical with I, II and III but in a different quantity.

It can be stated from the thin-layer chromatogram that D_{13} oil contains 8 substances and that D_{13b} gives spots which have the same R_F values as fractions VI and VII, consequently, it contains two substances. The substance exhibiting antitumour activity is in this fraction.

Identification and transformation of the active molecule will be consecutively reported.

* * *

The technical assistance of Mr. I. FÖLDEÁK is gratefully acknowledged.

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РАСТИТЕЛЬНЫЕ ВЕЩЕСТВА, ЗАДЕРЖИВАЮЩИЕ ВОЗРАСТАНИЕ ТУМОРА I

Изолироваине активного вещества из Arctium Lappa

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Из корня Arctium Lappa экстракцией при помощи диклорметана и после этого хроматографией было изолировано вещество, задерживающее возрастание тумора.

SYNTHESIS OF *m*-DIOXANS

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(Received May 5, 1964)

A number of 1,3-dioxan derivatives have been prepared by means of various methods.

In connection with the preparation of condensed trimethylene oxide [1], moreove with the study of γ-neighbouring group effect [2], greater amounts of stereochemically pure cis- and trans-2-hydroxy-methylcyclohexanol (A—1 and B—1) were required, respectively. The cis and trans isomers, however, beind accessible through the application of various synthesis methods, are always contaminated, usually with the other modification, too. For this reason some simple procedure has been looked for to separate the isomers, or to purify them, respectively. In the course of our preliminary experiments it has been observed that there is a preparatively useful difference in the physical constants of the benzal derivatives (C—1 and D—1) of the two modifications (A—1 and B—1). On this basis the two isomers might be separated from one another and from accompanying materials, as well, simply

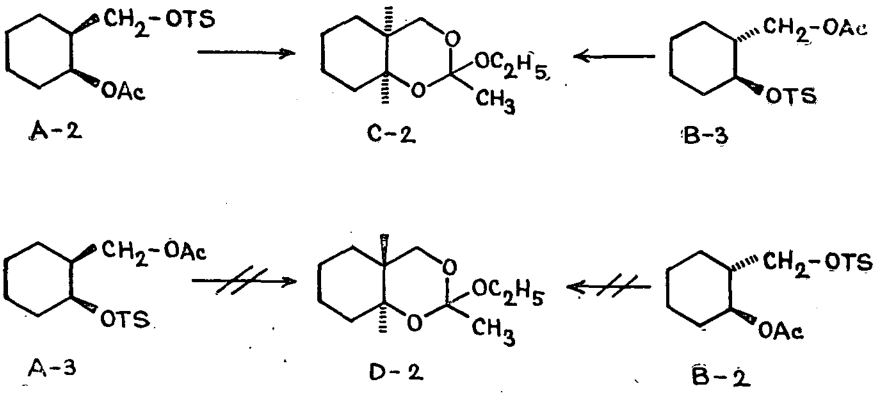


Fig. 1

by distillation, subsequent mild acidic hydrolysis resulting in the recovery of the diol (A—1 and B—1), respectively [3]. On the other hand, it has been shown [2] that ethanolysis of both cis-2-p-toluenesulphonyloxymethylcyclohexyl acetate (A—2) and trans-2-acetoxymethylcyclohexyl p-tosylate (B—3), proceding presence of potassium acetate affords cis-1,3-dioxadecalin derivative (C—2), while the corresponding trans modification (D—2) could not be detected in the similar reaction of either cis-2-acetoxymethylcyclohexyl tosylate (A—3) or trans 2-p-toluenesulphonyloxymethylcyclohexyl acetate (B—2).

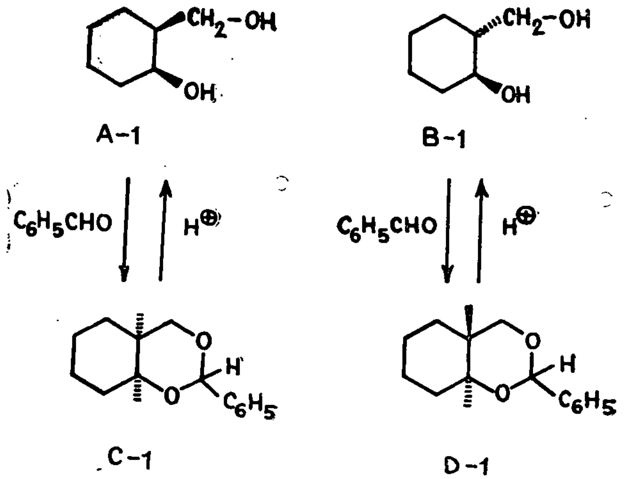


Fig. 2

On basis of the foregoing it has been assumed that the difference originating in the molecular structure of cis and trans-1,3-dioxadecalin derivatives (C—1, D—1, C—2, D—2) appears also in the reactivity of these compound pairs, from the numerical data of which conclusions might be drawn concerning the conformation of the bicyclic compound examined, moreover the configuration of the starting 1,3-diol. Such kind of investigations is known in the case of the 1,3-dioxolan derivative [4—6] obtainable from cis and trans-1,2-cyclohexanediols, showing essentially greater difference in stability and reactivity, furthermore the kinetics of hydrolysis of 1,3-dioxolan and 1,3-dioxan derivatives, available from aliphatic 1,2- and 1,3-diols has been studied as well [7—11].

First the relative rates of hydrolysis of acetals and ketals, obtainable from A—1 and B—1, were intended to be examined. To this the derivative had to be selected, which might be measured kinetically the best, that is to say, the suitable oxo-component. Since we had had some experience in the field of aliphatic 1,3-propanediols [12], this compound class was chosen as model to study the above viewpoints. Thus in the course of our experiments some formals, acetals and ketals of the basic compound, 1,3-propanediol, moreover of its derivatives, *e. g.* 2,2-dimethyl-, 2,2-diethyl-, and 2-ethyl-2-n-butyl-1,3-propanediol, of pentaerythritol and of 1,3-butanediol were prepared, respectively.

Preparation of the formals and acetals followed the usual procedure [13], the diol and the oxocomponent were reacted in beneze (Method A), or in ether (Method B) in the presence of sulphuric acid (A), or dry hydrogen chloride (B), respectively. The acetonals and the aromatic acetals were prepared in benzene solution in the presence of catalytic amount of p-toluenesulphonic acid (Method C), or sulphuric acid (Method D), with the simultaneous removal of water formed by means of azeotropic distillation. Some acetals (XX, XXIV, XXXIII, XXXVIII) were obtained through transacetalation (Method E) [4, 14]. In the preparation of the acetals of furfural (VI, XVIII) p-toluenesulphonic acid was used as catalyst to avoid the partial polymerization of the oxo-component. The preparation of the mono and diacetals of pentaerythritol (XXVIII—XXXII, XXXVII—XLII) was accomplished in benzene -dioxan mixture, because of the polar character of the starting tetraol. The ketal of cyclopentanone (XII) smoothyl hydrolyses even under the effect of carbon dioxide dissolved in the water; the phenomenon has been explained by BROWN and coworkers [15] with the I-strain principle. In the case of preparation of compound XI more than catalytic amount of sulphuric acid was applied in order to complete the reaction.

In the D—1 and D—2 conformational equilibrium of derivatives $R_1 = R_2$, $R_3 \neq R_4$ (II, IV—VII, X, XI, XIV—XVIII, XX, XXXIII, XXXVI) one of the conformers containing the more bulky group at carbon atom C_2 in equatorial position is preponderant [16—18], owing to the interaction of the axial hydrogens being in meta position relatively to ieach other at carbon atoms C_4 and C_6. The same does not hold true to derivative XXI ($R_1 \neq R_2$, $R_3 = R_4$), because of the absence of meta axial hydrogens. On the other hand, compound XXIV ($R_1 \neq R_2$, $R_3 \neq R_4$) exists in two diastereoisomeric forms [4, 19], the separation of which is to be reported in a later publication.

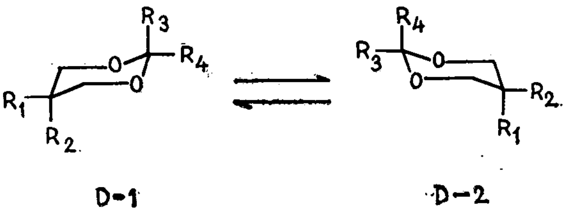
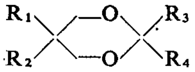


Fig. 3

At about the time of completion of the experiments [20] the authors got knowledge of the publications of RONDESTVEDTNEK [19] and CONRAD and coworkers [21], respectively, dealing with similar topic and reporting the preparation of some of the compounds occuring also in the present paper, accomplished in partly different way from those applied by us. The physical constants given there are in good agreement with the values found by us.

The reason why these investigations have been extended besides the above to the synthesis of 1,3-dioxans and within them to 1,3-dioxadecalins and 1,3-hydrindans, the latters being to be published in the future, is that according to recent literary data these derivatives are useful for the preparation of valuable intermediates, thus for instance their catalytic isomerization gives rise to β-alkoxyaldehydes [22], their perioxide oxidation to diol monobenzoates [23, 24], their bromination to bromobenzoates [23], and their reduction ($LiAlH_4 + BF_3$, or $LiAlH_4 + AlCl_3$) to diol monoethers [24], respectively.

Table I



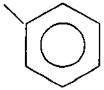
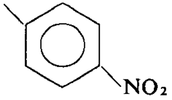
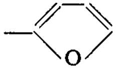
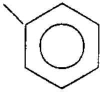
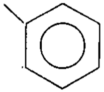
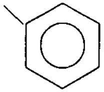
Nr.	R₁	R₂	R₃	R₄	Mp.:	Bp.:	n_d^{25}	Formula	Calcd %		Found %		Method
I.	H	H	H	H	104°		–	$C_4H_8O_2$	54,53	12,49	54,60	12,55	A
II.	H	H	CH_3	H		107°	1,4120	$C_5H_{10}O_2$	58,81	11,76	58,70	11,79	B
III.	H	H	CH_3	CH_3		125°	1,4159	$C_6H_{12}O_2$	62,08	10,42	61,90	10,30	C
IV.	H	H		H	50°		–	$C_{10}H_{12}O_2$	73,15	7,36	73,32	7,45	D
V.	H	H		H	111,5°		–	$C_{10}H_{11}O_4N$	57,41	5,30	57,50	5,49	D
VI.	H	H		H		102°/2 Hgmm	1,4885	$C_8H_{10}O_3$	62,35	6,54	62,53	6,52	C
VII.	H	H		$-CH_3$	57°		–	$C_{11}H_{14}O_2$	74,14	7,91	74,25	8,05	D
VIII.	H	H			112°		–	$C_{16}H_{16}O_2$	79,97	6,71	79,82	6,85	D
IX.	CH_3	CH_3	H	H		126°	1,4190	$C_6H_{12}O_2$	62,08	10,42	61,02	10,30	A

Table I (contd.)

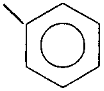
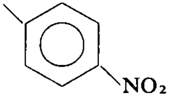
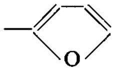
Nr.	R₁	R₂	R₃	R₄	Mp.: Bp.:	n_d^{25}	Formula	Calcd %		Found %		Method
X.	CH_3	CH_3	CH_3	H	58–60°/52 Hgmm	1,4134	$C_7H_{14}O_2$	64,58	10,84	64,50	10,83	B
XI.	CH_3	CH_3	$-CCl_3$	H	129°	–	$C_7H_{11}Cl_3O_2$	36,00	4,75	36,05	4,90	D
XII.	CH_3	CH_3	$-(CH_2)_4-$		103°/36 Hgmm	1,4520	$C_{10}H_{18}O_2$	70,55	10,66	70,60	10,52	C
XIII.	CH_3	CH_3	$-(CH_2)_5-$		116°/34 Hgmm	1,4610	$C_{11}H_{20}O_2$	71,69	10,94	71,50	10,86	C
XIV.	CH_3	CH_3	C_2H_5	H	76°/54 Hgmm	1,4227	$C_8H_{16}O_2$	66,61	11,19	66,90	11,15	B
XV.	CH_3	CH_3	C_3H_7	H	91°/20 Hgmm	1,4510	$C_{10}H_{20}O_2$	69,72	11,71	69,51	11,65	B
XVI.	CH_3	CH_3		H	120°/4 Hgmm	1,5010	$C_{12}H_{16}O_2$	74,96	8,39	74,82	8,35	D
XVII.	CH_3	CH_3		H	48°	–	$C_{12}H_{15}NO_4$	60,84	6,37	60,65	6,38	D
XVIII.	CH_3	CH_3		H	107°/12 Hgmm	1,4558	$C_{10}H_8O_3$	64,48	9,74	64,25	9,67	C
XIX.	CH_3	CH_3	CH_3	CH_3	143°	1,4178	$C_8H_{16}O_2$	66,63	11,18	66,36	10,98	C
XX.	C_2H_5	C_2H_5	CH_3	H	70°/5 Hgmm	1,4205	$C_9H_{18}O_2$	68,33	11,46	68,42	11,55	B; E
XXI.	C_2H_5	C_2H_5	CH_3	CH_3	198°	1,4241	$C_{10}H_{20}O_2$	69,75	11,70	69,80	11,76	C

Table I (contd.)

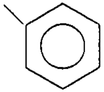
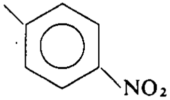
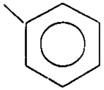
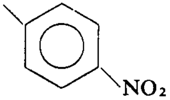
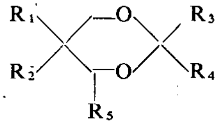
Nr.	R_1	R_2	R_3	R_4	Mp.: Bp.:	n_d^{25}	Formula	Calcd %		Found %		Method
XXII.	C_2H_5	C_2H_5		H	143°/3 Hgmm	1,5075	$C_{14}H_{20}O_2$	76,43	9,16	76,48	9,30	D
XXIII.	C_2H_5	C_2H_5		H	92°	–	$C_{14}H_{19}O_4N$	63,38	7,21	63,40	7,35	D
XXIV.	C_4H_9	C_2H_5	CH_3	H	94°/5 Hgmm	1,4270	$C_{11}H_{22}O_2$	70,99	11,91	70,81	11,98	B; E
XXV.	C_4H_9	C_2H_5	CH_3	CH_3	120°/20 Hgmm	1,4282	$C_{12}H_{24}O_2$	71,96	12,07	77,00	12,15	C
XXVI.	C_4H_9	C_2H_5		H	172°/4 Hgmm	1,5029	$C_{15}H_{24}O_2$	76,25	10,24	76,30	10,28	D
XXVII.	C_4H_9	C_2H_5		H	54°	–	$C_{15}H_{23}O_4N$	64,11	8,25	64,20	8,14	D
XXVIII.	CH_2-OH	CH_2-OH	CH_3	CH_3	135°	–	$C_8H_{16}H_4$	54,73	8,61	54,65	8,55	C
XXIX.	CH_2-OH	CH_2-OH	CH_2-Cl	H	114°	–	$C_7H_{13}O_4Cl$	42,76	6,66	42,70	6,58	B
XXX.	CH_2-OH	CH_2-OH	C_3H_7	H	70°	–	$C_9H_{18}O_4$	56,84	9,47	56,70	9,52	B
XXXI.	CH_2-OH	CH_2-OH	C_4H_9	H	82°	–	$C_{10}H_{20}O_4$	58,82	9,80	58,76	9,85	B
XXXII.	CH_2-OH	CH_2-OH	$-(CH_2)_5-$		123°	–	$C_{11}H_{20}O_4$	61,11	9,25	61,25	9,30	C

Table II



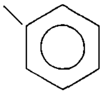
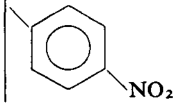
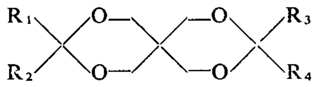
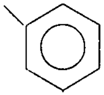
Nr.	R_1	R_2	R_3	R_4	R_5	Mp.: Bp.:	n_d^{25}	Formula	Calcd. %		Found		Method
									C	H	C	H	
XXVIII.	H	H	CH_3	H	CH_3	118°	1,4039	$C_6H_{12}O_2$	62,02	10,42	62,10	10,50	B E
XXIX.	H	H	CH_3	CH_3	CH_3	129°	1,4190	$C_7H_{14}O_2$	64,56	10,85	64,56	10,80	C
XXX.	H	H		H	CH_3	105°/5 Hgmm	1,5161	$C_{11}H_{14}O_2$	74,14	7,91	74,20	7,81	D
XXXI.	H	H		H	CH_3	104°C	–	$C_{11}H_{13}O_4N$	59,19	5,87	59,10	5,91	D

Table III



Nr.	$R_1=R_3$	$R_2=R_4$	Mp.: Bp.:	n_d^{25}	Formula	Calcd. % C	Calcd. % H	Found C	Found H	Method
XXXVII.	H	H	50°	–	$C_7H_{12}O_4$	52,50	7,50	52,47	7,52	A
XXXVIII.	CH_3	H	45°	–	$C_9H_{16}O_4$	57,40	8,57	57.42	8,59	B; E
XXXIX.	CH_3	CH_3	116°	–	$C_{11}H_{20}O_4$	61,07	9,33	61,02	9,45	C
XL.	C_2H_5	H	152°/10 Hgmm	1,4520	$C_{11}H_{20}O_4$	61,07	9,33	59,84	9,22	B
XLI.	C_3H_7	H	95°	–	$C_{13}H_{24}O_4$	63,88	9,90	63,94	9,98	B
XLII.		H	160°	–	$C_{22}H_{20}O_4$	73,08	6,41	73,15	6,52	D

Experimental

a) 1,3-Propanediol, b. p.: 214° $n_D^{25} = 1,4390$
b) 2,2-Dimethylpropanediol, m. p.: 206°
c) 2,2-Diethylpropanediol, m. p.: 60,5°
d) 2-Methyl-2-propylporpanediol, m. p.: 56,6°
e) 2-Ethyl-2-butylpropanediol, m. p.: 43,8°
f) 1,3-Butanediol, b. p.: 106° /15 mm., $n_D^{25} = 1,4398$ Chemische Werke HÜLS A. G./MARL.

Preparation of formals Method A

A 10% benzene solution of 1,2 moles of paraformaldehyde and 1 mole of 1,3-propanediol derivatives was treated with catalytic amount of concentrated sulphuric acid. The mixture was kept at the temperature of boiling water-bath for 6 hours. After cooling the acid and the unreacted diol were removed by washing the solution with water and subsequently with 10% sodium hydrogencarbonate solution, the organic phase was dried over anhydrous magnesium sulphate and the solvent evaporated. The residue was subjected to fractionated distallition.

Preparation of acetals (Method B)

1,2 Moles of acetaldehyde was added to a 10% solution of 1 mole 1,3-propanediol derivatives in ether with ice-cooling. Then dry hydrogen chloride gas was introduced to the solution for one hour. The reaction mixture was allowed to warm up to room temperature and washed subsequently with water, 10% sodium hydrogencarbonate solution and water again. The organic phase was dried over anhydrous magnesium sulphate and evaporated. The residue was distilled fractionately.

Preparation of acetonals (Method C)

1,2 Moles of acetone, a 10% solution of 1 mole of 1,3-propanediol derivative in benzene and catalytic amount of p-toluenesulphonic acid were placed in the lower container of a Soxhlet apparatus. The upper part of the apparatus was provided with a jacket containing anhydrous calcium chloride. The reaction mixture in the Soxhlet apparatus was refluxed for 24 hours by means of and infrared lamp. The reaction mixture was subsequently washed with water, 10% sodium hydrogencarbonate solution and water again. The benzene phase was dried over anhydrous magnesium sulphate and evaporated. The residue was fractionately distilled.

Preparation of aromatic acetals (Method D)

1,2 Moles of the aromatic aldehyde or ketone component was refluxed with 1 mole of 1,3-propanediol component in 10% benzene solution in the presence of catalytic amount of sulphuric acid in an apparatus fitted with a water-separatory device. Subsequent fitted with a water-separatory device. Subsequent to the distillation out of the necessary amount of water, the reaction mixture was washed until neutral, dried, and the solvent removed. The residue was either distilled or crystallized.

Transacetalation (Method E)

1 Mole of 1,3-propanediol derivative was refluxed with 5 moles of acetaldehyde diethylacetal in the presence of catalytic amount of benzoyl chloride for 6 hours. In order to complete the reaction, the theoretical amount of ethanol was distilled out of the reaction mixture by means of a Vigreux column. Then absolute ether was added to the solution and the mixture washed with 10% sodium hydrogencarbonate solution and water until neutral. Following the removal of ether and excess diethylacetal the product was fractionated.

Preparation of pentaerythritol acetals

All the above methods were suitable for the preparation of acetals of pentaerythritol of strongly polar character with the modification that benzene-dioxan (1:1) mixture was used as solvent in the case of methods A and D, respectively.

* * *

The authors gratefully acknowledge the help of Mrs. K. LÁNG and Mrs. G. B. BOZÓKI for microanalyses and Mr. R. FERENCI for his technical assistance.

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СИНТЕЗ М-ДИОКСАНОВ

Г. Шнейдер, Е. Ковач, М. Хинораи

Различными методами были синтезированы многие из 1,3-диоксандериватов.

PREPARATION AND PROPERTIES OF TRIMETHYLSILYL ETHERS OF SOME STEROIDS

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(Received May 5, 1964)

A method has been given for the preparation of trimethylsilyl ethers of some steroids. Behaviour of these compounds has been investigated.

Trimethylsilyl ethers of certain steroids have been prepared by LUUKKAINEN and coworkers [1] to study their gas chromatographyc behaviours, without mentioning however the physical and chemical properties of these derivatives. They reported a method for the preparation of these compounds using hexamethyldisilazine as silylating agent and trimethylchlorosilane as catalyst. It was SJÖVALL[1], who suggested the application of trimethylsilyl diethylamine for the preparation of trimethylsilyl ethers of bile acid esters, a method earlier applied by RÜHLMANN [2] in the preparation of silyl derivatives of amino acids. Now it has been found that trimethylsilyl diethylamine is a more convenient silylating agent, since the silylation reaction does not result any nonvolatile by-product. Trimethylsilyl ethers of Δ_5-3β-hydroxy-androsten-17-one, Δ_5-3β-hydroxy-cholestene and methyl-Δ_5-3β-hydroxy-cholenate were prepared in acetone in the presence of excess trimethylsilyl diethylamine at room temperature for 4 hrs., or at elevated temperature with shorter reaction period. After the evaporation of the solvent in vacuo a crystalline product remained, which could be examined in gas chromatograph, or recrystallized for analysis without further manipulations.

These silyl ethers decompose on boiling in ethanol solution in the presence of sodium ethoxide or *p*-toluenesulphonic acid in 30 minutes, but the hydrolysis of the trimethylsilyl ether of dehydroepiandrosterone on boiling in 75% ethanol does not proceed even in 4 hrs. The reduction of the latter silyl ether by means of $LiAlH_4$ in ether, or $NaBH_4$ in tetrahydrofuran results $\Delta_5$3β-trimethylsilyloxy-17β-hydroxy-androstene.

A preliminary report may also be given about the selectivity of the silylation reactions. Systematic gas chromatographic investigations of the silylation product of bile acid esters show that equatorial hydroxyl groups at the 3 and 6α positions react in a few hrs. at room temperature. The silylation of OH groups at 7β position is not complete in 20 hrs. at room temperature, while the 7α-OH group is not attacked under the same conditions. The 12α-OH groups do not react even at 100°.

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[1] Karolinska Institute, Institute of Chemistry, Stockholm.

Experimental

The silyl ethers were obtained either from purified trimethylsilyl diethylamine or from the crude reaction product of the preparation of trimethylsilyl diethylamine with the same results.

Trimethylsilyl ether of Δ_5-3β-hydroxy-androsten-17-one

300 mg Δ_5 – 3β-hydroxy-androstene-17-one in 2 ml acetone and 2 ml trimethylsilyl diethylamine were kept at 60° for 15 min., the mixture evaporated in vacuo and the residue crystallized from petrolether, m. p.: 158 °C. Anal.: Calc.: $C_{22}H_{36}O_2Si$ C 73,28 H 10,06; Found: C 72,84 H 9,87.

Trimethylsilyl ether of cholesterol.

It was prepared as above, m. p.: 130 °C (petrolether). Anal.: Calc.: $C_{30}H_{54}OSi$ C 78,52 H 11,86; Found: C 78,95 H 11,66.

Trimethylsilyl ether of methyl-Δ_5-3β-hydroxy-cholenate.

The compound was prepared as above and melted at 73 °C (cyclohexane). Anal.: Calc.: $C_{28}H_{48}O_3Si$ C 72,99 H 10,50; Found: C 72,64 H 10,27.

3-Trimethylsilyl ether of Δ_5-3β, 17β-dihydroxy-androstene.

A mixture of 200 mg trimethylsilyl ether of Δ_5-3β-hydroxy-androsten-17-one in 10 ml ether and 200 mg $LiAlH_4$ in 30 ml ether were stirred at 0 °C for 3 hours and a mixture of 1 ml water, 2 ml ethanol, 10 ml ether and 3 drops of acetic acid were added at the same temperature. The product was filtered, dried over Na_2SO_4 and evaporated in vacuo. The residue yielded on recrystallization from petrolether a product, m. p.: 163—164 °C. Anal.: Calc.: $C_{22}H_{38}O_2Si$ C 72,87 H 10,56; Found: C 73,00 H 10,50.

This compound gave on acidic alcoholysis Δ_5-3β-hydroxy-androsten-17-one.

Alcoholysis and hydrolysis of trimethylsilyl ether of Δ_5-3β-hydroxy-androstene-17-one.

30 mg samples of trimethylsilyl ether of Δ_5-3β-hydroxy-androsten-17-one in 5 ml abs. ethanol in the presence of traces of sodium ethoxide or benzene-sulphonic acid, or in 75% aqueous ethanol, respectively, were refluxed. Thin layer chromatography revealed the absence of starting materials in the first two cases in 30 min., while in the third case considerable amounts of starting material could be detected even in 4 hours.

ПРОИЗВОДСТВО НЕКОТОРЫХ ТРИМЕТИЛСИЛИЛ ЭФИРА СТЕРОИДОВ И ИХ СВОЙСТВА

И. Веис, З. Хаваш

Был разработан метод для производства триметилсилил эфира стероидов. Было изучено свойство этих соединений.

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PREPARATION OF PREGNADIENOLONE-20-C^{14}

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(Received May 5, 1964)

$\Delta_{5,16}$-Pregnadien-3β-ol-20-on-20-C^{14} has been prepared analogously as described by BUTENANDT [1] in the case of the inactive derivative, as follows:

Δ_5-3β-acetoxy-androsten-17-one → Δ_5-3β-acetoxy-androstene-17-cyanohydrin → → $\Delta_{5,16}$-3β-hydroxy-etiocholadienic acid nitril → $\Delta_{5,16}$-3β-hydroxypregnadien-20-one.

In the first step of the reaction sequence 3,55 g $KC^{14}N$ corresponding to 2,2 μc C^{14} activity, 1 g Δ_5-3β-acetoxy-androsten-17-one, 3,5 ml glacial acetic acid and 15 ml ethanol were reacted. The final product of the reaction sequence pregnadienolon-20-C^{14} was purified in a chromatographic way on Whatman N° 3 paper in formamide-hexane system, followed by crystallization from ethyl acetate till constant specific activity.

The substance obtained this way was 72 mg, melted at 214—216°. Specific activity 43 cpm/10 μg measured with a windowended GM tube. The purity of the product was checked by thin layer chromatography running it together and parallel with inactive pregnadienolone.

The radioactive yield could be enhanced up to 25—30% by means of exchange reaction between C^{14} N ion and the previously prepared inactive Δ_5-3β-acetoxy-androstene-17-cyanohydrine, as it had been described by KOUŘIM and ZIKMUND [2] for the synthesis of C^{14}-serine.

The utilization of the compound in the synthesis of progresterone and corticosteroids, and in the solution of certain analytical problems are in progress.

ПРОИЗВОДСТВО ПРЕГНАДИЕНОЛОНА-20-C^{14}

Предворительное сообщение

И. Веис, Ё. Ковач

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SOME EXPERIENCES
IN THE CONSTRUCTION OF GAS CHROMATOGRAPHS

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(Received May 5, 1964)

On basis of certain consideration our gas chromatograph has been fitted with thermal conductivity cell. The detector body is a wrought brass block, and it is a flow-detector type. As a gauge resistance-wire a tungsten spiral was used. Thermostation was accomplished with air thermostat. This thermostat might be used up till 250 °C with ±1 °C accuracy.

The rapid spreading of gas chromatography is due to the cheapness of the devices used, on the one, and naturally due to the wide field of application on the other. The employment of relatively simple appliances makes possible the successful approach to "domestic" construction of the instrument at universities and research institutes. A number of home and foreign textbooks [1, 2, 3, 4, 5, 6, 7] deal with the development achieved so far, which highly facilitates the possibility for domestic construction.

According to literature the construction of a gas chromatograph of any type (gas-solid, gas-liquid) is determined by the quality of the following three units:

detector
thermostation
recording of the detector signal.

Among detectors the thermal conductivity cells are the most wide-spread ones; though these are not the most sensitive devices, they accomplish certain taks satisfactorily. On basis of this consideration our gas chromatograph has been fitted with such a detector. The detector and its dimensions are shown in Figure 1.

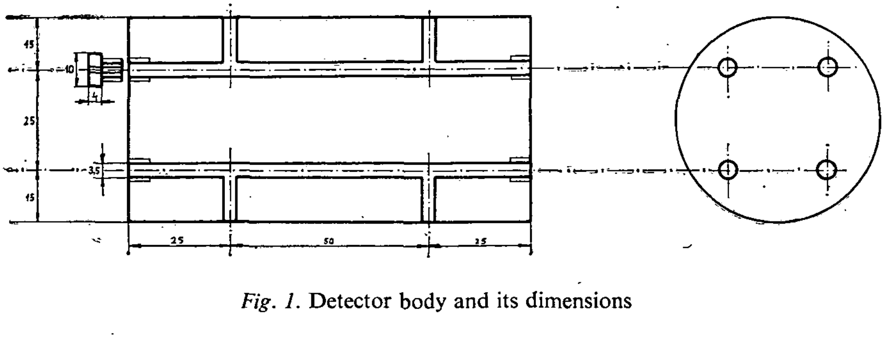

Fig. 1. Detector body and its dimensions

The detector body is a wrought brass block provided with four borings, of which two opposite ones are the comparing and measuring cells, respectively. The other two opposite borings contain the two wires of constant resistance of the Wheatstonebridge. Thus our device is of a flow-detector type. As gauge resistance-wire a tungsten spiral was used. The spirals were connected to brass wire by spelter and provided with bilateral terminals. The espace of gas was prevented by drawing home the screws in Figure 1, applying klingerit and asbestos packing. Using this packing experiments were carried out at 200 °C with absolute certainty.

The electric circuit of the detector is shown in Figure 2. The rough and fine compensation of the bridge is done with potentiometers R_5 and R_6, respectively. The total bridge-current is regulable with potentiometer R_7 within the range of 50 and 240 mA. The detector is fed with a 6V battery. The R_3 and R_4 constant resistances are placed in the detector body for the sake of thermostation, the output signal of the detector being thus insensitive against any change in temperature. $R_1 = R_2 = R_3 = R_4 = 20$ ohm, $R_5 = 5$ ohm, and $R_6 = R_7 = 100$ ohm.

The relationship between the integral detectorsignal and the amount of sample introduced was chacked. This proved to be linear (see Figure 3) in accordance with literary data (8).

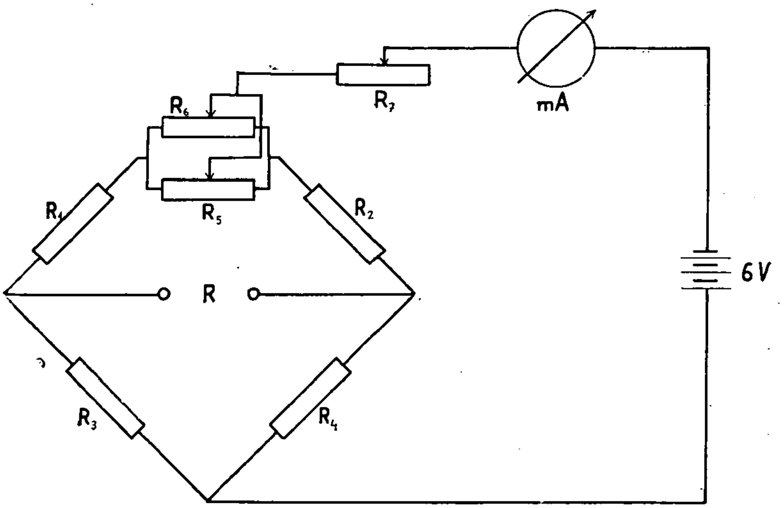

Fig. 2. Electric circuit of the detector

The sensitivity of the detector (change in signal over change in sample amount) is the slope of the corresponding straight lines in Figure 4. Figure 4 was obtained by plotting these slope values (sensitivity) against bridge-current. Similar results were obtained by M. Spalma, too (8).

Thermostation was accomplished with air-thermostat. The volume of the thermostat was 30 liter, since the apparatus is intended to be used for preparative purposes as well, in the future. The heatregulation circuit of the thermostat is shown in Figure 5. This thermostat might be used up till 250 °C with ± 1 °C. accuracy.

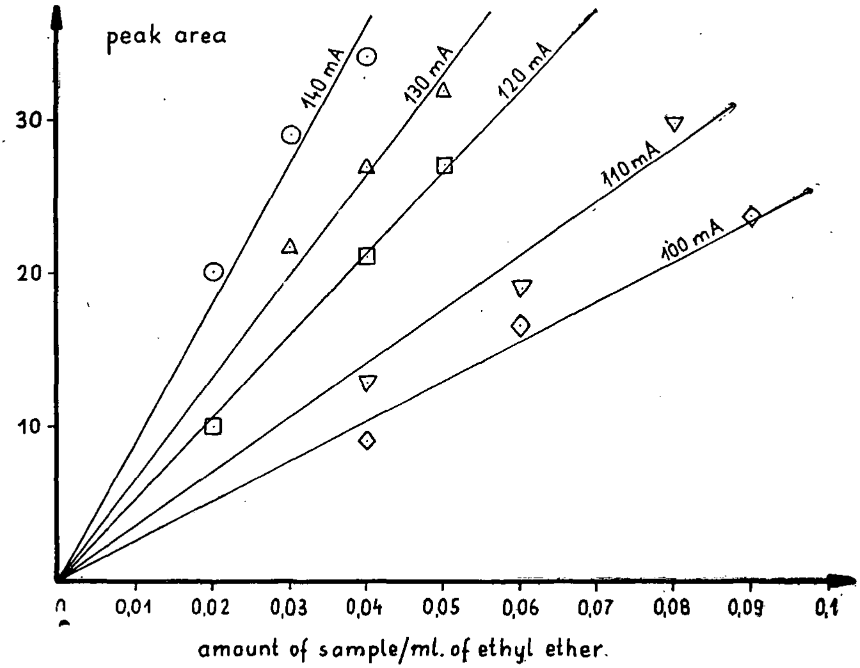

Fig. 3. Relationship between integral detectorsignal and sample amount

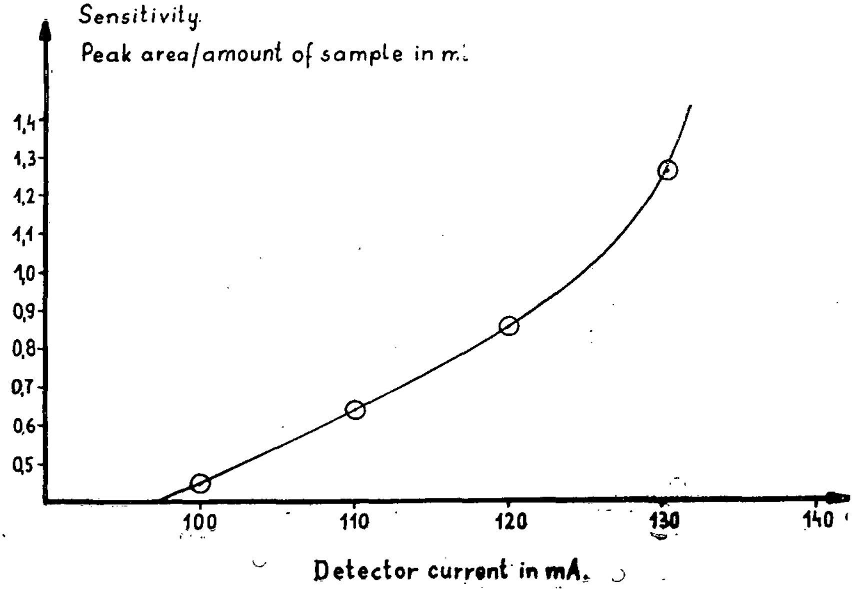

Fig. 4. Sensitivity of the detector

The principal arrangement of the thermostat was made on basis of scheme of the Organic Chemical Research Institute, Budapest. The detector signal was recorded by a J. C. Eckardt single trace compensograph of 0—2 mV measuring range. This compensograph could directly be connected to the Wehatstone-bridge, without any fitting parts.

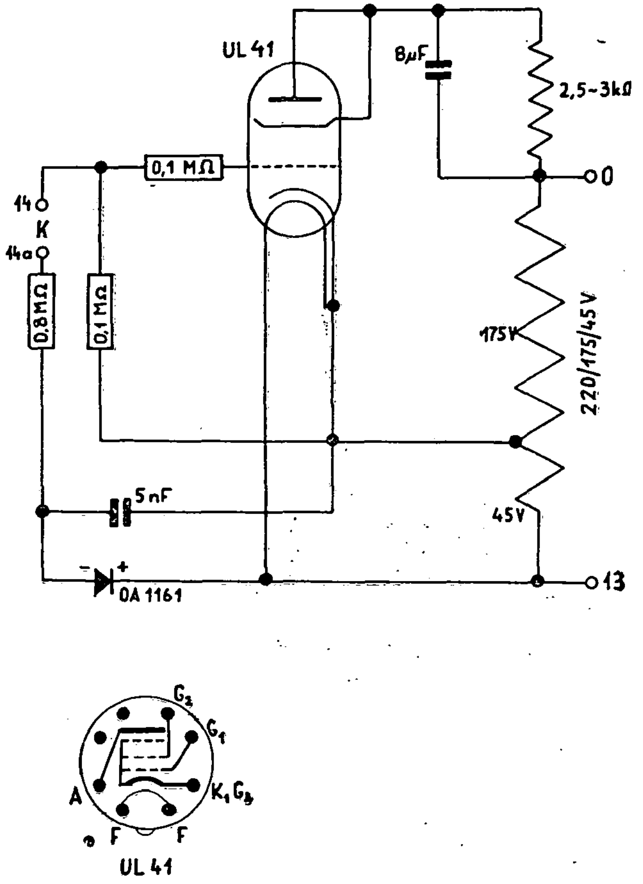

Fig. 5. Heat-regulation circuit of the thermostat

* * *

Thanks are due to Mr. S. KÓNYA technician of the department for the execution of the apparatus.

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ОПЫТЫ ПОСТРОЕНИЯ ГАЗХРОМАТОГРАФА

И. Кевари и С. Фени

На основе некоторых размышлений наш газхроматограф снабжен хорошей теплопроводящей камерой. Тело самого детектора приготовляется из кованной меди, переносного типа. В роде сопротивления употребилась волфрамная спираль. Воздушный термостат служил термостатом, регулирующий до 250 С точностью ±1°.

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