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CONTENTS

MIXED GAS ADSORPTION ON HETEROGENEOUS SURFACES

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Summary

The mixed gas adsorption on heterogeneous surfaces is studied on the basis of lattice statistical thermodynamics. Both mobile and localized adsorption on random and patchwise surfaces are treated as specific cases of a generalized model for the adsorption layer.

Key Words: Lattice statistical thermodynamics, Physical adsorption.

I. Introduction

In recent papers[1-3] the pure gas adsorption on homogeneous and heterogeneous surfaces as well as the mixed gas adsorption on homogeneous surfaces have been studied by means of the lattice theories of statistical thermodynamics. Here this type of treatment is extended to mixed gas adsorption on heterogeneous surfaces.

As in the papers[2,3] a generalized lattice model for the adsorption layer is suggested and analyzed. The localized as well as the mobile adsorption on random and patchwise heterogeneous surfaces are coming out as specific cases of this model.

II. Heterogeneous Adsorption of Binary Gas Mixtures

1. General equations

We make the same assumptions as in the case of unimolecular pure gas adsorption on heterogeneous surfaces[2]. In addition we accept that the adsorbed molecules are of two different kinds and that they can be considered as having similar diameters.

When N_1 molecules of type 1 and N_2 molecules of type 2 are adsorbed on the L sites of an homogeneous surface, then the partition function of the adsorption layer can be written as:

$$Q = \frac{L!}{N_1! \, N_2! \, (L - N_1 - N_2)!} \left(q_{in\,(1)} \, q_{t\,(1)} \, \exp \frac{U_1}{kT} \right)^{N_1} \cdot$$

$$\left(q_{in\,(2)} \, q_{t\,(2)} \, \exp \frac{U_2}{kT} \right)^{N_2} \cdot \exp \left(- \frac{Lu\,(0)}{2kT} \right) \qquad (1)$$

where
$$u(0) = c \{ \theta_1^2 u_{11}(0) + \theta_2^2 u_{22}(0) + 2\theta_1 \theta_2 u_{12}(0) \} \tag{2}$$

and
$$\theta_i = N_i/L \ , \ i = 1, 2 \tag{3}$$

In these equations $q_{in\,(i)}$ and $q_{t\,(i)}$ are the internal and the translational partition functions of an adsorbed molecule of type $i (= 1,2)$ respectively, U_i is the interaction energy of the ith type molecule with the adsorbing surface, c is the coordination number of the lattice of the adsorption surface and $u_{kh}(0)$ is the interaction energy between a pair of nearest -neighbouring molecules of type k and h respectively, when they are in the center of their cells.

When this binary gas mixture is adsorbed on a heterogeneous surface we assume, as in the case of pure gas adsorption on heterogeneous surfaces, that various cells have different interaction energies with the adsorbing surface.

We denote by L_{ij} the number of cells with adsorption energies U_{1i} and U_{2j}. Then we have:

$$L = \sum_{ij} L_{ij} \tag{4}$$

Let ξ be a distribution $\xi_{11}, \xi_{12}, ..., \xi_{21}, \xi_{22}, ...$ of the N molecules of the adsorption layer into the various cells. Then ξ_{kl} denotes that the number of molecules of type k (=1, 2) —each one of which interact with the adsorption surface with an energy U_{kl} (l=i or j) — is equal to $N_{\xi_{kl}}$.

For every ξ distribution Eq (1) can be written as:

$$Q_\xi = \exp\left(-\frac{Lu(0)}{2kT}\right) \cdot \prod_{ij} \frac{L_{ij}!}{N_{\xi_{1i}}! \, N_{\xi_{2j}}! \, (L_{ij} - N_{\xi_{1i}} - N_{\xi_{2j}})!} \cdot q_{1i}^{N\xi_{1i}} \cdot q_{2j}^{N\xi_{2j}} \tag{5}$$

where
$$q_{kl} = q_{in\,(kl)} \cdot q_{t\,(kl)} \exp\frac{U_{kl}}{kT} \ , \ k=1,2 \ , \ l=i \ or \ j \tag{6}$$

$$N = N_1 + N_2 = \sum_i N_{\xi_{1i}} + \sum_j N_{\xi_{2j}} \tag{7}$$

and
$$u(0) = c \{ \theta_1^2 u_{11}(0) + \theta_2^2 u_{22}(0) + 2\theta_1 \theta_2 {}_{12}(0) \} \tag{8}$$

when the cells of different energies are randomly distributed over the surface. In the case of a patchwise surface i.e. when the sites (cells) of equal energy are present in groups, instead of Eq. (8) we have:

$$u(0) = c \sum_{ij} \{ \theta_{1i}^2 u_{11}(0) + \theta_{2j}^2 u_{22}(0) + 2\theta_{1i} \theta_{2j} u_{12}(0) \} \tag{9}$$

where
$$\theta_{kl} = N_{\xi_{kl}}/L_{ij} \tag{10}$$

The total partition function Q is the sum of the partition functions Q_ξ:

$$(11) \qquad\qquad Q = \sum_\xi Q_\xi$$

and it can be calculated by the maximum term method. Then the logarithm of Q may be expressed by:

$$
\begin{aligned}
\ln Q = \sum_{ij} \Big\{ &L_{ij} \ln \frac{L_{ij}}{L_{ij} - N_{\xi_{1i}} - N_{\xi_{2j}}} - N_{\xi_{1i}} \ln \frac{N_{\xi_{1i}}}{L_{ij} - N_{\xi_{1i}} - N_{\xi_{2j}}} \\
&- N_{\xi_{2j}} \ln \frac{N_{\xi_{2j}}}{L_{ij} - N_{\xi_{1i}} - N_{\xi_{2j}}} + N_{\xi_{1i}} \ln \left(q_{in\,(1i)} \cdot q_{t\,(1i)} \right) \\
&+ N_{\xi_{2j}} \ln \left(q_{in\,(2j)}\, q_{t\,(2j)} \right) + \frac{N_{\xi_{1i}} U_{1i}}{kT} + \frac{N_{\xi_{2j}} U_{2j}}{kT} \Big\} - \frac{Lu\,(0)}{2kT}
\end{aligned}
\qquad (12)
$$

2. Mobile adsorption on a random surface

In this case we have:

$$q_{t\,(kl)} = \frac{2\pi m_k kT}{h^2}\, a_{f_{kl}} = \lambda_k \cdot a_{f_{kl}} \qquad (13)$$

and if we assume that in the case of a random cell distribution the free area is given by [1,3-5]:

$$a_{f_{kl}} = (1 - \theta)\, \omega \qquad (14)$$

where ω is the free area of a molecule having empty all its nearest-neighbouring sites, then the chemical potentials of the adsorbed molecules on the L_{ij} sites can be calculated from:

$$
-\frac{\mu_{\xi_{kl}}}{kT} = \left(\frac{\partial \ln Q}{\partial N_{\xi_{kl}}} \right) = \ln \left(q_{in(kl)} \cdot \lambda_k \omega \right) + \frac{U_{kl}}{kT} - \ln \frac{\theta_{kl}}{(1 - \theta_{1i} - \theta_{2j})(1 - \theta)}
$$

$$
- \frac{\theta}{1 - \theta} - \frac{c}{kT} \{ \theta_k u_{kk}(0) + \theta_m u_{12}(0) \} \qquad (15)
$$

where $k = 1,2$ $l = i$ or j, $m = 1,2$ $m \neq k$ and $\partial = \partial_1 + \partial_2$ $\qquad (16)$

The adsorption isotherms result from the following equilibrium relations:

$$\mu_{\xi_{kl}} = \mu_k^{gas} \quad k = 1,2 \qquad (17)$$

where μ_k^{gas} is the chemical potential of a molecule of type k in the bulk gas phase.

For a perfect bulk gas phase the isotherms obtained from Eqs. (17) may be expressed by:

$$\ln P_k = \ln \frac{\lambda_k^{1/2} kT q_{in}^{gas}(k)}{\omega q_{in(kl)}} + \ln \frac{\theta_{kl}}{(1 - \theta_{1i} - \theta_{2j})\ (1 - \theta)} + \frac{\theta}{1 - \theta} - \frac{U_{kl}}{kT}$$

$$+ \frac{c}{kT} \{\theta_k u_{kk}(0) + \theta_m u_{12}(0)\} \tag{18}$$

If the system of the isotherms (18) is solved with respect to θ_{kl}, then θ_{kl} is obtained as a function of P_k, θ_k and U_{kl}:

$$\theta_{kl} = \Theta_\kappa\ (P_1,\ P_2,\ \theta_1,\ \theta_2,\ U_{1l},\ U_{2l}) \tag{19}$$

Let x (U_1, U_2) be a fraction of sites (cells) with adsorption energies lying in the two dimentional region $(U_1, U_1 + dU_1) \times (U_2, U_2 + dU_2)$.

The function x (U_1, U_2) evidently must satisfy the normalization condition:

$$\int \int x\ (U_2,\ U_2)\, dU_1 dU_2 = 1 \tag{20}$$

and for a continuous distribution of the adsorption energies the fraction of the total surface covered with adsorbed molecules of type k is given by:

$$\theta_k = \int \int \Theta_k x\ (U_1,\ U_2)\ dU_1 dU_2 \tag{21}$$

The total adsorption isotherm is the sum of the partial isotherms (21):

$$\theta\ (P_1,\ P_2,\ T)\ =\ \theta_1(P_1,\ P_2,\ T) + \theta_2\ (P_1,\ P_2,\ T) \tag{22}$$

Therefore the determination of the adsorption isotherm requires the solution of the system of integral Eqs. (21), in which the distribution function x (U_1, U_2) is incorporated.

Usually this function is selected from the already known distribution functions.

3. Mobile adsorption on a patchwise surface

The analysis described above is subject to the condition that cells of different energies are randomly distributed over the surface. If we have a patchwise surface then instead of Eqs. (8) and (14) we have Eqs. (9) and (23):

$$a_{f_{kl}} = (1 - \theta_{kl}) \cdot \omega \tag{23}$$

Therefore the chemical potentials of the adsorbed molecules on cells L_{ij} are given by:

$$\frac{\mu \xi_{kl}}{kT} = \ln \frac{\theta_{kl}}{(1 - \theta_{1i} - \theta_{2j})^2} + \frac{\theta_{1i} + \theta_{2j}}{1 - \theta_{1i} - \theta_{2j}} + \frac{c}{kT} \{\theta_{kl_1} u_{kk}(0) + \theta_{ml_2} u_{12}(0)\}$$

$$- \frac{U_{kl}}{kT} - \ln\ (q_{in(kl)} \lambda_k \omega) \tag{24}$$

where $l_1 = i$ or $l_1 = j$ depending on whether $k = 1$ or $k = 2$ and $l_2 (= i$ or $j) \neq l_1$. The corresponding adsorption isotherms are expressed by:

$$\ln P_k = \ln \frac{\lambda_k^{1/2} kTq_n^{gas}(k)}{\omega q_{in\,(kl)}} + \ln \frac{\theta_{kl}}{(1 - \theta_{1i} - \theta_{2j})^2} + \frac{\theta_{1i} + \theta_{2j}}{1 - \theta_{1i} - \theta_{2j}} - \frac{U_{kl}}{kT}$$

$$+ \frac{c}{kT} \{\theta_{kl_1} u_{kk}(0) + \theta_{ml_2} u_{12}(0)\} \qquad (25)$$

Obviously these isotherms cannot be solved analytically with respect to θ_{kl}. Thus, as in the case of pure gas adsorption on heterogeneous surfaces, the use of numerical methods is necessary to obtain θ_{kl} as a function of P_k and U_{kl}:

$$\theta_{kl} = \Theta_k (P_1, P_2, U_{1l}, U_{2l}) \qquad (26)$$

The determination of the total adsorption isotherm, as in the previous case, is possible from Eqs. (21), (22) and (26).

4. Localized adsorption

In this case we have $q_{t\,(kl)} = 1$ and the resulting isotherms are the following:

$$\ln P_k = \ln \frac{\lambda_k^{3/2} kTq_{in}^{gas}(k)}{q_{in\,(kl)}} - \frac{U_{kl}}{kT} + \ln \frac{\theta_{kl}}{1 - \theta_{1i} - \theta_{2j}} + \frac{c}{kT} \{\theta_k u_{kk}(0)$$

$$+ \theta_m u_{12}(0)\} \qquad (27)$$

and

$$\ln P_k = \ln \frac{\lambda_k^{3/2} kTq_{in}^{gas}(k)}{q_{in\,(kl)}} - \frac{U_{kl}}{kT} + \ln \frac{\theta_{kl}}{1 - \theta_{1i} - \theta_{2j}} + \frac{c}{kT} \{\theta_{kl_1} u_{12}(0)$$

$$+ \theta_{ml_2} u_{12}(0)\} \qquad (28)$$

depending on whether we have a random or patchwise cell distribution. The total adsorption isotherms can also be determined from Eqs. (21), (22), (27) and (28) provided that $x(U_1, U_2)$ is known.

In the limiting case where $u_{kk}(0) = u_{kl}(0) = 0$ and $q_{in\,(kl)} = q(T)$ the isotherms (27) and (28) are reduced to:

$$\theta_{kl} = \frac{P_k A_k \exp(U_{kl}/kT)}{1 + P_1 A_1 \exp\dfrac{U_{1l}}{kT} + P_2 A_2 \exp\dfrac{U_{2l}}{kT}} \qquad k = 1,2 \quad l = i \text{ or } j \quad (29)$$

where

$$A_k = \frac{q(T)}{\lambda_k^{3/2} kT\, q_{in}^{gas}(k)} \qquad (30)$$

and therefore we have

$$\theta_k = \iint \theta_{k|} x (U_1, U_2) dU_1 dU_2 \tag{31}$$

In this case it can be shown that if the partition function $x (U_1, U_2)$ has the simple form

$$x (U_1, U_2) = \frac{1}{U_{1m} U_{2m}} \exp \left(- \frac{U_1}{U_{1m}} \right) \exp \left(- \frac{U_2}{U_{2m}} \right) \tag{32}$$

where U_{1m}, U_{2m} represent the mean adsorption energy over all sites of positive adsorption energy, then Eqs. (31) can be reduced further to the Freundlich isotherms[6,7]
Indeed from Eqs. (31) and (32) we have:

$$\theta_1 = \int \left\{ \frac{1}{U_{1m}} \int \frac{P_1 A_1 \exp (U_1/kT) \exp (- U_1/U_{1m})}{1 + P_1 A_1 \exp (U_1/kT + P_2 A_2 \exp (U_2/kT)} dU_1 \right\} \frac{1}{U_{2m}}$$

$$\exp (-U_2/U_{2m}) dU_2 \tag{33}$$

Now if we assume that $\qquad \dfrac{U_1}{U_2} = \dfrac{U_{1m}}{U_{2m}} = 1 \tag{34}$

and we integrate Eq. (33) between the limits $-\infty$ and $+\infty$ we find

$$\theta_1 = \frac{\pi kT/U_{1m}}{\sin (\pi kT/U_{1m})} \cdot \frac{P_1 A_1}{(P_1 A_1 + P_2 A_2)^{1 - kT/U_{1m}}} \tag{35}$$

from which the well known Freundlich isotherm is obtained:

$$\ln \frac{P_1}{X_1} = \frac{U_{1m}}{kT} \ln \theta + \text{const.} \tag{36}$$

where X_1 is the mole fraction of adsorbate 1.

In the case where $x (U_1, U_2)$ is a constant and under the approximation imposed by (34), Eq. (31) after integration between the limits 0 and U yields:

$$\theta_1 = ckT \frac{P_1 A_1}{P_1 A_1 + P_2 A_2} \ln \left\{ \frac{1 + (P_1 A_1 + P_2 A_2) e^{U/kT}}{1 + P_1 A_1 + P_2 A_2} \right\} \tag{37}$$

and also an analogous isotherm for θ_2.
Therefore

$$\theta = ckT \ln \frac{1 + (P_1 A_1 + P_2 A_2) e^{U/kT}}{1 + P_1 A_1 + P_2 A_2} \tag{38}$$

This isotherm can be reasonably considered as a generallized form of Temkin isotherm in the case of mixed gas adsorption.

III. Heterogeneous adsorption of r-component mixtures

The problem described previously is generallized for the case of the adsorption of a mixture consisting of r gases of similar diameters on a heterogeneous surface.

For the adsorption of a mixture of r gases, Eq. (5) is rewritten in the following form:

$$Q_\xi = \exp\left(-\frac{Lu(0)}{2kT}\right) \prod_i \left\{ \frac{L_i!}{\prod_k N_{\xi_{ki_k}}! \, (L_i - \Sigma N_{\xi_{ki_k}})!} \prod_k (q_{ki_k})^{N_{\xi_{ki_k}}} \right\} \qquad (39)$$

where $\mathbf{i}$ is the r-dimensional vector: $\mathbf{i} = (i_1, i_2, \ldots i_r)$,

$$q_{ki_k} = q_{in(ki_k)} \, q_{t(ki_k)} \, \exp(U_{ki_k}/kT) \qquad (40)$$

while $u(0)$ depends on the nature of the absorbing surface.

For a random surface, $u(0)$ is given by:

$$u(0) = c \sum_k^r \{\theta_k^2 u_{kk}(0) + 2 \sum_{k<l}^r \theta_k \theta_l u_{kl}(0)\} \qquad (41)$$

whereas for a patchwise surface we have

$$u(0) = c \sum_i \sum_k^r \{\theta_{ki_k}^2 u_{kk}(0) + 2 \sum_{k<l}^r \theta_{k_k} \theta_{li_l} u_{kl}(0)\} \qquad (42)$$

Following the same procedure with that of binary adsorption we obtain in general

$$\theta_{ki_k} = \Theta_k (\mathbf{P, U, \theta}) \qquad (43)$$

for the random surface,

and $$\theta_{ki_k} = \Theta_k (\mathbf{P, U}) \qquad (44)$$

for a patchwise heterogeneous surface, where $\mathbf{P} = (P_1, P_2, \ldots, P_r)$, $\mathbf{U} = (U_1, U_2, \ldots, U_r)$ and $\mathbf{\theta} = (\theta_1, \theta_2, \ldots, \theta_r)$.

For a continuous distribution of the adsorption energies, the surface coverage for the k component is

$$\theta_k = \int \Theta_k x(\mathbf{U}) \, d\mathbf{U} \qquad (45)$$

where the r-dimentional distribution function x satisfies the condition

$$\int x(\mathbf{U}) \, d\mathbf{U} = 1 \qquad (46)$$

The solution of the system of the r integral Eqs. (45) together with the relation:

$$\theta(\mathbf{P}) = \sum_{k} \theta_k \tag{47}$$

leads to the total adsorption isotherm of the system.

Περίληψη

Προσρόφηση μίγματος αερίων σε ετερογενείς επιφάνειες

Η εργασία αυτή αποτελεί επέκταση και γενίκευση προηγούμενων εργασιών πάνω στην προσρόφηση αερίων. Συγκεκριμένα μελετάται σε θεωρητικό επίπεδο η προσρόφηση μίγματος r αερίων πάνω σε ενεργειακά ετερογενείς επιφάνειες. Όπως και σε προηγούμενες εργασίες, προτείνεται και αναλύεται με βάση τη στατιστική θερμοδυναμική ένα γενικευμένο πλεγματικό μοντέλο της στιβάδας προσρόφησης, από το οποίο προκύπτουν σαν μερικές περιπτώσεις η κινητή και η τοπική προσρόφηση. Οι ισόθερμες προσρόφησης προκύπτουν με τη βοήθεια της προσέγγισης των Bragg-Williams και προσδιορίζονται από ένα σύστημα r ολοκληρωτικών εξισώσεων.

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EIN VERGLEICH DER LEWIS-BASIZITÄT VON N,N-DIMETHYL-FORMAMID MIT N,N-DIMETHYLTHIOFORMAMID.

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Zusammenfassung

B_2H_6 reagiert mit N,N-Dimethylformamid direkt und gibt N,N-Dimethylformamid-Boran. Die Darstellung von N,N-Dimethylthioformamid-Boran ist jedoch auf dieselbe Art und Weise nicht möglich.
Diese Tatsache führt zu der Frage nach der relativen Stärke der Lewis Basizität beider Amide bzw. nach deren Bau und Elektronenverteilung. Die NMR-Spektren der Amide und deren Borane, sowie andere experimentelle Fakten aus der Literatur ermöglichen es, den obengenannten Sachverhalt befriedigend zu deuten.

Key Words: Amide boranes, NMR

Einleitung

Die Einwirkung von Natriumboranat auf elementaren Schwefel in Gegenwart von Aminen, Amiden oder Ammoniak kann zur präparativen Darstellung von Amin-, Amid-oder Ammoniak-Boranen verwendet werden[1].

$$2 \; NaBH_4 + 1/8 \; S_8 \xrightarrow{\text{N-Lewis-Base}} BH_3\text{-N-Lewis-Base} + H_2 + Na_2S \quad (1)$$
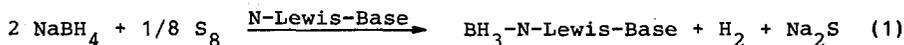
Wendet man die Reaktion nach Gl. (1) zur Darstellung von N,N-Dimethylformamid-Boran (DMF-BH$_3$) an, so zeigt das ^{11}B-NMR-Spektrum der Reaktionsmischung neben dem Quartett des DMF-BH$_3$ ein zweites Quartett, welches, wie wir nachweisen konnten, von dem N,N-Dimethylthioformamid-Boran (DMTF-BH$_3$) herrührt[1]. Während aber für das DMF-BH$_3$ auch der direkte Weg zu seiner Darstellung über einfaches Einleiten von Diboran in DMF eingeschlagen werden kann,

$$(2)$$
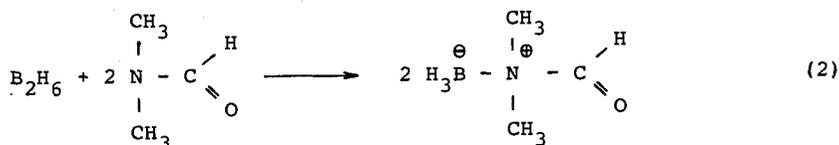
ist eine analoge Lewis-Säure-Lewis-Base-Reaktion mit DMTF nicht möglich. ·

$$B_2H_6 + 2 \; \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}} - C \overset{H}{\underset{S}{\diagdown}} \; \xrightarrow{\quad/\!\!/\quad} \; 2 \; H_3\overset{\ominus}{B} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{\oplus}{N}}} - C \overset{H}{\underset{S}{\diagdown}} \qquad (3)$$
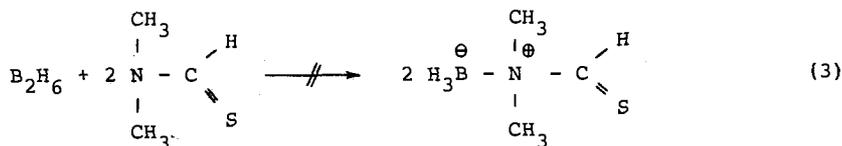
Das DMTF-BH$_3$ ist deshalb nicht auf diese Weise, sondern ausschließlich durch die Überführung der Carbonylgruppe des DMF-BH$_3$ in die Thiocarbonylgruppe zugänglich:

$$H_3\overset{\ominus}{B} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{\oplus}{N}}} - C \overset{H}{\underset{O}{\diagdown}} + \overset{\ominus}{S}H \; \xrightarrow{\quad DMF \quad} \; H_3\overset{\ominus}{B} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{\oplus}{N}}} - C \overset{H}{\underset{S}{\diagdown}} + \overset{\ominus}{O}H \qquad (4)$$
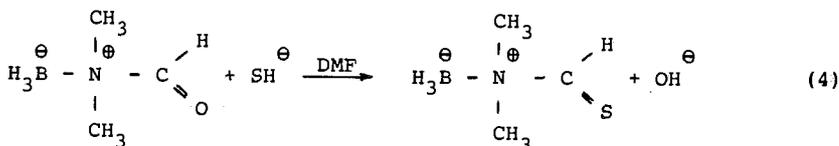
Experimentelles

In einem 250-ml-Dreihalskolben, versehen mit KOH-Trockenturm und Substanzbirne, werden zu 4,0 g (0,105 mol) NaBH$_4$ 150 mol DMF hinzugegeben. Im Laufe von 2 h werden 3,2 (0,1 mol) S$_8$ eingetragen. Die Außentemperatur beträgt etwa 60^{0}C.

Nach beendigter Reaktion destilliert man, ohne vorherige Abtrennung der Polysulfide, das DMF-BH$_3$ zusammen mit DMF bei 40^{0}C in Ölpumpenvakuum. Im Anschluß daran läßt man die Temperatur langsam bis auf 80^{0}C ansteigen, wobei eine hellgelbe Flüssigkeit überdestilliert, die neben DMTF-BH$_3$ noch DMF und DMTF enthält.

Zur Herstellung größerer Mengen an DMTF-BH$_3$ empfiehlt es sich, die direkte Thioformylierung durchzuführen[1].

Zu eine vorgelegten Lösung von DMF-BH$_3$ in DMF gibt man einen Überschuß an Na$_2$S. 9H$_2$O sowie etwas S$_8$; man erwärmt nun auf 60^{0}C und gibt gleichzeitig einige ml HCl (10%) hinzu. Die Umwandlung von DMF-BH$_3$ in DMTF-BH$_3$ erfolgt quantitativ, was ^{11}B-NMR-spektroskopisch verfolgt werden kann. Die Reaktion ist beendet, sobald nur noch das Quartett des DMTF-BH$_3$ erscheint. Die destillative Trennung erfolgt nach obigen Angaben. Ist das Destillat an Produkt hinreichend konzentriert, so werden beim stehenlassen im Laufe von zwei Wochen im Kühlschrank farblose Kristalle abgeschieden, die für die ^{1}H-NMR-Untersuchung des Produkts benutzt werden können.

Sämtliche chemische Verschiebungen sind für die ^{1}H-NMR-Spektren auf TMS, für die ^{11}B-NMR-Spektren auf BF$_3$O (C$_2$H$_5$)$_2$ als externen Standard bezogen. Positive δ-Werte bedeuten eine chemische Verschiebung nach niederer Feldstärke relativ zum jeweiligen Standard.

Die ^{11}B-bzw. ^{1}H-NMR-Spektren wurden mit dem Bruker WP 80 und WP 60 Kernresonanzspektrometer registriert. Für die Darstellung der beiden Borane wurden die im Handel erhältlichen Amide DMF und DMTF verwendet[1].

Deutung der experimentellen Befunde.

Die Tatsache, daß DMF-BH₃ leicht durch eine Lewis-Säure-Lewis-Base-Reaktion nach Gl. (2), DMTF-BH₃ dagegen auf analoge Weise, d. h. nach Gl. (3), nicht erhalten werden kann, wirft die Frage auf, weshalb sich die beiden Lewis-Basen DMF und DMTF gegenüber derselben Lewis-Säure BH₃ so unterschiedlich verhalten. Aufgrund der größeren elektronenziehenden Wirkung der Formyl-gegenüber der Thioformylgruppe wäre an sich am N-Atom des DMF eine größere Verarmung an Elektronenladung zu erwarten, als am N- Atom des DMTF. Dies hätte jedoch zur Folge, daß das DMTF eine stärkere Lewis-Base als das DMF wäre, und dies steht nicht im Einklang mit den experimentellen Ergebnissen, die das DMF als die stärkere Lewis-Base festlegen.

Das ¹H-NMR-Spektrum des DMF und DMTF indessen zeigt, daß das freie Eletronenpaar des N-Atoms beider Amide starken p-Charakter haben muß, eine Schlußfolgerung die unmittelbar aus der magnetischen Nichtäquivalenz der Methylprotonen beider Verbindungen gezogen werden kann. Die daraus resultierende sp²-Hybridisierung des N-Atoms bzw. die Planarität beider Amide ist zumindest für das DMF auch durch Elektronenbeugung in der Gasphase sichergestellt worden[2]. Für die beiden Amide lassen sich relevante 1,3-dipolare Resonanzstrukturen formulieren[3]:

Wendet man hier qualitativ die Hückel-Näherung an[4], d.h. betrachtet man σ-und π-Elektronengerüste der beiden Amide als unabhängig voneinander, so wird deutlich, warum die größere elektronenziehende Wirkung der Formyl-gegenüber der Thioformylgruppe nicht unbedingt zu einer verminderten Basizität des N-Atoms des DMF gegenüber dem des DMTF führen muß: Der größere -I-Effekt der Formyl-gegenüber der Thioformylgruppe wirkt sich ausschließlich im σ-Gerüst, dagegen nicht im π-Gerüst des DMF aus. Die gegen die Erwartung größere Lewis-Basizität des DMF im Vergleich zum DMTF läßt sich demnach befriedigend erklären, indem man für die 1,3-dipolare Resonanzstruktur IV einen wesentlich größeren Beitrag bei der Beschreibung des DMTF annimmt, als der Beitrag der Resonanzstruktur II für das DMF. Tatsächlich läßt sich diese Annahme durch eine Reihe von übereinstimmenden experimentellen Fakten zusätzlich stützen. So ergaben die Messungen der Dipolmomente der beiden Amide, daß das Dipolmoment des DMTF mit 4,37 Debye

größer als das große Dipolmoment des DMF mit 3,86 Debye ist[5]. Dieser überraschende Befund läßt sich durch das hohe relative «Gewicht» der dipolaren Resonanzstruktur IV erklären. Daß die Resonanzstruktur IV eine größere Bedeutung als die II hat, geht auch daraus hervor, daß die Torsionsbarriere beim DMF 21 kcal/mol gegenüber∼28 kcal/mol beim DMTF beträgt, und daß daher die freie Drehbarkeit der Dimethylaminogruppe des DMF bei 120°C, des DMTF dagegen erst bei 175°C erreicht wird[3,6].

Der aus der Resonanzstruktur IV resultierende Merkaptid-Charakter des DMTF ist sogar so stark ausgeprägt, daß man mit CH_3I eine S-und nicht etwa eine N-Methylierung erreichen kann[7]. Einen zusätzlichen Hinweis schließlich für die Bedeutung der Resonanzstruktur IV liefert uns das ^{1}H-NMR-Spektrum der beiden Amide der Abb. 2. Man findet dort:

DMF   DMTF

$\delta_{^1H}(CH_3,\ cis\quad zu\ O) = 2,92\ ppm$ $\delta_{^1H}(CH_3,\overset{\ominus}{cis}\quad zu\ S) = 3,15\ ppm$

$\delta_{^1H}(CH_3,\ trans\ zu\ O) = 2,82\ ppm$ $\delta_{^1H}(CH_3,\ trans\ zu\ S) = 2,98\ ppm$

Diese Tieffeldverschiebung beider CH_3-Signale des DMTF gegenüber den CH_3-Signalen des DMF läßt sich in Übereinstimmung mit den obengenannten Fakten auf eine größere, partiell positive Ladung des N-Atoms in IV als in II zurückführen, obwohl das Vorhandensein der Formylgruppe in II bzw. I das Gegenteil nahelegt. Daß die Tieffeldverschiebung der CH_3-Signale des DMTF primär auf das stärkere elektrostatische Feld des N-Atoms zurückzuführen ist, läßt sich zusätzlich durch die vorerwähnte S-Methylierung stützen.
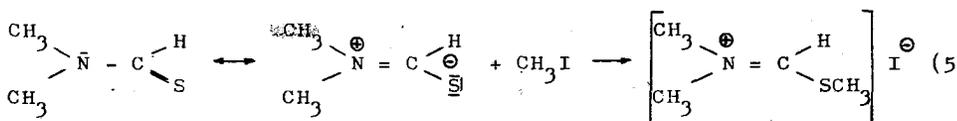
Man erreicht also hier durch eine solche Überführung des DMTF zum N,N-Dimethyl-Imidothioesterjodid den Übergang eine partiellen Formalladung am N-Atom in eine echte volle Ladung. In voller Übereinstimmung mit der Erwartung resultiert eine verstärkte Verschiebung der C-H-Bindungselektronen in Richtung zum Kohlenstoffatom und als Folge davon erscheinen die beiden N-Methylsignale noch mehr tieffeldverschoben[8]. Aus allen diesen experimentellen Ergebnissen läßt sich demnach die eindeutige Schlußfolgerung ziehen, daß das DMTF eine sehr schwache N-Lewis-Base ist. Hier liegt die Begründung, daß eine direkte BH_3-Anlagerung an das DMTF-anders als beim DMF-nicht in Frage kommt, und daß ein Zugang zum DMTF-Boran ausschließlich über eine Umwandlung des DMF-Borans nach Gl. (4) möglich ist. Der größere Beitrag der 1,3-dipolaren Resonanzstruktur IV gegenüber der 1,3-dipolaren Resonanzstruktur II steht in Übereinstimmung mit der Doppelbindungsregel, wonach Elemente der dritten und höheren Periode eine geringe Tendenz haben kovalente-p-p-π-Bindungen einzugehen. Dieser allgemeine Sachverhalt ist auch im Verhältnis von DMTF zum DMTF-Boran zu beobachten. Während das DMTF

wegen seiner Mesomeriefähigkeit stabil und monomer ist, führt die durch die BH_3^-
Anlagerung hervorgerufene Aufhebung der Mesomerie zu einer Fixierung der
Kohlenstoff-Schwefel-Doppelbindung.

Versucht man aber danach das DMTF-Boran lösungsmittelfrei zu erhalten, so
weicht das Molekül dieser Fixierung der C = S-Doppelbindung durch Polymerisation
aus. Vermutlich geht die Polymerisation folgendermaßen vor sich:

$$n \; H_3\overset{\ominus}{B} - \overset{\overset{\oplus}{CH_3}}{\underset{CH_3}{N}} - C\overset{H}{\underset{S}{\diagdown}} \longrightarrow \left[\begin{array}{c} H \\ - C - S - \\ \oplus \\ CH_3 - N - CH_3 \\ \underset{BH_3}{\ominus} \end{array} \right]_n \qquad (6)$$
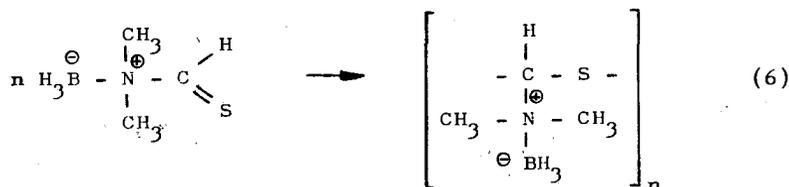
Die Tatsache, daß das DMTF-BH_3 im DMTF praktisch unbegrenzt ohne
Polymerisation aufbewahrt werden kann, läßt sich auf zwei naheliegende Ursachen
zurückführen. Die erste davon rührt von der elektronenziehenden Wirkung der
Dimethylboranoaminogruppe her, wodurch eine gewisse Verarmung an
Elektronenladung am C-Atom und mithin eine partielle Stabilisierung der C = S-
Doppelbindung resultiert. Die zweite Ursache dürfte in einer intermolekularen Donor-
Akzeptor-Beziehung zwischen dem DMTF und dem DMTF-BH_3 liegen, wodurch der
Doppelbindungscharakter der C-S-Bindung abgeschwächt wird. Die hohe
Assoziationstendenz des DMTF aufgrund seines hohen Dipolmoments ist in der
Literatur dokumentiert[5]:

$$H_3\overset{\ominus}{B} - \overset{\overset{\oplus}{CH_3}}{\underset{CH_3}{N}} - \overset{H}{\underset{S}{C}} \longleftarrow \overset{\ominus}{S} - \overset{H}{C} = \overset{\overset{H}{} \; CH_3}{\underset{CH_3}{N}\oplus}$$
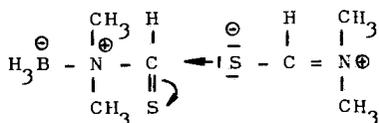
Zur chemischen Verschiebung der NMR-Signale von DMF-BH₃ und DMTF-BH₃.
Wie weiter oben ausgeführt, erscheinen im [1] H-NMR-Spektrum die CH_3-Signale des
DMTF bei niedrigerem Feld, als die von DMF. Führt man hingegen die BH_3^--
Anlagerung in den beiden Amiden durch, so kehrt sich diese Reihenfolge um.
Sämtliche am N-Atom gebundenen Gruppen mit resonanzfähigen Kernen liefern
NMR-Signale, die bei der Thiocarbonylverbindung bei höheren Feld erscheinen, als
bei der Carbonylverbindung (vgl. Abb. 1 und 2):

DMF–BH_3

$\delta_{^{11}B} = -6,7$ ppm, q,

$^1J(^1H-^{11}B) = 93,75$ Hz

$\delta_{^1H}(BH_3) = 2,07$ ppm, q,

$^1J(^1H-^{11}B) = 93,75$ Hz

$\delta_{^1H}(CH_3) = 2,7$ ppm, s

DMTF–BH_3

$\delta_{^{11}B} = -12,3$ ppm, q,

$^1J(^1H-^{11}B) = 92$ Hz

$\delta_{^1H}(BH_3) = 1,75$ ppm, q,

$^1J(^1H-^{11}B) = 92$ Hz

$\delta_{^1H}(CH_3) = 2,4$ ppm, s

Wie ersichtlich, sind bei den Boranen die freien Elektronenpaare am N-Atom durch die BH_3-Gruppe gleichermaßen blockiert bzw. es kann bei keinem der beiden Borane ein sich über das ganze Molekül erstreckendes π-Gerüst existieren. In-
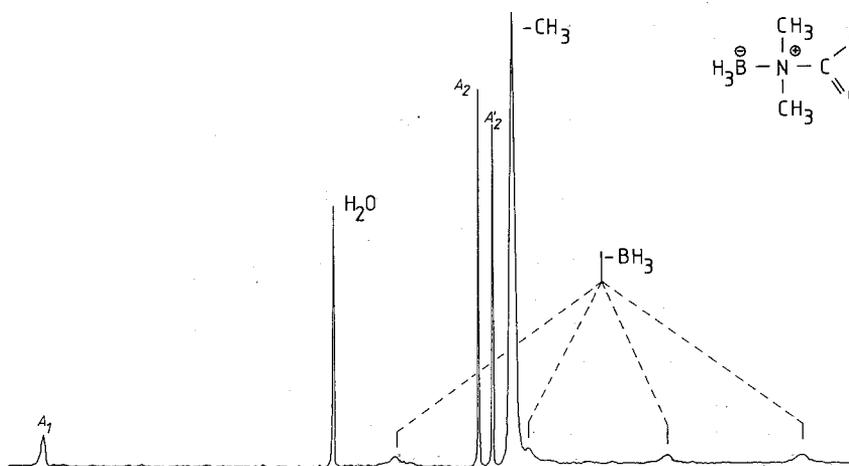
ABB. 1: *¹H-NMR-Spektrum von DMF-BH₃ in DMF/H₂O. Die Signale A₁,A₂,A′₂ stammen von DMF. Das vom Formylproton des Borans verursachte Signal liegt unter A₁.*
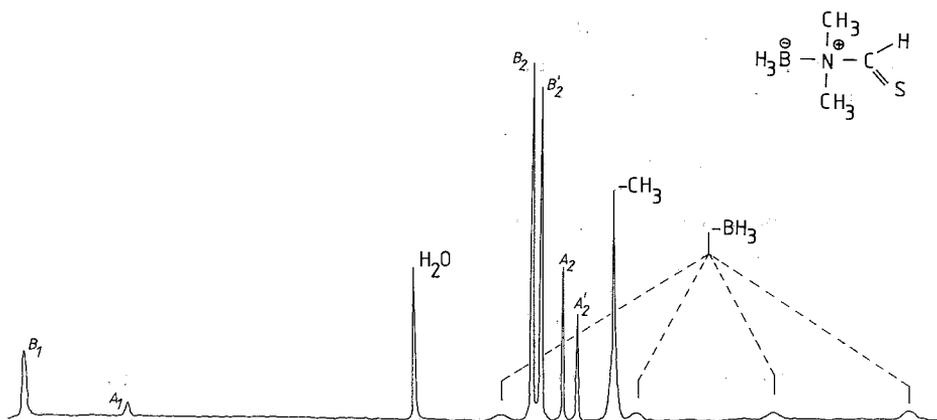
ABB. 2: *¹H-NMR-Spektrum von DMTF-BH₃ in DMF/DMTF/H₂O. Die Signale B₁,B₂,B′₂ stammen von DMTF. Das vom Thioformylproton des Borans verursachte Signal liegt unter B₁.*

folgedessen kommt nunmehr ausschließlich die größere elektronenziehende Wirkung

der Formyl-gegenüber der Thioformylgruppe in Betracht. Diese führt naturgemäß zu einer größeren Elektronenverarmung des N-Atoms des DMF-BH₃ gegenüber dem N-Atom des DMTF-BH₃, und somit zu einer verminderten Abschirmung der Kerne des ersteren gegenüber den Kernen des letzteren, so daß die beobachtete Umkehrung der Reihenfolge der Signale verständlich wird.

Summary

A comparison of Lewis-basicity between N,N-dimethylformamid and N,N-dimethylthioformamid.

B_2H_6 acts on N,N-dimethylformamide to give N,N-dimethylformamide borane. The preparation of N,N-dimethylthioformamide borane, on the other hand, is not possible with the same method. This fact raises the question to the relative strength of the Lewis basicity of both amides. The NMR spectrum of both amides and of their boranes, in connection with other experimental facts from the literature, makes it possible to give a satisfactory answer to this question.

Περίληψη

Μια σύγκριση της Λούις-βασικότητας ανάμεσα στο N, N-διμεθυλοφορμαμίδιο και στο N,N-διμεθυλοθειοφορμαμίδιο.

Με απ' ευθείας αντίδραση του B₂H₆ με Ν,Ν — διμεθυλοφορμαμίδιο παρασκευάζεται το βοράνιο του Ν,Ν-διμεθυλοφορμαμιδίου. Η κατά παρόμοιο τρόπο όμως παρασκευή του βορανίου του Ν,Ν-διμεθυλοθειοφορμαμιδίου δεν είναι εφικτή. Το δεδομένο αυτό θέτει το ερώτημα αναφορικά με τη σχετική ισχύ της Λούις-βασικότητας και κατ' επέκταση αναφορικά με τη δομή και τον καταμερισμό του ηλεκτρονικού φορτίου των δύο αμιδίων.

Τα NMR-φάσματα των δύο αμιδίων και των βορανίων τους καθώς και άλλα πειραματικά δεδομένα από την βιβλιογραφία καθιστούν δυνατό το δόσιμο ικανοποιητικής ερμηνείας στο πάρα πάνω φαινόμενο.

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THE USE OF NON-IONIC SURFACE ACTIVE AGENTS AND ORGANIC ACIDS ON THE DYEING OF ALUMINIUM WITH DISPERSE DYES

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Summary

The use of non-ionic surface active agents during the dyeing of anodized aluminium with disperse dyes has not a positive influence apart from a few cases (i.e. Marlophen 83).

Pretreatment of anodized samples in aqueous solutions of organic acids had by itself a positive action on colour depths. Subsequent dyeing, with parallel addition of non-ionic surface active agent, didn't show any further improvement in colour depth. On the contrary, when the acid was strong enough i.e. Sulphosalicylic acid and the dyeing took place in the presence of an excess of non-ionic surfactant, no colouring was observed.

Introduction

Aluminium presents great interest all over the world and specially in Greece, because Bauxite, the main ore for aluminium production occurs in large amounts in several parts of Greece.

The surface protection and dyeing of aluminium is of particulr importance for its use. Apart from the electrolytic colouring methods, many excellent commercial dyes (usually water soluble acid, acid mordant, complex metallic dyes and a few mordant dyes) are available for the dyeing of anodized aluminium. The dyeing process is analogous with that of protein fibres. The main bonds between these dyes and porous oxide film are of ionic type (anion exchange). Some covalent bonding between dye and film may also occur.[1]

In previous paper[2] it has been reported that some commercial disperse dyes, which are available for colouring synthetic fibres, are satisfactory as well as for the colouring of anodized aluminium from aqueous solutions in many modern colours. They must have active protons in a suitable position in the molecule in order that stereochemical hindrance does not exist and hydrogen bridges can be formed between dye and substrate. In this case, the main forces between film and dye are hydrogen bonds.[1, 2] In cases where the disperse dye has groups in the o-position suitable to form complexes, semi-polar bonds can also be developed.[1, 3]

Disperse dyes have no water solubilizing groups. They are suspended in the water bath in form of very fine particles. The use of surface active agents improves the dye dispersion stability.

The uniformity of particle size and the choice of dispersing agent according to in-dividual dye overcame most of the difficulties in regard to the dispersion stability.[4]

The intent of this study is to investigate the role of non-ionic surface active agents to produce better finishes of anodized aluminium in terms of colour depth with commercial disperse dyes.

The influence of a pretreatment of anodized aluminium in a series of aqueous solutions of organic acids on these colour depths was also investigated.

The surface active agent has been added in the dyeing bath in concentration above the critical micelle concentration (C.M.C.), in order to achieve a mono-molecular dispersion after some hours. The other conditions of dyeing (temperature, dyeing time, disperse dye concentration, electrolyte concentration etc.) have not been changed.

It appears that, with the above conditions remaining stable, the structure of the dye molecule, its size, its polarity, the degree of its solubility in water, the dye disper-sion stability and the degree of dye aggregation, influence the dyeing of anodized aluminium.

The first four conditions depend on the structure of the dye, while the others de-pend on the types and concentration of the dispersing agent, the mechanical pretreat-ment and the dispersion technique, the life time of dye suspension and its tem-perature.[5, 6]

Experimental Part

Aluminium foils 0.5mm thick of 99.5% purity (Eloxal quality) were degreased in trichloroethylene, etched for a few minutes in alkali hydroxide solution at 50°C, rin-sed well, immersed for a few minutes in 1:1 nitric acid at room temperature, rinsed again and anodized in 175g/l sulphuric acid solution at $20 \pm 2°C$ for about an hour. The current density was 1.2 A/dm^2 and the aluminium content was between 5-7g/l.

After anodizing, the samples were rinsed well in running water and the dyeing process followed in aqueous solutions of commercial disperse dyes in conc. 3g/l and non-ionic surface active agents in conc. usually 2g/l at 40°C for 2 hours. For com-parison, a dyeing, without the addition of non-ionic surface active agents was also performed.

The differences in colour depths were assessed with the S.D.C. Grey Scale for assessing change of colour (1S0 Recommendation R 105).

The dye-baths were made 24h earlier in order to establish a stable aqueous dye dispersion.

The dyeing took place in the apparatus LINITEST. The ratio between the volume of the dye bath (ml) and the surface of aluminium for dyeing (cm^2) was 5:1. The pH of the dye bath was almost neutral.

Anodized samples were treated before dyeing and immediately after anodizing, in aqueous solutions of organic acids in conc. 200g/l (Note 1) at room temperature with continuous agitation for 3h. After a minimum drying, there followed dyeing in baths and conditions as were reported above. The dyes, surface active agents and acids used are reported in Table II.

Note 1: Salicylic and itaconic acids are sparingly soluble in water and were used in the form of their saturated solution.

Results and Discussion

The non-ionic surface active agents, which were used, were as follows:

A. Fatty alcohols-polyoxyethylated products

1) Eumulgin OIO: Oleyl-cetylalcohol with appr. 10 moles of ethylene-oxide (Henkel).

2) Dehydol LS2: Fatty alcohol polyglycol ether with an average 5-10 ethylene-oxide links (Henkel).

3) Dispersogen ASN: Fatty alcohol (C_{12-15}) polyglycol ether (Hoechst).

B. Alkylphenol-polyoxyethylated products

4) Marlophen 83: Alkylphenolpolyglycolether (Hüls).

5) Lissapol NX: A condensate of nonylphenol with ethylene-oxide (I.C.I.).

6) Hostapal H Konz: A condensate of nonylphenol with appr. 10 moles of ethylene-oxide (Hoechst).

C. Fatty acids-polyoxyethylated products

7) Cremophor EL: A condensate of 1 mole of castor oil with 40 moles of ethylene-oxide (BASF).

Agents 1 and 2 have good emulsifying and wetting action. Agent 4 is an effective dispersing agent and possesses, according to the oxyethylation degree, excellent emulsifying wetting, washing and dispersing properties. Agent 5 is emulsifying, wetting and an effective dispersing agent and finds applications in the preparation of fine stable aqueous dispersions of solids, even in low pH values. Agent 6 is a wetting agent, a detergent for the fibre finishing and a good levelling agent for the dyeing. Agent 7 is a very good dispersing and solubilising agent.

The disperse dyes, which were used can be divided in the following two groups:

a) Monoazodyes which have as diazo-compound p-nitroaniline or his chlorinated products and as coupling component aniline or substituted aniline:

CIBACET ORANGE 2R (C.I.11005), DISPERSOL SCARLET B (C.I.11110), DISPERSOL RUBINE B (C.I.11115), DISPERSOL RED R (C.I. 11130), TERASIL SCARLET 2G (C.I. 11080), CIBACET RED 2G (C.I. 11210).

b) Substituted aminoanthraquinones:

TERASIL BLUE 2R (C.I. 61110), DISPERSOL BLUE BG (C.I. 63305) DISPERSOL VIOLET BG (C.I. 60725(S)) and DISPERSOL ORANGE DG (C.I. 60710).

The above dyes[2] (with the exception of the azodyes C.I. 11005, 60710 and the aminoanthraquinone dye C.I. 63305) had, under normal conditions, moderate results on the dyeing of aluminium, probably because the affinity of these dyes to the substrate was small i.e. the active proton forms, in preference, hydrogen bonds between the dye molecules and not between dye and substrate. On the contrary, the dyes C.I. 11005, 60710 and 63305 dyed anodized aluminium well and very well, respectively.

From Table I it is obvious that none of the non-ionic surface active agents, which were used, had a remarkable positive influence on the dyeing of anodized aluminium with disperse dyes, although these agents are reported as wetting, dispersing, emulsifying and levelling agents and that they help in there being more dye in molecular state in water. This may be ought to the following reason. These agents

are of non-ionic nature, while the substrate has positively charged sites in the water and generally appear to have a high polarity. So their micelles have difficulties in being transfered to the surface, adsorbed, and finally connected with the substrate. So they can't carry the dye molecules in the substrate or act as a binder between dye and substrate in the cases where there isn't affinity between them.

On the contrary, anionic surface active agents, which are extensively adsorbed from the substrate by ion exchange, have a remarkable positive influence on the dyeing with disperse dyes.[8]

The observed small improvement in colour depths for certain combinations of non-ionic surface active agent and dye should originate from the fact that in these cases the concentration of the monomolecularly dispersed dye in the aqueous phase increases, because the surface active agent stabilizes the solubilized disperse dye molecules.

The different influence of the same surface-active agent for each dye can be explained from the fact that the interaction between dye-surface active agent depends on the properties of the whole dye molecule (i.e. polarity, solubility) and on the structure of the surfactant.

It is reported[9] that the structure and the polymerisation degree of non-ionic surface active agent of the general type $R[OCH_2CH_2]_nOH$ plays an important role on

TABLE I: Influence of non-ionic surface active agents on colour depths of anodized aluminium, dyed by disperse dyes.

Improvement in depth with the use o non-ionic surface active agents in the dye bath

Non-ionic surface active agent Conc. 2g/1	C.I. 11130	C.I. 11110	C.I. 11115	C.I. 11005	C.I. 61110	C.I. 63305	C.I. 60710
1	worse	1-2	—	1	—	worse	2
2	worse	2-3	2	1-2	—	worse	2
3*	worse	1	1	2	—	1	1-2
4	1-2	3-4	2-3	2-3	4-5	1	worse
5**	1	worse	worse	2	1	1	1
6	worse	2-3	2	1-2	—	1	1
7	worse	2	1	1-2	—	1	—

The oxide-film thickness was 25 ± 2 μm and measured using an eddy-current technique.[7] The differences in depths of dyeing with disperse dyes (with and without the addition of the above surfactants) are indicated using the following gradings in terms of the SDC Grey Scale for assessing the change of colour (1S0 Recommendation R 105):

1. No improvement in depth
2. Very slight improvement in depth
3. Appreciable improvement in depth
4. Distinct improvement in depth

5. Great improvement in depth
* Concentration 8g/1
** Concentration 10g/1

the above interaction. The favourable influence is higher when R is phenyl or alkyl than acyl group. In this work some polyglycol ethers with R = alkyl of fatty alkohol

TABLE II: Influence of non-ionic surface active agents on colour depths of anodized aluminium, which was treated with organic acids and subsequently dyed by disperse dyes.

Colour Index number Disperse dye	Non-Ionic surface active agent Conc. 2g/1	Improvement in depth after treatment with organic acids. a) Without addition of non-ionic surface-active agent in the dye bath. b) With addition of non-ionic surface-active agent in the dye-bath.											
		Maleic		Lactic		D-Tartaric		Salicylic		Itaconic		S-Sulphosalicylic	
		a	b	a	b	a	b	a	b	a	b	a	b
11080	2	2-3	3	3	2-3	2-3	3	3-4	1	3-4	3-4	4-5	No dyeing
11130	2	2	1-2	2	—	2	—	3-4	—	2	—	3-4	—
61110	3*	2	—	2-3	2-3	2-3	3	2	1	3-4	2	4-5	No dyeing
11110	5*	2	2	2-3	2-3	4	2-3	3-4	▲	3	2	4-5	» »
60725 (S)	5*	2	2	2	2-3	2-3	—	2-3	No dyeing	3-4	2-3	3-4	» »
11115	6	3	2-3	2-3	3	4	3	4	1-2	4	3-4	4-5	» »
11210	6	2	2	3	3	3	2-3	4	No dyeing	3-4	3-4	4	» »

The oxide-film thickness was 25 ± 2 µm and measured using an eddy-current technique.[7] The differences in depths of dyeing with disperse dyes are indicated using the same gradings with those of table I.
* Concentration 8g/l.

or alkylphenyl group had a positive influence on the dyeing with certain disperse dyes. On the contrary, the surface active agent 7 did not have a positive influence on the dyeing. However, it has a high molecular weight.

Similar investigations[10] with a non-ionic ethoxylated product and two commercial water soluble ionic dyes, suitable for dyeing of Aluminium showed, that they have practically no influence on the dyeing.

From Table II it is concluded that the observed improvement on colour depths is due in fact, not in the presence of surfactant, but to the action of organic acids. These modify the crystal structure, increase the dye adsorption and act as binders.[11]

In the cases, where the pretreatment took place with strong acids i.e. sulphosalicylic acid and the dyeing took place in the presence of non-ionic surfactants, no colouring of aluminium was observed. This may be due to the partial destruction of the oxide film.[11, 12]

Περίληψη

Χρήση μη ιοντικών επιφανειακά δραστικών μέσων και οργανικών οξέων στη βαφή του αλουμινίου με χρώματα διασποράς

Η χρήση μη ιοντικών επιφανειακά δραστικών μέσων κατά τη βαφή του ανοδιωμένου αλουμινίου με χρώματα διασποράς, δεν είχε ιδιαίτερα θετική επίδραση, εκτός από λίγες περιπτώσεις (π.χ. Marlophen 83).

Προκατεργασία ανοδιωμένων δειγμάτων σε υδατικά διαλύματα οργανικών οξέων είχε σαν αποτέλεσμα βελτίωση των πυκνοτήτων, δηλ. του βάθους των χρωματισμών. Στην περίπτωση όμως, όπου μετά την κατεργασία ακολούθησε βαφή με ταυτόχρονη προσθήκη μη ιοντικών επιφανειακά δραστικών μέσων, δεν παρατηρήθηκε καμμία περαιτέρω βελτίωση του βάθους των χρωματισμών. Αντίθετα, όταν το χρησιμοποιούμενο οξύ ήταν αρκετά ισχυρό όπως π.χ. το σουλφοσαλικιλικό και ακολούθησε βαφή με την παρουσία, σε περίσσεια, ενός μη ιοντικού επιφανειακά δραστικού μέσου, τότε δεν παρατηρήθηκε χρωματισμός των δειγμάτων.

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MOISTURE SORPTION ISOTHERMS OF SULTANA RAISINS

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Summary

Moisture sorption isotherms of Sultana raisins at 30°C were determined, using a standard method, developed in the collaborative project COST 90 "Water Activty" of the European Economic Community. Three samples of raisins were studied, i) commercial raisins, ii) raisins dried in the laboratory after alkali pretreatment and iii) raisins dried in the laboratory without pretreatment.

The isotherm of raisins at 30°C was similar to that of sucrose-fructose mixtures at the same temperature. Raisins characteristically sorb large quantities of water at high water activities. Pretreatment of the raisins had a small effect on the sorption isotherm. Optimum water activity for storage of the raisins at 15% moisture content and 30°C was about 0.6.

The experimental adsorption data were best described by the Halsey equation. The GAB equation, suggested by the COST-90 project, failed to describe the isotherms in the entire range of water activity.

Abbreviations and terminology

α_w = Water activity (0-1), BET = Brunauer - Emmet - Teller, RH = Relative Humidity, P = Partial vapor pressure of water, P_0 = Saturation vapor pressure of water, X = Moisture content, kg water/kg dry solids, X_M = Moisture content of monomolecular layer, GAB = Guggenheim - Anderson - de Boer equation, exp = Exponential (power of e), ln = Natural logarithm.

Introduction

The sorption isotherm of a food material is best described as a plot of the amount of water adsorbed at equilibrium as a function of the water activity of the food, at constant temperature. The water activty of a material at equilibrium with the surrounding space is defined by equation (1):

$$\alpha_w = \frac{P}{P_0} = \frac{\%RH}{100} \tag{1}$$

where: P: water vapor pressure, exerted by the food material at equilibrium

P_0: vapor pressure of pure water at the equilibrium temperature of the system

%RH: % relative humidity of the surrounding space (air).

It is generally accepted that the water activity of a food is more closely related to its physical, chemical and biological properties than the total moisture content.[1] Measurements of water activity provide a simple and convenient method for the estimation of the water binding ability and the physical, chemical and microbial stability of the food. Microbial spoilage is considered to stop generally below $\alpha_w = 0.70$.[2] Non-enzymic browning rate is affected by α_w, with a maxmum occuring between 0.30-0.70.[2, 3] The rates of enzymatic reactions and lipid oxidation reactions are also affected by α_w.[2, 3]

The relationship between water activty and moisture content has been studied for many foods.[3] However, because the sorption characteristics exhibited by a product are influenced by many factors, data for a specific product of different origin usually differ widely from each other and are comparable only under certain restrictions. For a better comparability of the sorption data it is necessary to establish a standardized procedure for the measurement of the moisture sorption isotherms of foods.

The Council of the European Community adopted in 1974 the action programme COST 90 with the general aim to supply the food industry (as well as university research centres and manufacturers of food processing equipment) with data relating to the physical properties of food products. Within the frame-work of this project, the sub-group "Water Activity" studied the sorption of water by foods. At the first stage a reference material (microcrystalline cellulose) was selected for the collaborative study and a standard method for the measurement of moisture sorption isotherms was developed.[4, 5] This method was used by our laboratory and it is recommended for measuring the sorption isotherms of food materials, in order to obtain comparable results for various food products.

Raisin sorption isotherms have been determined by Pixton and Warburton (1972), Katsuras (1973) and Bolin (1980). Pixton and Warburton studied Sultana raisins only to a limited degree and their moisture determination procedure used excessively long drying times, which may give inaccurate results.[6] Katsuras also studied Sultana raisins to a limited degree and his results can only serve as a rough estimation of the sorption behaviour of the product.[7] Bolin determined the adsorption and desorption isotherms of raisins at 25°C.[8] More information is therefore needed as to the relationship between moisture content and water activity for different types of raisins as well as for different temperatures. This study was undertaken to develop a set of moisture isotherms for Sultana raisins, using the developed method, to determine how the various variables affect these isotherms and to test the empirical equations suggested in the literature, which best describe the isotherms.

The empirical relations reported in the literature include the following equations:[3, 9]

(a) BET:
$$\frac{\alpha_w}{(1-\alpha_w) X} = \frac{1}{X_M \cdot C} + \frac{\alpha_w (C-1)}{X_M \cdot C}$$
(2)

(b) Bradley:
$$\ln\left(\frac{1}{\alpha_w}\right) = B(2) \cdot B(1)^X \tag{3}$$

(c) Halsey:
$$\alpha_w = \exp\left[-B(2)/X^{B(1)}\right] \tag{4}$$

(d) Henderson:
$$1 - \alpha_w = \exp\{-[B(2) \cdot X^{B(1)}]\} \tag{5}$$

(e) Iglesias-Chirife I:
$$X = B(1)\left[\alpha_w/(1-\alpha_w)\right] + B(2) \tag{6}$$

(f) Iglesias-Chirife II:
$$\ln\left[X + (X^2 + X_{0.5})^{1/2}\right] = B(1)\alpha_w + B(2) \tag{7}$$

(g) Kuhn:
$$X = \frac{B(1)}{\ln \alpha_w} + B(2) \tag{8}$$

(h) Oswin:
$$X = B(2)\left[\alpha_w/(1-\alpha_w)\right]^{B(1)} \tag{9}$$

(i) Smith:
$$X = B(2) - B(1)\ln(1-\alpha_w) \tag{10}$$

(j) GAB (Guggenheim - Anderson - de Boer):

$$\frac{X}{X_M} = \frac{ck\alpha_w}{(1-k\alpha_w)(1-k\alpha_w + ck\alpha_w)} \tag{11}$$

In all the above equations:
α_w: water activity
X: moisture content, kg H_2O/kg of dry material
X_M : monomolecular moisture content
$X_{0.5}$: moisture content at $\alpha_w = 0.5$
c, k : constants
B(1), B(2): constants

The parameters of each equation are calculated using the least squares method and the adequacy of the fit is checked by calculating the percent relative mean square root of the error (RMS%):

$$RMS\% = \sqrt{\frac{\sum\left[(X_{exp} - X_{cal})/X_{exp}\right]^2}{N}} \times 100 \tag{12}$$

where,
X_{exp} : experimental moisture content
X_{cal} : calculated moisture content
N: number of experimental points

Experimental Materials and Methods

Three samples of seedless Sultana raisins were used in this investigation. The first one was a sample of normal commercial raisins (origin Heraklion, Crete). Hence, it

had been picked from the vine at the stage of full maturity, immersed into an emulsion of potassium carbonate of density 8-$10B^{me}$ and 0.5% olive oil. The grapes were sun-dried in the field and treated with sulfur dioxide. The second sample consisted of pretreated raisins (grown in Zemena - Corinthos), dried in our Laboratory. Pretreatment was carried out by immersion of raw grapes into a 0.5% sodium hydroxide solution for 10 sec. The third sample was the same as the second, only untreated.

The sorption isotherm of microcrystalline cellulose, the reference material recommended by COST-90, was measured for comparison purposes. The cellulose sample, packed in a 100 g polyethylene-coated aluminum pouch, was obtained from the Federal Research Institute for Nutrition, Karlsruhe, which coordinated the COST-90 project on Water Activity of Foods.

The standardized method, recommended by the European Cooperative Project COST 90 on Water Activity was used in all experiments. This is a static gravimetric method, where the dried fruit samples are placed over saturated salt solutions of known concentration. 10 saturated salt solutions with varying partial pressure of water vapor were used, and corresponding water activity values ranging between 0.112 and 0.903 (Table I).

TABLE I: Salt and water quantities required for the preparation of the saturated salt solutions.[4, 5] All salts were from Fluka Company, p.a.

	Salt	α_w	Quantities for 1 hygrostat	
			salt (g)	water (ml)
1	LiCl	0.112	150	85
2	CH_3COOK	0.226	200	75
3	$MgCl_2$	0.327	200	25
4	K_2CO_3	0.438	200	90
5	$Mg(NO_3)_2$	0.529	200	30
6	NaBr	0.577	200	70
7	$SrCl_2$	0.708	200	50
8	NaCl	0.753	200	60
9	KCl	0.843	200	80
10	$BaCl_2$	0.903	200	70

The experimental apparatus consisted of a constant temperature bath, equipped with a temperature sensor (Haake TP 32) for the regulation and control of the temperature. The hygrostats containing the sample were simple preserve jars of 1 l capacity. All measurements reported here were performed at 30°C.

Each sample consisted of a single raisin, cut into thin slices of uniform thickness ($\sim$1mm). The samples were placed in weighing bottles, dried in a dessicator over P_2O_5 at room temperature for 15 days and then placed in the hygrostats, over the saturated salt solutions. Results reported are the average of two replicates. We confirmed that equilibrium was reached within 15 days, which is the time recommended by the COST 90 project. The moisture content was determined by drying the sample in a Gallenkamp OV-930 vacuum oven at 70°C and 50 mm Hg absolute pressure for 6 hours.

At high water activities ($\alpha_w > 0.6$) crystalline thymol was placed in the hygrostat to prevent the microbial spoilage of the raisins.

Results and Discussion

Sorption results are shown in Table II and in Figures 1, 2, 3 and 4. Fig. 1 shows

TABLE II: Sorption measurements of three samples of raisins.
The standardised method, recommended by the European Cooperative Project COST 90 on Water Activity was used in all measurements.

α_w	% X (g$H_2$0/100 g dry material)		
	1st sample	2nd sample	3rd sample
0.112	3.28	2.49	3.20
0.226	3.74	3.28	4.02
0.327	5.12	4.80	5.50
0.438	7.66	8.34	8.46
0.529	11.12	12.41	10.96
0.577	13.46	14.80	15.40
0.708	24.73	26.59	25.26
0.753	36.51	34.52	34.17
0.843	52.95	56.49	53.84
0.903	88.08	76.41	86.47

1st sample: Normal commercial raisins
2nd sample: Raisins dried in the laboratory after alkali pretreatment of the grapes
3rd sample: Raisins dried in the laboratory without pretreatment of the grapes.

the adsorption isotherm of the reference material, microcrystalline cellulose, at 30°C, which is in good statistical agreement with the results obtained in the cooperative study of COST 90. The raisins gave isotherms similar to those of mixtures of sucrose and fructose, with a slight difference observed only at the lower end of the curve. This was to be expected, since raisins contain 82-88% sugars, (sucrose and fructose) on a dry basis. The remaining solids consist of pectin, polysaccharides and other biopolymers, which sorb more water than pure oligosaccharides at low water activities.

The effect of the growing and processing conditions on the water sorption of dried raisins requires some discussion. At first, it seems that the sorption isotherms of the three samples are quite similar, below $\alpha_w = 0.7$. Some differences exist above $\alpha_w = 0.7$, where an exudation (extraction) of sugars into solution was observed (this did not have a significant effect on the isotherm). The maturity of the fresh fruit seems to affect the sorption isotherm, since there is a lowering of the α_w in the more mature commercial fruit (Fig. 2), when compared with that dried in the laboratory after pretreatment (Fig. 3). This is also to be expected because maturity of the fruit increases its total sugar content. Pretreatment of the fresh fruit also seems to affect the isotherm, as can be seen by comparison of Figures 3 and 4. It is quite possible that the pretreatment of the fruit (that is, immersion into a sodium hydroxide
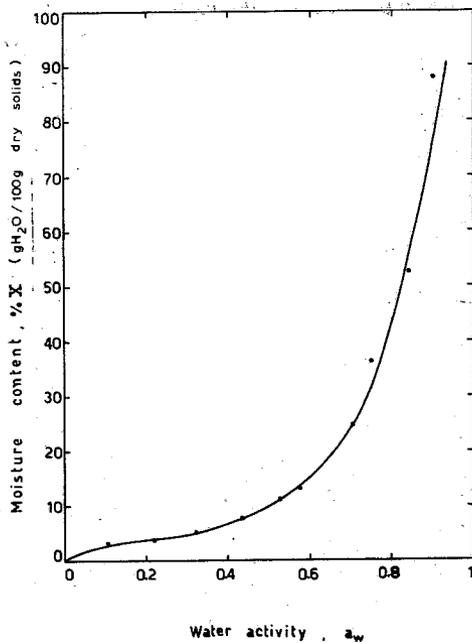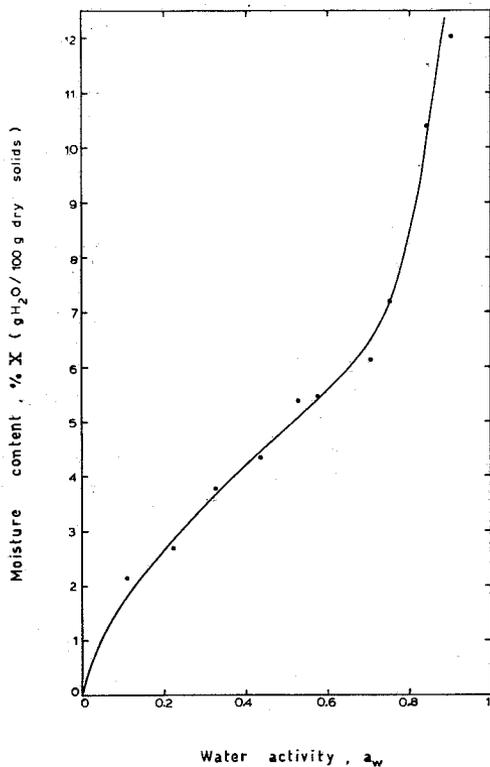
FIG. 1: *Moisture sorption isotherm of microcrystalline cellulose.*

FIG. 2: *Moisture sorption isotherm of the first sample of raisins (commercial raisins).*
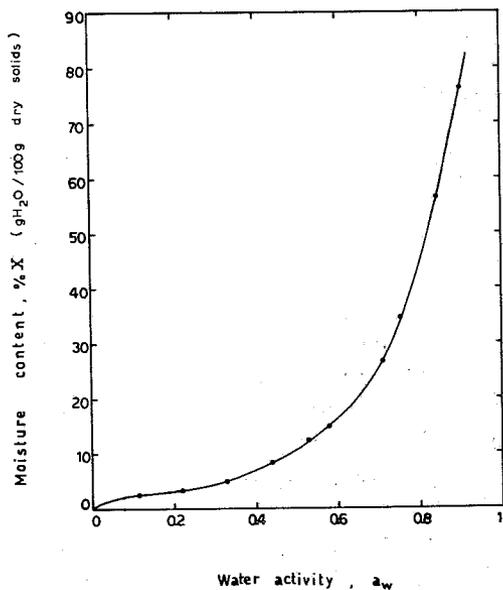
FIG. 3: *Moisture sorption isotherm of the second sample of raisins (pretreated dried).*
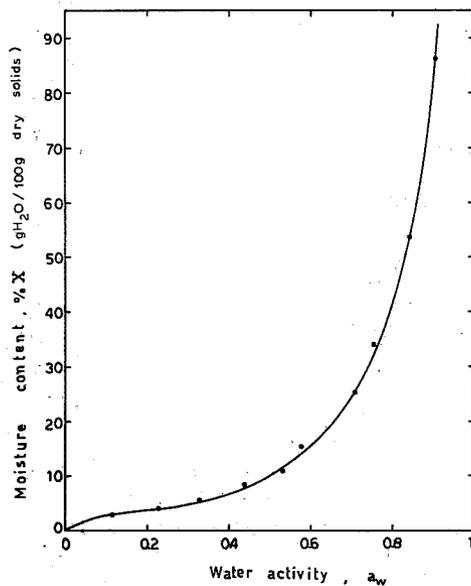
FIG. 4: *Moisture sorption isotherm of the third sample of raisins (untreated dried).*

solution) reduces its sugar content by leaching, so that there may be some differences at high water activities.

The application of the empirical equations, mentioned in the Introduction, to each experimental point determined gave the results shown in Table III. It is quite clear

TABLE III: Application of the empirical equations to the experimental points of the sorption measurements of the three samples of raisins.

Equation	*RMS %		
	1st sample	2nd sample	3rd sample
BET	18.2	14.9	15.3
Bradley	239.5	231.7	228.2
Halsey	11.6	15.9	9.3
Henderson	30.3	22.9	27.4
Iglesias and Chirife I	13.1	38.9	11.6
Iglesias and Chirife II	21.1	14.7	18.1
Kuhn	16.6	32.4	12.3
Oswin	19.6	14.6	16.4
Smith	113.4	107.1	106.2
GAB	68.8	39.2	37.3

$$*RMS\% = \sqrt{\frac{\sum [(X_{exp} - X_{cal})/X_{exp}]^2}{N}} \times 100$$

that none of these equations is able to completely describe the experimental results over the whole range of water activities of the three samples. However, the Halsey e-quation seems to give the best fit, compared to the others, which are close to that (Iglesias and Chirife I and II, Kuhn, and Oswin equations). The GAB equation gave a rather poor fit over the whole range of water activities. This was surprising, since the GAB model has recently gained a great popularity among the laboratories par-ticipating in the COST-90 Project "Water Activity".[5] The GAB equation was applied to different sets of experimental points. The results are shown in Table IV. It is in-

TABLE IV: Application of the GAB equation to different sets of experimental points of the three samples of raisins.

Number of points	*RMS %		
	1st sample	2nd sample	3rd sample
1-9	23.4	21.8	21.7
1-8	20.1	20.3	19.8
1-7	11.1	14.8	10.4
2-8	3.1	4.0	5.0

$$*RMS\% = \sqrt{\frac{\sum |(X_{exp} - X_{cal})/X_{exp}|^2}{N}} \times 100$$

teresting that although this equation fails to describe the sorption isotherm of raisins over the whole range of water activities, it gives a satisfactory fit in the "commercial" range of water activities (0.226 < a_w < 0.753).

The Greek Government standards limit the upper moisture level of raisins to 18% (dry basis).[10] Hence the safe storage conditions of bulk (unpacked) Sultana raisins, can be achieved by maintaining the raisins at a relative humidity of about 60%, for a storage temperature of 30°C. Lower relative humidities could be used, but the product would become harder and should be partially hydrated before consumption.

Other factors affecting the sorption isotherm of a product, e.g. temperature, must be investigated. Data on the deteriorative changes taking place in stored and packaged raisins should be considered in order to determine the optimum storage conditions and shelf life of each particular product.

Περίληψη

Ισόθερμοι ροφήσεως υγρασίας της σταφίδας σουλτανίνας

Η εργασία αυτή είχε σαν σκοπό την εύρεση των ισοθέρμων ροφήσεως υγρασίας της σταφίδας σουλτανίνας, χρησιμοποιώντας την πρότυπη μέθοδο που αναπτύχθηκε στα πλαίσια του συλλογικού προγράμματος της Ευρωπαϊκής Κοινότητας COST 90 "Water Activity" και τον έλεγχο των εμπειρικών εξισώσεων περιγραφής των ισοθέρμων που αναφέρονται στη βιβλιογραφία. Χρησιμοποιήθηκαν τρία δείγματα σταφίδας: σταφίδα του εμπορίου, σταφίδα ξηραμένη μετά προκατεργασία και σταφίδα ξηραμένη χωρίς προκατεργασία. Επειδή η ροφητική συμπεριφορά των διαφόρων τροφίμων επηρεάζεται από πολλούς παράγοντες (προϊστορία και προκατεργασία τροφίμου, μέθοδο προσδιορισμού της ισοθέρμου κλπ.), τα δεδομένα της βιβλιογραφίας για ένα συγκεκριμένο προϊόν που προέρχονται από διαφορετικές πηγές, συνήθως διαφέρουν πολύ μεταξύ τους και δεν είναι άμεσα συγκρίσιμα. Γεννήθηκε λοιπόν η ανάγκη μίας πρότυπης μεθόδου μετρήσεως των ισοθέρμων, η οποία αναπτύχθηκε μέσα στα πλαίσια του Ευρωπαϊκού προγράμματος COST 90. Η πρότυπη αυτή μέθοδος είναι μία στατική ζυγιστική μέθοδος, που χρησιμοποιεί 10 κορεσμένα διαλύματα αλάτων για την επίτευξη σταθερής σχετικής υγρασίας. Έτσι, όλα τα εργαστήρια που ασχολούνται με μετρήσεις ισοθέρμων προμηθεύονται με ένα πολύτιμο εργαλείο, ώστε τα αποτελέσματά τους να είναι άμεσα συγκρίσιμα. Η μέθοδος αυτή χρησιμοποιήθηκε κατά την εργασία μας για τη μέτρηση των ισοθέρμων της σουλτανίνας στους 30°C.

Οι ισόθερμοι των τριών δειγμάτων παρουσιάζουν μικρές διαφορές μεταξύ τους, που οφείλονται στο διαφορετικό βαθμό ωρίμανσης και τη διαφορετική προκατεργασία καθενός δείγματος. Η εξίσωση που περιγράφει καλύτερα τις ισόθερμες της σταφίδας σε όλο το εύρος ενεργοτήτων νερού είναι η εξίσωση Halsey, ενώ αρκετά καλή προσέγγιση έχουν οι εξισώσεις Iglesias και Chirife I και II; η εξίσωση Kuhn και η εξίσωση Oswin. Η εξίσωση GAB, που έχει προταθεί στα πλαίσια του COST 90, δεν δίνει καλή προσέγγιση σε όλο το εύρος των ενεργοτήτων νερού, περιγράφει όμως τις ισόθερμες στη λεγόμενη «εμπορική» περιοχή ενεργοτήτων νερού 0.226 < a_w < 0.753.

Η απαιτούμενη σχετική υγρασία του χώρου αποθήκευσης, για διατήρηση της περιεκτικότητας υγρασίας της σταφίδας στην τιμή 18% στους 30°C, βρίσκεται από τις ισόθερμες ότι είναι περίπου 60%.

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DETERMINATION OF THIOCYANATE AND THIOSULPHATE IONS BY OXIDATION WITH BIS (TRIFLUOROACETOXY) IODOBENZENE

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Introduction

Several methods have been proposed for the determination of thiocyanate and thiosulphate ions[1,4]. Belcher and co-workers determined thiocyanate and thiosulphate ions by oxidation with iodine in alkaline solution to sulphate ions. In both procedures, the excess of iodine is extracted with chloroform and then determined. Vasatova and Zyka[6] oxidized thiocyanate and thiosulphate ions using cobalt (III). Attempts to utilize these oxidations quantitatively were unsuccessful and only in 9N HCl solutions they stabilized the potential of the reactions in 10 min.

In a previous work the oxidation of a number of inorganic and organic substances with bis (trifluoroacetoxy) iodobenzene has been studied in water - acetonitrile media[2].

In the present paper we report the oxidation of thiocyanate and thiosulphate ions with bis (trifluoroacetoxy) iodobenzene which allows the indirect titrimetric and gravimetric determination of the above two ions.

Experimental

Reagents: Bis (trifluoroacetoxy) iodobenzene was prepared as it has been described previously[2,3].

Standard solution of bis (trifluoroacetoxy) iodobenzene was prepared by dissolving the appropriate amount of it in acetonitrile.

Potassium thiocyanate: The analytical reagent grade material, was dried under vacuum at 75° for 12h, was weighed out and dissolved in 1l of distilled water. This stock solution was stable over a long period.

The standardization of this solution was done by titration with silver nitrate solution conductometrically[5].

Sodium thiosulphate: A 0.100M solution was prepared by a titrisol ampule (Merck AE). This solution is stable for a period of time when kept in dark. A 1.000 × 10^{-3}M solution was prepared daily and was used as the stock solution for investigation of the determination of thiosulphate.

This solution was standardized against iodine solution.

Recommended Procedure

a) *For the titrimetric determination of thiocyanate:* To 5 ml of 5.07×10^{-3}M KSCN was added 5 ml of 2.19×10^{-2}M reagent solution in acetonitrile, the mixture was diluted with water to 50 ml allowed for 10 min and titrated with a 1.000×10^{-2}N $Na_2S_2O_3$ solution to determine unreacted bis (trifluoroacetoxy) iodobenzene.

Back-titration of unconsumed bis (trifluoroacetoxy) iodobenzene: An excess of potassium iodine was added to the above solution and the liberated iodine was titrated with standard solution of sodium thiosulphate[2].

$$PhI(OCOCF_3)_2 + 2I^- \rightarrow I_2 + PhI + 2CF_3COO^- \qquad (1)^{\,7}$$
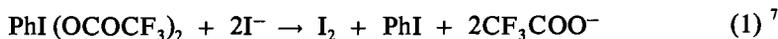
From the difference between the total mmoles of bis (trifluoroacetoxy) iodoben-zene added and the unconsumed mmoles, we found the amount of the reagent reac-ted with the thiocyanate ions to sulphate, according to the following equation (2).

$$SCN^- + 3PhI(OCOCF_3)_2 + 4H_2O \rightarrow SO_4^= + 3PhI + 6CF_3COO^- + 7H^+ + HCN$$
$$(2)$$
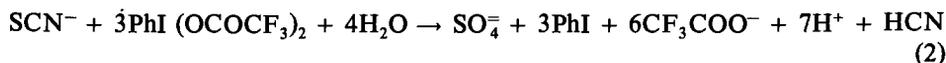
The above mentioned reaction must take place in a fume hood.

b) *For the gravimetric determination of thiocyanate:* A 5 to 8 ml aliquot of 5.07×10^{-3}M KSCN was added 3 to 5 ml 4.38×10^{-2}M solution of bis (trifluoroacetoxy) iodobenzene in acetonitrile, allowed for 10 min, diluted to 100 ml and warmed for removal of acetonitrile. To the hot solution, a solution of 5 ml 2.5×10^{-1}M $BaCl_2 \cdot 2H_2O$ was added under stirring. The white precipitate of barium sulphate formed settled down on digestion of 30 min on water bath leaving a clear supernatant fluid. The precipitate was filtered after 5 h through a filter paper (Green box, ashless) and was washed throughly with hot water. The precipitate obtained was dried at 110°C ignited and weighed as $BaSO_4$.

c) *For the titrimetric determination of thiosulphate:* To 8 ml of 1.00×10^{-3}M $Na_2S_2O_3$ was added 5 ml of 2.35×10^{-2}M solution of bis (trifluoroacetoxy) iodoben-zene in acetonitrile, the mixture was diluted with water to 40 ml allowed for 5 mn and an excess of KI was added to this solution. The liberated iodine was titrated with standard solution of 1.00×10^{-2}N $Na_2S_2O_3$.

From the difference between the total mmoles of the reagent added and uncon-sumed mmoles we found the amount of the reagent consumed for the oxidation of thiosulphate ions to sulphate $(3)^1$.

$$S_2O_3^= + 4PhI(OCOCF_3)_2 + 5H_2O \rightarrow 2SO_4^= + 4PhI + 8CF_3COO^- + 10H(3)$$

d) *For the gravimetric determination of thiosulphate:* A 20 to 32 ml aliquot of 2.50×10^{-4}M $Na_2S_2O_3$ was added 5 ml 2.35×10^{-2} solution of bis (trifluoroacetoxy) iodobenzene in acetonitrile allowed for 5 min and diluted with water to 50 ml and warmed for evaporation of acetonitrile. Then the sulphate ions were determined as in procedure (b).

Results and discussion

Analysis of aqueous thiocyanate and thiosulphate ions gave the experimental

results shown in tables I and II. Each mmol, as we can see from the reactions given, of thiosulphate and thiocyanate ions needs 4 and 3 mol of bis (trifluoroacetoxy) iodobenzene respectivelly.

TABLE I: Experimental results from titrimetric and gravimetric determination of aqueous thiocyanate solutions.

Compound	Added (mmol)	No of expts done	Found[a] (mmol)	
			By titration	Gravimetrically
Thiocyanate	0.0253	8	$0.0233 \pm 0.8 \times 10^{-3}$	$0.0249 \pm 0.6 \times 10^{-3}$
	0.0304	8	$0.0311 \pm 1.1 \times 10^{-3}$	$0.0301 \pm 0.7 \times 10^{-3}$
	0.0355	8	$0.0361 \pm 0.9 \times 10^{-3}$	$0.0351 \pm 1.0 \times 10^{-3}$
	0.0405	8	$0.0391 \pm 1.2 \times 10^{-3}$	$0.0409 \pm 1.1 \times 10^{-3}$

a Average value of eight determinations ± standard deviation.

TABLE II: Experimental results from titrimetric and gravimetric determination of aqueous thiosulphate solutions.

Compound	Added (mmol)	No of expts done	Found[a] (mmol)	
			By titration	Gravimetrically
Thiosulphate	0.0050	8	$0.0052 \pm 1.2 \times 10^{-4}$	$0.0049 \pm 0.8 \times 10^{-4}$
	0.0060	8	$0.0058 \pm 2.1 \times 10^{-4}$	$0.0059 \pm 1.4 \times 10^{-4}$
	0.0070	8	$0.0073 \pm 1.8 \times 10^{-4}$	$0.0072 \pm 2.6 \times 10^{-4}$
	0.0080	8	$0.0077 \pm 2.5 \times 10^{-4}$	$0.0081 \pm 1.3 \times 10^{-4}$

a Average value of eight determinations ± standard deviation.

The successful titrations and gravimetric determinations of these compounds is due to the fast oxidation at room temperature.

We had not interferences from the common ions such as Ca^{++}, Mg^{++}, Al^{+++}, Ni^{++}, Co^{++}, Zn^{++}, Cd^{++}, NO_3^-, PO_4^{---}, CH_3COO^- etc.
We had interference from ions which participated in redox reactions with bis (trifluoroacetoxy) iodobenzene[2, 8].

Summary

Thiocyanate and thiosulphate ions are oxidized by bis (trifluoroacetoxy) iodobenzene to sulphates which enable the indirect determination of these ions by back-titration or gravimetrically. Each mmol of thiocyanate and thiosulphate ions needs 3 and 4 mmoles of the reagent respectivelly to give sulphate ions.

Περίληψη

Προσδιορισμός θειοκυανιούχων και θειοθειϊκών ιόντων κατόπιν οξείδωσης με διτριφθοροακετοξυιωδοβενζόλιο

Στην εργασία αυτή περιγράφεται μια μέθοδος οξείδωσης των θειοκυανιούχων και θειοθεικών ιόντων με ακετονιτριλικό διάλυμα διτριφθοροακετοξυιωδοβενζολίου. Τα θεοκυανιούχα και θειοθεικά ιόντα οξειδώνονται προς θειικά και προσδιορίζονται με επανογκομέτρηση και σταθμικά. Βρέθηκε πειραματικά, ότι κάθε mmol θειοκυανυούχων και θειοθεικών ιόντων χρειάζεται 3 και 4 mmoles από το αντιδραστήριο αντίστοιχα για να οξειδωθεί προς θειικά ιόντα. Με βάση τη στοιχειομετρία αυτή δίνονται και οι χημικές εξισώσεις της οξείδωσης.

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SHORT PAPER

SOME CHEMICAL AND PHYSICAL CHARACTERISTICS OF PUMPKIN SEED OIL

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Introduction

Many members of Cucurbitaceae produce seeds rich in oil and protein. Although none of these oils has yet been utilized on an industrial scale, they are used as cooking oil in some countries of Africa and Middle East[1,2].

In Greece it has not been produced oil from such seeds, but pumkin seeds (Cucurbita pepo and Cucurbita maxima) are consumed in large amounts in the form of salted dried seeds.[3] They constitute a food rich in oil and protein. It should be pointed out that the plants Cucurbita pepo and Cucurbita maxima can be cultivated with good yields in sandy and fairly infertile soils without irrigation. The fruits of these plants constitute an important source of animal feed and simulataneously contain significant amounts of seeds.

Although data on the utilization of various cucurbit seeds is extensive in the literature,[2,4,5,6,7,8] the present study was undertaken to determine the characteristics of oil from C. maxima and C. pepo seeds. They are utilized as food in the above referred form. Also the utilization could not only help maximize available resources but at the same time minimize waste disposal problems.

Materials and Methods

Preparation of the oil

Ripe fruits of Cucurbita maxima and Cucurbita pepo variety Thessaloniki (white) were collected from the same field with sandy soil, from the province of Didymotikhon Evros (Thrace) in August 1983. The ripe fruits were crushed and the seeds separated and sundried. The sundried seeds were then ground into powder using a 2.00 mm sieve. Amounts of 100g of the ground seeds were extracted with petroleum ether (b.p. 40° - 60°C) in a Soxhlet extractor. After extraction of the oil the solvent was evaporated under reduced pressure. The obtained oil was kept in sealed bottles under refrigeration for further analyses.

Chemical Analyses of Seeds and Oil

Proximate seed analyses including determinations of moisture, crude protein, crude oil, crude fiber and ash content were performed in triplicate in accordance with AOAC procedures.[9]

Chemical analyses of the oil including acidity, iodine value, saponification number, unsaponifiable matter, Hehner value and Reichert-Meissl number were performed according to the AOAC procedures.[9] All were determined in triplicate and the mean values were reported. Refractive index was determined by an Abbe refractometer with temperature adjustment (Bellingham + Stanley Ltd.). The ultraviolet spectra of the oils were made with oil solutions 0.20% w/v in cyclohexane (spectral grade). The solutions were analysed in 1-cm quartz cells on a Varian 634 Spectrophotometer with slit setting of 1.00 nm.

Characterization of fatty acids

The characterization of fatty acids was done by gas-liquid chromatography (GLC). The preparation of the methyl esters was performed according to AOAC procedure.[9] The oil was treated with 0.5 N methanolic NaOH and BF_3-MeOH. Methyl esters were extracted with hexane or ethyl ether and the extract was dried with anhydrous sodium sulfate. The analyses of methyl esters were performed with a gas-liquid chromatograph (Varian model 3700) equipped with a hydrogen flame ionization detector using a 0.3 × 210 cm stainless steel column packed with DEGS 20%. The column was operated isothermally with a temperature of 170°C. Injector and detector temperature was 300°C. The carrier gas was nitrogen with flow rate of 12 ml/min. The total flow rate of the gases (H_2, N_2, air) was 40 ml/min. Methyl esters were identified and quantified by comparing the retention time and peak area of the unknowns with those of the fatty acid methyl esters standards.

Results and Discussion

The oil content of the seeds of two species, C. maxima and C. pepo var. Thessaloniki (white) was 44.64% and 41.23% respectively, while the moisture content was 5.44 and 5.37% respectively. The values of oil content are high and comparable to those of other oil seeds such as sunflower, soybean and peanut[10, 11] as well as to other cucurbitaceae.[2, 4, 6, 11, 12, 13, 14, 15, 16, 17]

The proximate composition of the seeds is presented in Table I. The crude protein content was 29.32 and 30.14% respectively for C. maxima and C. pepo var. Thessaloniki (white), values that fall in the reported range of 25-35%.[11-17] The ash content, 5.51 and 5.18% respectively, was significant and as reported by Kamel et al.[11] pumkin seeds may be good sources of minerals. Also, the crude fiber content was significant, 5.06 and 5.95% respectively.

In the Table I are shown some physical and chemical characteristics of the extracted seed oils. As we can see the oils from C. maxima and C. pepo var. Thessaloniki (white) had similar characterictics. They had low values for acidity, unsaponifiable matter and Reichert-Meissl numbers comprable to other reported values.[11-17] However, these and Hehner value were in accordance with the values of other vegetable oils.[10] The saponification number was in the range reported in literature.[11-17] The oils had relatively high iodine values, although lower from those reported by El-Gharbawi et al.,[12] thus reflecting a high degree of unsaturation.

The ultraviolet spectra of the oils in cyclohexane were identical and exhibited two maxima at 272 and 218 nm. The slight variation between λmax of these species and

TABLE I: Proximate composition of the seeds and characteristics of the seed oil extracted from C. maxima and C. pepo var. Thessaloniki (white).

Assay	Value	
	C. maxima	C. pepo var. Thessaloniki
Seed composition:		
Moisture, %	5.44	5.37
Crude oil, %	44.64	41.23
Crude protein (N×6.25), %	29.32	30.14
Crude fiber, %	5.06	5.95
Carbohydrates (by difference), %	10.03	12.13
Ash, %	5.51	5.18
Oil characteristics:		
Acidity, % as oleic	0.80	0.35
Iodine value, Wijss	103.89	102.50
Saponification number	191.50	199.70
Unsaponifiable matter, %	0.62	0.78
Hehner value	73.15	72.95
Reichert-Meissl number	0.95	0.85
Refractive index, n (40°C)	1.4617	1.4615

the literature values could be attributed to the environmental effect of other components present in the oils.

In the Table II it is shown the fatty acid composition of the two oils. GLC analyses of the fatty acid methyl esters showed that the degree of unsaturation was over 80%. Linoleic acid ($C_{18:2}$) was found to be the dominant fatty acid, 44.06 and 42.18% respectively, followed by oleic ($C_{18:1}$), 37.23 and 38.36% respectively. Total saturated

TABLE II: Fatty acid composition of crude oil of Cucurbita maxima and Cucurbita pepo var. Thessaloniki (white) seeds.

Fatty acids	Wt %	
	C. maxima	C. pepo var. Thessaloniki (white)
$C_{12:0}$	0.01	0.02
$C_{14:0}$	0.10	—
$C_{16:0}$	12.25	13.10
$C_{16:1}$	0.12	0.15
$C_{17:0}$	0.04	0.08
$C_{18:0}$	5.54	5.25
$C_{18:1}$	37.23	38.36
$C_{18:2}$	44.06	42.18
$C_{18:3}$	0.26	0.29
$C_{20:0}$	0.25	0.26

fatty acids were 18.19 and 18.71% for C.maxima and C. pepo var. Thessaloniki (white) respectively. Palmitic acid ($C_{16:0}$) was found to be the dominant saturated fatty acid, 12.25 and 13.10% respectively, followed by stearic acid ($C_{18:0}$), 5.54 and 5.25% for the two species respectively.

In very low quantities were found lauric ($C_{12:0}$), Hexadecenoic ($C_{16:1}$), linolenic ($C_{18:3}$) and arachidic ($C_{20:0}$) acids. Myristic acid ($C_{14:0}$) was found only in the oil from C. maxima seeds. Both oils were found that contained heptadecanoic ($C_{17:0}$) acid. On the basis of these results the oils from C. maxima and C. pepo var. Thessaloniki (white) seeds fall in the linoleic - oleic acid oils category (semi-dried). They may be considered similar to several other vegetable oils such as corn, cotton and soybean oil.

The results of this investgation show that pumkin seeds could be utilized successfully in oil extraction and as a source of protein concentrates. Such utilization could not only help maximize available resources but at the same time minimize waste disposal problems.

Summary

The characteristics and composition of the crude oil extracted from Cucurbita maxima and Cucurbita pepo var. Thessaloniki (white) seeds were examined. Data obtained for the two species were respectively: iodine value 103.89 and 102.50, saponification number 191.50 and 199.70, unsaponifiable matter 0.62 and 0.78%, acidity (as oleic) 0.80 and 0.35%, Hehner value 73.15 and 72.95, Reichert-Meissl value 0.95 and 0.85 and refractive index (40°C) 1.4617 and 1.4615. The UV spectra exhibited two maxima at 272 and 218 nm for both oils. The major fatty acid was linoleic ($C_{18:2}$) at concentrations of 44.06 and 42.18% respectively, followed by oleic, 37.23 and 38.36% respectively. Also were found palmitic ($C_{16:0}$), 12.25 and 13.10%, stearic ($C_{18:0}$), 5.54 and 5.25%, and in very low concentrations lauric ($C_{12:0}$), hexadecenoic ($C_{16:1}$), heptadecanoic ($C_{17:0}$), linolenic ($C_{18:3}$) and arachidic ($C_{20:0}$) acids. Myristic acid ($C_{14:0}$) was found only in the oil from C. maxima seeds. The proximate composition of the seeds from the two species was respectively: moisture content 5.44 and 5.37%, crude oil 44.64 and 41.23%, crude protein (N × 6.25) 29.32 and 30.14%, crude fiber 5.06 and 5.95% and ash 5.51 and 5.18%.

Key words: Cucurbita maxima, C. pepo seeds, composition, oil characteristics, fatty acid GLC analysis.

Περίληψη

Μερικά χημικά και φυσικά χαρακτηριστικά του λαδιού από σπόρους κολοκυθιού

Εξετάσθηκαν τα χαρακτηριστικά και η σύνθεση του λαδιού που εκχυλίσθηκε από σπόρους των ειδών Cucurbita maxima και Cucurbita pepo ποικιλία Θεσσαλονίκη (λευκό). Τα στοιχεία που ελήφθησαν για τα δύο είδη ήταν αντιστοίχως: αριθμός ιωδίου 103,89 και 102,50, αριθμός σαπωνοποιήσεως 191,50 και 199,70, ασαπωνοποίητα συστατικά 0,62 και 0,78%, οξύτητα (σαν ελαϊκό) 0,80 και 0,35%, αριθμός Hehner 73,15 και 72,95, αριθμός Reichert-Meissl 0,95 και 0,85 και δείκτης διαθλάσεως (40°C) 1,4617 και 1,4615. Τα UV φάσματα έδειξαν δύο μέγιστα στα 272 και 218 nm για και τα δύο λάδια.

Το κύριο λιπαρό οξύ·ήταν το λινελαϊκό ($C_{18:2}$) σε συγκεντρώσεις 44,06 και 42,18% αντιστοίχως, ακολουθούμενο από το ελαϊκό ($C_{18:1}$) 37,23 και 38,36% αντιστοίχως. Επίσης ανευρέθησαν παλμιτικό οξύ ($C_{16:0}$) 12,25 και 13,10%, στεατικό οξύ ($C_{18:0}$) 5,54 και 5,25%, και σε πολύ μικρές συγκεντρώσεις λαουρικό ($C_{12:0}$), δεκαεξενοϊκό ($C_{16:1}$), δεκαεπτανοϊκό ($C_{17:0}$), λινολενικό ($C_{18:3}$) και αραχιδικό ($C_{20:0}$) οξύ. Μυριστικό οξύ ($C_{14:0}$) βρέθηκε μόνο στο λάδι από C. maxima.

Η προσεγγιστική σύνθεση των σπόρων από τα δύο είδη ήταν αντιστοίχως: υγρασία 5,44 και 5,37%, λάδι 44,64 και 41,23%, πρωτεΐνη ($N \times 6,25$) 29,32 και 30,14%, ακατέργαστες ίνες 5,06 και 5,95% και τέφρα 5,51 και 5,18%.

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SHORT PAPER

MASS SPECTRAL STUDY OF BIS-ARYLHYDRAZONES OF CYCLO-DECANE-1,6-DIONE AND THEIR OXIDATION PRODUCTS 9,10-BIS-ARYLAZO-DECALINES

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Summary

The fragmentation pattern upon electron impact at 70eV of the title compounds is studied. An interesting feature concerning the cyclodecane-ring derivatives is their fragmentation mode via a transannular pathway as well as the appearance of an aza-propellane type fragment. A correlation between the mass spectra of the two classes of compounds is also made.

Key words: Cyclodecane-1,6-dione bis-arylhydrazones, 9,10-bis-arylazo-decalines, aza-propellane, transannular.

Introduction

Oxidation[1] of the bis-arylhydrazones of cyclodecane-1,6-dione (1) with silver oxide leads to the formation of 9,10-bis-arylazo-decalines (2).

NNHAr		N=NAr	
	$\xrightarrow{Ag_2O}$		
NNHAr		N=NAr	
(1)		(2)	
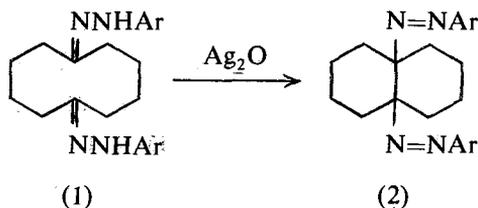
(a): $Ar=C_6H_5 -$ (d): $Ar=-C_6H_4 - NO_2(-p)$

(b): $Ar=-C_6H_4 - CH_3(-p)$ (e): $Ar=-C_6H_4 - CH_3(-o)$

(c): $Ar=-C_6H_4 - Cl(-p)$ (f): $Ar=-C_6H_4 - NO_2(-o)$

In this paper the mass spectra of the above compounds are reported and their characteristic fragment ions are indicated and discussed.

Results and discussion

The principal fragment ions in the mass spectra of compounds (1) and (2) are

given in tabular form in Tables I and II respectively, while general fragmentation pathways of the compounds (1) and (2) are given in Schemes I and II respectively.

In all mass spectra of compounds (1) the molecular ion peak appears with low relative intensity, whereas the ion Ar-N$_2^+$ (IV) appears to be the base peak or one of the prominent peaks in the spectrum with an exception for compounds (1b) and (1e), where the prominent peaks are those of m/z 91 which probably correspond to the tropylium ion. An important daughter ion which appears with moderate relative in-

TABLE I: Principal fragment ions in the mass spectra of bis-arylhydrazones of cyclodecane-1,6-dione (1).

Compound	
(1a)	m/e 348 (31)M$^{+\cdot}$, 346 (1), 256 (15), 241 (100), 150 (14), 136 (8), 107 (77), 105 (54), 92 (30), 77 (94).
(1b)	m/e 376 (4)M$^{+\cdot}$, 372 (2), 270 (4), 255 (15), 150 (10), 136 (8), 121 (13), 119 (40), 106 (50), 91 (100), 77 (23).
(1c)	m/e 420/418/416 (7)M$^{+\cdot}$, 418/416/414 (1), 292/290 (4), 277/275 (29), 150 (5), 143/141 (68), 141/139 (100), 136 (48), 113/111 (63), 77 (7).
(1d)	m/e 438 (2)M$^{+\cdot}$, 436 (2), 406 (1), 301 (<0.5), 286 (51), 152 (10), 150 (100), 136 (15), 122 (96), 92 (69), 77 (51).
(1e)	m/e 376 (1)M$^{+\cdot}$, 374 (<0.5), 270 (2), 255 (4), 150 (5), 136 (21), 121 (12), 119 (10), 106 (100), 91 (84), 77 (30).
(1f)	m/e 438 (12)M$^{+\cdot}$, 436 (<0.5), 301 (<0.5), 286 (25), 152 (10), 150 (100), 136 (10), 120 (52), 91 (62), 77 (90).

TABLE II: Principal fragment ions in the mass spectra of 9,10-bis-arylazo-decalines (2).

Compound	
(2a)	m/e 346 (5)M$^{+\cdot}$, 241 (7), 136 (2), 105 (100), 77 (99).
(2b)	m/e 374 (12)M$^{+\cdot}$, 255 (22), 136 (6), 119 (99), 91 (100), 77 (9).
(2c)$_1^a$	m/e 418/416/414 (<0,5)M$^{+\cdot}$, 277/275 (6), 141/139 (100), 136 (23), 113/111 (45), 77 (17).
(2c)$_2^a$	m/e 418/416/414 (2)M$^{+\cdot}$, 277/275 (7), 141/139 (100), 136 (13), 113/111 (70), 77 (7).
(2d)	m/e 436 (<0.5)M$^{+\cdot}$, 406 (<0.5), 286 (4), 150 (100), 136 (42), 122 (68), 77 (22).
(2e)$_1^a$	m/e 374 (<0.5)M$^{+\cdot}$, 255 (<0.5), 136 (9), 119 (26), 107 (8), 91 (100), 77 (12).
(2e)$_2^a$	m/e 374 (3)M$^{+\cdot}$, 255 (5), 136 (1), 119 (49), 91 (100).
(2f)	m/e 436 (<0.5)M$^{+\cdot}$, 286 (5), 150 (100), 136 (12), 122 (68), 77 (15).
(2g)^a	m/e 406 (20)M$^{+\cdot}$, 271 (17), 136 (44), 135 (97), 107 (100), 77 (46).

^{a} Compounds (2c)$_1$ and (2e)$_1$ are 9,10-bis-arylazo-trans-decaline isomers, whereas compounds (2c)$_2$ and (2e)$_2$ are 9,10-bis-arylazo-cis-decaline isomers.

^{b} Compound (2g) is 9,10-bis-(p-methoxy-phenylazo)-decaline and has been received directly from the preparation reaction of the corresponding bis-hydrazone, which has not been isolated.

tensity is ion $[M-ArNHNH]^+$ (III), which is formed from the molecular ion by a transannular scission of the arylhydrazine function. This transition is accompanied in all cases by the appropriate metastable ion peak and it has been also observed in the mass spectra of other bis-arylhydrazones[2]. Another transition confirmed in several cases by the corresponding metastable ion peak is that leading to the formation of ion $[M-ArNH]^+$ (II).
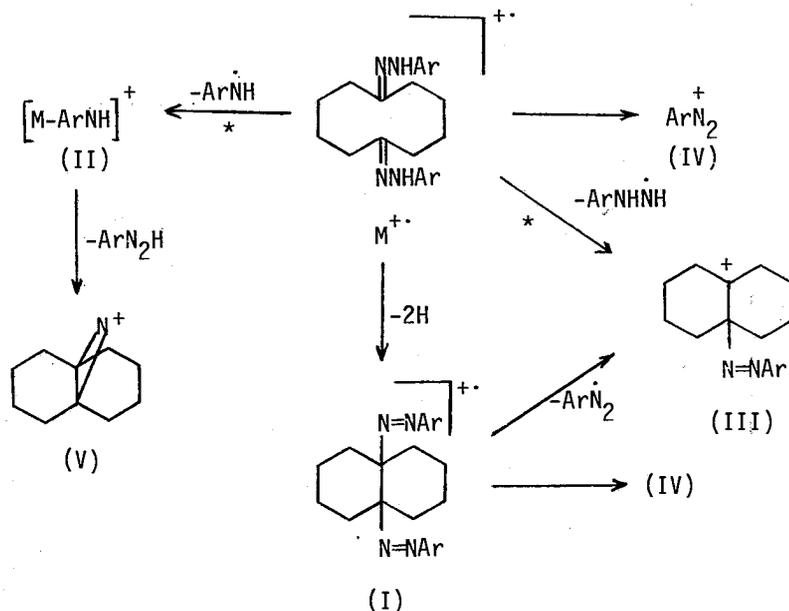
Scheme I. *Schematic representation of general fragmentation of bis-arylhydrazones of cyclodecane-1,6-dione (1).*

An interesting fragmentation pathway is that, which results to the formation of ion I, obviously by transannular elimination of hydrogen from the molecular ion, as follows:
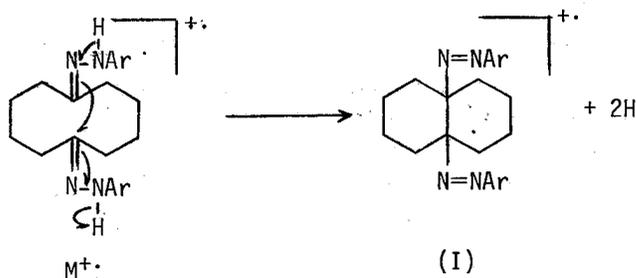
Analogous transannular reactions have been observed upon oxidation of bis-arylhydrazones (1) with lead tetraacetate or silver oxide[1]. The ion of m/z 150 is

found in all spectra and it is probably attributed to the propellane type ion (V). In the cases of compounds (1d) and (1f) of course the peak of m/z 150 also corresponds to the ion $O_2N-C_6H_4N_2^+$. A typical mass spectrum of compound (1a) is shown in Figure 1.
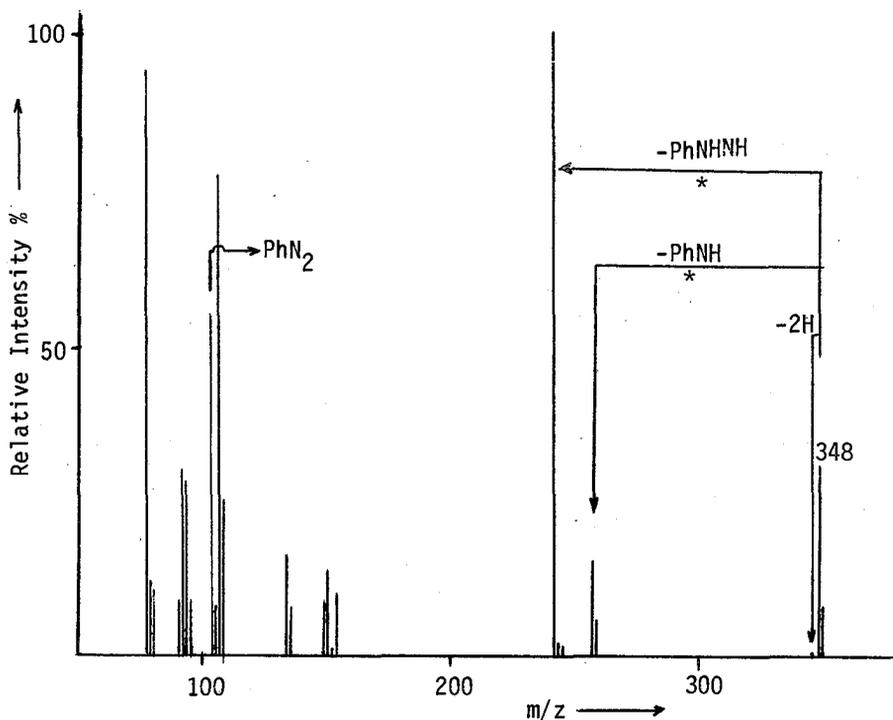
Figure 1. *Mass spectrum of the compound (1a).*

The fragmentation pattern observed in the mass spectra of the 9,10-bis-arylazo-decalines (2) is quite simple. In these spectra the molecular ion appears with low intensity, whereas the base peak is that corresponding to the ions (IV) or (VI). Scission of one arylazo- function from the molecular ion leads to ion $[M-ArN_2]^+$ (III), which appears with low to moderate relative intensity. This transition is followed in some cases with the appropriate metastable ion peak (Scheme II).

It is of interest to mention that the present compounds (2) lack of any peak corresponding to the $[M—ArN]^+$ ion although this ion peak has been found to be one of the most prominent in the mass spectra of 1,2-bis-arylazo-ethylenes[3].

Figure 2 is a representation of the mass spectrum of compound (2b).

In conclusion, comparing the mass spectra of compounds (1) and (2) we notice similarities as well as differences concerning their fragmentation patterns. Thus, they both show in the mass spectra the presence of the molecular ion in low relative intensity and the ion ArN_2^+ as base peak or one of the most prominent. A difference ob-
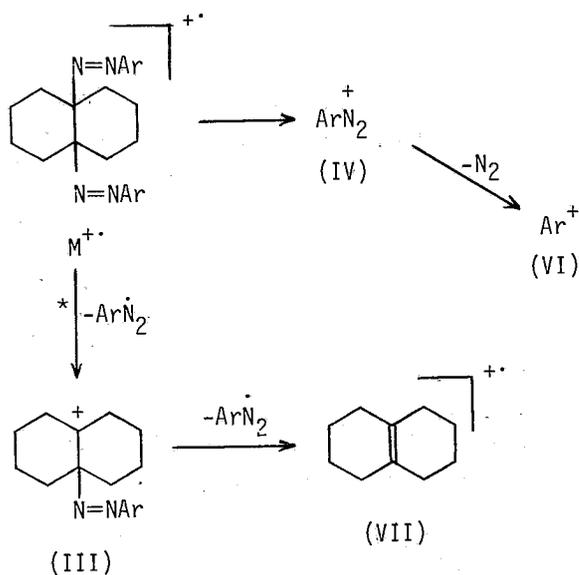
Scheme II. *Schematic representation of general fragmentation of 9,10-bis-arylazo-decalines (2).*
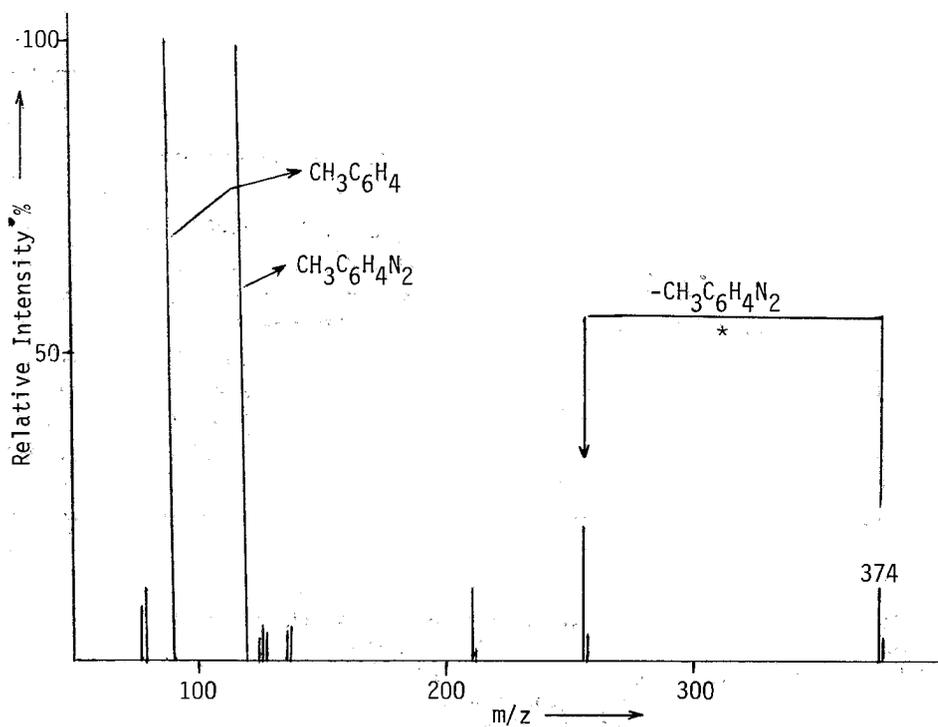
Figure 2. *Mass spectrum of the compound (2b).*

served is the complete absence of any ion of m/z 150 in the spectra of bis-arylazo-decalines (2) except from the cases of compounds (2d) and (2f) where it corresponds to the nitro-phenylazo- group. Additionally, an interesting point in the spectra of the bis-arylhydrazones (1) is the appearance of the 9,10-bis-arylazo-decaline ion (I), resulting by abstraction of hydrogen from the molecular ion.

Experimental

All mass spectra were run at 70eV on a RMU-GL Hitachi-Perkin-Elmer single focusing mass spectrometer, using the direct probe insertion for the samples. Probe temperature was in the range of 100-290°.

The compounds studied were prepared according to the following procedures:

Preparation of bis-arylhydrazones of cyclodecane-1,6-dione (1). The bis-aryl-hydrazones (1) were prepared upon treatment of cyclodecane-1,6-dione with two e-quivalents of the appropriate arylhydrazine in ethanol solution at room tempera-ture[1,4].

Preparation of 9,10-bis-arylazo-decalines (2). The 9,10-bis-arylazo-decalines (2) were received by the oxidation of bis-arylhydrazones of cyclodecane-1,6-dione (1) with silver oxide. The oxidation[5] was carried out under reflux in ether solution and the products (2) were received in high yields (90-100%), except from nitro- compounds (2d) and (2f) which were received in almost 20% yield.

Περίληψη

Μελέτη φασμάτων μαζών των διαρυλο-υδραζονών της κυκλοδεκανοδιόνης-1,6 (1) και των 9,10-διαρυλαζω-δεκαλινίων (2).

Στην εργασία αυτή γίνεται μελέτη των φασμάτων μαζών κατά το βομβαρδισμό με δέσμη ηλεκτρονίων σε 70eV των προαναφερομένων ενώσεων. Οι διαρυλο-υδραζόνες της κυκλοδεκανοδιόνης-1,6 (1) εμφανίζουν μικρής σχετικής εντάσεως μοριακά ιόντα, ενώ τα σπουδαιότερα θραύσματα που παρατηρούνται είναι αυτά που προκύπτουν με υπερκυκλική απόσπαση υδρογόνου ή μιας ομάδας ArNHNH—. Χαρακτηριστική είναι επίσης και η εμφάνιση ιόντος με m/z 150, στο οποίο αποδίδεται η προπελλανικού τύπου δομή (V). Μικρότερο ενδιαφέρον παρουσιάζουν τα φάσματα μαζών των 9,10-διαρυλαζω-δεκαλινίων (2), στα οποία επίσης εμφανίζεται μικρής σχετικής εντάσεως μοριακό ιόν.

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SHORT PAPER

HPLC ANALYSIS OF ERGOSTEROL FROM *PINUS HALEPENSIS* POLLEN

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Introduction

Ergosterol (provitamin D_2) is the predominante sterol component of most fungi and is either absent or a minor constituent in most higher plants[1, 2] and to my knowledge, there is no mention up to day of its presence in Pine pollens.

Analysis of pollen sterols from several plant species, including pine species, by gas chromatography and mass spectrometry as their acetate or trimethylsilyl ether derivatives, yielded mainly β-sitosterol or 24-methylene-cholesterol as the main components and cholesterol, stigmasterol, campesterol and desmosterol as minor constituents, but the presence of ergosterol was not confirmed.[3] These results can be compared to the distribution of the predominant pollen phytosterols found in Pine species, β-sitosterol in *Pinus sylvestris, P. mygo* and *P. montana,* campesterol and cholesterol in *P. montana* and 24-methylene-cholesterol in *P. sylvestris*.[4] Several standard phytosterols have been analyzed by gas chromatography as trimethylsilyl ether derivatives on varios column substrates[5, 6], including ergosterol[6], but only cholesterol, stigmasterol and β-sitosterol have been determined in the free form[5].

Free sterols and ergosterol can be succesfully separated on a preparative scale by liquid column chromatographic methods but the required elution times are very long[7]. Thin layer chromatography (TLC) on reverse phase mode has provided satisfactory separation of ergosterol[8] but this method is also time consuming.

High pressure liquid chromatography (HPLC) on reverse phase mode was used for the separation of ergosterol from other sterols, as their acetate derivatives[9] and the reverse phase HPLC separation of ergosterol from other sterols in the free form has so far been only partially succesful[10]. Normal phase HPLC determination of ergosterol has been used by Seitz and coworkers as a mesure of fungal growth by UV detection at 282 nm[11].

In this paper the isocratic normal phase HPLC analysis of ergosterol by UV detection at 292 nm is reported. At this wavelength no interference from other sterols is observed. The above results were confirmed in the analysis of the pollen sterol fraction from the common in mediterranean climate *P. halepensis* species.

Experimental

Materials

Pollen was collected by hand from the Pine tree *Pinus halepensis (Miller)* in ear-
ly May at Chalandri of Attica (Greece). All reagents and chemicals were of
analytical grade (Merck, Darmstadt, F.R.G.). Standard plant sterols were purchased
from Supelco (Bellefonte, Pensulvania, U.S.A.) and HPLC solvents from Ruthburn
(Walkerburn, Peeblesshire, Scotland, G.B.). TLC was performed on 20cm × 20cm
glass plates coated with silica gel G, 0.50mm thikness.

Instrumentation

Perkin-Elmer (Norwalk, Connecticut, U.S.A.) instruments were used throughout
this work.

HPLC analyses were performed with a Series 3B liquid chromatograph fitted
with a Rehodyne, model 7105, loop valve injector and equipped with a model 551
UV-VIS spectrophotometer as detector, fitted with 8 μl special HPLC flow
microcells.

The above equipments were coupled to a model 2 integrator-calculator printer
and a model 550 recorder.

UV spectra were obtained by the model 551 spectrophotometer, fitted with 1.0
ml special cells and were recorded on the model 550 recorder.

Methods

Total pollen lipids were extracted by the method of Kates[12]. Total free sterols
were separated from other lipid classes by the unidimentional TLC system ether-
acetic acid, 100:3 (V/V) up to Rf 0.4 followed by petroleum ether (b.p. 40-60°C) -
ether-acetic acid, 80:20:1 (V/V/V) and were purified by TLC using the system
petroleum ether (b.p. 40-60°C) -ether-acetic acid, 80:20:3 (V/V/V). The recovery of
sterols from the plates was effected by extracting the scrapped off silica bands with
chlorofrom-methanol, 9:1 (V/V).

The HPLC chromatographic conditions are given in the figure legend.

Results and Discussion

By an our recent work pollen lipids of *P. halepensis* have been isolated and iden-
tified[13]. The total lipid content of pollen was found 2.5 ± 0.2% and the sterol content
1.254% of total lipids. β-Sitosterol was determined by gas chromatogrpahy as the
predominante component (0.958% of total lipids) followed by ergosterol (0.154%),
stigmasterol (0.095%) and cholesterol (0.025%), but the ergosterol and campesterol
standards were partially overlaped and no complete separation could be achieved
although several chromatographic conditions were tested. Therefore HPLC was em-
ployed for additional determination and quantitation of ergosterol.

UV spectra of plant sterol standards were obtained as 0.02% solutions in
chloroform. As is shown in Fig. 1, stigmasterol, desmosterol, β-sitosterol, cam-
pesterol, cholesterol, lanosterl and ergosterol standards possess λ maxima in the
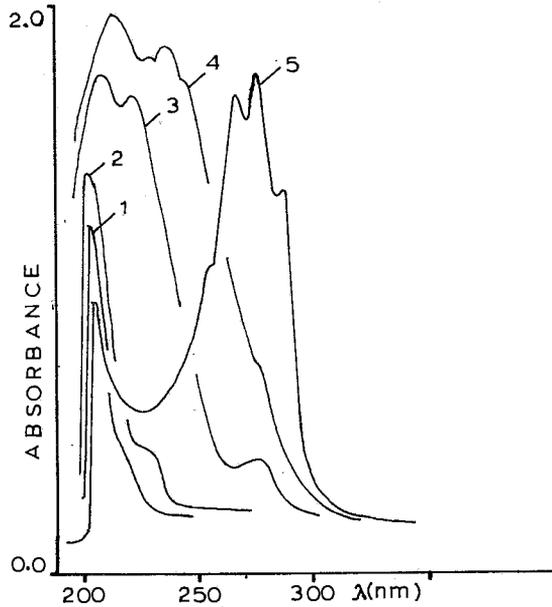
FIG. 1: *UV spectra of plant sterol standards. Concentration, 0.02% each sterol in chloroform; sample volume 0.5 ml; Scan 10 nm/min; 2.0 a.u.f.s.; curves: 1, stigmasterol or desmosterol; 2, β-sitosterol or campesterol; 3, cholesterol; 4, lanosterol; 5, ergosterol.*
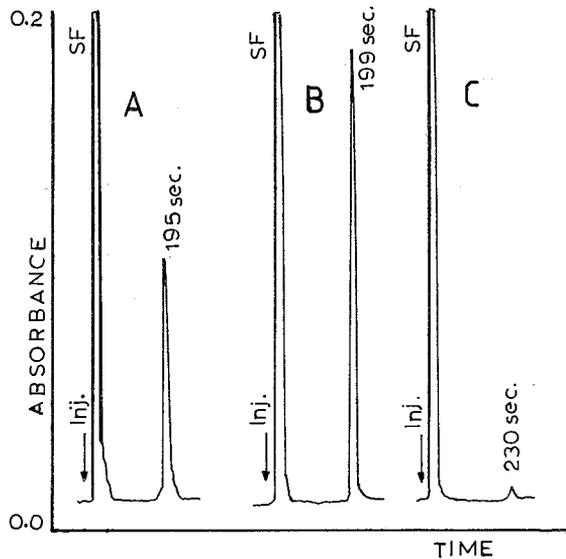
FIG. 2: *HPLC analysis of ergosterol. Chromatographic conditions: column, Perkin-Elmer, Silica A/10 (stainless steel, 25 cm × 2.6 mm I.D.); mobile phase, isopropanol-cyclohexane (1:99, V/V) with isocratic elution; detection, UV 292 nm, 0.2 a.u.f.s.; flow rate, 1.0 ml/min; temperature, ambient; injections, 100 μl chloroform solutions. A; Sterols from 5 mg total lipids of P. halepensis pollen. B, 0.01% ergosterol standard. C, mixture of plant sterol standards (0.01% each) exept ergosterol. The peak at 230 sec. tested by TLC (8) = impurities.*

205-215 nm region. Ergosterol possesses also λ maxima in the 262-292 nm region. The absorbance of cholesterol (and lanosterol) at 280 nm may be owning to its 7-dehydro-artefact which anyway is minimized at 292 nm. The detection, therefore, of ergosterol at 292 nm is free from interferences from the other pollen phytosterols and also from other, usually found in plants, absorbing phytosterols.

Following the above methodoloty only one peak was obtained from the HPLC analysis of *P. halepensis* pollen sterols, corresponding to ergosterol, Fig. 2A. Quantitative determination of ergosterol in the *P. halepensis* total lipids furnished a value of 0.134% when compared with standard ergosterol runs, Fig. 2B. It is also worth noting that, as already stated above, a mixture of the aforementioned standard phytosterols, exept ergosterol, could not be detected and identified by HPLC at this wavelength, Fig. 2C.

By these means ergosterol was identified and determined quantitivelly in the free sterol content of a pine species without interferences from the other phytosterols. The determination was performed without derivatization of ergosterol, as in the previously reported reverse phase method[9]. In addition in the represented method, ergosterol is alouted in about 3 min at a flow rate of 1 ml/min (with the mobile phase isopropanol-cyclohexane 1:99 V/V) and as compared to the aforementioned reverse phase HPLC methods[9, 10] and to the 9 min and 1.7 ml/min (with the mobile phase dichloromethane - cyclohexame 1:99, V/V) of the method of Seitz and coworkers[11], has the advantage of economizing time and solvents. This advantage is essential for experiments involving a large number of samples.

Summary

A rapid isocratic method for the idendification and quantitation of ergosterol in a sterol mixture by high pressure liquĩd chromatography and detection at 292 nm, is described. At this wavelength no interference from other common plant sterols is observed. Lipids are injected in 100 μl of chlorophorm on a silica column and eluted with a solvent mixture of isopropanol - cyclohexane 1:99 (V/V) at a flow rate of 1 ml/min. The above results were confirmed in the pollen sterol fraction of the pine species *Pinus halepensis (Miller)* and ergosterol was found 0.134% of pollen total lipids.

Key Words: Pine, *Pinus halepensis,* pollen, TLC, UV, sterols, ergosterol.

Abbreviations

HPLC, high pressure liquid chromatography; TLC, thin layer chromatography; SF, solvent front; UV, ultraviolet.

Περίληψη

HPLC ανάλυση της εργοστερόλης, από τη γύρη του πεύκου Pinus halepensis

Σε αυτή την εργασία παρουσιάζεται η ανάλυση της εργοστερόλης με υγρή χρωματογραφία υψηλής πίεσης (HPLC) από ένα είδος μεσογειακού πεύκου, το *Pinus halepensis (Miller),* με ανίχνευσή της στο υπεριώδες (UV) σε μήκος κύματος 292 nm, στο οποίο οι άλλες φυτοστερόλες της γύρης δεν απορροφούν.

Η έκλουση της εργοστερόλης γίνεται σε στήλη Siliςa A/10 με το μίγμα διαλυτών ισοπροπανόλη - κυκλοεξάνιο, (1:99, κ.ο.) στα 3 λεπτά περίπου, με ροή 1 ml/min.

Η περιεκτικότητα της εργοστερόλης, που ανιχνεύεται για πρώτη φορά στα κωνοφόρα, βρέθηκε 0.134% των συνολικών λιποειδών της γύρης.

Acknowledgments

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