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## THE NECESSITY OF USING NON-KOH COLUMNS FOR THE GLC ANALYSIS OF DIMETHYLPROPION AND TWO OF ITS METABOLITES

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### Summary

Decomposition of dimethylpropion (2-dimethylaminopropiophenone) and 2-aminopropiophenone was observed during (GLC) gas-liquid chromatography on KOH coated columns. Decomposition products were characterized by GLC and GLC-MS and it was confirmed that dehydrogenation, caused by the presence of KOH and the temperature used, occurred. N-primary and tertiary 2-aminopropiophenones decomposed to significantly different extents.

A GLC analytical method using a non-KOH coated column and a single step extraction with chloroform is adopted for the analysis of dimethylpropion and two of its metabolites. The method can be used for the determination of these compounds in urine for at least 24 hours after oral administration of dimethylpropion hydrochloride in a dose of 50mg.

**Key Words:** Dimethylpropion, Monomethylpropion, 2-Aminopropiophenone, Methylpseudoephedrine. Decomposition of Aminopropiophenones.

### Abbreviations

#### Chemical Names

#### Abbreviated Names

2-Dimethylaminopropiophenone (Dimethylpropion)  
2-Methylaminopropiophenone (Monomethylpropion)  
Methylephedrine/Methylpseudoephedrine  
2-Aminopropiophenone

DMP I  
DMP II  
DMP IV  
DMP III

### 1. Introduction

The  $\alpha$ -aminoketone-type compounds, of which diethylpropion, dimethylpropion (DMP I) and 2-aminopropiophenone (DMP III) are examples, have been reported to be unstable in the presence of alkali<sup>1,2</sup>. Two neutral and one acidic product (benzoic

acid), as a result of instability during alkaline extraction and GLC analysis, were found.

Van Zwol (1966)<sup>3</sup> studied the decomposition of some sympathomimetic amines (among which was diethylpropion) during separation on gas chromatographic columns. He mentioned that this decomposition was promoted by high injector and detector temperatures and probably some stationary phases.

Decomposition and rearrangement of diethylpropion and its ketone metabolites, 2-ethylaminopropiophenone and 2-aminopropiophenone, during GLC analysis on KOH treated supports was also reported to occur<sup>4,5</sup>. Banci et al (1971)<sup>4</sup> attributed this decomposition to a keto-enolic equilibrium or to another rearrangement.

In the present study, decomposition of dimethylpropion (DMP I) and 2-aminopropiophenone (DMP III) during GLC analysis on KOH-coated supports, was observed and the structure of their decomposition products was investigated by means of GLC-MS.

The results of these investigations led to the development of a new method for the determination of DMP I and two of its metabolites by GLC using non-KOH coated supports.

## 2. Experimental section

### 2.1. Apparatus used:

PYE '104' Chromatograph fitted with a flame ionisation detector and incorporating a Perkin Elmer (model 56) Recorder.

### 2.2. GLC Columns used:

One meter glass columns were used containing:

- Chromosorb G (AW DMCS, 100-120 mesh) coated with 10% KOH, 2% Carbowax 20M and 10% Apiezon L.
- Chromosorb G (AW DMCS, 100-120 mesh) coated with 2% Carbowax 20M and 10% Apiezon L.
- Chromosorb G (AW DMCS, 100-120 mesh) coated with 5% KOH and 2% Carbowax 20M.
- Chromosorb W coated with 10% KOH and 10% Apiezon L.

### 2.3. Working Conditions:

For columns a, b and d:

N<sub>2</sub> pressures 87, 100 and 135 kPa; flow rates: I, 1.25 and 1.66 cm<sup>3</sup>s<sup>-1</sup> respectively; column temperature 200°, injection port temperature 250°; H<sub>2</sub> and air pressures 135 kPa.

For column c:

The same as with the other columns except with a column temperature of 150°.

### 2.4. Gas Liquid Chromatography-Mass Spectrometry (GLC-MS)

Gas liquid chromatography-mass spectra were recorded on a VG 12F Mass

Spectrometer with VGDS 2135 data system (ionization potential 70eV) linked to a Pye-104 gas chromatograph.

Direct inlet mass spectra of the compounds examined were obtained on the same instrument at an ionization potential of 70eV.

### 2.5 Preparation of Solutions for GLC-MS Studies

Solutions of DMP I and DMP III were obtained by dissolving their hydrochlorides in methanol or chloroform, or by extracting alkaline aqueous solutions of their salts with freshly distilled diethyl ether. Each solution contained approximately 2 $\mu$ g base per  $\mu$ l, with the exception of the solution of 2-aminopropiophenone (DMP III) examined on the column (b) where concentrations were ca. 20 $\mu$ g/ $\mu$ l. 2-3 $\mu$ l of the prepared solutions were chromatographed.

### 2.6 Preparation of samples of DMP I and its metabolites DMP II and DMP IV for GLC analysis

To 1-4ml of aqueous solution or urine, containing from 4 to 400 $\mu$ g of DMP I, DMP II and DMP IV, in a tapered centrifuge tube, 1ml of internal standard solution (ethylephedrine hydrochloride) was added. The mixture after dilution to 6ml with distilled water or blank urine, was alkalinised (pH 10.5) with diluted ammonia solution (0.5ml of 30% v/v NH<sub>3</sub>) and then extracted with 100 $\mu$ l freshly distilled chloroform by shaking the tube for 2.25min on a Fison Whirlimixer. After centrifugation of the tube at 6000 r.p.m. on a MSE Speed Bowl for 10min to separate the 2 immiscible phases, 50 $\mu$ l of acetic anhydride was injected into the chloroform layer by means of a 100 $\mu$ l Hamilton syringe. The mixture was allowed to stand overnight. The next morning 1-2 $\mu$ l of the chloroform extract was removed using a 5 $\mu$ l SGE glass syringe fitted with a 3cm needle. The chloroform was removed by placing the tip of the syringe needle directly into the chloroform layer, below the aqueous layer, and withdrawing the required volume. The chloroform was then injected into the GLC column for analysis.

## 3. Results and Discussion

GLC analysis of DMP I and DMP III using column (a) produced two peaks for DMP I and a single peak for DMP III (FIG 1). The smaller peak derived from compound DMP I had a longer retention time (Rt) than the main peak. Phenylvinylketone and phenylmethyldiketone, the proposed decomposition products (formed by beta elimination) of the 2-aminopropiophenones<sup>6</sup>, chromatographed under the same conditions, showed very short Rt 1.8-2.0 min. A process of beta elimination occurred to a small extent in DMP I and DMP III during the process of extraction from alkaline medium, but peak(s) with short Rt corresponding to phenylvinylketone and phenylmethyldiketone were almost immeasurable. Since the observed GLC decomposition on column (a) did not correspond to a beta elimination reaction, the structures of decomposition products were examined by GLC-MS.

Direct inlet mass spectrums of DMP I (M.W. 177) and DMP III (M.W. 149) showed base peaks, at m/e 72 and m/e 44 respectively, formed by  $\alpha$ -cleavage.

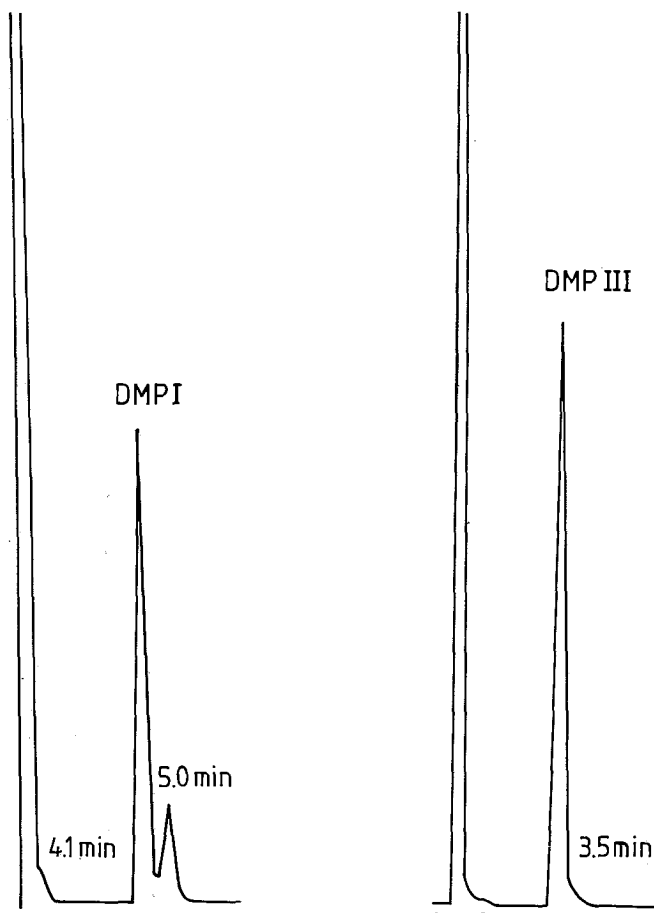


FIG. 1: GLC Chromatograms of the 2-Aminopropiophenones Using Column (a)

The GLC-MS results showed that the spectrum of the first peak of DMP I (Rt 4.1min) produced a base peak  $m/e$  72, corresponding to the direct inlet mass spectrum of DMP I. The GLC-MS of thesecond peak of DMP I (Rt 5.0min) and the single peak of DMP III showed the highest masses, two mass units lower than those corresponding to molecular ions ( $M^+$ ) of these compounds and characteristic fragments. The  $m/e$  175 (16%) and peak at  $m/e$  70 (100%) was obtained from DMP I and  $m/e$  147 (6%) and peak at  $m/e$  42 (100%) from DMP III. These results showed that decomposition was almost complete for the N-primary aminopropiophenone (DMP III), since this compound gave only *one* peak using column (a) and this peak had a mass spectrum in which  $m/e$  147 ( $M^+-2$ ) instead of  $m/e$  149 ( $M^+$ ) was obtained. In the case of the N-tertiary aminopropiophenone, DMP I, about 20-25% decomposition occurred i.e. much less than with DMP III.

In the GLC-Mass Spectra of DMP I and DMP III there were no  $m/e$  units corresponding to the direct inlet mass spectra of phenylvinylketone and phenylmethylidketone.

Decomposition of the compounds examined on the KOH-coated column (a) always took place, but the extent of the change depended on the gas chromatographic conditions and varied daily. Decomposition did not depend on the solvent used as a very similar picture was obtained using methanol and chloroform solutions as well as ether extracts of the compounds examined.

Very similar results were obtained with DMP I and DMP III using two other KOH-coated columns (c and d) and this indicated that stationary phases did not influence the decomposition of these compounds. For this reason column (b) which was the same as column (a) but with KOH omitted, was prepared. Using the same gas chromatographic conditions on column (b), DMP I showed a single peak (FIG 2). Best peaks were obtained when the following conditions were used with this column:  $N_2$  flow rate  $1.25\text{ cm}^3\text{ s}^{-1}$ ,  $H_2$  and Air pressures 135 kPa and oven temperature  $200^\circ$ . The GLC-MS of DMP I now corresponded to its direct inlet mass spectrum; only a small amount (1.3%) of the fragment corresponding to its decomposition product could be seen. At the concentration usually used on column (b) i.e.  $2\mu\text{g}/\mu\text{l}$ , it was not possible to detect any 2-aminopropiophenone (DMP III). But using higher concentrations (10-20 times higher) a peak for DMP III was observed (FIG 2) which

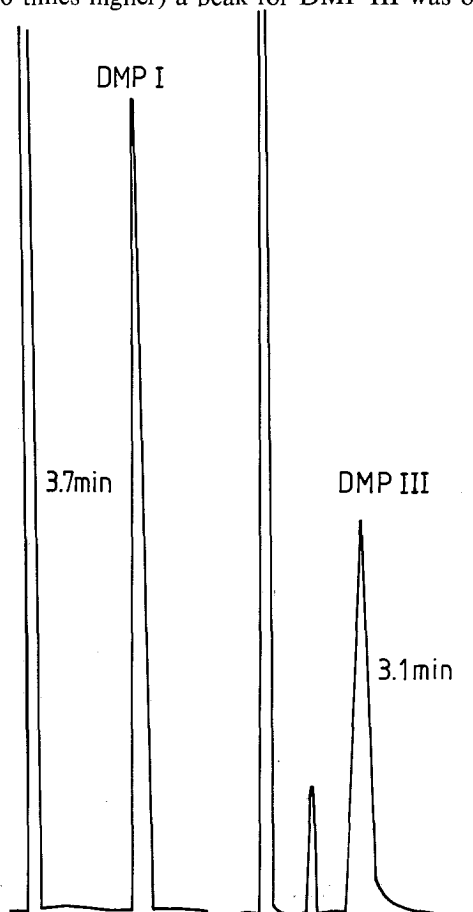


FIG. 2: GLC Chromatograms of the 2-Aminopropiophenones Using Column (b).



was not as sharp as the peak on column (a) (FIG 1). GLC-MS confirmed that the peak was a mixture of unchanged DMP III and decomposition product (in almost equal amounts) indicating that because of its thermolability, dehydrogenation of DMP III occurred to some extent *without* catalysis by KOH.

To confirm that both the compounds and their decomposition products had alkaline character and that an alkali during the process of extraction did not influence decomposition observed on the column, ether extracts of the compounds examined were washed with HCl (1N) and chromatographed. No peaks were observed. Acid layers were again made alkaline (5N NaOH), extracted with ether and chromatographed. Two peaks from DMP I were observed using column (a) and a single peak using column (b).

On the basis of the above, a probable chemical mechanism for the GLC decomposition of DMP I and DMP III on KOH-treated columns was proposed (see FIG 3). Hydrogen abstraction leading to dehydrogenation via free radical mechanisms is

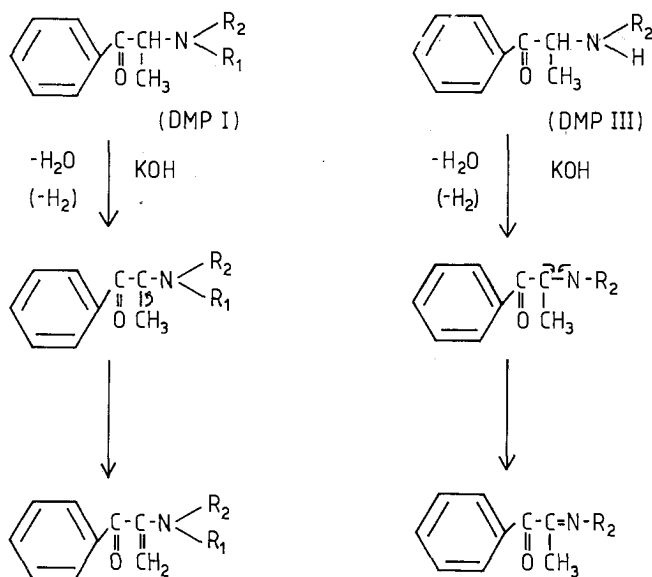


FIG. 3: Chemical mechanisms for the GLC decomposition of the 2-Aminopropiophenones on KOH treated columns

mainly based on the following facts: -The reaction takes place in the gas phase and under conditions which favour energetically the homolytic process. The reaction is initiated by KOH which under these conditions generates free radicals by heating.

Having established that DMP I did not produce a decomposition peak with column (b), this column was adopted for the GLC analysis of DMP I in urine and water.

Metabolites of DMP I i.e. methylpseudoephedrine, DMP IV, and monomethylpropion, DMP II<sup>7</sup>, extracted from aqueous solution or urine in the same way as DMP I (see 2.6) and injected onto column (b), under the same conditions, gave satisfactory peaks for quantitative analysis. However, the retention time of DMP II was exactly the same as DMP I (3.0 min.). It was therefore proposed to separate the pa-

rent compound (DMP I) from the metabolite DMP II by acetylating the secondary amine DMP II using acetic anhydride as the reagent (DMP I and DMP IV both being tertiary amines could not be derivatized by this method). The acetylated DMP II gave a retention time of 12.6min. FIG 4 represents one of the chromatograms

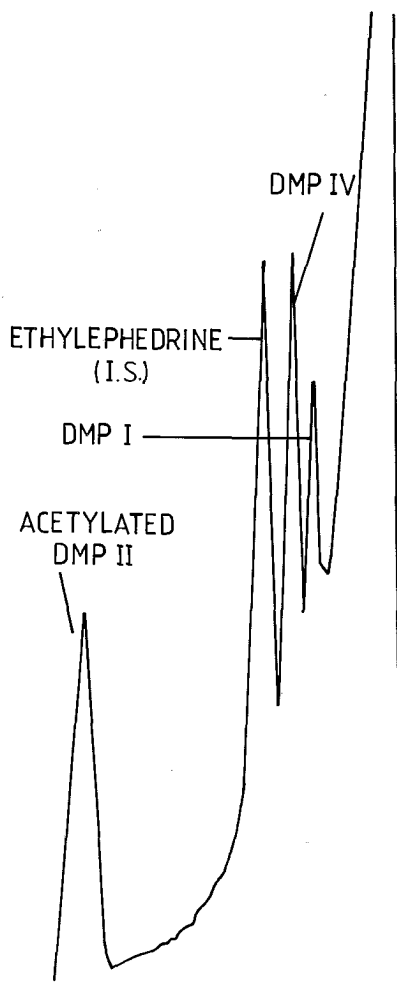


FIG. 4: A Chromatogram showing the Separation of DMP I, DMP II, DMP IV and Ethylephedrine extracted from Urine and injected onto Column (b).

showing the separation of DMP I, DMP II, DMP IV and the internal standard ethylephedrine. The reproducibility of extraction of these compounds from water or urine, determined by GLC, gave coefficients of variation not exceeding 4.0%. The extraction efficiency of the method from both water and urine was between 80-100% for DMP I,II,IV and ethylephedrine. Calibration curves gave correlation coefficients of 0.998 and more.

Markantonis (1982)<sup>7</sup> found that DMP I was not metabolised to DMP III, so quantitative GLC analysis of the compound was not required.

## Acknowledgements

I would like to thank Temmler-Werke, Marburg/Lahn for kindly supplying dimethylpropion hydrochloride and all its metabolites.

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## Περίληψη

«Η αναγκαιότητα χρησιμοποίησης στηλών χωρίς ΚΟΗ για την αεριοχρωματογραφική ανάλυση του διμεθυλοπροπίου και δύο μεταβολιτών του».

Κατά τη διάρκεια αερίου χρωματογραφίας με στήλες που περιείχαν ΚΟΗ παρατηρήθηκε αποσύνθεση του διμεθυλοπροπίου και της αμινοπροπιόφαινόνης. Τα προϊόντα διάσπασης χαρακτηρίστηκαν με GLC και GLC-MS και επιβεβαιώθηκε ότι πρόκειται για αφυδρογόνωση που προκαλείται από την επίδραση του ΚΟΗ και της θερμοκρασίας.

Τελικά προτάθηκε η χρησιμοποίηση στήλης χωρίς ΚΟΗ για τον αεριοχρωματογραφικό ποσοτικό προσδιορισμό του διμεθυλοπροπίου και δύο μεταβολιτών του. Η μέθοδος αυτή αποδείχτηκε αποτελεσματική για τον ποσοτικό προσδιορισμό των ουσιών αυτών στις συγκεντρώσεις που υπάρχουν στα ούρα για 24 τουλάχιστο ώρες μετά τη χορήγηση 50 mg διμεθυλοπροπίου από το στόμα.

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## **APPLICABILITY OF DISSOLVED - AIR FLOTATION FOR THE RECOVERY OF FINE MINERAL PARTICLES**

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### **Summary**

In most mineral beneficiation operations much of the losses are attributed to the fine size fraction of the ore. Application of conventional flotation techniques for the recovery of fine mineral particles is not possible for a number of reasons. The suitability of dissolved-air flotation, a separation method established in wastewater engineering, was examined on calcite fines at a laboratory batch stage. The process is known to produce fine bubbles. Parameters studied were the conditioning time, flotation recovery, agitation, fatty acid concentration, pulp density, and flotation time. The problems associated with the presence of fine particles during flotation processing were discussed and reviewed.

**Key Words:** Dissolved-air flotation, fine mineral particles processing.

### **Introduction**

The problem of processing fine particles poses an immense challenge today to the researchers both in mining and mineral processing areas, with the increasing demand for minerals and the continuously diminishing grade of ores. Since mineral recoveries are generally difficult to achieve at the fine particle size, much of the losses in most mineral beneficiation operations may be attributed to the fine size fraction of the ore.

The processing of ores containing fine mineral particles can be classified into two broad categories, namely: (a) those in which the desired mineral almost entirely occurs in the fine size range, due to liberation reasons and in this instance, the process (ideally) should be designed to recover virtually all the particles at this size range, and (b) those in which the desired mineral extends from coarse sizes down into the fine size range and in this case, the fines or slimes often interfere with the concentration of coarser particles and are usually removed (and simply discarded).

Examples of ores that consist mostly of fine particles are taconites, tin ores containing cassiterite, certain sulphide ores, and mainly those encountered in the clay industry. There are numerous examples of processing systems in which the ore must be deslimed. Perhaps the best example is the Florida phosphate industry, where approximately one third of the phosphate is discarded as a slime. It is known that

nowadays roughly one fifth of the world tungsten and one half of Bolivian tin are lost in slime, because of the lack of a suitable method of separation at fine particle sizes<sup>1</sup>.

Because of the losses of mineral and metal values in the fine size range, considerable interest is growing in developing new processes and in improving old ones for the recovery of fine particles. Flotation is by far the most important unit operation of mineral processing. However, the application of conventional flotation techniques for the separation of mineral fines is generally uneconomical and present several scientific and technological problems.

Particle - bubble collision, adhesion, and detachment are the three major sub-processes during flotation. The first is non-selective in that both hydrophobic and hydrophilic particles have the same probability of collision. Theoretical treatment of the particle - bubble collision process assumes that bubbles move through pulp so that there is a streamline flow of fluid around the bubble. At constant bubble size the collision rate decreases with decreasing particle size<sup>2</sup>.

If, on the other hand, the bubble size is reduced in proportion to the particle size, the rate of collision remains unchanged. This indicates that flotation with fine bubbles would be an effective way of recovering fine particles.

Scope of this paper is to study the technique of dissolved-air flotation applied to the separation and recovery of fine particles. The background of the field will be also briefly reviewed. Dissolved-air flotation has found increasing value during the 1970's, particularly in the area of water and wastewater treatment.

Our parallel work on electrolytic flotation as a separation method for fines has been also reported recently<sup>3</sup>. The two techniques are known to produce bubbles of an average diameter of approximately 50  $\mu\text{m}$ , compared with the size range of 0.6 - 1 mm produced in froth flotation cells.

A dissolved -air (pressure) flotation system consists essentially of a flotation unit and a saturator. The flotation unit serves to separate the solid phase from the liquid phase and the saturator dissolves air into water under pressure. The pressure - saturated water is introduced to the flotation unit through a reducing valve. Just downstream of the valve the pressure is virtually atmospheric and the saturator feed becomes highly super-saturated with air (Henry's law). The air precipitates out of solution in the form of very small bubbles, which are blended with the feed.

The technique was reviewed by one of the authors<sup>4</sup>, among others. The operational experience with a 2,300  $\text{m}^3/\text{day}$  pilot plant installed by a Water Company has been described<sup>5</sup>, and a cost comparison between dissolved-air flotation and alternative clarification processes was also attempted<sup>6</sup>. While, a design example was included in an excellent article on the process<sup>7</sup>.

Only two papers were found in the literature dealing with dissolved-air flotation for the separation of mineral particles, and both studies were carried out, more or less, at the same time with ours. In the first<sup>8</sup>, the method was applied at ultrafine particles (less than 10  $\mu\text{m}$ ) and as an example, the separation of fine coal from coal washery wastewater was chosen. The second paper<sup>9</sup> investigated the possibility of using the method for the separation of fine cassiterite.

## Experimental

The dissolved-air flotation batch experiments were conducted<sup>10</sup> in a portable jar tester for laboratory use, pioneered by Water Research Centre (UK) and manufactured by Aztec Environmental Control Ltd. The system, although was primarily designed for sedimentation tests, could readily be adapted with a special 1,500 cc calibrated jar and a mini saturator having a content of 10 l, for dissolved-air flotation evaluations. The jar, having a conical bottom with a drain and two side sampling points, was equipped with a stirrer motor giving stable speeds, fast for initial mixing and slow to assist flocculation in effluent treatment. Water saturated with air (from a compressor), under a saturator's pressure of around  $5 \times 10^5$  Pa, was introduced to the base of the unit via a nozzle specifically designed. The operation for the dissolution of air needs attention<sup>7</sup>.

As material natural calcite was used having the chemical analysis shown in Table I, and certified by an x-ray crystallographic analysis. The material was crushed,

TABLE I: Analysis of Material  $\text{CaCO}_3$ .

Loss on ignition	43.71%
$\text{SiO}_2$	1.93
$\text{R}_2\text{O}_3$	0.04
MgO	0.98
CaO	51.28

ground and sieved in the laboratory and the - 45  $\mu\text{m}$  fraction (- 325 mesh) was taken. As collector the Acintol FA1 tall oil fatty acid was selected, supplied by Arizona Chemical Company. It was containing mainly linoleic and oleic acids. Previous experiments on the floatability of calcite have been also carried out and reported elsewhere<sup>11</sup>.

## Results and discussion

Not all minerals, of course, show maximum recovery in exactly the same size range. To get some idea of the differences between minerals, the observed size ranges of maximum flotation recovery have been published<sup>12</sup> in a review paper on the floatability of very fine particles; as for instance, 50-150  $\mu\text{m}$  for fluorite, 37-295  $\mu\text{m}$  for galena, 15-100  $\mu\text{m}$  for sphalerite, 50-150  $\mu\text{m}$  for pyrite, etc.

As the particle size is reduced two characteristics begin to dominate: the specific surface becomes large and the mass of the particle becomes very small. A schematic diagram was given<sup>13</sup>, which is drawn as Figure 1, to illustrate the relationship between the physical and chemical properties of fine particles and their behaviour in flotation. The arrows indicate the various factors contributing to a particular phenomenon observed in flotation of fine particles. Certain phenomena affect the recovery, as low flotation rate, high reagent consumption and rapid oxidation; other the grade, as fine particle entrainment and non specific collector adsorption; while there are some affecting both recovery and grade, as froth stabilization and higher dissolution.

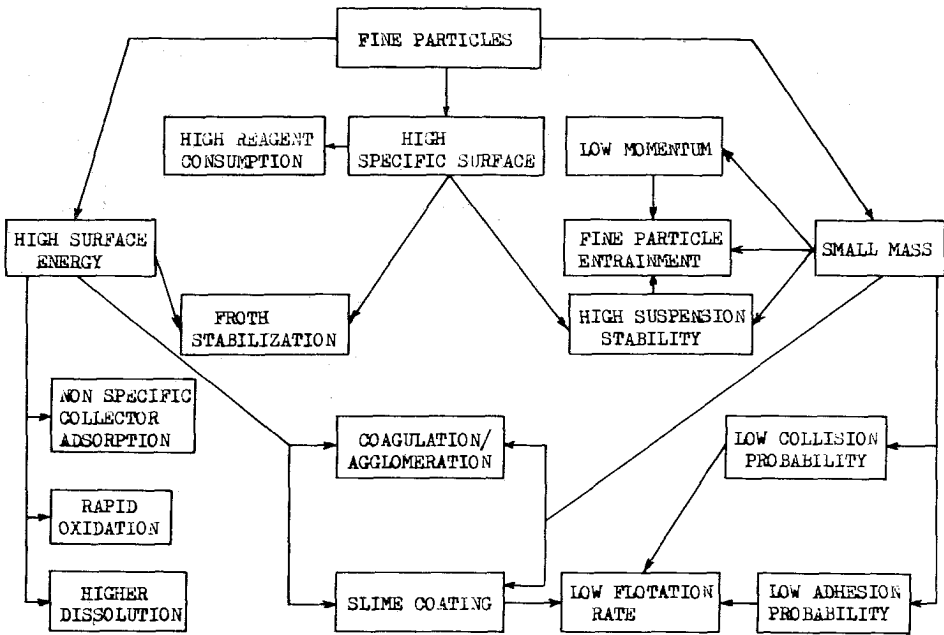


FIG. 1: Relationship between the properties of fine particles and their behaviour in flotation (after Fuerstenau).

One of the first parameters studied during the batchwise laboratory work was the effect of flotation time, expressed here as volume of water saturated with air, that was added in the cell. The results are shown in Figure 2. The initial liquid content of the flotation cell was 800 cc, the weight of calcite particles 8.4 g, the collector's concentration 40 ppm and the conditioning time 5 min. The values given are the average.

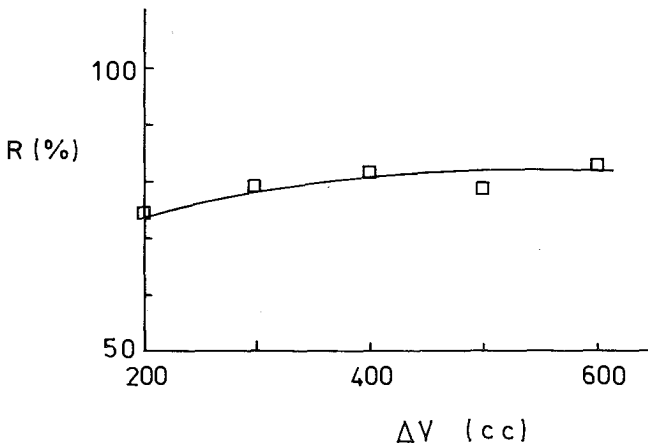


FIG. 2: Effect of time of dissolved-air flotation on recovery of calcite fines.

of two (or three sometimes) tests. On the ordinate in the figure, it is customary in flotation tests to calculate the flotation recovery,  $R$ , expressed per cent. It is seen from the experimental results that with an introduced volume of 200 cc, or in other words a recycle of 25%, the recovery reached 75%.

The speed of stirring was another variable and the results are presented in Table II. A recovery of over 80% was noticed with 200 rpm. In this case, the added

TABLE II: Effect of agitation during flotation on recovery.

rpm	R %
45	66.5
100	54.5
200	83.0

volume of saturated water was 500 cc and the other parameters as above. The same principle stands for the rest of the paper, unless stated otherwise. It was obvious that agitation, even with fine particles, was a necessity to keep them in dispersion and prevent them from settling towards the bottom of the flotation tank.

Because of the small mass and momentum of fine particles, it is known that they may be carried into the froth after getting either entrained in the liquid, or mechanically entrapped with particles being floated. This phenomenon was also noticed during the next round of experiments, when no collector was used giving a recovery of 13% roughly. Figure 3 shows this effect of flotation reagent concentra-

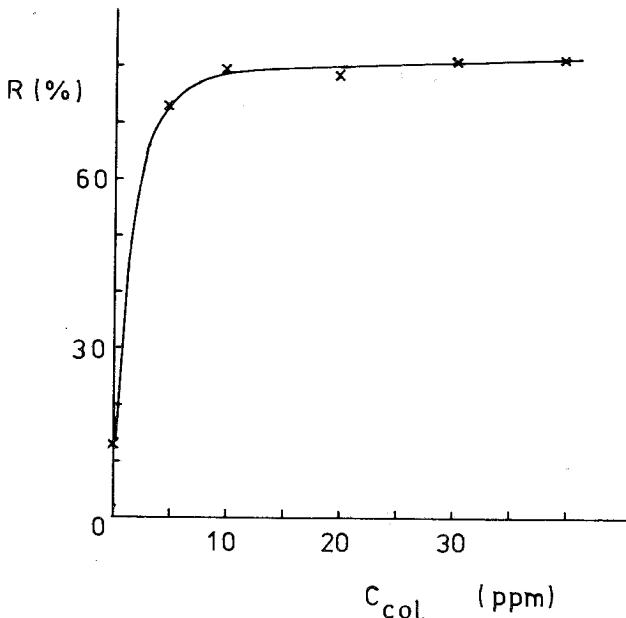


FIG. 3: Study of collector concentration on flotation recovery.



tion on dissolved-air flotation recovery. A 10 ppm concentration was separating 80% of calcite fines. It is accepted that the mechanism of fatty acids adsorption on salt-type minerals is predominantly by chemisorption in neutral and basic pH<sup>11</sup>.

Chemisorption, generally, helps to improve the flotation recovery of fine particles. This was explained<sup>13</sup> due to one or more of the following reasons: (a) Specific chemical interactions between the collector ion or molecule and metallic cation sites on the mineral surface, maintain the selectivity even at finer sizes. (b) Because of large free energies of adsorption in chemisorbing systems, the residual concentration of collector in solutions is lower, which results in lower reagent consumption. (c) If collector adsorption occurs by exchange or neutral molecule adsorption, the electrical charge on the mineral is lower leading to better recovery of fine particles. (d) Reduced adsorption of collector on bubble surfaces contributes to better recovery of fine mineral particles.

The next parameter tested was the pulp density. Satisfactory results, shown in Figure 4, of the order of 80% recovery, were observed with a pulp density of 2%.

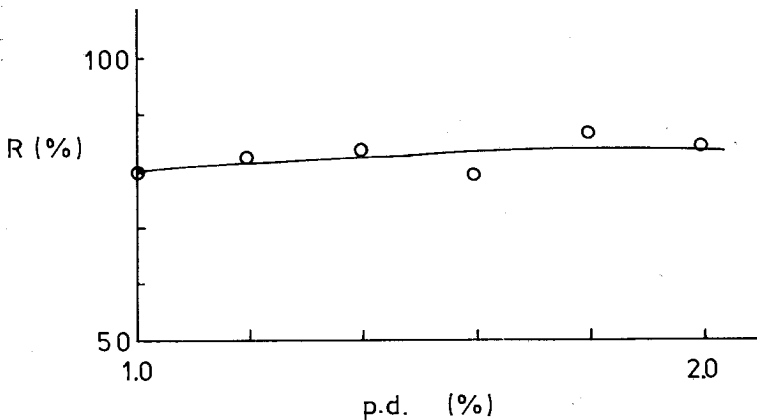


FIG. 4: *Effect of pulp density on calcite recovery.*

This might be a problem for the application of the process on industrial scale, particularly in places where there is scarcity of water.

Similar range of pulp density was also found for electrolytic flotation<sup>3</sup>, compared with an average pulp dilution of 15% solids in commercial nonmetallic circuits. Pulp densities of as high as 55% and as low as 8% solids have been mentioned for flotation separations<sup>14</sup>.

Figure 5 shows the experiments where the effect of conditioning time was tested. An optimum of 4 min was observed.

Because of the extremely complicated physico-chemico-mechanical conditions existing in the flotation process, the problems associated with the presence of fine particles are most pronounced in flotation processing. Attempts to develop theories which explain the slower flotation of fines have had limited success. A lower rate of attachment of particles to bubbles appears to be a contributing factor, but the relative contributions of the processes of collision and adhesion have not been resolved.

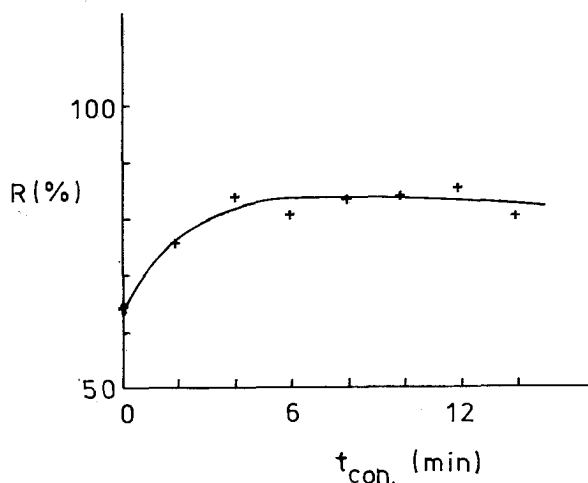


FIG. 5: Studying the conditioning time as a parameter.

The most plausible theory described the behaviour of fine particles in terms of their lower rate of collision with bubbles and their low particle momentum, which reduces the chance of adhesion. However, it must be stressed that this useful working hypothesis lacks experimental proof<sup>12</sup>.

Other postulates were found inconsistent either with the limited data available or else with relevant theoretical considerations. These included collision by diffusio-phoretic motion, attachment through rotation of angular particles, an increasing dynamic contact angle, older surfaces, increased solubility, increased surface stress, and an increased rate of adsorption. Certainly the whole problem of fines does not look simple at all.

Many researchers carried out investigations on the tenacity of attachment of particles to bubbles, measuring the contact angle and relating the size of bubbles to the floatability of particles. Volkova was one of the first in 1940 (quoted in reference 15), who actually worked with calcite. Her work has played a significant role in development of the theory of mineralization of bubbles in flotation. Volkava's experimental results, among others, showed that fine particles float better with fine bubbles.

In conclusion, the results on dissolved-air flotation for the processing and recovery of fine mineral particles are considered promising. It would be interesting to investigate the possibilities of this technique for the selective separation of minerals and in this area our work is continued.

## Περίληψη

*Δυνατότητα Εφαρμογής της Επίπλευσης Διαλυμένου Αέρα για την Ανάκτηση Λεπτών Σωματιδίων Ορυκτών*

Με την αυξανόμενη ζήτηση των ορυκτών και τη συνεχώς ελαττωνόμενη ποιότητα των κοιτασμάτων, το πρόβλημα της επεξεργασίας και εμπλουτισμού των λεπτών σωματιδίων

προβάλλει σήμερα έντονο. Στις εγκαταστάσεις εμπλουτισμού μεταλλευμάτων οι περισσότερες απώλειες αποδίδονται στα λεπτά σωματίδια, που είναι γενικά δύσκολο ν' ανακτηθούν. Το αυξανόμενο ενδιαφέρον των ερευνητών στρέφεται είτε στη βελτίωση παλιών γνωστών μεθόδων, είτε στην ανακάλυψη και μελέτη νέων. Διάφορες τεχνικές επίπλευσης έχουν δοκιμασθεί, αφού η κλασική αερο-επίπλευση παρουσιάζει τεχνολογικά και επιστημονικά προβλήματα σ' αυτό τον τομέα και θεωρείται μη οικονομική. Μια απ' αυτές τις δυνατότητες είναι και η επίπλευση διαλυμένου αέρα, που έχει καθιερωθεί στο πεδίο της τεχνολογίας του περιβάλλοντος και ως γνωστό παράγει μικρές φυσαλίδες αέρα. Στην εργασία εξετάζεται σαν υλικό λεπτός ασβεστίτης και οι παράμετροι που μελετήθηκαν ήταν ο χρόνος προοδοποίησης, η ανάμιξη, η συγκέντρωση συλλέκτη λιπαρού οξέος, η ανάκτηση, η πυκνότητα του πολφού και ο χρόνος επίπλευσης. Τα διάφορα προβλήματα που εμφανίζονται με την παρουσία των λεπτών σωματιδίων κατά την επίπλευση συζητούνται και αναλύονται.

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## **TIME DEPENDENT ADSORPTION AT THE INTERFACE BETWEEN A STATIONARY SPHERICAL ELECTRODE AND THE ELECTROLYTE SOLUTION**

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### **Summary**

The effect of diffusion on the rate of attainment of adsorption equilibrium is examined for the case of a stationary spherical electrode surface, by means of a time dependent expression for the electrode surface coverage. This expression is derived from the solution of the differential equation representing Fick's second law for symmetrical spherical diffusion.

The analysis is also extended to the derivation of equations which enable a time dependent isotherm analysis.

Application of literature data for the adsorption of naphthyl compounds on mercury reveals a satisfactory agreement between the experimental and calculated values of the free energy of adsorption, while the agreement between the experimental and the calculated adsorption isotherms is limited only to the potential of maximum adsorption.

**Key words:** Time, dependence, adsorption, stationary, electrode.

### **Introduction**

Time dependence of the interfacial behaviour of surface active substances is usually introduced either by a slow diffusion<sup>1</sup> or a slow adsorption<sup>2</sup> process. The case of a slow diffusion step towards a large variety of electrode surfaces, including plane, spherical, stationary, rotating and growing<sup>2-6</sup> electrodes is the most frequently encountered in practice.

Spherical symmetrical diffusion has been systematically studied<sup>7-8</sup> on a theoretical as well as experimental level for the case of diffusion of electroactive species.

Enough attention has been also given to the diffusion controlled adsorption of electroinactive substances on plane electrodes as well as on growing mercury drop electrodes<sup>2,9</sup>.

However the diffusion controlled adsorption of electroinactive substances, the so called surfactants, to a stationary spherical electrode, like the hanging mercury drop electrode (HMDE), has yet received no attention, although such a study should set the time effects on a quantitative basis. Such a study is attempted on a theoretical level at the first part of this work. Here equations are derived for the time dependen-

ce of the electrode coverage while adsorption isotherms are introduced into these equations.

At the second part, we use literature data<sup>10</sup> for the adsorption of naphthyl compounds on Hg in order to test the applicability of the expressions previously derived. Plots of surface coverage against time are calculated at various concentrations of the adsorbates and the calculated adsorption isotherms and the values of the standard free energy of adsorption are checked against experimental data.

### Symmetrical spherical diffusion of a surface active substance

It can be shown<sup>2,3,5</sup> that the fundamental differential equation describing symmetrical spherical diffusion of an electroactive substance to the surface of a spherical electrode is given by Fick's second law expressed in spherical coordinates:

$$\frac{\partial c_{(r,t)}}{\partial t} = D \left( \frac{\partial^2 c_{(r,t)}}{\partial r^2} + \frac{2}{r_0} \frac{\partial c_{(r,t)}}{\partial r} \right) \quad (1)$$

where  $c_{(r,t)}$  is the concentration of the diffusing substance, at a distance  $r$  from the center of the electrode,  $D$  is the diffusion coefficient and  $r_0$  is the electrode radius. Obviously this equation is also applicable to the case of the diffusion controlled adsorption of electroinactive species.

Equation (1) is analogue to the equation:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

for linear diffusion, except the term  $2/r_0(\partial c/\partial r)$  which accounts for the curvature of the diffusion plane.

The solution of (1) can be obtained under the following initial conditions:

at  $t=0$  and  $r=\infty$  (bulk)  $c = c^*$

at  $t=0$  and  $r=r_0$  (electrode surface)  $c = 0$

at  $t>0$  and  $r=r_0$   $c \neq 0$ , and it is given by:

$$\frac{\partial c_{(r,t)}}{\partial r} = c^* \left( \frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt}} \right) \quad (3)$$

If the first law of Fick is transformed to spherical coordinates then we obtain:

$$\frac{dn}{dt} = qD \frac{\partial c_{(r,t)}}{\partial r} \quad (4)$$

where  $q$  is the area of the electrode surface and  $n$  is the number of moles transported by diffusion.

Therefore from equations (3) and (4) we obtain:

$$\frac{dn}{dt} = Dqc^* \left( \frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt}} \right) \quad (5)$$

It is seen that eq. (5) is composed of a constant and a time dependent term.

The latter is the same as for linear diffusion. For large time values the steady state term predominates. Therefore the times required to reach the steady state, even with electrodes of large diameters are relatively short. As it is pointed out by Delahay<sup>11</sup> for the case of electrolysis current at a HMDE, the contribution of the steady state term is relatively small at the initial stage.

Therefore equations for linear diffusion are applicable to our case only when time is sufficiently short (a few seconds) and the radius of the electrode is not too small ( $r_0 > 0.05$  cm).

From (5) integrating between 0- $N_t$  and 0- $t$  we obtain:

$$N_t = Dgc^*(t \cdot r_0^{-1} + 2D^{-1/2}\pi^{-1/2}t^{1/2}) \quad (6)$$

where  $N_t$  is the number of moles diffusing to the electrode surface within time  $t$ . It is known<sup>4,9</sup> that the surface excess concentration of the adsorbate,  $\Gamma_t$ , is related to  $N_t$  by  $\Gamma_t = N_t/q$  (mole/cm<sup>2</sup>).

Therefore

$$\Gamma_t = Dc^*(t \cdot r_0^{-1} + 2D^{-1/2}\pi^{-1/2}t^{1/2}) \quad (7)$$

By means of equation (7) a relation can be established for the time dependence of the degree of the electrode coverage.

Since  $\theta_t = \Gamma_t/\Gamma_s$ , where  $\Gamma_s$  is the  $\Gamma$  value at saturation coverage, then:

$$\theta_t = (Dc^*r_0^{-1}t + 1.128D^{1/2}c^*t^{1/2})\Gamma_s^{-1} \quad (8)$$

where  $\theta_t$  is the time dependent value of the degree of the electrode coverage,  $\theta$ . This equation can be used for the calculation of the time dependence of the surface coverage, provided that  $D$ ,  $r_0$ ,  $c^*$  and  $\Gamma_s$  are given.

However the study of the interfacial behaviour of surfactants enters a quantitative level when the adsorption data are subjected to an isotherm analysis. Such an analysis can be enabled by introducing the adsorption isotherms into equation(8).

It is known that the adsorption isotherm can be generally represented by

$$\beta c^* = f(\theta)g(B_i; \theta) \quad (9)$$

where  $\beta$ ' is the adsorption equilibrium constant, in cm<sup>3</sup>/mole,  $f(\theta)$  is the configurational term standing for the entropy of mixing of the adsorbed species,  $g(B_i; \theta)$  is the energetic term which accounts for the interactions between the adsorbed particles<sup>12</sup> and  $B_i$  is the interaction parameter which depends on the certain adsorption isotherm used.

If (9) is written in the form  $\beta c = F(\theta, B_i)$  then we have:

$$\theta_t = (Dr_0^{-1}t + 1.128 D^{1/2}t^{1/2}) \beta^{-1} \Gamma_s^{-1} F(\theta, B_i) \quad (10)$$

The adsorption equilibrium constant is related to the standard free energy of adsorption by:

$$\beta = \frac{1}{c_s} \exp\left(-\frac{\Delta G_{\text{ads}}^0}{RT}\right) \quad (11)$$

where  $c_s$  is the concentration of the solvent in moles/lit.

Therefore we obtain:

$$\theta_t = (Dr_0^{-1}t + 1.128 D^{1/2}t^{1/2}) \Gamma_s^{-1} c_s \exp\left(\frac{\Delta G_{\text{ads}}^0}{RT}\right) F(\theta, B_i) \quad (12)$$

Thus when the corresponding pair values of  $\theta_t$  and  $t$  are determined by means of equation (8), we can obtain through equation (12) the  $\Delta G_{\text{ads}}^0$  vs  $\theta$  dependence.

Finally we must define the certain form of the  $F(\theta, B_i)$  term.

For the most commonly used isotherm for adsorption from solutions namely the Frumkin isotherm<sup>13</sup>, equation (10) takes the following form:

$$\theta_t = (Dr_0^{-1}t + 1.128 \cdot D^{1/2}t^{1/2}) \beta^{-1} \Gamma_s^{-1} \frac{\theta_e}{1-\theta_e} \exp(-2a\theta_e) \quad (13)$$

where  $a$  is the interaction parameter and  $\theta_e$  is the equilibrium surface coverage. It must be pointed out that the results obtained for  $\theta_t$  at any instant of time retain their physical meaning when the condition  $0 \leq \theta_t \leq 1$  is fulfilled. In other words equations (8) to (13) do not account for the formation of multimolecular films.

Another limitation of the above relations is that the  $\theta_t$  values are derived actually almost independently of the certain polarization conditions existing at the electrochemical system.

Nevertheless the effect of the electric field is indirectly introduced in equation (10) through the adsorption equilibrium constant  $\beta$ , which is known to depend on the electric variable (electrode potential or charge) of the system, however leading to very complicated expressions.

#### **Application to the adsorption of naphthyl compounds at the mercury-solution interface**

The applicability of the above outlined theory can be tested against experimental data for the adsorption of surface active substances derived from the literature. Our choice from the vast variety of the available data was guided by the need to know the values of the maximum surface excess concentration,  $\Gamma_s$  and of the corresponding diffusion coefficients.

The availability of these parameters enables us to verify to what extent our theoretical treatment is valid for the case of a stationary spherical Hg electrode, namely the hanging mercury drop electrode (HMDE).

On the basis of the experimental  $\Gamma_s$  and  $D$  values for *a*-naphthol, *a*-naphthaldehyde and *a*-naphthoic acid derived from ref. 10, provided in table I, we calculated the  $\theta_t$  vs  $t$  dependence for the above substances by means of equation (8).

TABLE I. Maximum surface excess and diffusion coefficient values (Taken from ref. 10)

Substance	$\Gamma_s \cdot 10^{10}$ mole/cm <sup>2</sup>	$D \cdot 10^6$ cm <sup>2</sup> /s
$\alpha$ -C <sub>10</sub> H <sub>7</sub> OH	2.8	6.7
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CHO	2.9	6.4
$\alpha$ -C <sub>10</sub> H <sub>7</sub> COOH	2.2	6.1

The radius used for the HMDE is taken equal to 0.1 cm, in agreement to Delahay's suggestions<sup>11</sup>.

In figures 1,2 and 3 the calculated  $\theta_t$  vs  $t$  plots for various concentrations of *a*-naphthol, *a*-naphthaldehyde and *a*-naphthoic acid are respectively provided.

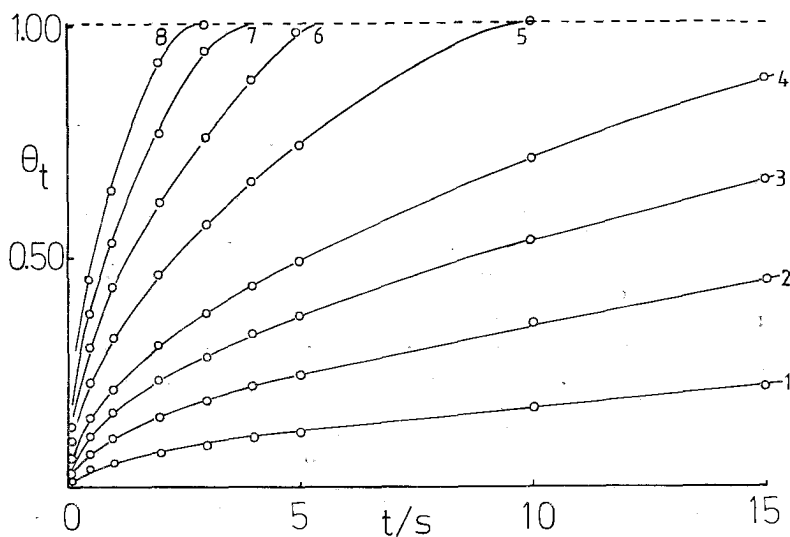


FIG. 1: Calculated  $\theta_t$  vs  $t$  curves of 0.1N HCl aqueous solutions in the presence of the following *a*-naphthol concentrations: 1)  $0.5 \cdot 10^{-5}$ , 2)  $1 \cdot 10^{-5}$ , 3)  $1.5 \cdot 10^{-5}$ , 4)  $2 \cdot 10^{-5}$ , 5)  $3 \cdot 10^{-5}$ , 6)  $4 \cdot 10^{-5}$ , 7)  $5 \cdot 10^{-5}$ , 8)  $6 \cdot 10^{-5}$  moles/l.



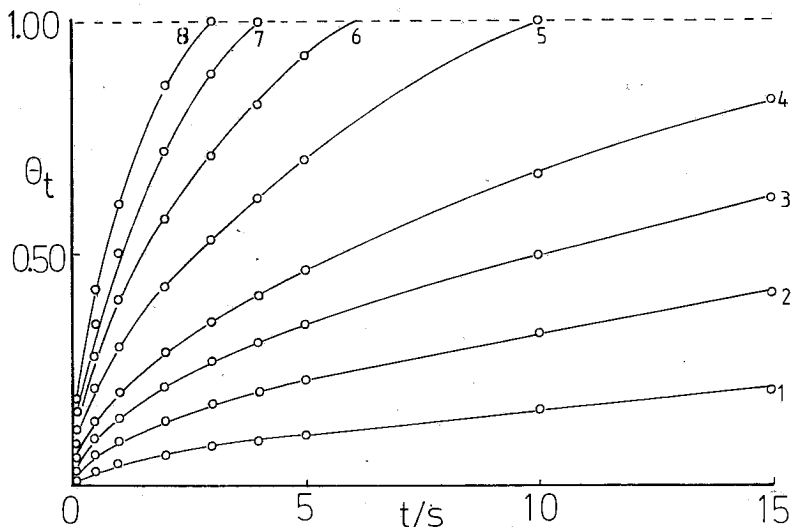


FIG. 2: Calculated  $\theta_t$  vs  $t$  curves of 0.1N HCl aqueous solutions in the presence of the following  $\alpha$ -naphthaldehyde concentrations: 1)  $0.5 \cdot 10^{-5}$ , 2)  $1 \cdot 10^{-5}$ , 3)  $1.5 \cdot 10^{-5}$ , 4)  $2 \cdot 10^{-5}$ , 5)  $3 \cdot 10^{-5}$ , 6)  $4 \cdot 10^{-5}$ , 7)  $5 \cdot 10^{-5}$ , 8)  $6 \cdot 10^{-5}$  moles/lt.

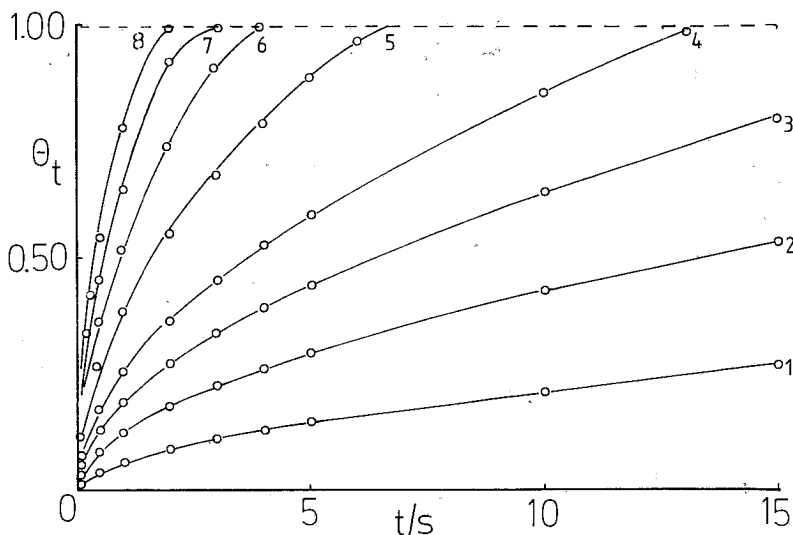


FIG. 3: Calculated  $\theta_t$  vs  $t$  curves of 0.1N HCl aqueous solutions in the presence of the following naphthoic acid concentrations: 1)  $0.5 \cdot 10^{-5}$ , 2)  $1 \cdot 10^{-5}$ , 3)  $1.5 \cdot 10^{-5}$ , 4)  $2 \cdot 10^{-5}$ , 5)  $3 \cdot 10^{-5}$ , 6)  $4 \cdot 10^{-5}$ , 7)  $5 \cdot 10^{-5}$ , 8)  $6 \cdot 10^{-5}$  moles/lt.

It is seen that for low enough concentrations ( $c^* < 2 \cdot 10^{-5} \text{M}$ ) equilibrium is slowly attained. At this concentration range it is also seen that the equilibrium surface coverages are markedly below the value  $\theta = 1$ . For higher concentrations saturation coverage is attained within short time intervals ( $\leq 10\text{s}$ ). It must be pointed that at this concentration range the increase of the exposition times, leads to values of  $\theta > 1$

which lack of physical meaning and they are produced by the inability of equation (8) to account for the formation of multimolecular layers. However the almost immediate attainment of the value  $\theta = 1$  for  $c^* > 3 \cdot 10^{-5} \text{M}$  makes these concentrations inappropriate for further calculations.

From the comparison of figures 1 to 3 conclusions are drawn about the adsorbability of these substances. Comparing the  $\theta_t$  values corresponding to certain time instances it is seen that  $\alpha$ -naphthaldehyde presents the higher adsorbability, followed by  $\alpha$ -naphthol and  $\alpha$ -naphthoic acid. This order is in agreement with our literature data<sup>10</sup>. However such a comparison is of a qualitative character.

A quantitative comparison of the adsorbabilities of these substances is enabled by means of the values of the adsorption equilibrium constant, contained in equation (10).

In order to facilitate our calculations we don't account for particle-particle interactions, thus assuming a Langmuirian<sup>13</sup> behaviour. Under these conditions, (10) takes the following form:

$$\theta_t = (Dr_0^{-1}t + 1.128D^{1/2}t^{1/2}) \beta^{-1} \Gamma_s^{-1} \frac{\theta_e}{1 - \theta_e} \quad (14)$$

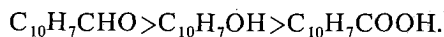
For the calculation of the values of  $\beta$ , we set the following requirements: concentrations must be limited below  $1.5 \cdot 10^{-5} \text{M}$  in order to obtain<sup>10</sup>  $\theta_e \leq 0.5$ , within reasonable time intervals ( $t < 50\text{s}$ ).

The calculated values of the adsorption equilibrium constant are provided in table II, together with the values of  $\Delta G_{\text{ads}}^0$  calculated by equation (11) and also the experimental values of  $\Delta G_{\text{ads}}^0$  taken from reference 10.

TABLE II. Adsorption equilibrium constants and standard free energies of adsorption for  $\theta_e = 0.25$  and  $T = 298 \text{ K}$ .

Substance	$\beta_{\text{calc.}} \cdot 10^{-4}$ cm <sup>3</sup> /mole	$(-\Delta G_{\text{ads}}^0)_{\text{calc.}}$ kcal/mole	$(-\Delta G_{\text{ads}}^0)_{\text{exp.}}$ (ref.10) kcal/mole
$\alpha$ -C <sub>10</sub> H <sub>7</sub> OH	2.89	8.46	8.80
$\alpha$ -C <sub>10</sub> H <sub>7</sub> CHO	4.33	8.70	9.00
$\alpha$ -C <sub>10</sub> H <sub>7</sub> COOH	1.86	8.20	8.60

It is again seen that the adsorbability follows the order:



We must also point out the reasonable agreement between the calculated and the experimental values of  $\Delta G_{\text{ads}}^0$ .

The fact that the calculated values are systematically lower than the experimental ones must be attributed to the Langmuirian behaviour assumed that is to the fact that the interaction between the adsorbed particles was not taken into account.

Finally the  $\theta$  vs  $c$  adsorption isotherms were calculated by means of eq (8) at various time instants and they are comparatively provided in figure 4 together with the corresponding experimental ones.

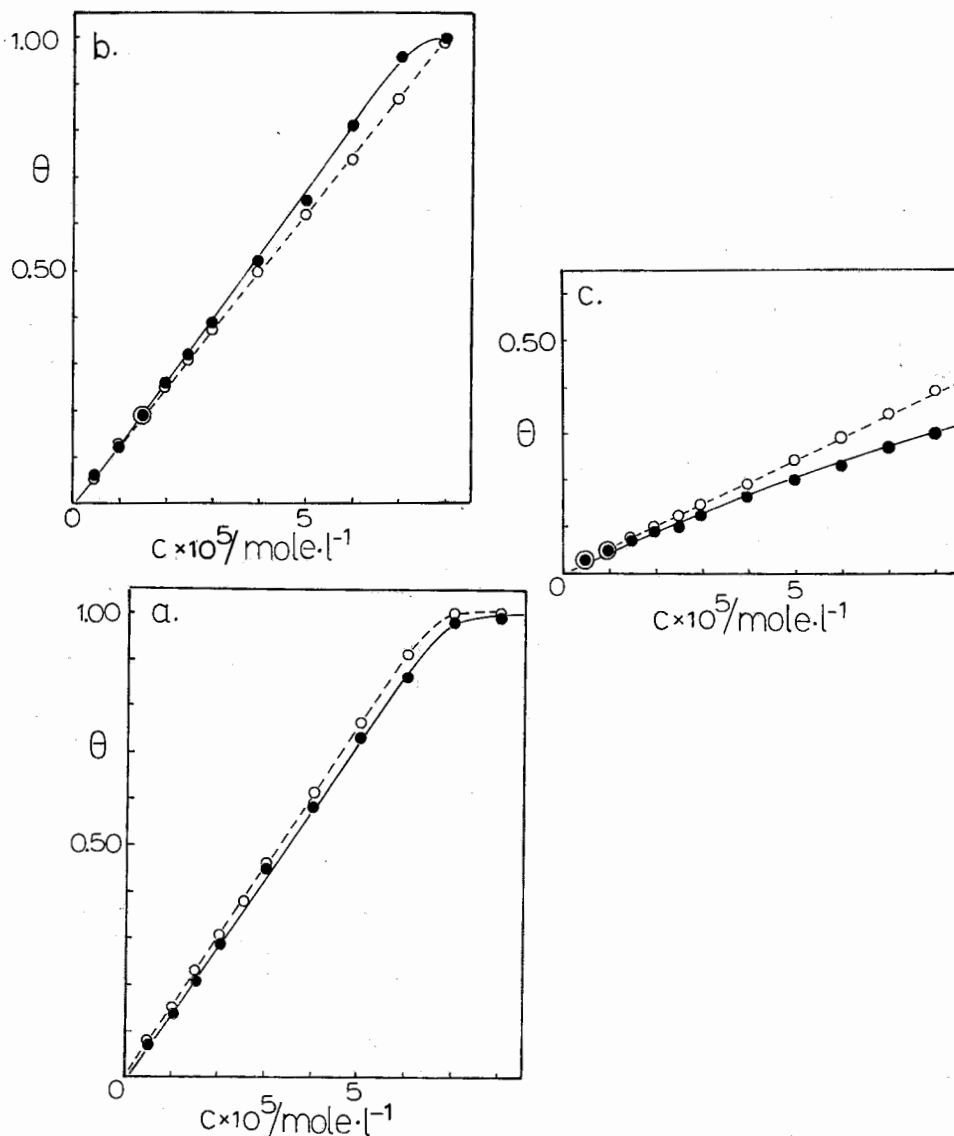


FIG. 4. Experimental adsorption isotherms (solid lines) of a-naphthol (a), a-naphthaldehyde (b) and a-naphthoic acid (c) at  $E=0.4$  V(SCE) in 0.1N HCl aqueous solutions, according to reference 10. Broken lines represent adsorption isotherms at  $t=2s$  (a),  $t=2s$  (b) and  $t=0.15s$  (c) calculated by means of equation (8).

It is seen that although eqn. (8) does not account for the polarization conditions existing at the interface, we can establish a satisfactory agreement by changing the exposition times. This is achieved only for the potential of maximum adsorption of the

substances studied, which is located<sup>10</sup> at  $-0.4V/SCE$ . Therefore in figure 4 we see that a fairly satisfactory agreement is obtained for a-naphthol and a-naphthaldehyde for  $t=2s$ .

For a-naphthoic acid at  $t=0.15s$  the agreement is less satisfactory. At other potentials no agreement was detected.

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## Περίληψη

*Επίδραση της διάχυσης στο ρυθμό επίτευξης της ισορροπίας προσρόφησης για την περίπτωση ενός στατικού σφαιρικού ηλεκτροδίου.*

Στην παρούσα εργασία μελετάται η επίδραση που έχει η διάχυση πάνω στο ρυθμό επίτευξης της ισορροπίας προσρόφησης για την περίπτωση ενός στατικού σφαιρικού ηλεκτροδίου.

Παράγεται μία χρονικά εξαρτώμενη εξίσωση για το ποσοστό επικάλυψης της ηλεκτροδιακής επιφανείας, μέσω της επίλυσης της διαφορικής εξίσωσης του 2ου νόμου του Fick, εκφρασμένης σε σφαιρικές συντεταγμένες.

Η ανάλυση επίσης περιλαμβάνει και την παραγωγή εξισώσεων οι οποίες επιτρέπουν μία χρονικά εξαρτώμενη εφαρμογή των ισοθέρων προσρόφησης.

Η εφαρμογή βιβλιογραφικών δεδομένων για την προσρόφηση των ουσιών α-ναφθόλη, α-ναφθαλδεύδη και α-ναφθοϊκό οξύ στον υδράργυρο, αναδεικνύει την ύπαρξη ικανοποιητικής συμφωνίας ανάμεσα στις υπολογιζόμενες και τις βιβλιογραφικές τιμές της πρότυπης ελεύθερης ενέργειας προσρόφησης. Ευρίσκεται επίσης ικανοποιητική συμφωνία ανάμεσα στις υπολογιζόμενες και τις πειραματικές ισόθερμες προσρόφησης μόνο όμως για αρνητικά δυναμικά και ειδικά για το δυναμικό μέγιστης προσρόφησης των ουσιών αυτών.

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## **$\gamma$ -RADIOLYSIS OF SOME OESTROGEN HORMONES IN ALKALINE SOLUTIONS**

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### **Summary**

Some oestrogens were studied by  $\gamma$ -radiolysis in alkaline solutions. The influence of the substituents of the five member D ring of the Oestrogen's framework was investigated. The reaction rate constants of the hormones with the oxidizing and reducing species were determined and found to be:

$$k_{O^{\cdot-} + \text{Oestradiol}} = (3.33 \pm 0.11) \times 10^9 \text{M}^{-1}\text{s}^{-1},$$

$$k_{O^{\cdot-} + \text{Oestriol}} = (4.55 \pm 0.19) \times 10^9 \text{M}^{-1}\text{s}^{-1},$$

$$k_{O^{\cdot-} + 17\alpha\text{-Ethynyloestradiol}} = (6.71 \pm 0.20) \times 10^9 \text{M}^{-1}\text{s}^{-1},$$

$$k_{e_{\text{aq}}^{\cdot-} + \text{Oestradiol}} = (2.42 \pm 0.20) \times 10^{10} \text{M}^{-1}\text{s}^{-1},$$

$$k_{e_{\text{aq}}^{\cdot-} + \text{Oestriol}} = (2.35 \pm 0.15) \times 10^{10} \text{M}^{-1}\text{s}^{-1},$$

$$k_{e_{\text{aq}}^{\cdot-} + 17\alpha\text{-Ethynyloestradiol}} = (2.60 \pm 0.20) \times 10^{10} \text{M}^{-1}\text{s}^{-1}.$$

**Key words:** Oestrogens/Radiolysis/rate constants/oxidation/reduction

### **Introduction**

The role of oestrogens hormones in the living organism is of great importance. Thus, the knowledge of their reactivity toward oxidation-reduction agents helps to understand their transformation mechanism in the cellular system. In order to follow these reactions in various systems several methods have been reported<sup>1,2,3</sup>.

We have tried to elucidate the influence of the two distinct functional groups of the oestrogenic A and D rings on the rate constant of the reaction of  $O^{\cdot-}$  radical-ions and  $e_{\text{aq}}^{\cdot-}$ , produced by  $\gamma$ -radiolysis of alkaline solutions with the oestrogen molecule. We have irradiated oestrogen hormones under conditions where only  $O^{\cdot-}$  radical-ions or  $e_{\text{aq}}^{\cdot-}$  were present, and we calculated the corresponding rate constants.

### **Materials and Methods**

The hormones used were Merck or Serva, biochemical purity. All experiments were carried out using compounds of the same lot number without any further purification.

Recrystallized Safranin T [further in the text as (S)] (trade name of 3,6-diamino-2,7-dimethyl-10-phenylphenazonium chloride) was Merck's für Mikroskopie und Bakteriologie.

Solutions were deaerated by flashing Ar or N<sub>2</sub>O before irradiation and they were scrubbed with V<sup>2+</sup>. Irradiations were carried out using a <sup>60</sup>Co γ-irradiation source (~700Ci) with a dose rate of ~900 rad min<sup>-1</sup>. Dosimetry was performed with the Fricke dosimeter, using GFe<sup>3+</sup> = 15.6.

Experiments were carried out by irradiating the deaerated aqueous oestrogen solutions in air tight spectrophotometric cells. Changes of the optical density (O.D.) before and after irradiation were followed on a Perkin-Elmer 551 spectrophotometer.

In some experiments Safranin T was added as a competitor to the oestrogens solutions. The spectrum of (S) was the same in alkaline, neutral or slightly acid solutions. The determination of the dye concentration was measured spectrophotometrically using the reported<sup>4,5</sup> calibration curve at 520 nm and the ε value of 43333 M<sup>-1</sup>cm<sup>-1</sup>.

## Results and discussion

The absorption maxima and the ε of the studied hormones were found as listed in Table I.

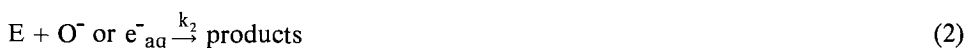
TABLE I. Maximum wavelength and ε of hormone alkaline solutions

Oestrogens	$\lambda_{max}$ (nm)	$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )
Oestrone	292, 240	2940, 9290
Oestradiol	297, 239	2680, 8503
Oestriol	297, 239	2963, 9245
17 $\alpha$ -Ethinyl-oestradiol	296, 233	2756, 9380

The most important reactive groups of oestrogen's molecule are the phenolic A ring and the substituents of the five carbon D ring.

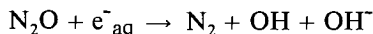
Using Safranin T as reference system the competition of hormones and (S) for the reducing and oxidizing species was followed. It is reported<sup>6,7</sup> that HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> do not react with the dye which is also stable<sup>1</sup> in high pHs.

Considering that the reactions (1) and (2) take place between (S) and (E) and k<sub>1</sub> is known, the unknown k<sub>2</sub> can be calculated.

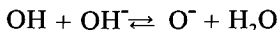


**Reaction of Oestrogens with O<sup>-</sup> radical-ions,**

It has been established that e<sup>-</sup><sub>aq</sub> are transformed to OH via the reaction:



It is also known that at high pHs' the OH radical dissociates:



with a pK = 11.9<sup>8</sup>.

The reaction of O<sup>-</sup> radical-ion with oestrogens was studied following the UV-Vis spectra of irradiated alkaline solutions, added with (S) as competitor, and saturated with N<sub>2</sub>O. Thus, the disappearance of (S), by measuring the G(-S), served to follow the competition of the two substances for the O<sup>-</sup>.

The final products do not interfere in the spectrophotometric determination of (S). As shown in Fig. (1), G(-S) results asymptotically to a constant non-zero value

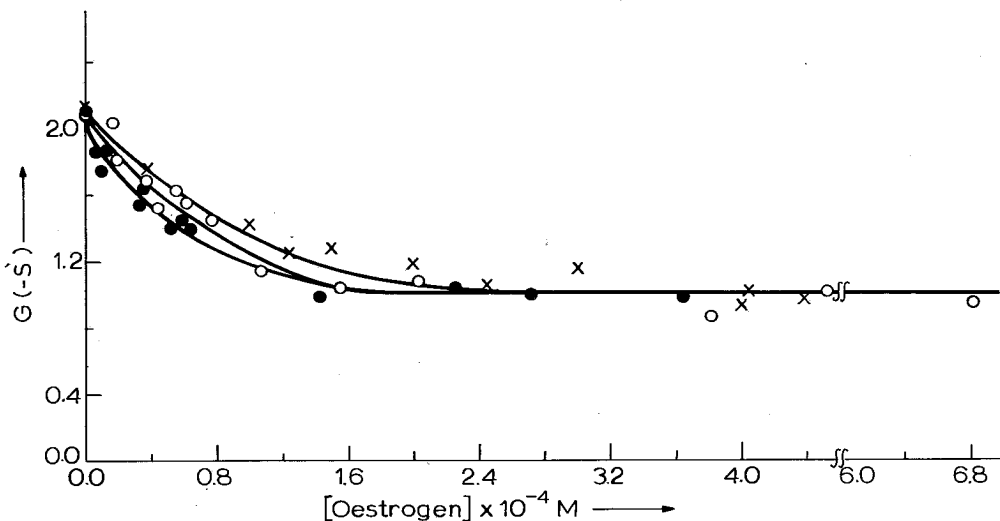


FIG. 1: Safranine T disappearance as a function of oestrogen concentration. [S] ~ 2.5 × 10<sup>-4</sup> M, N<sub>2</sub>O-saturated, pH = 13. ● Oestradiol, ○ Oestriol, × 17α-Ethinyloestradiol.

at «infinite» oestrogen concentration. Considering the competition between reactions (1) and (2), equation (3) was obtained:

$$\frac{1}{(G(-S) - A)} = \frac{1}{(1/3G_{OH} - A)} + \frac{1}{(1/3G_{OH} - A)} \cdot \frac{k_2[E]}{k_1[S]} \tag{3}$$

where A is the extrapolated constant value of G(-S) at «infinite» oestrogen's concentration, and [E], [S] are the concentrations of oestrogen and safranine T, respectively. The A values were measured in each case from Fig. 1. As shown in Fig. 2, the

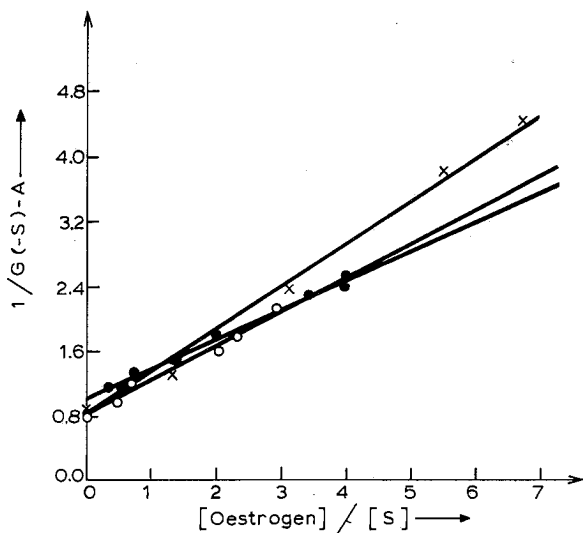


FIG. 2. Variation of  $1/G(-S)-A$  as function of oestrogen concentration.  $[S] \sim 2.5 \times 10^{-4} M$ ,  $N_2O$ -saturated,  $pH = 13$ . ● Oestradiol, ○ Oestriol, ×  $17\alpha$ -Ethynloestradiol.

plots of  $1/|G(-S)-A|$  vs  $\{E\}/\{S\}$  are linear, as expected. It is found that the oxidation of (S) in alkaline solution is a three one-electron equivalent processes.

From the plot of Fig. 2 we calculated the slopes in each case, and using  $G_{OH} = 6.3$  (the sum of the G values of oxidizing and reducing species), with  $k_1 = k_{O^+S} = 9.3 \times 10^9 M^{-1}s^{-1}$  and with the A values measured as above, we found the rate constants  $k_2 = k_{O^+Oestrogen}$ .

TABLE II. Rate constants of the reactions of the studied hormones in alkaline solutions.

Oestrogen	$k_{O^+Oestrogen}$ $\times (10^9 M^{-1}s^{-1})$	$k_{e_{aq}^+Oestrogen}$ $\times (10^{10} M^{-1}s^{-1})$
Oestrone <sup>1</sup>	$2.12 \pm 0.32$	—
Oestradiol	$3.33 \pm 0.11$	$2.42 \pm 0.20$
Oestriol	$4.55 \pm 0.19$	$2.35 \pm 0.20$
$17\alpha$ -Ethynyl-oestradiol	$6.71 \pm 0.20$	$2.60 \pm 0.20$

Considering that the A ring is the same for all investigated oestrogens, we can conclude that the substituents of the D ring influence the oxidation rate of the hormone molecule.



**Reaction of Oestrogens with  $e^-_{aq}$**

Using the same competition technique we can calculate the rate constants of  $e^-_{aq}$  with oestrogens. Using as reference electron scavenger the complex  $\{Co(en)_3\}^{3+}$  (where  $(en) = NH_2CH_2CH_2NH_2$ ), and  $k_{e^-_{aq} + \{Co(en)_3\}^{3+}} = 7.3 \times 10^{10} M^{-1}s^{-1}$ <sup>9</sup>, we recalculated the  $k_{e^-_{aq} + S} = 4.88 \times 10^{10} M^{-1}s^{-1}$  which is very close to the reported<sup>10</sup> value.

The competition curves of Safranin T and oestrogens for  $e^-_{aq}$  for the irradiations carried out in Ar-saturated solutions with 0.5M t-butanol present, are given in Fig. 3.

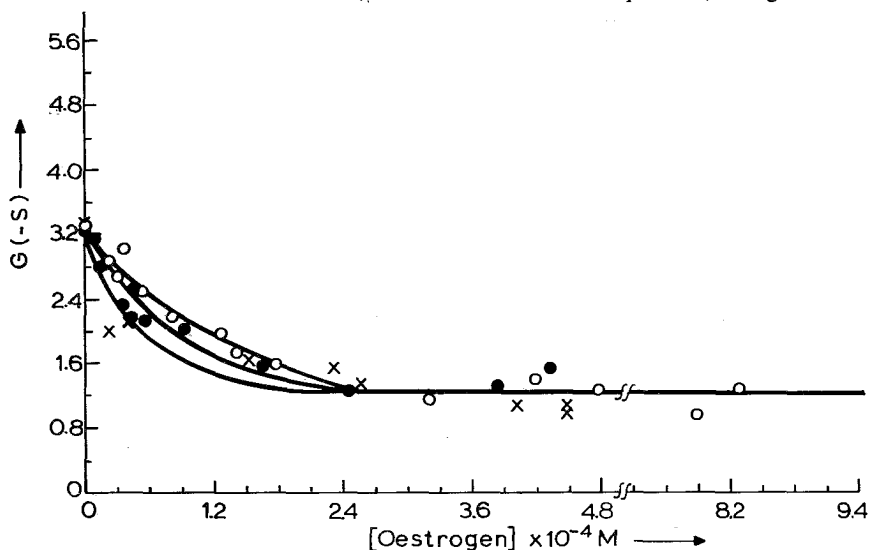


Fig. 3: Safranin T disappearance as a function of oestrogen concentration.  $[S] \sim 2.5 \times 10^{-4} M$ , Ar-saturated, pH = 13, 0.5M t-Butanol. ● Oestradiol, ○ Oestriol, × 17α-Ethinyloestradiol.

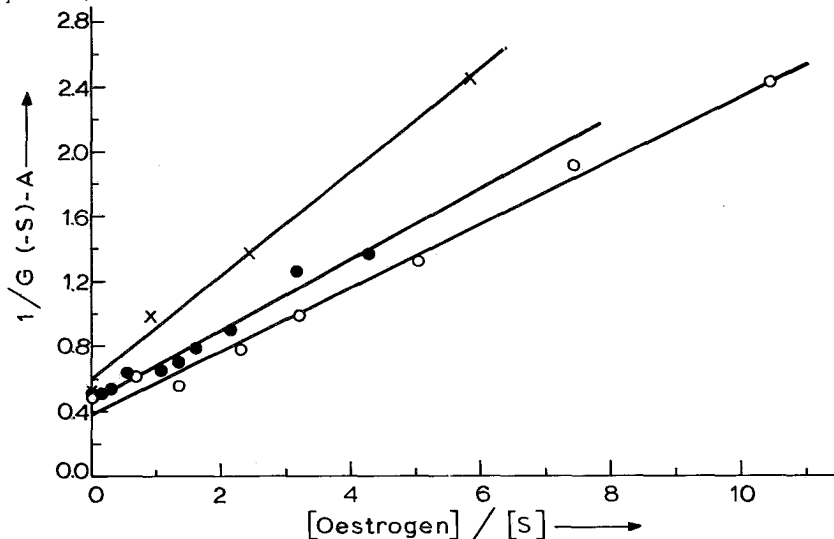


FIG. 4: Variation of  $1/G(-S)-A$  as a function of oestrogen concentration.  $[S] \sim 2.5 \times 10^{-4} M$ , Ar saturated, pH = 13, 0.5M t-Butanol. ● Oestradiol, ○ Oestriol, × 17α-Ethinyloestradiol.

The reduction of (S) by  $e^-_{aq}$  is an one electron equivalent process and equation (3) is transformed to (4).

$$\frac{1}{(G(-S)-A)} = \frac{1}{(Ge^-_{aq}-A)} + \frac{1}{(Ge^-_{aq}-A)} \cdot \frac{k_2[E]}{k_1[S]} \quad (4)$$

The experimental results are shown in Fig. 4. From the slopes of this Figure  $Ge^-_{aq} = 3.3$ , and from Fig. 3  $A = 1.2$ ,  $k_2 = k_{e^-_{aq} + \text{oestrogen}}$  was calculated.

The similar rate constants of the reducing species with the investigated hormones may be connected with the fact that the attack takes place at a common site of the molecules, i.e., the phenolic A ring, or at least, that the rate determining step for the reduction is the same in all cases. It also may mean that, contrary to the oxidizing species attack, the substituents of D ring have no influence in this case.

## Περίληψη

*γ- Ραδιόλυση μερικών Οιστρογόνων Ορμονών σε αλκαλικά διαλύματα*

Μελετήθηκαν μερικές Οιστρογόνες Ορμόνες σε αλκαλικά διαλύματα με  $\gamma$ -ραδιόλυση.

Ερευνήθηκε η επίδραση υποκαταστατών στον πενταμελή D δακτύλιο του στεροειδούς σκελετού. Προσδιορίστηκαν οι σταθερές ταχύτητας αντιδράσεως των οιστρογόνων ορμονών με τις οξειδωτικές και αναγωγικές ρίζες.

## Acknowledgements

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## ΠΑΡΑΓΩΓΗ ΜΟΝΟΥΔΡΟΞΥΣΤΕΑΤΙΚΩΝ ΟΞΕΩΝ ΜΕ ΥΔΡΟΧΛΩΡΙΩΣΗ ΤΟΥ ΕΛΑΪΚΟΥ ΟΞΕΟΣ

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(Παρελήφθη 28 Φεβρουαρίου 1985)

### Περίληψη

Για την παραγωγή μονοϋδροξυστεατικών οξέων από ελαϊκό οξύ αναπτύχθηκε η παρακάτω μέθοδος, που περιλαμβάνει δύο βασικές χημικές διεργασίες: i) την προσθήκη αερίου υδροχλωρίου υπό πίεση στο διπλό δεσμό του ελαϊκού οξέος, που οδήγησε σε χλωροστεατικό οξύ με υψηλή απόδοση 95% και ii) την υδρόλυση σε αυτόκλειστο του προϊόντος προσθήκης με υδατικά αλκαλικά διαλύματα, που έδωσε μίγματα με μέγιστη περιεκτικότητα σε μονοϋδροξυστεατικά οξέα 50%. Μια σειρά φυσικοχημικών προσδιορισμών εφαρμόστηκε για την ποιοτική και ποσοτική εξέταση των προϊόντων των αντιδράσεων (αριθμός ιωδίου, αριθμός υδροξυλίων, αριθμός οξύτητας, προσδιορισμός χλωρίου, σ. τήξεως, αέριος χρωματογραφία).

**Λέξεις κλειδιά:** μονοϋδροξυστεατικό οξύ, ελαϊκό οξύ, υδροχλωρίωση, σαπωνοποίηση.

### Εισαγωγή

Μια σύγχρονη τάση στη σύνθεση βιοαποικοδομήσιμων επιφανειακά ενεργών ουσιών<sup>1</sup>, που σήμερα παράγονται κυρίως από το πετρέλαιο, είναι η χρησιμοποίηση φυτικών ανανεώσιμων πρώτων υλών, όπως είναι τα φυτικά έλαια. Η ευθείας αλυσίδας αλκυλομάδα των ανωτέρων λιπαρών οξέων, βασικών συστατικών των τριγλυκεριδίων, θα μπορούσε να αποτελέσει το υδρόφοβο τμήμα ενός αμφίφιλου μορίου<sup>2</sup>. Επειδή όμως στην πλειοψηφία τους τα λιπαρά οξέα των φυτικών ελαίων περιέχουν στο μόριό τους μεγάλο αριθμό ατόμων άνθρακα (14-18), κατέχουν έντονα υδρόφοβο (λιπόφιλο) χαρακτήρα. Μείωση του υδρόφοβου χαρακτήρα μπορεί να επιτευχθεί με την εισαγωγή υδρόφιλων ομάδων στο μέσον της υδρόφοβης αλυσίδας<sup>3,4,5</sup>. Στην περίπτωση του ελαϊκού οξέος (18 άτομα C στο μόριο) απαιτείται η ελάττωση της υδροφοβικότητας, ώστε το τασιενεργό που θα προκύψει από την προσθήκη σ' αυτό ενός υδρόφιλου τμήματος να έχει τις επιθυμητές ιδιότητες που χαρακτηρίζουν τις επιφανειακά ενεργές ενώσεις π.χ. υδατοδιαλυτότητα, κατάλληλη αναλογία υδρόφιλου προς υδρόφοβο τμήμα (HLB) κλπ.

Είναι γνωστό ότι η σημασία των πυρηνελαίων στο χώρο των απορρυπαντικών υλών, έχει αισθητά μειωθεί από τη σε μεγάλο βαθμό αντικατάσταση των κοινών σαπωνιών από τις συνθετικές απορρυπαντικές ύλες. Η χρησιμοποίησή τους για παρα-

γωγή βιοαποικοδομήσιμων συνθετικών επιφανειακά ενεργών ουσιών θεωρείται ότι θα αποτελούσε μια σημαντική αξιοποίηση του εγχωρίου αυτού προϊόντος.

Σκοπός της παρούσας εργασίας ήταν η ανάπτυξη νέων τεχνολογικών μεθόδων για αναβάθμιση των ελαίνων, με τη μετατροπή του κύριου συστατικού τους, του ελαϊκού οξέος σε υδροξυλιωμένα παράγωγα του στεατικού οξέος παρόμοια του πολύτιμου 12-υδροξυστεατικού οξέος, που παράγεται από το κικινέλαιο (castor Oil-φυσικό προϊόν με υψηλή οικονομική σημασία).

Η προσθήκη υδραλογόνων στο διπλό δεσμό των μονοακορέστων οξέων που συνοδεύεται από σαπωνοποίηση αποτελεί γενική μέθοδο της σχετικής βιβλιογραφίας για παρασκευή υδροξυοξέων και οδηγεί σε μίγμα μονοϋδροξυοξέων, ακορέστων και λακτονών<sup>6,7</sup>. Ας σημειωθεί ότι η υδροχλωρίωση του ελαϊκού οξέος έχει πολύ λίγο μελετηθεί. Στη βιβλιογραφία αναφέρονται ερευνητικές προσπάθειες με χρησιμοποίηση διαφόρων διαλυτών και καταλυτών<sup>8,9,10</sup>. Όσον αφορά τη σαπωνοποίηση, χαμηλές αποδόσεις υδροξυ-οξέων αναφέρονται στη βιβλιογραφία κατά την αντίδραση αλογονωμένων παραγώγων του παλμιτικού οξέος με υδροξείδιο του καλίου<sup>6</sup>, ενώ η συγκεκριμένη υδρόλυση δεν έχει μελετηθεί στις συνθήκες της παρούσας εργασίας.

### Πειραματικό μέρος

α. *Υλικά που χρησιμοποιήθηκαν.* Ελαϊκό οξύ (pure Merck Art 471) ΑΙ: 90 (μέση περιεκτικότητα σε ελαϊκό οξύ 85%)  
 – Υδροχλώριο αέριο (χημικά καθαρό, άνυδρο).  
 – Θεϊκό οξύ (Merck 96-98%)  
 – Υδροξείδιο του νατρίου (pure Merck)  
 – Πετρελαϊκός αιθέρας (Merck DAB 7 ειδ. βάρος: 0,66 σ. ζέσεως: 40-60°C).  
 – Τα αντιδραστήρια, που χρησιμοποιήθηκαν στους χημικούς προσδιορισμούς αρ. ιωδίου κατά Wijs, αρ. οξύτητας, αρ. υδροξυλίων, αναφέρονται στις πρότυπες μεθόδους<sup>11</sup>. Για τον προσδιορισμό της περιεκτικότητας σε χλώριο σε οργανικές ενώσεις χρησιμοποιήθηκαν τα αντιδραστήρια της μεθόδου Schöniger<sup>12</sup>.

β. *Όργανα που χρησιμοποιήθηκαν* – Για την υδροχλωρίωση του ελαϊκού οξέος χρησιμοποιήθηκε αυτόκλειστο, χωρητικότητας 468ml, από ανοξείδωτο χάλυβα, εφοδιασμένο με μανόμετρο και με θερμόμετρο, που έφερε πλάγια οπή για την τροφοδότηση του αερίου υδροχλωρίου. Η αντίδραση διεξαγόταν σε γυάλινο κύλινδρο με εξωτερική διάμετρο 40 mm, εσωτ. διάμετρο 37 mm, μήκος 27 cm που κατέληγε σε κώνο ύψους 1,5 cm.

– Για τη σαπωνοποίηση του χλωροστεατικού οξέος χρησιμοποιήθηκε αυτόκλειστο, χωρητικότητας 1 lt, από ανοξείδωτο χάλυβα εφοδιασμένο με σύστημα ανάδευσης, μανόμετρο, θερμαντικό μανδύα, θερμόμετρο και αυτόματο σύστημα ελέγχου της θερμοκρασίας.

– Για την ανάλυση των προϊόντων χρησιμοποιήθηκε η συσκευή Schöniger<sup>12</sup> (προσδιορισμός χλωρίου) και αέριος χρωματογράφος (Perkin Elmer). Το λιπαρό μίγμα μετά τη σαπωνοποίηση εστεροποιήθηκε για την παρασκευή των μεθυλεστέρων των λιπαρών οξέων, που αναλύθηκαν στο χρωματογράφο σε συνθήκες: Θερμοκρασία στήλης 210°C, πληρωτικό υλικό APIEZON L (20%) σε Chromosorb W, πίεση αερίου (He) 1,3Kp/cm<sup>2</sup>.

γ. *Διαδικασία υδροχλωρίωσης-σαπωνοποίησης* Τροφοδοτούσαμε το αυτόκλειστο με

υδροχλώριο, που αντιδρούσε με το περιεχόμενο ελαϊκό οξύ (0.5 mole). Πραγματοποιήθηκαν υδροχλωρώσεις με συνεχή τροφοδοσία υδροχλωρίου (σταθερή πίεση) και με ασυνεχή τροφοδοσία υδροχλωρίου (μεταβαλλόμενη πίεση). Μελετήθηκε η απόδοση της αντίδρασης σε προϊόν προσθήκης. Για το διαχωρισμό της λιπαρής φάσης εφαρμόστηκε εκχύλιση του μίγματος της αντίδρασης με πετρελαϊκό αιθέρα, πλύση με αποσταγμένο νερό και απόσταξη του διαλύτη υπό κενό. Η απόδοση της αντίδρασης μετρήθηκε με προσδιορισμό του αριθμού ιωδίου (ακορεστότητα) με τη μέθοδο Wijs και με προσδιορισμό του χλωρίου με τη μέθοδο Schöniger. Το προϊόν προσθήκης μετά την ανακρυστάλλωση από διαιθυλαιθέρα έδειξε σ. τήξεως 40°-41°C, Α.Ι.:1,1, Α.Ο:176,5, περιεκτικότητα σε χλώριο 10,9%.

Το κορεσμένο προϊόν από τη διεργασία της υδροχλωρίωσης μεταφέρθηκε στο αυτόκλειστο της σαπωνοποίησης για να υδρολυθεί σε συνθήκες: αναλογία moles χλωροστεατικού οξέος προς καυστικό νάτριο 1:3,2, διαλύματα NaOH: 7% και 10%, θερμοκρασίες 125-200°C, χρόνοι 5-20 ώρες. Μετά το τέλος της αντίδρασης προσθέταμε αραιό διάλυμα θειϊκού οξέος 15% κ.ο. για το διαχωρισμό της οργανικής φάσης. Το λιπαρό μίγμα συγκεντρωνόταν στην επιφάνεια, εκχυλιζόταν με διαλυτικό μέσον και ακολουθούσαν εκπλύσεις με θερμό αποσταγμένο νερό μέχρι τελικά τα εκπλύματα να δείχνουν ουδέτερη αντίδραση. Για τη διευκόλυνση του διαχωρισμού των φάσεων προστέθηκε διάλυμα NaCl 10% κ.β. Τέλος το εκχυλιστικό μέσον (πετρ. αιθέρας) αποσταζόταν υπό κενό.

Στο λιπαρό μίγμα της αντίδρασης προσδιοριζόταν ο αριθμός ιωδίου, ο αριθμός υδροξυλίων, η περιεκτικότητα σε χλώριο για την εκτίμηση της περιεκτικότητας των ακόρεστων οξέων (ελαϊκό οξύ-αφυδραλογόνωση), των υδροξυστεατικών οξέων και του χλωροστεατικού οξέος, που δεν υδρολύθηκε, αντιστοίχως. Χρωματογραφική ανάλυση σε αέριο χρωματογράφο, μετά τη μετατροπή των λιπαρών οξέων στους αντίστοιχους μεθυλεστέρες, συμπλήρωνε την εξέταση της ποιοτικής και ποσοτικής σύστασης του λιπαρού μίγματος. Για την παραλαβή των υδροξυστεατικών οξέων εφαρμόστηκε ανακρυστάλλωση από διαιθυλαιθέρα.

### Αποτελέσματα και συζήτηση

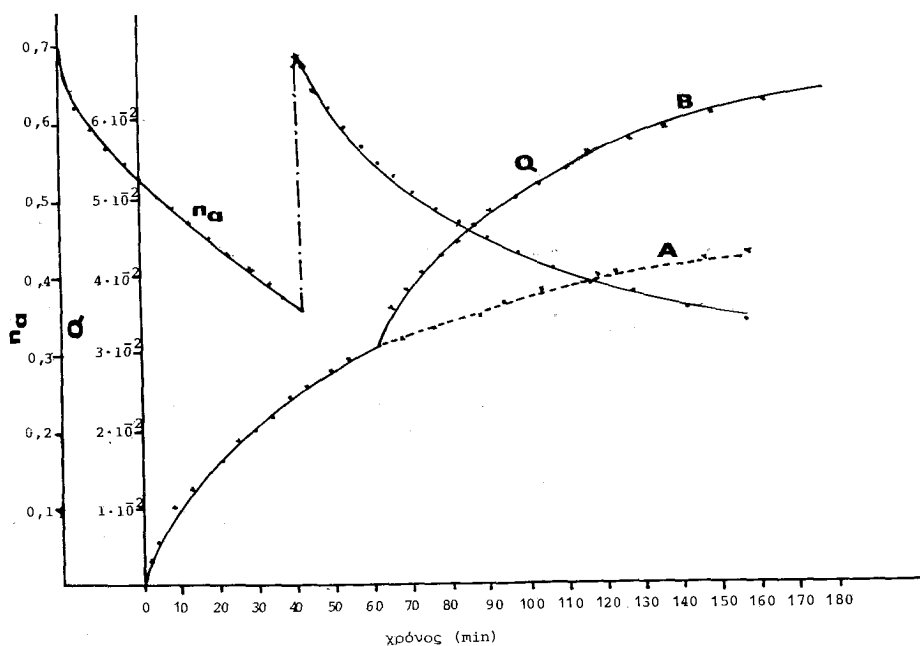
*Υδροχλωρίωση του ελαϊκού οξέος.* Η πορεία της υδροχλωρίωσης του ελαϊκού οξέος με σταθερή πίεση HCl 40 atm δίνεται στον Πίνακα I μέσα από τη μεταβολή της σύ-

ΠΙΝΑΚΑΣ I: Μετατροπή του ελαϊκού οξέος σε χλωροστεατικό οξύ κατά την υδροχλωρίωση με σταθερή πίεση 40 atm

Χρόνος αντιδράσεως t σε min	Αριθμός Ιωδίου κατά Wijs	Μετατροπή ελ. οξ. %	Cl %	Χλωροστεατικό οξύ (%)
30	78,9	12,3	1,3	11,7
60	64,3	28,5	3,1	27,9
90	55,5	38,3	4,3	38,6
120	42,9	52,3	5,7	51,2
150	29,1	67,7	7,5	67,4
180	17,6	80,4	8,8	79,3
210	9,5	89,4	10,1	90,1
240	2,5	97,2	10,6	95,5

στασης του αντιδρώντος μίγματος. Η μετατροπή του ελαϊκού οξέος σε χλωροστεατικό οξύ ανήλθε σε ποσοστό ανώτερο του 95% σε χρονικό διάστημα 4 ωρών, που θεωρείται εξαιρετικά υψηλή. Στους παραπάνω υπολογισμούς έγινε η παραδοχή ότι το ελαϊκό οξύ ήταν τελείως καθαρό (100%). Η μεγάλη όμως περιεκτικότητα σε ελαϊκό οξύ μας επιτρέπει να συμπεράνουμε ότι το χλωροστεατικό οξύ κυριαρχεί στο λιπαρό μίγμα, γεγονός που επιβεβαιώνεται από τα αποτελέσματα των προσδιορισμών και προβλέπεται από θεωρητική άποψη. Ας σημειωθεί, ότι η θερμοκρασία διατηρήθηκε σταθερή στους 21°C κατά την αντίδραση.

Η ασυνεχής υδροχλωρίωση μελετήθηκε για αρχικές πιέσεις υδροχλωρίου 40-50 atm, με μονή ή διπλή διοχέτευση υδροχλωρίου (νέα τροφοδότηση υδροχλωρίου όταν η πίεση έπεσε στις 25 atm) και καταγράφηκε η πτώση πίεσης και η μεταβολή της θερμοκρασίας. Με βάση τα πειραματικά αυτά δεδομένα υπολογίστηκε η κατανομή των moles υδροχλωρίου στην αέρια και υγρή φάση κατά την εξέλιξη της αντίδρασης. (Σχήμα 1). Είναι φανερό ότι η μεγαλύτερη συγκέντρωση του διαλυμένου



$n_a$ : moles υδροχλωρίου στην αέρια φάση

$Q_v$ : συνολικά moles υδροχλωρίου στην υγρή φάση moles/cm<sup>3</sup>

A, B: ρόφηση με χημ. αντίδραση (απλή και διπλή αντιστοίχως).

ΣΧΗΜΑ 1: Υδροχλωρίωση σε ασυνεχή λειτουργία (Μονή και διπλή τροφοδοσία HCl).

υδροχλωρίου έχει ευνοϊκή επίδραση στη μετατροπή του ελαϊκού οξέος, αφού οι υψηλές πιέσεις οδήγησαν σε μεγαλύτερες αποδόσεις σε προϊόν προσθήκης, ενώ αντίθετα η θερμοκρασία μείωσε την απόδοση, γεγονός που αναμένεται αφού η αντίδραση είναι ισχυρά εξώθερμη (Πίνακας II).

ΠΙΝΑΚΑΣ Π: Υδροχλωρίωση ελαϊκού οξέος με μεταβαλλόμενη πίεση

α/α	Απλή διοχέτευση H Cl		AI	Cl %	%μετατροπή του ελαϊκού οξέος σε προϊόν προσθήκης
	P (max) atm	T (°C)			
1	40	22	30,8	7,2	66
2	40	26	34,9	6,8	61
3	50	22	16,7	8,9	81
Διπλή διοχέτευση H Cl (T=22°C)					
	P <sub>1</sub> (max)	P <sub>2</sub> (max)			
1	50	50	0,6	10,9	100
2	48	48	0,7	10,8	100
3	45	45	5,5	10,3	93,9
4	42	42	10,2	9,7	88,6
5	40	40	14,9	9,1	83,4

Οι τιμές των φυσικοχημικών προσδιορισμών στο ανακρυσταλλωμένο προϊόν (AI:1,1, AO:176,5 Cl%:10,9σ.τ. (°C): 40-41) συγκριτικά με τις θεωρητικές και τα ελάχιστα βιβλιογραφικά δεδομένα<sup>13</sup> (AI:0, AO:175,5, Cl%: 11,1, σ.τ.: 39-41) οδηγούν στο συμπέρασμα ότι το προϊόν της αντίδρασης αποτελείται πρακτικώς από χλωροστεατικό οξύ.

**Σαπωνοποίηση.** Κατά την υδρόλυση του χλωροστεατικού οξέος διαπιστώνεται ότι χωρούν ταυτόχρονα δύο βασικές αντιδράσεις, η αφυδραλογόνωση και η αντικατάσταση του αλογόνου από μια υδροξυλομάδα. (Πίνακες III και IV) όπως προβλέπεται και θεωρητικά. Η παρατηρούμενη αύξηση της ακορεστότητας ευνοείται κατ' αρχήν με την αύξηση της θερμοκρασίας, ενώ στις υψηλές θερμοκρασίες παρουσιάστη-

ΠΙΝΑΚΑΣ III: Ανάλυση και σύσταση του προϊόντος της σαπωνοποίησης (διάλυμα NaOH 7%)

α/α	Χλωριωμένο προϊόν AI	Υδρόλυση		Προϊόν υδρολύσεως							Σύνολο ακορ.+OH +χλωρ/ προϊόν
		T (°C)	t (h)	AI	Cl%	AOH	ακόρεστο προϊόν	κεκορεσμ. προϊόν	Υδροξύ προϊόν	Χλωροπροϊόν	
1	0,6	125	5	37,3	1,90	65,0	41,4	58,6	34,8	17,0	93,2
2	0,6	125	10	40,0	0,90	71,0	44,4	55,6	38,0	8,1	90,4
3	0,6	125	15	42,8	0,34	74,5	47,6	52,4	39,9	3,0	90,5
4	0,6	125	20	42,0	0,04	70,5	46,7	53,3	37,8	0,0	84,5
5	0,6	150	5	40,0	1,55	71,0	44,4	55,6	38,0	14,0	96,4
6	0,6	150	10	42,0	0,67	75,0	46,7	53,3	40,2	6,0	92,9
7	0,6	150	15	46,3	0,40	78,0	51,4	48,6	41,8	3,6	96,2
8	0,6	150	20	48,5	0,33	65,9	53,9	46,1	35,3	3,0	92,2
9	0,6	175	5	41,9	1,00	72,5	46,6	53,4	38,8	9,0	94,4
10	3,0	175	10	48,0	0,30	77,7	53,3	46,7	41,6	2,7	97,6
11	2,2	175	15	45,6	0,20	79,2	50,7	49,3	42,4	1,8	95,1
12	2,2	175	20	43,3	0,00	69,0	48,1	51,9	37,0	0,0	88,9
13	1,5	200	5	49,5	0,57	69,5	55,0	45,0	37,2	5,1	97,3
14	2,9	200	10	53,3	0,22	74,5	59,2	40,8	39,9	2,0	101,1
15	2,9	200	15	45,7	0,12	77,3	52,8	49,2	41,4	1,1	93,3
16	2,9	200	20	44,2	0,00	67,0	49,1	50,9	35,9	0,0	85,0

ΠΙΝΑΚΑΣ IV: Σαπωνοποιήσεις χλωροστεατικού οξέος με διάλυμα NaOH 10% κ.β. T = 150°C.

t(h)	AI	ΑΟΗ	Cl%	%ακόρ.	%κεκόρ.	%OH	%Cl
5	41,0	96,7	0,25	45,6	54,4	51,8	2,2
10	43,0	97,2	0,10	47,8	52,2	52,1	1,0
15	49,4	84,6	0,04	54,9	45,1	45,3	0,0
20	51,0	79,0	0,00	56,7	43,3	42,3	0,0

κε μείωση που οφείλεται σε άλλες δράσεις. Η μεγαλύτερη απόδοση σε υδροξυπριόν επιτεύχθηκε σε χρόνο 15 ωρών για όλες τις θερμοκρασίες που εξετάστηκαν. Η αύξηση της θερμοκρασίας πάνω από τους 175°C οδήγησε σε μικρότερη απόδοση σε υδροξυστεατικά οξέα. Θετική ήταν η επίδραση πυκνότερου αλκαλικού διαλύματος (10%) κατά τη σαπωνοποίηση οπότε ελήφθησαν μεγαλύτερες αποδόσεις σε υδροξυπριόν σε μικρότερους χρόνους. Η μέγιστη απόδοση τοποθετείται στη χρονική περιοχή των 5-10 ωρών και ανήλθε σε 52%.

Η ανάλυση του μίγματος των λιπαρών μεθυλεστέρων στον αέριο χρωματογράφο έδωσε χρόνους ανάλυσης 44.40 min, 19.80 min και 44.50 min για τον υδροξυστεατικό μεθυλεστέρα, για τον ελαϊκό μεθυλεστέρα και τον 12-υδροξυστεατικό μεθυλεστέρα αντιστοίχως, που χρησιμοποιήθηκε σαν πρότυπη ουσία και η ποσοτική εκτίμησή τους συμφωνούσε με τα αποτελέσματα των χημικών προσδιορισμών.

Το υδροξυστεατικό οξύ μετά την ανακρυστάλλωση από διαιθυλαιθέρα έδωσε: ΑΟΗ:180-186 (έναντι 186,7 της θεωρητικής τιμής), ΑΟ: 182-187 (έναντι 186,7), ΑΙ:5 (έναντι 0,0), σ. τήξεως: 73-75 (έναντι 74-75 και 81-82 του 9- και 10-υδροξυδεκαοκτανοϊκού οξέος αντίστοιχα), χρώμα λευκό και λιπαρά υφή.

## Summary

*Production of monohydroxystearic acids by hydrochlorination of oleic acid.*

*D. Doulia and G. Valcanas*

A method for the production of monohydroxystearic acid from oleic acid was developed, which consists of two basic chemical reactions: i) the addition of gaseous hydrogen chloride to the double bond of oleic acid under pressure, which leads to 95% yield in chlorostearic acid and ii) the hydrolysis of the addition product in an autoclave, using aqueous sodium hydroxide solutions, which gives mainly mixtures with a maximum content in monohydroxystearic acids approximately 50%. The conditions of the above reactions were studied in order to increase the yields in chlorostearic acid and monohydroxystearic acid respectively. The physical and chemical determinations, which were employed for testing the reactions's products, included the iodine number, the hydroxyl number, the acid number, the chlorine content, the melting point and the G.L.C of the fatty acid methyl esters.

**Key words:** monohydroxystearic acid, oleic acid, hydrochlorination, saponification.



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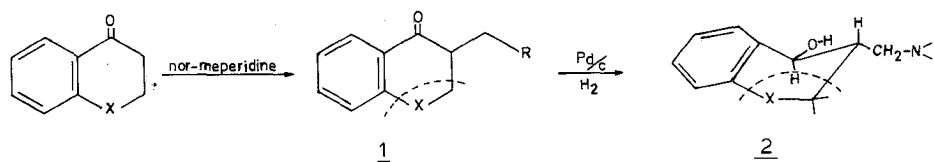


différence que la formation d'un cycle en six chaînons entre le carbone  $\beta$  par rapport à l'azote et le phényle par l'intermédiaire d'un hétéroatome ou pas assure la conformation S semi-rigide.

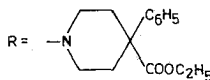
### Partie chimique

Nous avons préparé les composés des formules **1** et **2** en faisant réagir le chlorhydrate de la normépéridine avec la tétralone-1, chromanone-4 et N-méthyl dihydro-2, 3-quinolone-4 selon Mannich. Les bases **1** obtenues, qui se décomposent relativement facilement<sup>10</sup> sont soumises à une hydrogénation catalytique. On obtient ainsi les alcools **2** sous forme d'un seul stéréoisomère dans lequel les hydrogènes aux positions 1 et 2 du noyau cyclanique sont en position trans-diaxiale<sup>13</sup>.

Les réactions effectuées sont figurées dans le schéma II et les caractéristiques principales des produits synthétisés dans le tableau I.



X = CH<sub>2</sub>, O, N-CH<sub>3</sub>



SCHEMA II

TABLEAU I

Composé	X	F base (éther)	F <sub>HCL</sub> (éthanol-éther)	Formule
1a	CH <sub>2</sub>	103	173	C <sub>25</sub> H <sub>29</sub> NO <sub>3</sub>
1b	O	91	141	C <sub>24</sub> H <sub>27</sub> NO <sub>4</sub>
1c	N-CH <sub>3</sub>	104	176*	C <sub>25</sub> H <sub>30</sub> N <sub>2</sub> O <sub>3</sub>
2a	CH <sub>2</sub>	94	159	C <sub>25</sub> H <sub>31</sub> NO <sub>3</sub>
2b	O	112	188	C <sub>24</sub> H <sub>29</sub> NO <sub>4</sub>
2c	N-CH <sub>3</sub>	116	**	C <sub>25</sub> H <sub>32</sub> N <sub>2</sub> O <sub>3</sub>

(\*) dichlorhydrate

(\*\*) Dichlorhydrate hygroscopique, il se décompose à basse température.

## Partie Expérimentale

Les points de fusion ont été pris dans un appareil de Büchi et ne sont pas corrigés. Les microanalyses ont été effectuées par le Service Central de Microanalyse du C.N.R.S. et sont conformes aux valeurs théoriques à  $\pm 0,4\%$ . Les spectres RMN proton  $^1\text{H}$  ont été enregistrés sur un appareil Varian FT-80A; les déplacements chimiques sont donnés en  $\delta$  (ppm) par rapport au TMS en référence interne. Les spectres en IR ont été enregistrés sur un spectrophotomètre Perkin-Elmer 177.

La N-méthyl dihydro-2,3 quinolone-4 a été préparée selon<sup>11</sup> et la chromanone-4 selon<sup>12</sup>.

### *[(oxo-1 tétrahydro-1,2,3,4 naphyl-2) méthyl]-1 nor-méperidine 1a. (X=CH<sub>2</sub>)*

Un mélange de 2g (0,0074 mole) de chlorhydrate de nor-méperidine, de 1,26g de trioxyméthylène (0,014 mole), de 1,16g (0,008 mole) de tétralone-1, de 20 cm<sup>3</sup> d'éthanol absolu et de 5 gouttes d'éthanol saturé d'acide chlorhydrique est chauffé à reflux pendant 8h.

On évapore l'éthanol sous pression réduite, ajoute 100 cm<sup>3</sup> d'eau et extrait quatre fois à l'éther. La couche aqueuse est alcalinisée avec un excès d'une solution de bicarbonate de sodium saturée. On élimine sous pression réduite l'éther dissous dans la masse du mélange. Il se forme un précipité que l'on filtre et lave à l'eau. Le précipité est mis dans le même ballon, dissous dans 100 cm<sup>3</sup> d'éther et séchée sur Na<sub>2</sub>SO<sub>4</sub>. Après avoir évaporé sous pression réduite et à la température ambiante le solvant, on obtient la base qui est transformée par la suite en chlorhydrate (éthanol abs. - HCl). Rdt en chlorhydrate: 60%. IR base (nujol):  $\nu$  (C=O) ester 1720 cm<sup>-1</sup>,  $\nu$  (C=O) cétone 1680 cm<sup>-1</sup>, RMN (base-CDCl<sub>3</sub>)  $\delta$  1,18 ppm (t, 3H, CH<sub>3</sub>), 1,50-3,32 ppm (m, 15H, 2, 3, 4, CH<sub>2</sub>-N et pipéridiniques-H), 4,10 ppm (q, 2H, COOCH<sub>2</sub>), 6,90-7,55 ppm (m, 9H, aromatiques H).

De la même façon on prépare les bases de Mannich **1b** et **1c**.

### *[(oxo-4 chromanyl-3) méthyl]-1 nor-méperidine 1b (X=O)*

Rdt en chlorhydrate: 52% I.R. base (nujol):  $\nu$  (C=O) ester 1718 cm<sup>-1</sup>,  $\omega$  (C=O) cétone 1690 cm<sup>-1</sup>, RMN (base-CDCl<sub>3</sub>)  $\delta$  1,12 ppm (t, 3H, CH<sub>3</sub>), 1,56-3,12 ppm (m, 11H, 2, CH<sub>2</sub>-N, pipéridiniques-H), 4,08 (q, 2H, COOCH<sub>2</sub>), 4,25-4,68 (m, 2H, O-CH<sub>2</sub>), 6,75-7,93 (m, 9H, aromatiques).

### *[(méthyl-1 oxo-4 tétrahydro-1, 2, 3, 4-quinolyl-3) méthyl]-1 nor-méperidine 1c. (X=N-CH<sub>3</sub>)*

Rdt en dichlorhydrate: 57% I.R. base (nujol):  $\nu$  (C=O) ester 1720 cm<sup>-1</sup>,  $\nu$  (C=O) cétone 1668 cm<sup>-1</sup>, RMN (base-CDCl<sub>3</sub>)  $\delta$  1,18 ppm (t, 3H, CH<sub>2</sub>CH<sub>3</sub>), 3,00 ppm (s, 3H, N-CH<sub>3</sub>), 1,56-3,78 ppm (m, 13H, 2, 3, CH<sub>2</sub>-N, pipéridiniques H) 4,08 ppm (q, 2H, COOCH<sub>2</sub>), 6,58-7,87 ppm (triplet de multiplet, 9H, aromatiques). La base et son chlorhydrate sont de coloration jaune comme toutes les quinolones-4<sup>11</sup>.

### *[(hydroxy-1 tétrahydro-1, 2, 3, 4 naphyl-2) méthyl]-1 nor-méperidine 2a (X=CH<sub>2</sub>)*

La cétone **1a** est hydrogénée en présence de Pd-C à 10%. L'hydrogénation est effectuée au début à la température ambiante, puis vers 45° jusqu'à absorption complète du volume d'hydrogène calculé. Après filtration et évaporation du solvant sous

pression réduite, on vérifie la disparition de la bande du carbonyle à l'infra rouge. Le résidu est dissous dans l'éther et filtré sur alumine activée. Après évaporation du solvant le résidu cristallise dans un mélange éther-n-pentane. La base est transformée ensuite en chlorhydrate suivant les méthodes courantes et dans des conditions anhydres.

Rdt en base: 95%. IR base (nujol):  $\nu(\text{OH})$  3250  $\text{cm}^{-1}$  très large,  $\nu(\text{C}=\text{O})$  ester 1735  $\text{cm}^{-1}$ , RMN (base- $\text{CDCl}_3$ ):  $\delta$ 1,18 ppm (t, 3H,  $\text{CH}_3$ ), 1,35-3,37 ppm (m, 15H, 2, 3, 4,  $\text{CH}_2\text{N}$ , pipéridiniques-H), 4,10 ppm (q, 2H,  $\text{COOCH}_2$ ), 4,62 ppm (d, 1H,  $J=9\text{Hz}$ , 1-H), 6,81-7,68 ppm (m, 9H, aromatiques).

De la même façon on préparé les bases **2b** et **2c**.

*[(hydroxy-4 chromanyl-3) méthyl]-1 nor-méperidine 2b (X=O)*

Rdt en base: 80%. I.R. base (nujol):  $\nu(\text{OH})$  3440  $\text{cm}^{-1}$  très large,  $\nu(\text{C}=\text{O})$  ester 1724  $\text{cm}^{-1}$ , RMN (base- $\text{CDCl}_3$ )  $\delta$ 1,18 ppm (t, 3H,  $\text{CH}_3$ ), 1,68-3,31 ppm (m, 11H, 2,  $\text{CH}_2\text{N}$ , pipéridiniques-H), 3,56-4,25 ppm (m, 4H,  $\text{OCH}_2$ ,  $\text{COOCH}_2$ ), 4,66 ppm (d, 1H,  $J=9\text{Hz}$  1-H), 6,56-7,50 ppm (m, 9H, aromatiques).

*[(hydroxy-4 méthyl-1 tétrahydro-1, 2, 3, 4 quinolyl-3) méthyl]-1 nor-méperidine 2c. (X=N- $\text{CH}_3$ )*

Rdt en base: 83%, I.R. base (nujol):  $\nu(\text{OH})$  3380  $\text{cm}^{-1}$  très large,  $\nu(\text{C}=\text{O})$  ester 1728  $\text{cm}^{-1}$ , RMN (base- $\text{CDCl}_3$ ):  $\delta$ 1,15 ppm (t, 3H,  $\text{CH}_3$ ), 1,81-3,18 ppm (m, 13H, 2, 3,  $\text{CH}_2\text{N}$ , pipéridiniques-H), 4,06 ppm (q, 2H,  $\text{COOCH}_2$ ), 4,62 ppm (d, 1H,  $J=9\text{Hz}$ , 1-H), 6,37-7,50 (m, 9H, aromatiques).

## Sommaire

Des bases de Mannich de la nor-méperidine avec la tétralone-1, chromanone-4 et N-méthyl dihydro-2, 3-quinolone-4 ont été synthétisées. Ces amines cétones ont été transformées aux amines alcools correspondants par hydrogénation catalytique. Les deux séries des composés obtenus possèdent les caractéristiques structurales nécessaires, selon Janssen, pour une éventuelle activité neuroleptique et analgésique.

**Key words:** Mannich bases of 1-tetralone, 4-chromanone, N-méthyl-2, 3-dihydro-4-quinolone.

## Summary

*Synthesis of nor-meperidine derivatives with a possible analgetic and neuroleptic action*

In this paper the preparation of Mannich bases of 1-tetralone, 4-chromanone and N-methyl-2, 3-dihydro-4-quinolone with nor-meperidine is described. These bases were converted to amino alcohols by catalytic hydrogenation. The two series of products show the Janssen structural characteristics for a possible neuroleptic and analgetic activity.

## Περίληψη

*Σύνθεση παραγώγων της nor-μεπεριδίνης με πιθανή αναλγητική και νευροληπτική δράση*

Παρασκευάστηκαν βάσεις του Mannich της 1-τετραλόνης, 4-χρωμανόνης και N-μέθυλο-2, 3-διυδρο-4-κινολόνης με την nor-μεπεριδίνη που μετετράπηκαν σε άμινο αλκοόλες με κα-

ταλυτική υδρογόνωση. Οι δύο σειρές των προϊόντων παρουσιάζουν τα δομικά χαρακτηριστικά, σύμφωνα με τον Janssen, για μια πιθανή νευροληπτική και αναλγητική δράση.

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# SHORT PAPER

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## CONFIRMATION OF STRUCTURE OF DEGRADATION PRODUCT OF BUTYLATED HYDROXYTOLUENE ISOLATED FROM FOOD GRADE POLYETHYLENE PELLETS

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### Introduction

Polyethylene is the most widely used polymeric packaging material in the world today including food and drug packaging applications. Upon aging polyethylene undergoes oxidative degradation under the influence of heat, light or radiation<sup>1</sup>. Depending on nature of oxidizing agents and conditions of oxidation nearly 20 oxidation products of the antioxidant BHT have been isolated and characterized<sup>2</sup>.

To prevent such degradation and to increase the stability of polyethylene, antioxidants are added in small amounts to the polymer, the major one by far being butylated - hydroxytoluene (BHT). These compounds inhibit oxidation by blocking free radical formation but in turn oxidize themselves to produce colored substances<sup>3</sup>. An oxidation product of BHT causing a marked yellow discoloration of clear polyethylene film was identified as 3,3',5,5'-tetrakis (tert-butyl) stilbenequinone<sup>4</sup> and was isolated from cooking oil to which BHT was added<sup>5</sup>.

This work was undertaken with the objective to isolate and identify the compound or compounds responsible for the yellow discoloration of polyethylene pellets destined to be used in food packaging applications and possibly to confirm the formation of the above mentioned stilbenequinone derivative.

### Experimental

#### *Samples*

Two different samples of PE pellets were supplied by a local manufacturer. The "control" sample, white in color and the "oxidized" sample ranging from bright yellow to off white in color.

#### *Isolation of colored compound*

A series of organic solvents were tested for solubility of the yellow colored compound without simultaneous dissolution of the polymer. Methanol was chosen for the above purpose. Both samples were extracted in a Soxhlet apparatus for 8 hrs with

methanol. The solvent was subsequently evaporated in a vacuum evaporator until a bright yellow colored solution resulted. The control sample gave a colorless solution.

#### *Oxidation of pure BHT*

A small amount of BHT was dissolved in methanol, placed in a glass vial which was sealed with a rubber stopper and an aluminum crimp cap and purged with oxygen. The vial was simultaneously heated on a heating plate at 60° C. Oxidation of BHT was stopped when a bright yellow colored solution was formed.

#### *TLC analysis*

TLC analysis of the following samples was run on Eastman Chromogram 13181 Silica gel sheets using acetone as the separation medium and iodine vapors as the developing medium:

- a. Oxidized BHT
- b. "Oxidized" sample extract
- c. "Control" sample extract
- d. Isolated yellow compound. This compound was purified by repeated preparative TLC analysis.

#### *HPLC analysis*

HPLC analysis was performed on the following samples:

- a. Oxidized BHT
- b. "Oxidized" sample extract
- c. "control" sample extract
- d. isolated yellow compound
- e. Pure BHT dissolved in methanol

Preliminary scanning of the above samples was performed using a UV detector between 180-390nm with the wavelength 232nm chosen for the analysis.

HPLC operational conditions:

column: partisil P×5 5/25 30cm × 0.65cm i.d.

injector: Rheodyne, model 7125

pump: Altex, model 110A

detector: Tracor, model 970A, variable wavelength UV detector at 232nm.

flow rate: 1ml/min

carrier medium: methanol,  $A_{max} = 202\text{nm}$

injection volume: 20 $\mu\text{l}$

#### *I.R. analysis*

I.R. analysis of samples a.b. and d. was performed using a Perkin Elmer, model 421 I.R. spectrophotometer.

#### *Mass spectrometry analysis*

Mass spectrometry analysis of samples a. and d. was performed using a Hewlett Packard, Model 5990A GC/MS system. To obtain a sufficiently purified sample for Mass spectrometry analysis, 3 TLC purifications were required. Samples were analyzed at 70 eV using temperature programming between 110 and 150° C.



## Results and discussion

TLC analysis of samples a,b, and d gave the same major yellow spot ( $R_f = 0.67$ ).

HPLC analysis of samples a,b,d and e, gave the same characteristic peak response ( $t_r = 3.44$ min) at  $\lambda = 232$ nm., for BHT and its oxidation product. There was no differentiation between the two. Sample c., gave no significant peak response at 232nm indicating the absence of both, excessive amounts of BHT and its oxidation product.

Samples a,b, and d, gave an IR spectrum with a major absorption band at  $1600\text{ cm}^{-1}$ . This is characteristic of a carbonyl group in a highly conjugated system and is indicative of a quinoid structure<sup>6</sup>.

TABLE I: Relative Abundance of Major Ions in Mass Spectra of Samples a\* and d\*.

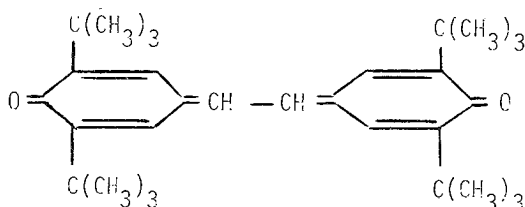
m/e	Sample a	Sample d
57	9	9
203	6	5
204	4	3
217	5	4
219	4	3
434	100	100
435	34	32
436	22	21
437	8	8

\* See text for description of samples a and d.

The mass spectra of both samples a, and d, exhibited a base peak at m/e 435 and additional peaks at m/e 437 and 57 (Table I), and were similar to those obtained previously<sup>4</sup>.

Based on data recorded in Table I, the m/e 434 peak was considered the molecular ion, the m/e 435 peak was attributed to the normal isotopic abundance of carbon-13, and the m/e 436 peak was attributed to the normal isotopic abundance of oxygen-18. The m/e 57 peak was assigned to a t-butyl ion ( $C_4H_{10}$ ).

Based on a molecular weight of 434 and establishing the number of carbon atoms present from mass spectra recorded<sup>7</sup>, the isolated yellow compound is confirmed to be an oxidation product of BHT<sup>4,5</sup> with a molecular formula of  $C_{30}H_{42}O_2$  and a structure that of stilbenequinone.



Extraneous peaks found in both spectra (Table I) were attributed to minor impurities present in the samples.

It is postulated that during compounding due to excessive content of BHT in the polyethylene, a significant portion of the antioxidant is oxidized to produce yellow discoloration in the polymer. BHT is regulated by government agencies (F.D.A., GREEK FOOD CODE)<sup>8,9</sup> and as a food additive it is permitted in certain foods at levels ranging from 10-200 ppm. However breakdown products of BHT such as stilbenequinone or stilbene are not regulated and their presence in large amounts as a result of excessive oxidation of BHT raises questions as to the acceptability of products containing them without proof of their safety. Foods therefore containing off color and/or off taste could lead to seizure by the appropriate Government agencies.

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## Summary

Butylated hydroxytoluene (BHT) is widely used as an antioxidant in the production of polyethylene. An oxidation product of this antioxidant was isolated from discolored polyethylene pellets, destined to be used in food packaging applications. The compound identified as a derivative of stilbenequinone, was isolated by extraction with methanol, purified by preparative TLC and its structure identified by IR, HPLC and Mass Spectrometry. The formation of this yellow colored oxidation product of BHT can cause discoloration of polyethylene and is not regulated as an indirect food additive.

**Key words:** BHT oxidative degradation, Polyethylene discoloration, TLC, IR, HPLC, MS analysis.

## Περίληψη

*Επιβεβαίωση της δομής προϊόντος αποικοδόμησης του βουτυλιωμένου υδροξυτολουολίου, απομονωθέντος από πελλέτες πολυαιθυλενίου προορισμένες για συσκευασία τροφίμων*

Το βουτυλιωμένο υδροξυτολουόλιο (BHT) χρησιμοποιείται σήμερα ευρύτατα σαν αντιοξειδωτικό στην παραγωγή του πολυαιθυλενίου. Στην εργασία αυτή απομονώθηκε και ταυτοποιήθηκε ένα προϊόν οξείδωσης του BHT προερχόμενο από κόκκους πολυαιθυλενίου που προορίζονταν να χρησιμοποιηθούν για την παραγωγή ειδών συσκευασίας τροφίμων. Η ουσία απομονώθηκε κατόπιν εκχύλισης με μεθανόλη, διαχωρίστηκε με παρασκευαστική TLC και ταυτοποιήθηκε με φασματοσκοπία IR, MS και HPLC σαν βουτυλιωμένο παράγωγο της στυλβενοκινόνης. Έτσι επιβεβαιώθηκε η δομή της ουσίας αυτής, η παρουσία της οποίας σε αντίστοιχα συστήματα, έχει αναφερθεί προηγούμενα στη βιβλιογραφία. Ο σχηματισμός αυτού του κίτρινου χρώματος, προϊόντος οξείδωσης του BHT, δυνατόν να προκαλέσει αφ' ενός μεν χρωματισμό του πολυαιθυλενίου, αφ' ετέρου πιθανόν προβλήματα υγείας στο καταναλωτικό κοινό, μιά και ουσίες σαν κι' αυτή δεν έχουν μελετηθεί και καταχωρηθεί στον πίνακα των επιτρεπόμενων έμμεσων προσθέτων στα τρόφιμα.

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## NOTE

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### MONO-OXYDATION DES TRISULFURES ORGANIQUES

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Nous avons montré l'intérêt des thiosulfates R-SO-S-R naturels dans certaines relations plantes-insectes<sup>1</sup> et cette classe de composés peu stables à activité biologique est intéressante en synthèse<sup>2</sup>. La nouvelle méthode d'obtention facile des trisulfures symétriques<sup>3</sup> nous a permis de synthétiser aisément des trisulfures monosulfoxydés de propriétés chimiques et biologiques analogues à celles des thiosulfates et qui sont plus stables. En particulier nos premiers résultats montrent que, par coupure de la liaison SO-S, ces composés s'additionnent sur les acétyléniques vrais et par ailleurs ils se sont révélés être aussi attractifs pour la teigne du poireau (*Acrolepiopsis assectella* Z.) que les thiosulfates et plus attractifs que les trisulfures correspondants lors de tests effectués dans un tube olfactométrique<sup>4</sup>.

Nous avons obtenu cette nouvelle classe de composés, dont deux exemples avaient déjà été cités<sup>5</sup>, avec un excellent rendement (80 à 95%) et sans sous-produits en oxydant par l'acide m-chloroperoxy-benzoïque (MCPBA) les trisulfures:



(R = Méthyl, Ethyl, Propyl, t-Butyl, Benzyl).

L'absorption IR à 1080 cm<sup>-1</sup> indique la fixation d'un seul oxygène et la RMN (<sup>1</sup>H) l'existence unique de la structure dissymétrique: par exemple, le diméthyltrisulfure monoxyde présente deux singulets à δ = 2,65 et 2,95 p.p.m.

#### Exemple de synthèse

A 0,1 mol (12,6g) de trisulfure de méthyle dans 50 ml de dichlorométhane, ajouter goutte à goutte en 1 heure 0,11 mol (19 g) d'acide m-chloroperoxybenzoïque dissout dans 200 ml de dichlorométhane à température comprise entre -5 et 0°C; laisser 2 h à température ambiante; éliminer le précipité apparu; laver au bicarbonate et à l'eau; sécher; évaporer le solvant. On obtient 0,085 mol (12,1 g) de diméthyltrisulfure monoxyde exempt de produit de départ selon la RMN et utilisable directement pour les synthèses ultérieures et les tests biologiques.

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**Resumé**

Les trisulfures symétriques sont oxydés par le MCPBA pour donner des trisulfures S-monoxydes stables et purs avec un très bon rendement. Cette nouvelle classe de substances semble avoir les mêmes propriétés chimiques et écologiques que les thiosulfates.

**Mots-clefs:** Trisulfures, Thiosulfates, mono-S-oxydation, relations plantes-insectes.

**Abréviation:** MCPBA: acide méta-chloroperoxybenzoïque.

**Summary***Mono-oxidation of organic trisulfides*

Symmetrical trisulfides are oxidized by MCPBA to give stable trisulfide monoxides in good yield and high purity. This new class of substances seems to have the same chemical and ecological properties as thiosulfates.

**Περίληψη***Μono-οξειδωση οργανικών τρισουλφιδίων*

Συμμετρικά τρισουλφίδια οξειδώθηκαν με MCPBA για να δώσουν σταθερά S-μονοξυτρισουλφίδια πολύ καθαρά και με μεγάλη απόδοση. Η καινούργια αυτή τάξη ουσιών φαίνεται να έχει τις ίδιες χημικές και οικολογικές ιδιότητες με τα θειοσουλφινικά (S-μονοξυδισουλφίδια).

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