

present as DDE 24 days after treatment. Our findings agree with those of Bowes (1972), who recently reported that *Skeletonema costatum* and *Cyclotella nana* produced low amounts of DDE. He did not observe any conversion of DDT to DDE by *Amphidinium carteri*, whereas our studies indicate that this organism was able to convert small amounts of DDT to DDE.

Tlc analysis of the cells incubated with [^{14}C]DDT indicated the presence of only one metabolite having an R_f value of 0.43, which corresponded to authentic DDE.

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Fate of Aldrin- ^{14}C in Potatoes and Soil Under Outdoor Conditions

Werner Klein,* Jagmohan Kohli, Irene Weisgerber, and Friedhelm Korte

Aldrin- ^{14}C has been applied to soils under outdoor conditions in Germany (2.9 kg/ha) and England (3.2 kg/ha) and potatoes have been sown. At harvest, more than 60% of the total radioactivity recovered from the soil and plants was due to metabolites, mainly dieldrin and a group of hydrophilic products, of which the main compound was identified as dihydrochlordene- ^{14}C dicarboxylic acid (1,2,3,4,8,8-hexachloro-1,4,4a,6,7,7a - hexahydro-1,4-endo-methyleneindene - 5,7-dicarboxylic acid). Photodieldrin- ^{14}C was also detected in small amounts in the

potato haulm from England, as were traces of photoaldrin- ^{14}C in both soils. The conversion of aldrin- ^{14}C was least in the upper soil layer and greatest in deeper soil layers (10-60 cm from surface) and in the plants. Only very low residues were detected in the deeper soil layers in England, whereas more radioactivity was found in the deeper soil samples in Germany. The leaching water of the experiment in Germany contained only dihydrochlordene- ^{14}C dicarboxylic acid (0.02 ppm).

The chlorinated insecticide aldrin (Figure 1) is widely used for the control of a range of soil pests. It may be applied to the soil before planting at dosage rates between 2 and 4 kg/ha or it may be used to dress seeds before sowing.

It is well established that aldrin is readily converted to its epoxide, dieldrin, in soil (Gannon and Bigger, 1958; Lichtenstein and Schulz, 1959, 1965) and in plants (Gannon and Decker, 1958; Glasser, 1955; Lichtenstein, 1959; Lichtenstein *et al.*, 1965, 1967). The conversion of aldrin to dieldrin by plant enzymes has also been demonstrated *in vitro*; e.g., by root homogenates (Yu *et al.*, 1971). Numerous studies have been reported on aldrin and dieldrin residues in crops and in soil (Decker *et al.*, 1965; Elgar, 1966; Harrison *et al.*, 1967; Lichtenstein, 1965; Onsager *et al.*, 1970), in food moving in commerce (Duggan and Weatherwax, 1967), and in total diets (Duggan and Lipscomb, 1969). With the exception of dieldrin and its photoisomer

photodieldrin (Lichtenstein *et al.*, 1970; Weisgerber *et al.*, 1970), no further conversion products of aldrin in plants or soil have been reported. Recently we reported (Weisgerber *et al.*, 1970) that under glasshouse conditions, 4 weeks after foliar application of aldrin- ^{14}C to cabbage, nearly 80% of the radioactivity detected in the plants consisted of metabolites which were more hydrophilic than metabolites of aldrin that had been identified previously. Application of aldrin- ^{14}C to spinach, carrot, and cabbage soil resulted in hydrophilic metabolites amounting to 62, 55, and 12%, respectively, of the total residues.

It is difficult to predict from glasshouse experiments the behavior of a compound under practical conditions. It is frequently found that the concentration of a metabolite that is found in indoor radiochemical studies is far greater than is subsequently found when the work is undertaken under practical field conditions. We have therefore studied the metabolism of aldrin- ^{14}C under outdoor conditions to complement the previous indoor studies. Different crops have been grown out-of-doors and have been treated in reasonable accordance with the recommended agricultural practice. However, plot sizes were necessarily limited since radioisotopes were being used. Experiments took place in Germany and in England to permit a comparison of the overall effect of different climatic conditions, soil

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Table I. Cultural Details for Potatoes Grown with Aldrin-¹⁴C Treatment

Growth parameter	Details for site indicated	
	Woodstock Kent/UK	Birlinghoven Westphalia/Germany
Variety	Majestic	Grata
Number of tubers	4	4
Date of planting	April 30, 1969	April 18, 1969
Depth of planting	8 cm	8 cm
Treatment: K ₂ O	150 (as KCl)	96 (as KH ₂ PO ₄)
P ₂ O ₅ (in kg/ha)	96 (as "Super")	143 (as KH ₂ PO ₄)
N	40 + 40	40 + 40 (as Kalkammonsalpeter)
Aldrin- ¹⁴ C (as HHDN, 25% EC)	3.2 kg/ha (117 mg)	2.9 kg/ha (103 mg)
Date of harvest	October 3, 1969	September 18, 1969
Specific activity of aldrin- ¹⁴ C	5.6 nCi/μg	8.2 nCi/μg
Watering	As necessary, near 5 l. weekly in dry weather	Little watering needed
Soil: texture	Sandy clay loam	Sandy loam
organic matter	2.0%	3.5%
sand	65%	67.3%
silt	7.2%	16.7%
clay	25.8%	12.5%
pH	7.4	8.1
Total rainfall during crop growth, mm	290	554
Range of maximum daily temperature, °C	13-26	9-29

textures, and local cultural practices. A brief and preliminary account of the results of this work has been given previously (Klein, 1972; Korte, 1972) and the full results obtained from experiments with potatoes are described in this paper. The results with other crops will be reported later.

APPARATUS

Radioactivity was counted in extracts using Packard liquid scintillation counters (Tri-Carb model 3380 or 3375) with external standardization. Thin-layer plates were examined qualitatively on chromatogram scanners of Bertold-Frieseke GmbH, Karlsruhe, with one of them being fitted with a dot printer. Gas chromatography was performed on a Packard unit, Series 7400, with electron capture and flame ionization detectors and fitted with a glass column (diameter 4 mm; length 1.65 m) packed with 1% OV1 on Chromosorb G AW-DMCS, 80-100 mesh. The carrier gas was nitrogen (40 ml/min). An auxiliary Packard fraction collector 852 was used with anthracene tubes for the collection of radioactive substances.

Mass spectra were determined after gas chromatography using a gc-ms LKB 9000, from LKB-producter, Bromma, Sweden. The glc conditions were as described above except that the carrier gas was helium.

REAGENTS

Aldrin-¹⁴C was supplied by Shell Development Company, USA, and purified by tlc until above 99% radiochemical purity. Dieldrin-¹⁴C was supplied by The Radiochemical Centre, Amersham, UK (ca. 97% purity).

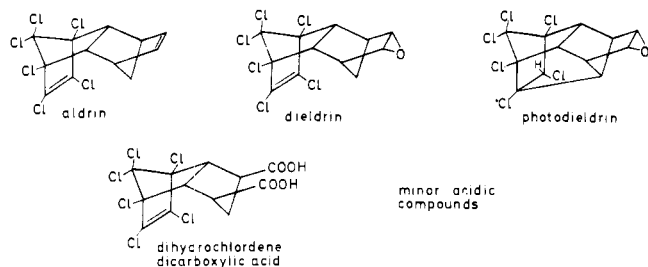


Figure 1. Formula of aldrin and its conversion products.

Dihydrochlordene dicarboxylic acid was obtained by oxidation of aldrin (Lay, 1971). Its bridged isomer was prepared from it by oxidation of photodieldrin (Klein *et al.*, 1970), and photodieldrin and photoaldrin were prepared by irradiation of dieldrin and aldrin (Fischler and Korte, 1969).

A liquid scintillator based on dioxan was used for counting of extracts and tlc zones. A toluene-based scintillator containing phenethylamine was used for absorbing and for counting ¹⁴C₂.

Silica gel, 0.05-0.2 mm, from Merck was used for column chromatography. Kieselgel G (Merck) was used for the preparation of tlc plates and ready-coated plates (Merck) with 0.25-mm layers of Kieselgel or aluminum oxide were also used. Methylation of the hydrophilic metabolites was performed in dimethylformamide. Methyl iodide and sodium hydride were added and the mixture was shaken at room temperature.

PROCEDURE

Cultural Conditions of Plant Growing. The potatoes were grown in boxes 60 × 60 × 60 cm constructed from water-resistant plywood. The base of the box contained holes to permit the drainage of excess water, which was collected in a metal splash tray. The box was wrapped in aluminum foil on the outside to prevent temperature increases from the sunlight. The bottom 25 mm of the box was packed with stone chips of near 25 mm diameter, and the stones were covered with a 25-mm layer of well-rotted turf. The box was filled with soil to 1 cm from the top. The soil was allowed to settle for 1 month before planting. The box was sunk into a large pit such that the upper surface of the soil was level with the surrounding ground.

The soils were typical for potato growing in the two locations. Fertilizers were applied as in agricultural practice. The aldrin-¹⁴C was applied as a diluted 30% emulsifiable concentrate using commercial surfactants. Application rate and specific activity of aldrin-¹⁴C and cultural details are given in Table I. The concentrate was diluted 100 times with water before application. The insecticide was incorporated in the soil to a 10 cm depth and then four potatoes were planted in each box. Air temperature, humidity, and pressure, as well as rainfall, were recorded during the vegetation period. A summary of the

climatic conditions, as well as the analysis of both soils, is included in Table I.

Working-Up of Plant Material and Soil. At harvest time, the total crop resulting from four potato plants was examined and the plant growth and yield were normal. The total crop was analyzed. Root, haulm, peeled tubers, and peel were analyzed separately. Soil samples of ca. 750 g were taken at depths of 0–10, 10–20, 20–40, and 40–60 cm immediately after the harvest. Samples taken in England were shipped frozen, cooled with solid carbon dioxide. All samples were stored at below -20° . To avoid loss of radioactivity by evaporation, they were not dried before analysis. The moisture content of soil samples was determined by drying in a vacuum desiccator at room temperature to constant weight. Dried samples were not used for quantitative analysis.

Plant samples were cut to small pieces and homogenized with methanol in a blender or with an ultraturax. The residues of plants as well as soil samples were reextracted with methanol in a Soxhlet for 48 hr. This extraction method is more efficient for hydrophilic compounds than the methods which have been reported for the insecticides themselves and their organosoluble metabolites. Efficiency for the two main radioactive products was dieldrin, 99.9%, and the Na salt of dihydrochlordene dicarboxylic acid, 80.8%.

Radioactive Measurements. *Extracted Radioactivity.* The radioactivity in methanolic extracts was determined by counting samples of 100, 200, and 500 μ l in a liquid scintillation counter. The data obtained were corrected by counting blanks of inactive extracts prepared in the same manner as the active ones.

Unextracted Radioactivity. Unextracted radioactivity in soil was determined by the combustion of 200 mg of soil after extraction and drying in a vacuum desiccator at room temperature. The combustion was performed at 850° for 15 min. Untreated soil was used to determine the blank value. The unextracted residues in plant samples were determined by the combustion of 200 mg of dried material after extraction. Data were corrected for blank values which were obtained from inactive samples.

Total Radioactivity. The total radioactivity of each sample was determined by summing up the values of extracted and unextracted residues. For soils these results were confirmed by combustion of unextracted samples.

Separation and Quantitative Determination of Radioactive Compounds. For the determination of aldrin and its conversion products, the methanolic extracts were concentrated in a rotary evaporator to $\frac{1}{10}$ of their original volume, followed by evaporation to dryness by freeze-drying at -50° and dissolution of the residue in 5–10 ml of methanol. This extract was chromatographed by tlc on silica gel in cyclohexane–hexane–dioxan 86.5:10:3.5. Zones of 1 cm were removed from the plates, and the radioactivity of each zone was desorbed with 15 ml of dioxane scintillator and counted in a liquid scintillation counter. The efficiency of this method was checked by tlc plates with dieldrin- ^{14}C and dihydrochlordene- ^{14}C dicarboxylic acid, along with plant coextractives. The recovery of both substances was about 99%.

Isolation of Conversion Products. Dieldrin, photodieldrin, and photoaldrin were isolated by repeated tlc and identified by comparison with authentic samples by tlc and glc. For the isolation of the main hydrophilic plant metabolite, the methanolic extracts of the different parts of the plants were mixed together and evaporated to dryness. The residue was taken up in water (pH 7) and extracted several times with diethyl ether in order to remove aldrin, dieldrin, and other nonpolar compounds. The aqueous solution was then acidified with 2 N HCl and extracted continuously with diethyl ether for 48 hr. The ether fraction was purified by repeated tlc. The purified

component was dissolved in dimethylformamide and methylated with methyl iodide in the presence of NaH. The reaction mixture was evaporated to dryness, and the residue was dissolved in methanol and applied to a tlc plate which was developed in cyclohexane–acetone 4:1 (v/v). The main product was desorbed with benzene and purified on a silica gel column, followed by repeated tlc. Approximately 5 μ g of methylated metabolite was obtained.

By the same procedure, the main hydrophilic metabolite was isolated from soil extracts and from the leaching water. The metabolite was, in all cases, identical with authentic dihydrochlordene- ^{14}C dicarboxylic acid on tlc. After methylation, it was identified by tlc, glc, and mass spectrometry.

RESULTS AND DISCUSSION

Identification of Metabolites. In all soil and plant samples most of the radioactivity was due to conversion products (Figure 1). Levels of aldrin were similar in the soils to those of dieldrin. Traces of aldrin were found in potato haulm and peeled tubers. Small amounts of aldrin were detected in the peel.

Dieldrin constituted the main metabolite in most of the potato samples and in the upper soil layers sampled in Germany. It was identified by comparison with authentic dieldrin in several tlc solvent systems and by glc at various temperatures. Since dieldrin has been described as a metabolite of aldrin in many studies, further attempts to confirm its identity were considered unnecessary.

In soil extracts a substance (Metabolite X) was found in very small amounts (0.01 ppm or less) which possessed an R_f value between that of aldrin and dieldrin. Further purification proved unsuccessful due to its instability. This substance was also detected in small amounts in the weeds (*Stellaria media*) that were growing between the potatoes.

In the potato haulm taken from the experiment in England, but not in that from Germany, a substance was found which behaved on tlc like photodieldrin (Figure 1). It accounted for 13.6% of the total radioactivity recovered from the haulm. In Table II, it is recorded together with "hydrophilic metabolites." Small amounts (below 1%) of the radioactivity in the soil of both experiments were due to photoaldrin, and this was identified by tlc and glc.

The greatest part of the recovered radioactivity, other than aldrin and dieldrin, was accounted for in all samples by a group of hydrophilic substances, consisting of a main product and two by-products. The major product in this group (more than 60%) was found to be dihydrochlordene- ^{14}C dicarboxylic acid (1,2,3,4,8,8-hexachloro-1,4,4a,6,7,7a-hexahydro-1,4-endo-methylene-indene - 5,7-dicarboxylic acid). Its identity was confirmed by cochromatography of an authentic sample of the free acid as well as of its dimethyl ester on tlc. Glc analysis of the dimethylated product showed that the methylated metabolite had the same retention time as an authentic sample of the dimethyl ester. Further confirmation of its identity was obtained by comparison of the mass spectra (Figures 2 and 3), which also showed clearly that it was not the photoisomer. Figures 2 and 3 show the mass spectra of dihydrochlordene dicarboxylic acid dimethyl ester and its photoisomer. Both have a molecular weight of 454. The main difference exists in the retro-Diels–Alder fragments which are not found with the bridged photoisomer, but are present in the mass spectrum of the metabolite which is, in all fragmentations, identical with the unbridged reference compound. Using ir it was also shown that the dicarboxylic acid was the only radioactive compound present in leaching water (Moza *et al.*, 1972). The occurrence of dihydrochlordene dicarboxylic acid demonstrates that the carbon ring skeleton was cleaved by oxidation in soil and

Table II. Residues of Aldrin-¹⁴C and Its Conversion Products in Potatoes and Soil Following Soil Application (Expressed as Equivalent ppm of Aldrin)

Sample	Germany						England					
	Aldrin	Metabolite X	Dieldrin	Hydrophilic metabolites and photodieldrin (extracted)	Unextracted residue	Total residue	Aldrin	Metabolite X	Dieldrin	Hydrophilic metabolites and photodieldrin (extracted)	Unextracted residue	Total residue
Roots	0.20	n.d.	1.68	0.38	0.08	2.34	0.58	n.d.	2.26	0.76	0.33	3.93
Peel	0.10	n.d.	0.39	0.12	0.01	0.62	0.36	n.d.	1.16	0.14	0.02	1.68
Peeled tubers	<0.01	n.d.	0.04	0.02	<0.01	0.06	<0.01	n.d.	0.08	0.02	<0.01	0.10
Haulm	<0.01	n.d.	0.06	0.04	0.01	0.11	0.03	n.d.	0.53	0.85	0.43	1.84
Soil, 0-10 cm from surface	0.58	0.01	0.62	0.11	0.11	1.43	0.59	0.01	0.40	0.74	0.27	2.01
Soil, 10-20 cm from surface	0.23	n.d.	0.26	0.05	0.08	0.62	<0.01	<0.01	<0.01	0.01	0.06	0.07
Soil, 20-40 cm from surface	0.02	<0.01	0.02	0.02	0.03	0.09	<0.01	n.d.	<0.01	0.01	0.03	0.04
Soil, 40-60 cm from surface	<0.01	<0.01	<0.01	0.02	0.03	0.05	<0.01	n.d.	<0.01	0.01	0.01	0.02

plants. It is not likely that this reaction takes place *via* dieldrin, for we were able to demonstrate in earlier experiments (Weisgerber *et al.*, 1970) that after dieldrin application to soil, only small amounts of hydrophilic metabolites are formed. Cyclodiene insecticides containing a carbon-carbon double bond in the nonchlorinated ring such as aldrin, isodrin (Klein *et al.*, 1972), and heptachlor (Weisgerber *et al.*, 1972) are converted more readily to hydrophilic metabolites than dieldrin. It may be concluded that nonchlorinated double bonds easily undergo ring cleavage.

The minor hydrophilic metabolites in potato plants and soil were not examined in detail but also show the properties of acids, and these will be investigated further.

Some radioactivity remained in the soils after extraction with organic solvents, as indicated in Table II. Extraction with dilute sodium hydroxide isolated a further 55% of the remaining radioactivity and this was also identified as dihydrochlorodene dicarboxylic acid by tlc, glc, and mass spectrometry.

Quantitative Residue Measurements. The amounts of aldrin and its conversion products, as well as the total residues in all samples, are shown in Table II. The residues in ppm are based on the fresh weight of the plant sample with the exception of haulm from England, which dried on the field. With the soil samples the residues are based on dry weight. In the experiments in both countries, the concentration of radioactive products (ppm) was highest in the upper soil layer (0-10 cm from surface) where the radioactivity had been applied. It decreased with increasing depth. In plant samples the radioactivity was higher in roots and tuber peel and lower in haulm and peeled tubers. The high residue in the haulm from England is due to the dry state of the sample. The total residues in the peeled tubers (0.06-0.10 ppm) were lower than those in the other parts of the plants and were mainly dieldrin. Residues of aldrin, dieldrin, and hydrophilic metabolites were detected in the peels at a higher level than in the tubers. In Germany, the weeds growing among the potato plants were also analyzed. They were found to contain 0.14 ppm of the total radioactivity, a level similar to that found in potato haulm.

The plants grown in England showed higher total residues than those grown in Germany. The dosage rate was a

little higher in England than in Germany, but there were also other differences, including the soil type, the climate, and the variety and yield of the crop. It is not possible from these experiments to indicate which factor contributed most to the difference in residues. The residues of the radioactive products at the soil surface were higher in England than in Germany, whereas the deeper soil layers (10-60 cm from the surface) contained more radioactive residues in the German experiment, indicating a greater leaching of radioactivity in the German soil used. This was more likely due to the higher rainfall in Germany. The water collected at a depth of 60 cm contained virtually no radioactivity in the experiment in England, but 0.02 ppm was detected in the experiment in Germany.

Conversion Rate. Dieldrin was the main metabolite in most of the plant samples and the soil samples in the ex-

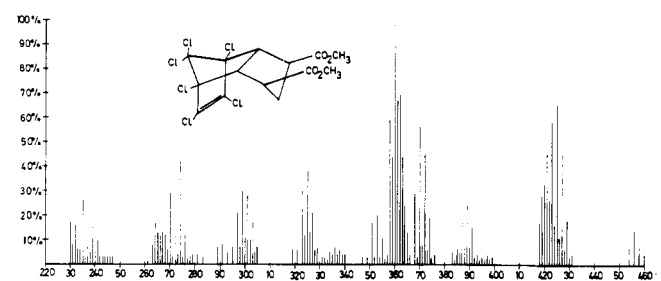


Figure 2. Mass spectrum of dihydrochlorodene dicarboxylic acid dimethyl ester.

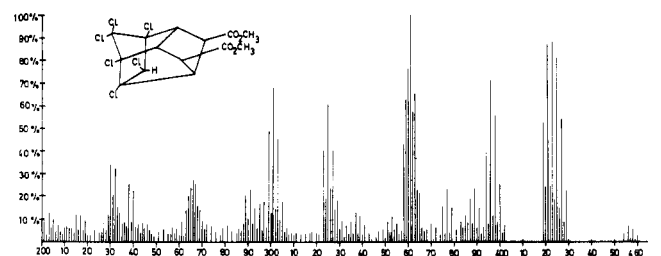


Figure 3. Mass spectrum of bridged isomer of dihydrochlorodene dicarboxylic acid dimethyl ester.

periment in Germany, whereas extractable hydrophilic metabolites constituted the main part of the radioactivity in the haulm of plants from England. The deeper soil layers, especially in the experiment in England, contained mostly compounds which were not extractable by organic solvents and probably were hydrophilic products, as considered previously.

The residues in the weeds (0.14 ppm) collected in Germany consisted of 20% of aldrin, 2.3% of metabolite X, 38.2% of dieldrin, 32.8% of hydrophilic metabolites, and 6.7% of unextractable residues. Generally, the proportion of hydrophilic metabolites and the proportion of unextractable compounds in soils increased with increasing depth of the samples. In the case of soil samples from England, the sum of hydrophilic metabolites and unextractable residue increased with increasing depth.

These two experiments show that the conversion of aldrin and its epoxide, dieldrin, to hydrophilic products and unextractable residues was slightly higher in the experiment in England than that carried out in Germany, with the exception of tuber and peel. The differences are caused by several factors which were not investigated separately in these experiments.

CONCLUSIONS

It is shown that under outdoor conditions aldrin is transformed mainly to dieldrin but also in varying amounts to acidic metabolites, the main product being dihydrochlorodene dicarboxylic acid.

In our Institute, studies are in progress to investigate whether hydrophilic metabolites occur, besides dieldrin, in other edible crops. It is possible that they exist in many edible crops containing dieldrin resulting from aldrin application. It seems to be useful to develop analytical methods to detect these residues in market samples.

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Metabolism of 1-(4'-Ethylphenoxy)-6,7-epoxy-3,7-dimethyl-2-octene (R 20458) in the Rat

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Oral administration of *trans*-1-(4'-ethylphenoxy-¹⁴C)-6,7-epoxy-3,7-dimethyl-2-octene (R 20458), an insect juvenile hormone analog, to rats resulted in the excretion of numerous urinary and fecal metabolites. Approximately 100% of the administered dose was recovered in equal amounts in urine and feces. No significant radiocarbon was detected in tissues or expired air. Metabolites were identified by chromatographic and

spectrometric analyses. The chemical nature of the metabolites indicates that R 20458 is metabolized *via* the following biotransformations: α and ω oxidation of the 4'-ethyl moiety; hydration of the trans olefin; hydration of the 6,7-epoxy group; and ether cleavage. The results of this study indicate that R 20458 is a highly biodegradable compound which is unlikely to leave persistent or toxic residues in animals or the environment.

The insect juvenile hormone analog *trans*-1-(4'-ethylphenoxy)-6,7-epoxy-3,7-dimethyl-2-octene (R 20458 of Stauffer Chemical Company) has shown promise as a selective insect control agent (Pallos and Menn, 1972; Pallos

et al., 1971). This terpene derivative represents a novel class of insect growth regulators.

The metabolic fate of terpenes has not been extensively studied. Gill *et al.* (1972) showed that R 20458 administered intraperitoneally (ip) to rats gave rise to numerous relatively polar products in urine and feces. One metabolite detected in feces cochromatographed with 1-(4'-ethyl-

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