solution to stand at the reaction temperature for a time corresponding to 10 half-lives of the undeuterated derivative. By this method an average of 100% of the olefin, 97% of the ethyl ether, and 99% of the thiol ester were recovered.

Kinetic Procedures.—The reaction rates of d_0-, d_3-, and d_6-cumyl chloride in ethanol were determined conductometrically at 25.0°. The reactions were run in a 2.5 × 15 cm test tube into which a Radiometer electode, type CDC 140, was placed. In each run, 25 ml of ethanol was added to the test tube and equilibrated in a water bath maintained at 25.00 ± 0.01°. Then a 0.245-ml aliquot of the chloride in pentane was added and the solution was briefly agitated. Usually 90–100 resistance measurements were taken at intervals varying from 15 sec to 3 min with an Industrial Instruments, Inc., conductivity bridge, Model RC-15. The reactions were followed to at least 62%, and infinity readings were taken after 10 half-lives. At least 20 measurements selected at appropriate times were used to calculate the rate constant. A weighted, least-squares FORTRAN program for the IBM-7094 computer took the measured resistance and time data for the run, converted the resistance into concentration, and applied the first-order equation. A calibration of resistance *vs.* concentration of hydrochloric acid in ethanol was determined, and a third-order polynomial was fitted to the data. The hydrochloric acid–ethanol solutions used in the calibration were *ca.* 1% in pentane, as were the solutions used in the kinetic and product runs.

The usual sealed-ampoule technique was used for the determination of the rates of solvolysis of the cumyl *p*-nitrobenzoates.[3] For all determinations a deuterated ester and an undeuterated ester were run concurrently in the same constant-temperature bath maintained at 100.00 ± 0.02°. In an additional method, a specially constructed titration apparatus was used which electronically detected a bromthymol blue end point. This method was also used to determine the rates of solvolyses of the benzhydryl *p*-nitrobenzoates.

The rates of ethanolysis of cumyl chloride and of cumyl thionbenzoate at 50° were determined by the use of a photometric titrator.[10,11] The apparatus consisted of a light source and an optical system which collimated the light on a band pass filter (λ_{max} 600 mμ) before it passed through a stirred and thermostated reaction cell to a phototransistor.

A servo-system controlled the addition of titrant from a piston buret so that the energy falling on the sensor was constant. The reaction cell had two cavities sealed by screw-caps containing silicone rubber plugs. Syringe needles were used for the introduction of titrant, substrate, and nitrogen gas. In a kinetic run, *ca.* 20 ml of solvent containing thymol blue indicator (*ca.* 2×10^{-5} *M*) was thermostated at the reaction temperature. Dry nitrogen was bubbled through the solution very briefly and the indicator was brought to the appropriate end point. The introduction of the chlorides into the reaction cell was by injection of pentane solutions. Thionbenzoates were added as solids. The apparatus added titrant (maximum volume was *ca.* 2 ml) as necessary to maintain the selected indicator end point. Readings at appropriate times were selected from the resulting titration volume *vs.* time curve and used directly to calculate the integrated first-order rate constant.

The solvolysis of benzhydryl thionbenzoates was studied in sealed, degassed ampoules thermostated in Carbowax-400 baths maintained at 75.00 ± 0.02 and 100.00 ± 0.02°. At appropriate times the ampoules were removed from bath, cooled to room temperature, and analyzed for absorption at 436 mμ with a Beckman DU spectrophotometer.

Calculations.—First-order rate constants were calculated with a FORTRAN program and IBM-7094 and -1800 computers. The program calculated the best fit, least-square line through the points of a plot of ln *Y* *vs.* time. The points were weighted in proportion to the relative magnitude of the *Y* values.

Registry No.—Acetophenone-d_3, 17537-31-4.

Effect of Solvent on the Photolysis of α-Lipoic Acid[1]

Phyllis R. Brown[2] and John O. Edwards

Metcalf Laboratory, Brown University, Providence, Rhode Island 02912

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The photolysis of α-lipoic acid in different solvents was followed by tlc and uv. It was found that a number of products are formed in each solution and the number and kind of product are dependent on the solvent. The chain length is determined by the kind of solvent; the length of the polymer chain decreased with increased availability of hydrogen atoms in the solvent. The amounts of products as well as the rate of formation of products are also solvent dependent. A mechanism is postulated in which the disulfide bond is broken homolytically in the first step. It is postulated that the reaction proceeds by chain transfer of hydrogen atoms from the solvent, causing short chains; by attack of the radicals on the other lipoic acid molecules, forming chains of longer length; or by the hydrolysis of the thio ketone formed by intramolecular abstraction of the tertiary hydrogen.

Because α-lipoic acid (1,2-dithiolane-3-valeric acid) has been found to be important biologically in the oxidative decarboxylation of α-keto acids,[3] and because it is thought to participate in photosynthesis,[4-7] several studies have been made of the photolysis of α-lipoic acid and the related compound, 1,2-dithiolane.[4,8,9]

In 1954, Barltrop, *et al.*,[4] reported that the photolysis of 1,2-dithiolane in neutral solution resulted in polymerization. They found that in acidified ethanol, the dithiolane ring was destroyed but no polymerization occurred. They suggested that the dithiyl radicals, produced by photolysis, reacted with the solvent. When Whitney and Calvin[8] photolyzed α-lipoic acid, the uv spectra indicated that a definite set of products was formed. These products were not identified. They also conducted a number of exploratory experiments on the relations between water concentration, pH, and polymerization, and concluded that polymer formation is not a simple consequence of the fission of the S–S bond. They postulated that the ultraviolet light causes slight polymerization and then inhibits it. They also felt that the failure of the biradicals to polymerize in ethanol solution was consistent with the views of Zimm and Bragg[10] that it is improbable for biradicals to form long chains. In 1956, while studying

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[1] This paper is abstracted in part from the Doctoral dissertation of P. R. Brown, submitted to the Graduate School of Brown University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June 1968.

[2] Union Carbide Fellow, 1966–1967. National Institute of Health Special Research Fellow, 1967–1968, Grant 1-F1-GM-35,937-01.

[3] L. J. Reed in "Comprehensive Biochemistry," M. Florkin and E. Stotz, Ed., **14**, Chapter II, Elsevier Publishing Co., Amsterdam, Holland, 1966.

[4] J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Amer. Chem. Soc.*, **76**, 4348 (1954).

[5] M. Calvin, H. Griseback, and R. C. Fuller, *ibid.*, **77**, 2659 (1959).

[6] M. Calvin and J. A. Barltrop, *ibid.*, **74**, 6153 (1952).

[7] M. Calvin, *Fed. Proc.*, **13**, 697 (1954).

[8] R. Whitney and M. Calvin, *J. Chem. Phys.*, **23**, 1750 (1955).

[9] E. Walton, A. Wagner, F. Bachelor, L. Peterson, F. Holly, and K. Folkers, *J. Amer. Chem. Soc.*, **77**, 5144 (1955).

[10] B. Zimm and J. Bragg, *J. Polym. Sci.*, **9**, 476 (1952).

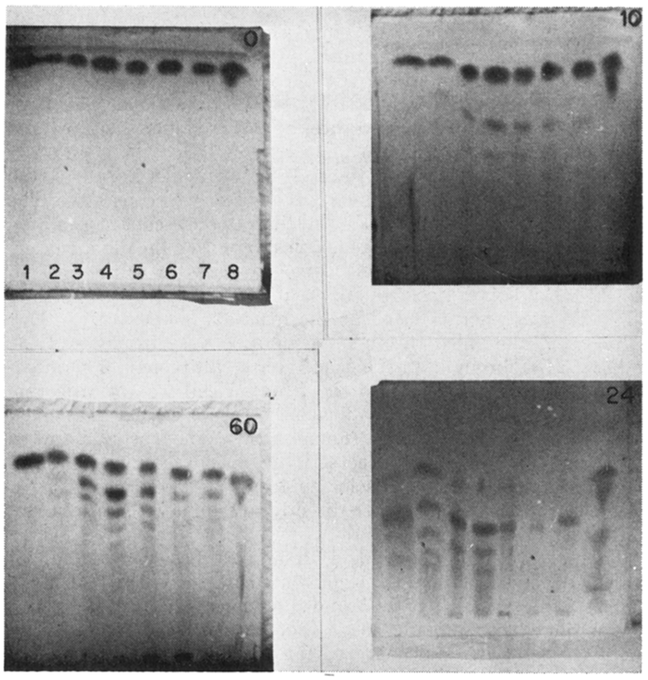

Figure 1.—Formation of products with time in photolysis of lipoic acid in different solvents as run on analytical tlc plates. The time of photolysis (in minutes except for 24 which is 24 hr) is noted on each plate. The 7 × 10^{-3} *M* solutions of lipoic acid were made up in the following solvents and applied from left to right: (1) 95% EtOH, (2) $(CH_3)_2CHOH$, (3) $CHCl_3$, (4) Et_2O, (5) C_6H_6, (6) C_6H_{12}, (7) CCl_4, (8) H_2O, OH^-.

the properties and derivatives of α-lipoic acid, Walton, *et al.*,[9] found that the ultraviolet spectra of solutions of α-lipoic acid (LA) in cyclohexane, ether, or benzene changed considerably on exposure to ordinary light for 2 days. The absorption at 3300 Å decreased and the absorption in the 2500-Å region increased. They postulated that linear disulfide polymers were formed once the cyclic disulfide bond was broken. No product studies were made, and the data collected was based on ultraviolet spectroscopy, which showed a decrease in the amount of cyclic disulfide present and an increase in absorption in the region of 2900–1900 Å. The absorption in this region is characteristic of many functional groups;[4,11] so the uv spectra provide no strong evidence for any one structure. No attempt was made to find out the effect of solvent on the course of the reaction.

Therefore, this study was made to investigate the effect of solvent on the photolysis of α-lipoic acid in order to elucidate the general mechanism of these photoreactions in various media.

Experimental Section

Materials.—The solvents used, CH_3OH, C_2H_5OH, $(CH_3)_2CHOH$, $(CH_3)_3COH$, Et_2O, C_6H_6, cyclohexane (herein referred to as C_6H_{12}), CCl_4, and C_6F_6, were spectral or reagent grade. The Et_2O, CH_3OH, C_2H_5OH, and $(CH_3)_2CHOH$ were either freshly distilled or were taken from containers that had been opened just prior to use so that peroxides would not be present. The α-lipoic acid (LA) was obtained from Sigma Chemical Co. A sample of dihydrolipoic acid (DHL), which was used as a reference compound, was also obtained from the same company.

Methods.—The photolysis reactions were followed by analytical tlc, using silical gel HR as adsorbent, $CHCl_3$–CH_3OH–$HCOOH$ (8:1:1) as developing solution, and I_2 as visualizing agent. They were also followed by uv. The uv source was an 8-W Sylvania Blacklight Blue uv tube lamp (no. F 8T5/BLB), which radiates the major part of its energy in the ultraviolet, peaking in the 3560-Å region.

The following extinction coefficients of LA in various solvents at λ_{max} = 3330 Å were determined, using a Hitachi Perkin-Elmer 139 uv-visible spectrophotometer: 95% EtOH, 139; $(CH_3)_2CHOH$, 145; $CHCl_3$, 169; Et_2O, 158; C_6H_6, 148; C_6H_{12}, 169; CCl_4, 232; H_2O, OH^-, 121.

The products of the photolysis in Et_2O were isolated by preparative tlc, using silica gel PF 254 as adsorbent and the solvent system described for the analytical tlc. The bands were located using a "hot wire" technique.[12] The structure of the major reaction product was determined on the basis of uv, ir, DTNB sulfhydryl determinations, reaction of product with base, reaction of product with $NiCl_2$, elemental analysis, and molecular weight determinations.

Results

In following the photolysis of LA by tlc, the products were designated A, B, C, etc., until they could be identified. Product A was the product that had the highest R_f value on tlc, B was the product that had the second highest, etc. No product had an R_f value higher than LA. The product with an R_f value of 0 was designated as a polymer, because it was found that increasing molecular weights caused decreasing R_f values. It should be noted that the fact that two compounds have the same R_f value does not necessarily mean that they have identical compositions. However, because of the distinct nature of the spots on tlc, they must be similar. Therefore, the product we call product A in Et_2O may differ in detail from product A in C_6F_6. Samples of typical plates are shown in Figure 1. All reactions were followed by sampling on tlc plates the solutions which had been photolyzed for 0, 5, 10, 20, 30, 45, 60, and 120 min and 24 hr.

In order to find the effect of oxygen on the products, duplicate photolyses on solutions of LA in Et_2O and C_6F_6 were run, one in air and one under nitrogen. No differences in the products formed could be observed on tlc in either solvent. The role of water in the photolysis was investigated by comparing the photolysis products in absolute ethanol, 95% EtOH, 66% EtOH, 33% EtOH, and H_2O. It was found that, after photolysis of the LA in absolute EtOH for 2 hr, there was only a trace of H_2S (both by odor and by $Pb(Ac)_2$ paper), but in all the others H_2S was a significant product. The effect of ease of abstraction of a hydrogen atom from similar solvents was followed by photolyzing LA in CH_3OH, C_2H_5OH, $(CH_3)_2CHOH$, and $(CH_3)_3COH$. Only traces of H_2S were found after photolysis of these solutions for 2 hr; however, after 24-hr photolysis, a significant amount of H_2S was found in the CH_3OH and C_2H_5OH but not in the secondary and tertiary alcohols. DHL was not formed in $(CH_3)_3COH$ but was a major product in the other three alcohols. The tlc results of the formation of products with time in the various solvents are tabulated in Tables I–III.

From the results obtained, it is evident that photolysis of α-lipoic acid is solvent dependent. The number of products and the kind, amount, and rate of formation are dependent on the solvent in which the photolysis takes place. From tlc plus the gross observations and uv, it is apparent that the photolysis of the solutions did not proceed identically. For example, H_2S was

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(11) C. Price and S. Oae, "Sulfur Bonding," Ronald Press Co., New York, N. Y., 1962.

(12) Detailed experimental procedures and results can be found in the Ph.D. Thesis of P. R. Brown, Chemistry Department, Brown University, Providence, R. I., 1968.

Table I

Products of Photolysis of α-Lipoic Acid in Various Organic Solvents[a]

Solvent	Time, min				
	5	10	30	60	1440
C_2H_5OH	...	Trace A	Trace A	DHL, Traces A–C	DHL, A, smear
$(CH_3)_2CHOH$	...	Traces A, B	Traces A, B	DHL, Traces A–C	DHL, A, smear
$CHCl_3$	Trace A	A–E	A–E	A–E	A–E
$C_2H_5OC_2H_5$	Trace A	A–E	A–E	A–E	50% A–E
C_6H_6	Trace A	A–E	A–E	A–E	Trace A, rest polymer
C_6H_{12}	...	A–E	A–E	A–E	Trace A, rest polymer
CCl_4	...	A–E	A–E	A–E	Trace A, rest polymer
C_6F_6	...	A–E	A–E	A–E	Polymer

[a] The products were designated A, B, C, etc., and polymer until they could be identified. Product A had the highest R_f value of all of the products, but its R_f value was lower than that of LA. The polymer had an R_f value of 0. The term "smear" indicates that products were present as indicated by analytical tlc but that distinct separation of the spots was not obtained under the conditions used.

Table II

Products of Photolysis of α-Lipoic Acid in Various Alcohols[a]

Solvent	Time, min				
	5	10	30	60	1440
CH_3OH	...	...	Trace A	Traces A–C	DHL, A, B, smear
C_2H_5OH	...	Trace A	Trace A	DHL, traces A–C	DHL, A, smear
$(CH_3)_2CHOH$	...	Traces A, B	Traces A, B	Traces A, B	DHL, A, smear
$(CH_3)_3COH$	...	A–C	A–C	A–C	A, smear

[a] See Table I, footnote *a*.

Table III

Products of Photolysis of α-Lipoic Acid in Ethanol–Water[a]

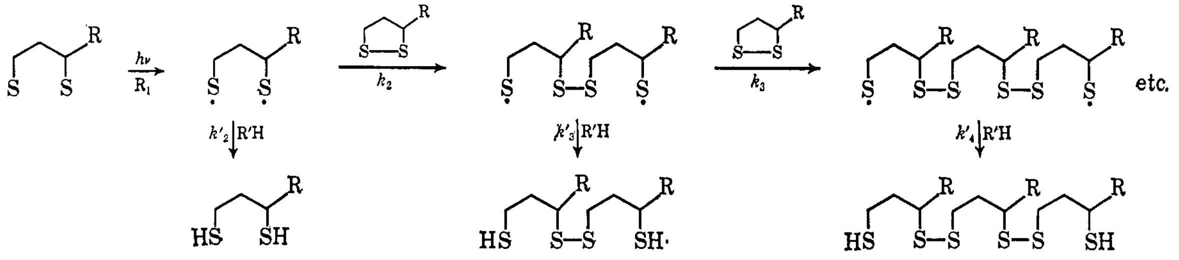
Solvent	Time, min				
	5	10	30	60	1440
100% EtOH	...	Trace A	Trace A	DHL, trace A–C	DHL, A, smear
95% EtOH	...	...	...	Traces A–C	DHL, A, A′, smear
66% EtOH	...	...	Traces A, B	Traces A, A′, B, C, D	Smear
33% EtOH	...	...	Traces A, B	Traces A, A′, B	Smear
H_2O	Smear	Smear	Smear	Smear	Smear

[a] See Table I, footnote *a*. Product A′ was a product that had a higher R_f value than A but lower than LA, and was found only in certain photolyses after the initial experiments were carried out.

detected [by odor and $Pb(Ac)_2$ paper] only in the alcohol and aqueous solutions. This indicates that there was breakup of at least some of the lipoic acid molecules in these solutions, and therefore different products must have formed.

The products developed at different rates with the various solvents. For example, a definite product was seen in $CHCl_3$, Et_2O, and C_6H_6 solutions after photolysis for only 5 min, whereas in $(CH_3)_2CHOH$ a distinct product was not detected until the solution had been photolyzed for 10 min, and in CH_3OH a product was not detected for still longer. After 24-hr photolysis, traces of a compound with the R_f value of α-lipoic acid were seen in $CHCl_3$, Et_2O, and C_6H_6, but not in C_6H_{12}, C_6F_6, and CCl_4. Only in the CH_3OH, EtOH, and $(CH_3)_2CHOH$ was there a significant amount of DHL observed. The major product in Et_2O after 24-hr photolysis was product A; in no other solution was product A present in such high concentration. The spots which were detected by tlc in all the organic solvents were similar, but the intensity of each spot (indicating concentration of the product) was dependent on the particular solvent in which the LA was photolyzed. The products with the higher R_f, which appeared in the C_6H_6, C_6H_{12}, and CCl_4 solutions early in the photolysis, either disappeared completely or decreased in concentration on photolyzing for 24 hr. None of the products in the Et_2O solutions, however, either disappeared or diminished in concentration on further photolysis. In solutions of LA in Et_2O (photolyzed for 24 hr) that were allowed to stand in the dark for one month, there was no change in the amount or kind of products present; no LA re-formed nor did the concentration of product A diminish. The alcohol solutions, however, showed a significant change in 1 month. The tlc showed breakdown of the DHL that had been present immediately after photolysis. In place of the DHL, there was a spectrum of many unidentified products, some of which were not seen in other experiments. In contrast to the DHL, there was no breakdown of product A; after a month it was still present and its concentration had not decreased. Polymer formation is seen (both from the turbidity of solutions photolyzed for 24 hr and from tlc) in C_6H_6, C_6H_{12}, C_6F_6, and CCl_4, but not in the alcohols or in Et_2O. All solutions remained colorless on photolysis except the basic aqueous solution, which turned yellow. The yellow color is probably due to the depolymerization of products which takes place in basic solutions.[3,12] The C_6H_5, C_6H_{12}, CCl_4, and C_6F_6 solutions became cloudy on photolysis, Scheme I

Postulated Mechanism for Photolysis of Lipoic Acid

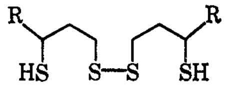


$R = (CH_2)_4COOH$

$R'H = \text{solvent}$

whereas the other remained clear. Since the products of the aqueous solutions were not well separated using this particular tlc procedure, no conclusions can be drawn as to the products formed in the photolysis of LA in aqueous solutions. However, from the work done on the photolysis of LA in ethanol solutions containing varying amounts of H_2O, it can be seen that H_2O has a definite effect on the formation of H_2S and hence on the breakup of LA molecules.

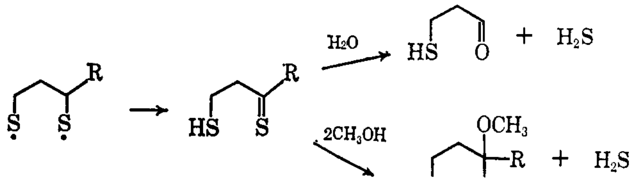
Using preparative tlc, small samples of product A (from photolysis of LA in Et_2O) were obtained and were characterized by several techniques.[12] Product A comprised approximately 50% of the total yield of products found in the Et_2O solution. Elemental analysis showed that no major change in atomic ratios occurred when LA is converted to product A. Experimental molecular weights were in the range of an oligomer with two LA units. The presence of sulfhydryl groups was shown by the appearance of the distinct red-brown color when nickel ion was added to product A solutions,[13] by the initial bleaching of iodine color at the product A spot in analytical tlc,[14] and by the DTNB determination for sulfhydryl content.[15] Product A depolymerized in the presence of base to form LA and DHL in equal amounts; this indicates a dimeric structure for product A. The infrared spectrum showed characteristic bands for C-H, S-H, and CO_2H groups. The ultraviolet spectrum had no bands in the area where the dithiolane ring absorbs, but adsorption was noted in the lower wavelength regions where the linear S-S and S-H groups absorb. When all the evidence is considered, it seems conclusive that product A is a linear dimer of the type where $R = (CH_2)_4CO_2H$. The actual disposition of the R groups is not known, and indeed product A may be a mixture of structural and geometric isomers.



Product B was isolated and analyzed in similar fashion. This product has the properties generally expected for a linear timer. We presume, therefore, that the lower spots represent higher molecular weight oligomers.

Discussion

From the results, a mechanism can be postulated for the photolysis of LA in which the disulfide linkage is broken homolytically in the first step (Scheme I). If the reaction proceeds by chain transfer of hydrogen atoms, in a type of chain transfer involving solvents that has been known for years,[16] short chains are formed. In solvents where a hydrogen atom is either not available or else not readily abstractable, the reaction can proceed by attack of the radicals on another LA molecule. If the reaction proceeds by subsequent attacks on other LA molecules, longer chains are formed. From our results, we feel that the conclusion of Whitney and Calvin[8] that light causes polymerization and then inhibits it and the conclusion of Zimm and Bragg[10] that it is improbable for diradicals to form long chains must be considered in terms of the specific system. The length of the chain of the products obtained in this particular reaction depends to a significant extent upon the solvent; the length of the polymer chain increases with decreased availability of hydrogen atoms in the solvent. In the photolysis of LA in Et_2O, the reaction proceeds primarily *via* the "chain transfer involving solvents" mechanism is which the significant products are oligomers. The results indicate that the photolysis in Et_2O and the alcohols involves hydrogen abstraction from the solvent. It is worth noting, however, that no DHL or H_2S was found in the Et_2O solution, whereas both products were found in the primary alcoholic solvents. The mechanism in these alcohols and water, therefore, is more complicated, since there is definite evidence for some breakup of the LA molecule in these photolyzed solutions. It is postulated that the mechanism of the photolysis of LA in hydroxylic solvents proceeds by one of two paths. If, as in the case of H_2O, the high bond energy of O-H prevents hydrogen abstraction from the solvent, then an intramolecular abstraction of a tertiary hydrogen may take place and a thio ketone is formed. Hydrolysis of the thio ketone leads to the formation of H_2S and a



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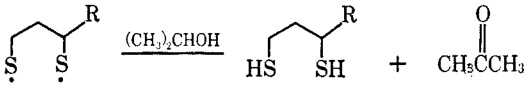
[13] P. R. Brown and J. O. Edwards, in press.

[14] P. R. Brown and J. O. Edwards, *J. Chromatog.*, **38**, 10.4, 543 (1968).

[15] G. L. Ellman, *Arch. Biochem. Biophys.*, **82**, 70 (1959).

[16] C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, Chapter 4.



ketone. If the solvent is CH_3OH, H_2S and a ketal may be the end products. In a solvent such as 2-propanol, where a hydrogen is easily abstracted from the hydroxylic carbon, dihydrolipoic acid and acetone are formed along with product A and the other oligomers. Since these are only preliminary experiments, it is indicated that a thorough product study should be made of the aqueous and alcoholic solutions. In solvents such as C_6F_6, where the products are mainly long chain polymers, it is evident that the reaction is a simple attack of the dithiyl radicals on other LA molecules. In solvents such as $CHCl_3$, CCl_4, C_6H_6, and C_6H_{12}, other products are formed as well as fair amounts of polymer. This indicates the possibility of other reactions proceeding at the same time as polymerization. Such possibilities include the abstraction of a chlorine atom from CCl_4 and formation of a chloro-LA derivative, the formation of a π-bond complex with benzene, the abstraction of a hydrogen atom from $CHCl_3$ and a subsequent coupling of the thiyl radical with the trichlorocarbon radical, etc.

Therefore it is concluded that the photolysis of LA is solvent dependent and that the final products formed are dependent on the ease of hydrogen abstraction and upon the presence or absence of water.

Registry No.—α-Lipoic acid, 62-46-4.

The Structure of Jegosapogenol (Barringtogenol C, Aescinidin) and the Configuration at C-21 and C-22 in Barringtogenol D, Aescigenin, Protoaescigenin, and Isoaescigenin[1,2]

T. NAKANO,[3] M. HASEGAWA, T. FUKUMARU, L. J. DURHAM, H. BUDZIKIEWICZ, AND CARL DJERASSI

The Department of Chemistry, Instituto Venezolano de Investigaciones Científicas (I. V. I. C.),
Apartado 1827, Caracas, Venezuela,
and the Department of Chemistry, Stanford University, Stanford, California 94305

Received October 16, 1968

The structure of jegosapogenol was established as $3\beta,16\alpha,21\beta,22\alpha,28$-pentahydroxyolean-12-ene (**1a**) on the basis of chemical as well as spectroscopic data and this triterpene was shown to be identical with barringtogenol C (aescinidin). The configuration at C-21 and C-22 in barringtogenol D, aescigenin, protoaescigenin, and isoaescigenin is discussed on the basis of nmr spectra, and their structures are revised to **12b**, **24a**, **25a**, and **26**, respectively.

The fruits of *Styrax japonica* Sieb. *et* Zucc. (Japanese name "egonoki") were once used as a substitute for soaps and as a fish poison. In 1899, Keimatsu[4] isolated from the skins of this fruit a saponin named jegosaponin. Since then, the elucidation of the chemical structure of this saponin has been the subject of a number of investigations.[5] However, in spite of these intensive studies, no structure could be proposed for this fish poison.

The earlier workers[5] reported that the acid hydrolysis of jegosaponin yielded 2 equiv each of glucuronic acid and glucose[6] as well as a sapogenin which, on digestion with alkali, was hydrolyzed to tiglic acid and jegosapogenol. For the sake of brevity, we have at the outset given the correct formula **1a** for jegosapogenol and will summarize later the relevant evidence. The nmr spectra of the acetyl derivatives (**1b**, **1c**, **1d**, **1e**, and **1f**) (see Table I) indicated that jegosapogenol has one primary hydroxyl group, which was confirmed by the preparation of a monotrityl ether **1g**, and all the remaining hydroxyl groups are secondary, one of which may be more hindered than the rest. From a biogenetic point of view, one hydroxyl group is assumed to be located at C-3, and a quartet (spacings of 6 and 12 Hz) at τ 5.28 in the 100 MHz nmr spectrum (benzene) of the pentaacetate **1b** corresponds to the axially oriented proton at C-3.[7]

The mass spectrometric fragmentation patterns[8] of jegosapogenol and its tetraacetate **1c** and also the detection of seven quaternary C-methyl groups as sharp singlets in the 100-MHz nmr spectrum (benzene) of the pentaacetate **1b**[1] suggested that jegosapogenol must be a β-amyrin-type triterpene alcohol, whose one primary and three secondary hydroxyl groups are located on rings D and E.

The uv spectrum of jegosapogenol exhibited an absorption maximum at 203 mμ (ϵ 6000), which was

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[1] Preliminary accounts of this work were presented in T. Nakano, M. Hasegawa, T. Fukumaru, S. Tobinaga, C. Djerassi, L. J. Durham, and H. Budzikiewicz, *Tetrahedron Lett.*, 365 (1967), and T. Nakano, M. Hasegawa, and J. B. Thomson, *ibid.*, 1675 (1967). The present paper represents part III in the series "Terpenoids" by T. Nakano and part LXIII in the series "Terpenoids" by C. Djerassi, *et al.*

[2] This work was supported by Research Grants GM-09362 and GM 06840 of the National Institutes of Health.

[3] To whom correspondence concerning this paper should be addressed.

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[5] Y. Asahina and K. Momoya, *Arch. Pharm.*, **252**, 56 (1914); *Yakugaku Zasshi*, **34**, 105 (1914); **35**, 1 (1915); C. Sone, *Acta Phytochim.* (Tokyo), **8**, 23 (1934); **9**, 83 (1936); S. Tobinaga, *Yakugaku Zasshi*, **78**, 526, 529 (1958).

[6] Matsunami [*J. Pharm. Soc. Jap.*, **545**, 87 (1927)], however, identified glucuronic acid (1 mol), rhamnose (1 mol), and glucose (2 mol) in this hydrolysis.

[7] This proton appears as a triplet (spacing of 8 Hz) at around τ 6.5 and 5.5, respectivey, in the 60 MHz nmr spectra of the C-3-OH (β) derivatives and the acetates (see Table I). This signal constitutes the X part of an ABX pattern and its change of appearance in different solvents is consistent with a change of the relative positions of A and B. These chemical shifts are in good accordance with those of the axial proton of α- and β-amyrin and taraxerol and their acetates [see M. Shamma, R. E. Glick, and R. C. Mumma, *J. Org. Chem.*, **27**, 4512 (1962)].

[8] H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 3688 (1963).