sured in the field in September 1976 during the microclimatic conditions chosen to simulate the leaf temperatures in Fig. 1. Similar mean leaf sizes were also measured in the field for the other four large-leafed species based on selection of sun versus shade leaf types during rapid growth periods (Table 1). This correlation provides evidence that leaf size may have an important functional role in the regulation of leaf temperature and, in combination with high transpiration rates, may act to reduce leaf temperatures to more optimal photosynthetic levels, particularly for rapid growth periods when water is abundant. Without abundant water and high transpiration rates a larger leaf size contributes to warmer leaf temperatures, often well above air temperature, and the accompanying changes in transpiration and photosynthesis.

A major portion of the photosynthetic production of these perennials may occur during relatively short periods following rainfall at almost anytime of the year (*6*). The probability of rain is nearly the same for any month except May and June, with substantial precipitation occurring in the late summer and fall months. Average maximum air temperatures for these months are generally above 30°C, while absolute maximum temperatures average above 40°C. In addition, these high temperatures usually persist for up to 6 or 7 hours during the day, over 50 percent of the total daily photosynthetic period. During these warm periods following rainfall, temperature reductions favoring photosynthesis appear to take priority over water conservation. This relationship is in contrast to the high water conservation of smaller leaves with moderately low leaf conductances that are characteristic of most desert species (*10*), although maximizing photosynthesis at some cost to water-use efficiency has been previously considered as a potential strategy for desert plants (*4, 11*). This adaptive pattern may represent an evolutionary alternative to the biochemical alterations needed for raising the temperature range for optimal photosynthesis, a prerequisite for water-conserving desert plants with relatively large leaves or photosynthetic stems.

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Photoejection of Electrons from Flavins in Polar Media

Abstract. *Riboflavin and 12 of its derivatives have been shown to form solvated electrons under ultraviolet irradiation (253.7 nanometers) in various water-methanol solvent mixtures. The highest quantum yield of solvated electrons (about 0.03) was obtained for flavins containing tyrosine on a side chain in the isoalloxazine N-3 or N-10 position. The splitting of hydrogen atoms from excited flavin molecules was also observed. From the results presented here, it can be determined that the semiquinone transients are formed not only by way of the flavin triplet, as usually suggested, but also by the attack of the electrons and hydrogen atoms on flavin molecules in the ground state. This is important, because the flavin radicals remaining after the electron-ejection or hydrogen-splitting processes must also be considered in the subsequent reaction mechanisms. The electron-ejection process from electronically excited flavins has important implications in the photobiology of these compounds.*

It has been shown that riboflavin and other isoalloxazines with substituents on the N-10 position in air-free polar solutions can be photobleached, and alteration to the aliphatic side chain is mainly responsible for this process (*1–4*). The solvent influences the kind of products formed in the photochemical reactions, which can be divided into two groups: reversible and irreversible. In the first group of products, the carbon skeleton of the side chain remains intact; however, it is oxidized. As a result of investigations of kinetic isotope effects with specifically deuterated isoalloxazines that have substituents on the N-10 position, it has been found that these processes can be initiated by intramolecular hydrogen abstraction (*2, 4, 5*). In the second group, at least a part of the carbon skeleton of the side chain is removed or the isoalloxazine nucleus is fragmented (*6*). Hydrogen abstraction occurs preferentially from the OH-bearing side-chain carbon most proximal to the ring system.

In addition, a completely reversible photoreduction of riboflavin has also been observed (*1, 2, 7*). Flash photolysis investigations showed that the reduction process is easier to achieve in alcohols with sufficiently labile hydrogens than in other solvents. The following solvents have been used, with the effectiveness decreasing in the order: 2-propanol, *tert*-butanol, 2-propyl acetate, and *tert*-butyl acetate (*8*). The same investigators found

Table 1. Substituents in formula **1**.

Compound	Substituents
1	$R_1 = CH_2(CHOH)_3CH_2OH$; $R_2 = H$ (riboflavin)
2	$R_1 = (CH_2)_5CONHCH(COOCH_3)CH_3$; $R_2 = H$
3	$R_1 = (CH_2)_5CONHCH(COOH)CH_2CH_2SCH_3$; $R_2 = H$
4	$R_1 = CH_2CONHCH(COOCH_3)CH_2C_6H_5$; $R_2 = H$
5	$R_1 = CH_2CONHCH(COOCH_3)CH_2C_6H_4CH_3$; $R_2 = H$
6	$R_1 = CH_2CONHCH(COOCH_3)CH_2C_6H_4OH$; $R_2 = H$
7	$R_1 = (CH_2)_5CONHCH(COOCH_3)CH_2C_6H_4OH$; $R_2 = H$
8	$R_1 = CH_2CONHCH(COOCH_3)CH_2$-indole; $R_2 = H$
9	$R_1 = (CH_2)_5CONHCH(COOCH_3)CH_2$-indole; $R_2 = H$
10	$R_1 = CH_3$; $R_2 = CH_2CONHCH(COOCH_3)CH_2C_6H_5$
11	$R_1 = CH_3$; $R_2 = CH_2CONHCH(COOCH_3)CH_2C_6H_4OH$
12	$R_1 = CH_3$; $R_2 = CH_2CONHCH(COOCH_3)CH_2$-indole
13	8α-*S*-(*N*-Acetyl)-L-cysteinylriboflavin

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that a flavin semiquinone radical is more prevalent in alcohols than in water. Two possible processes have been proposed to explain the formation of the semiquinone radical: the reactive flavin triplet can abstract hydrogen from its own side chain or from a photooxidizable compound, for example, an alcohol (*9*), or there can be an exchange of hydrogens immediately after the primary photoreduction step by means of the alkoxy radical. Flash photolysis studies also established that phenolic and indolic compounds are good quenchers of the flavin triplet (*10*). As a result, the quencher is oxidized and the flavin is reduced to the semiquinone radical. Tyrosine and its *N*-acetyl and ethyl ester derivatives serve equally well as photoreductants, whereas 4-methoxyphenylalanine is less effective (*11*). From these findings, it is clear that the spectral and photochemical properties of flavins are influenced by amino acid residues (for example, tyrosine or tryptophan) within certain flavoproteins (*9, 12*).

In contrast, it was shown very recently that the photochemistry of isoalloxazines in alcoholic solvents, although somewhat different from that in water, does not involve a primary photoreduction with the solvent, and photodegradation still dominates (*13*). The ultraviolet (UV) irradiation of riboflavin in air-free mixtures of 2-propanol and water showed that the physical properties of the solvent influence the photodegradation efficiency.

In addition, the formation of solvated electrons (e^-_{aq}) from certain electronically excited aromatic compounds [for example, phenols and phenolates (*14, 15*), tyrosine (*16*), tryptophan (*17*), indole (*18*), aromatic amines (*19*), and monophenylphosphate (*20, 21*)] in aqueous solutions is well established. In this connection, the irradiation of aromatic residues (for example, tyrosine or tryptophan) within proteins also leads to the production of e^-_{aq}, which can influence enzymic activity (*22*).

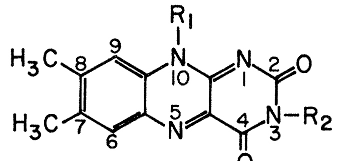
It was therefore of special interest to investigate whether or not electronically excited flavins in polar media can eject electrons. If so, these electrons can subsequently react with flavin to form the corresponding semiquinone radical. We have studied the photoejection of electrons from various flavins in methanol-water solvent mixtures. In this investigation, alanine, tyrosine, tryptophan, and other amino acid residues and their methyl esters were appended from alkyl chains in the N-3 or N-10 positions of the flavin (*23*); a cysteinyl function was substituted at the 8α-position (*24*). We also studied riboflavin as the basic compound for comparison.

Table 2. Quantum yields $Q(N_2) = Q(e^-_{aq})$ and $Q(H_2)$ formed by the UV irradiation at a wavelength of 253.7 nm of various flavins in water-methanol solvent mixtures. All solutions were saturated with N_2O.

Compound (Table 1)	Methanol concentration (mole liter^{-1})	Q (× 10^{-3})	
		$N_2(e^-_{aq})$	H_2
1	1	4.9	0.14
1	6.25	6.7	0.17
2	6.25	6.5	0.35
3	6.25	19	0.74
4	6.25	6.4	0.20
5*	6.25	14	0.50
6	12.5	22	0.60
7	12.5	33	0.62
8*	6.25	4.2	0.25
9	6.25	2.7	0.20
10	6.25	3.0	0.15
11	6.25	24.7	0.45
12	12.5	8.1	0.64
13	6.25	5.0	0.12

*Partly precipitated during irradiation.

The model substrates for formula **1** are given in Table 1. For the UV irradiation at 253.7 nm we used a vessel with double walls connected with a thermostat to maintain the temperature at 30° ± 0.5°C (*25*). A low-pressure Hg lamp (Osram Corporation, type HNS 10-W, ozone-free) with an incorporated filter for cutting off the light at 184.9 nm was used. The lamp intensity at 253.7 nm was determined by actinometry under the same experimental conditions with aqueous 2*M* monochloroacetic acid saturated with argon [at 30°C, the quantum yield of $Cl^- = 0.34$ (*26*)]. The light intensity was controlled periodically.



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We prepared the solutions (100 ml of $10^{-4}M$ to $5 \times 10^{-3}M$ flavin, $pH \simeq 7$), using water that had been distilled at least four times and reagent grade methanol (E. Merck, Darmstadt), which also served as a scavenger for the OH radicals [$k(OH + CH_3OH) = 0.9 \times 10^9$ liter mole^{-1} sec^{-1}] (*27*) and for the H atoms that eventually form [$k(H + CH_3OH) = 2.5 \times 10^6$ liter mole^{-1} sec^{-1}] (*28*). The CH_3OH concentrations varied from 5*M* to 12*M*. The solutions were saturated with N_2O, which acts as a specific scavenger for e^-_{aq} [$k(e^-_{aq} + N_2O) = 0.56 \times 10^{10}$ liter mole^{-1} sec^{-1}] (*29*). After irradiation, the yield of N_2, a product of e^-_{aq}, and the H_2 were pumped out of the solution (vacuum line) and determined by gas chromatography (molecular sieve, 5 Å). The Q values of N_2 and H_2 (Table 2) represent mean values of at least two experiments. The characteristic absorption maxima of the flavins in the vicinity of 488, 360, 266, and 220 nm were used occasionally for calculation of the respective flavin concentration.

From the data in Table 2 it is obvious that all the flavins we investigated in water-methanol mixtures are able to eject electrons under UV irradiation at a wavelength of 253.7 nm. Riboflavin and the flavins with a benzene ring (compounds 4, 5, and 10) or tryptophan residue (compounds 8, 9, and 12), and compounds 2 and 13 possess a low quantum yield, $Q(e^-_{aq}) = Q(N_2) \simeq 3 \times 10^{-3}$ to 14×10^{-3}. However, flavins having a tyrosine as a side chain in the N-3 or N-10 positions (compounds 6, 7, and 11) and compound 3 show relatively higher yields of e^-_{aq}. The Q value of tyrosine-containing compounds is about the same as for phenol [$Q(e^-_{aq}) = 0.03$] (*15*). Since the absorption at 253.7 nm by the phenolic part of the molecule is only 3.3 percent compared with that of, for example, compound 6 (phenol: molar extinction coefficient $\epsilon_{253.7} = 140$ m^2 mole^{-1}; compound 6: $\epsilon_{253.7} = 4230$ m^2 mole^{-1}), it is obvious that the photoformation of e^-_{aq} is not due to a direct excitation process of the phenol group but is probably a result of intramolecular energy transfer. Moreover, an interaction between the primary excited flavin nucleus and the phenol group under structurally favorable conditions can also enhance the electron-ejection process in a way similar to that of phenylethylamine (*19*).

A simplified reaction mechanism for the e^-_{aq} formation from electronically excited flavin (ROH) is represented as

$$RHOH \xrightarrow{h\nu} (RHOH)^*$$

$$\rightarrow \text{luminescence} \quad (1)$$

$$\rightarrow RHO^{\cdot} + H^+_{aq} + e^-_{aq} \quad (2)$$

$$\rightarrow \dot{R}OH \text{ (or } RHO^{\cdot}) + H \quad (3)$$

$$e^-_{aq} + N_2O \rightarrow N_2 + OH^-_{aq} + OH \quad (4)$$

In the absence of N_2O, e^-_{aq} can react with a flavin molecule in the ground state, producing the semiquinone radical. This is principally a second possible pathway in addition to the triplet state pathway, whereby the flavin triplet may abstract a hydrogen from its own side chain or from a photooxidizable compound (*1–4, 12*). The third possible pathway for the formation of the semiquinone radical could be due to the reaction of photolytically formed hydrogen atoms with the flavin in the ground state, but, under the present conditions, the hydrogen atoms are scavenged by the methanol, forming H_2.

Since the Q of H_2 is, in general, much less than the $Q(e^-_{aq})$ value (see Table 2), it can be assumed that e^-_{aq} and the flavin triplet are mainly engaged in the formation of semiquinone and of the leuco (1,5-dihydro) form of the flavins. The electron-ejection process of flavins by illumination at 253.7 nm very likely takes place from the singlet manifold, as has already been demonstrated for phenol and related compounds (*15*), aromatic amines (*19*), and monophenylphosphate (*21*).

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Experiments with Controlled Langmuir Circulations

Abstract. *Laboratory experiments in which wind was blown gently over a regular crossed-wave pattern have clearly shown the existence of regular, steady, and reproducible Langmuir circulations. The circulations were present only when both the wind and the wave patterns existed at the same time. With circulations having an across-wind wavelength of 44 centimeters, the descending vertical motions carried turbulent surface water downward 39 centimeters to the bottom of the wind and wave tank. The observations are in general agreement with the mathematical model of Craik and Leibovich, although further experiments will be required to definitively test the analytical model.*

The phenomena known as Langmuir circulations (LC's) consist of longitudinal roll vortices in the surface mixed layers of lakes and oceans. Their axes lie more or less parallel to the wind direction, there may be more than one scale present at any time, and the spacings of the convergence lines of the largest scale may be comparable to the depth of the mixed layer (*1*). These circulations were first systematically studied by Langmuir (*2*), who pondered the cause of lines of seaweed in the open ocean with spacings of the order of 100 m and similar but smaller-scale (1 to 10 m) lines of floating debris in Lake George, New York. From a variety of ingenious experiments over a period of several years, he concluded that these circulations were "the essential mechanism by which the epilimnion is produced" (*2*, p. 123). He believed that wind stirring was the primary cause of mixing and that organized rolls (as opposed to more random turbulence) were the dominant mechanism for the vertical transport of heat and momentum. The importance of LC's for planktonic activity has long been recognized (*3*), for these circulations concentrate floating materials in lines and may cause slightly buoyant particles to undergo large vertical excursions into and out of the photic zone.

An understanding of the basic mechanism leading to the generation of LC's has been clouded by the complexity of the natural environment and the consequent lack of definitive observations. A number of plausible theories have been advanced but most of these have been shown to be inadequate (*4*). An idealized mathematical model by Craik and Leibovich (*5*), however, has recently attracted wide attention and has been followed by a series of papers (*6–9*) that extend the application of the basic Craik-Leibovich (CL) model to more realistic conditions. The significance of these later papers, however, rests on some of the same basic premises as the original CL model. Accordingly, the goal of this research has been to experimentally test the original idealized model. That model involves a nonlinear interaction of the shear flow produced by the wind stress with two crossing trains of surface waves. In brief, the spatially variable Stokes drift associated with the pattern of waves is believed to twist the vorticity of the shear flow into the vorticity of the LC's.

Figure 1 illustrates the essential geometry of a wind and wave tank in which a regular pattern of crossed waves is generated by a double wedge that oscillates vertically at a resonant frequency σ. A light wind is drawn over the waves by an exhaust fan at the far end of the tank. With the wind alone or with the waves alone no LC's occur. With both wind and waves, however, the well-organized circulations depicted in Fig. 2 are observed.

A series of experiments was carried out with the following conditions: wind speed $U = 173$ cm/sec measured at a height $z = 7$ cm above the water surface, $\sigma = 9.94\ \text{sec}^{-1}$, and wave geometry as indicated in Figs. 1 and 2. The circulation was determined from cine photography of surface floats and $KMnO_4$ crystals sprinkled over the bottom. Figure 2 shows how the floats (weighted polyethylene rods 2.54 cm long and 1.27 cm in

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