The maleic anhydride adduct of furan is readily aromatized to phthalic acid[9] by hydrobromic acid in acetic acid. Similarly, the maleic anhydride adduct (V) of 2-acetoxyfuran is converted by sulfuric acid in acetic anhydride in 57% yield to 3-acetoxyphthalic anhydride (IX). This reaction represents a convenient new method of preparation of the latter compound.

Acknowledgment.—We gratefully acknowledge the support of this work by the Quaker Oats Company.

Experimental

Liquid Phase Pyrolysis of 2,5-Diacetoxy-2,5-dihydrofuran (IV). A. Without Catalyst.—A mixture of 2,5-diacetoxy-2,5-dihydrofuran (IV)[5] (50.9 g.) and dibutyl phthalate (50 ml.) was heated in a salt-bath at 200° under 10 mm. pressure, the reaction flask being provided with a 40-cm. helix-packed column (column temperature maintained at 120°). During a period of 120 minutes a light yellow distillate (27.3 g.) was collected. This liquid, which contained acetic acid, was diluted with ether (50 ml.) and the mixture was washed with cold saturated aqueous sodium bicarbonate (100 ml.) and dried over magnesium sulfate. Removal of the ether and distillation of the residue gave pure 2-acetoxyfuran (III) (12.7 g., 35%), b.p. 55–58° (10 mm.) (reported[4] b.p. 49–50° at 9 mm.).

B. With a Basic Catalyst.—A mixture of 2,5-diacetoxy-2,5-dihydrofuran (10.0 g.), dibutyl phthalate (25 ml.) and potassium acetate (0.5 g.) was heated at 200° for 90 minutes under conditions similar to those used without catalyst. No material distilled over. The column temperature was raised to 165° and the pressure decreased to 4 mm. A liquid, b.p. 120° (4 mm.), was collected which had an infrared spectrum identical with that of the original 2,5-diacetoxy-2,5-dihydrofuran.

C. With an Acid Catalyst.[10]—A mixture of 2,5-diacetoxy-2,5-dihydrofuran (10.0 g.), dibutyl phthalate (25 ml.) and β-naphthalenesulfonic acid monohydrate (0.05 g.) was heated in a Claisen flask under 2 mm. pressure for 45 minutes, the temperature of the heating bath being raised slowly from 100 to 190°. The distillate (9.5 g., b.p. 28–65° at 2 mm.) was redistilled through a 3-inch packed column to give 2-acetoxyfuran (b.p. 30–45° at 3 mm., 59%). Repetition of this latter experiment on a large scale using 2,5-diacetoxy-2,5-dihydrofuran (113.6 g.), dibutyl phthalate (275 ml.) and β-naphthalenesulfonic acid monohydrate (0.25 g.) gave a yellow distillate (99 g.) which on fractionation yielded 2-acetoxyfuran (62.8 g., b.p. 30–40° at 3 mm., 81.5%). The infrared spectrum of this material indicated it was essentially pure 2-acetoxyfuran.

3-Acetoxy-3,6-epoxy-Δ⁴-tetrahydrophthalimide (VI).—To 2-acetoxyfuran (1.0 g.) was added a solution of freshly sublimed maleimide (0.80 g.) in benzene (4 ml.). Within 5 minutes, white needles began to separate. After standing overnight the product was filtered and recrystallized from benzene to give the imide VI (1.1 g., 61%), m.p. 191–192°.

Anal. Calcd. for $C_{10}H_9NO_5$: C, 53.81; H, 4.06; N, 6.28. Found: C, 54.34; H, 4.24; N, 6.35.

3-Acetoxy-3,6-epoxy-Δ⁴-tetrahydrophthalonitrile (VII).—To 2-acetoxyfuran (1.0 g.) was added a solution of freshly sublimed fumaronitrile (0.8 g.) in benzene (4 ml.). After standing overnight the precipitate was filtered and recrystallized from benzene–petroleum ether to give fine white needles of the nitrile VII (0.50 g., 31%), m.p. 130.0–130.6°.

Anal. Calcd. for $C_{10}H_8N_2O_3$: C, 58.82; H, 3.95; N, 13.72. Found: C, 58.79; H, 3.97; N, 13.80.

Dimethyl 3-Acetoxy-3,6-epoxy-3,6-dihydrophthalate (VIII).—To 2-acetoxyfuran (0.670 g.) was added dimethyl acetylenedicarboxylate (0.733 g.). Within one day the mixture became viscous, but after one week no solid had separated. Benzene (1 ml.) was added and the mixture warmed. On cooling and rubbing, a solid (900 mg.) slowly separated. After recrystallization from benzene the diester VIII (0.70 g., 50%), formed fine white crystals, m.p. 152.2–152.8°.

Anal. Calcd. for $C_{12}H_{12}O_7$: C, 53.73; H, 4.51. Found: C, 53.85; H, 4.55.

3-Acetoxyphthalic Anhydride (IX).—A mixture of 3-acetoxy-3,6-epoxy-Δ⁴-tetrahydrophthalic anhydride (V)[3] (2.0 g.), acetic anhydride (20 ml.) and sulfuric acid (4 drops) was heated at 120° for one hour. The acetic anhydride was removed by distillation at 1 mm. and the dark residue was boiled with benzene (25 ml.) and activated charcoal. The filtered benzene solution was concentrated and cooled to give yellowish crystals (1.3 g.), m.p. 112–113° (sealed tube). Recrystallization from benzene–petroleum ether gave the pure anhydride (1.1 g., 57%), m.p. 116.0–116.2° (sealed tube) (reported[11] 113.5–115.5°).

Anal. Calcd. for $C_{10}H_6O_5$: C, 58.26; H, 2.93. Found: C, 58.12; H, 3.04.

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(9) Reference 6, p. 59.

(10) The exact conditions of method B were not appropriate with an acid catalyst, since cracking occurred too rapidly to be controlled.

(11) D. S. Pratt and G. A. Perkins, THIS JOURNAL, **40**, 227 (1918).

[CONTRIBUTION FROM THE WEIZMANN INSTITUTE OF SCIENCE]

Reversible Formation and Eradication of Colors by Irradiation at Low Temperatures. A Photochemical Memory Model

BY YEHUDA HIRSHBERG

RECEIVED AUGUST 29, 1955

It has been found that the colored forms of three spiropyrans and of one bianthrone derivative, produced by ultraviolet irradiation at low temperatures, at which they are stable, could nevertheless be reversibly eradicated, on irradiation with different visible monochromatic lights even at those temperatures. The eradication strength of each of the monochromatic visible lights was measured for the four compounds dissolved in different media. A mechanism for the energy transitions during the formation and eradication of color is proposed. On the basis of the experimental results, for the different media, the chemical course for the whole cycle studied is discussed and presented schematically. The cycle of the appearance of the color on ultraviolet irradiation and the disappearance of the color by irradiation with visible light is proposed for the first time as a photochemical memory model.

Introduction

The reversible formation of colors when colorless solutions of certain compounds are irradiated at room temperature was first reported by Lifschitz.[1] The occurrence of this phenomenon in rigid media solutions of some compounds has been found by Lewis and Lipkin.[2]

In 1950 Hirshberg reported that compounds belonging to the bianthrone series, either thermochromic or non-thermochromic, produce reversibly stable colors when their solutions are irradiated with

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(1) J. Lifschitz, *Ber.*, **52**, 1919 (1919); **61**, 1463 (1928); *Z. physik. Chem.*, **97**, 426 (1921).

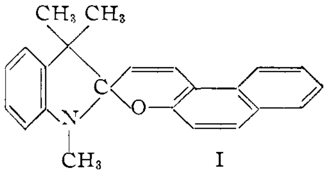
(2) G. N. Lewis and D. Lipkin, THIS JOURNAL, **64**, 2801 (1942).

ultraviolet light at 213°K.[3] A full account of this phenomenon (named, tentatively "photochromism") in compounds related to the bianthrone series and spiropyran series has been given in a number of publications.[4] It has been found that in those compounds which exhibit both thermochromism and photochromism the thermochromic and photochromic colors are spectroscopically identical.

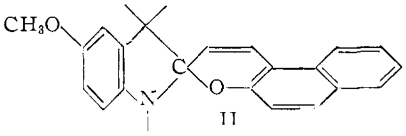
When the colors produced by ultraviolet irradiation are maintained at an appropriate low temperature they remain stable indefinitely, even after the ultraviolet irradiation has been discontinued. The rates of decay of the colors at higher temperatures are temperature dependent. When the temperature of the solution is finally raised to near 273°K. the original colorless modification is reformed.

In a preliminary note[5] it has been shown that the colored form of spiropyran (I), produced by ultraviolet irradiation and kept at a temperature at which it is stable, could, nevertheless, be reversibly eradicated by irradiation with visible light. The cycle can be repeated many times with the same solution.

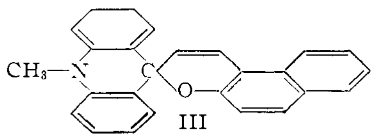
This phenomenon was now studied with four compounds and a detailed report on this work is the aim of this paper. The compounds used were



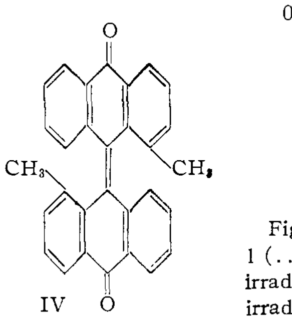
I



II



III



IV

Dilute solutions of each of these in either polar or non-polar solvents are colorless. When kept at an appropriate low temperature and irradiated with the 365 mμ triplet of a mercury arc (type A-H6) for a few seconds, strongly colored stable solutions result. Each of them possesses a characteristic absorption spectrum in the visible region with distinct absorption maxima.

The eradication of the color was done by irradiating successively with one of the monochromatic visible groups isolated from two different light sources. Before each experiment, the color was renewed by irradiation with the 365 mμ group of the above mentioned mercury arc. From the A-H6 mercury arc four monochromatic visible groups were isolated for the eradication process. They were the following: 578, 546, 436 and 405 mμ. The red light was isolated from the "Ediswan" Pointolite Lamp (1000 c.p.) by the red Corning filter No. 2418.

The velocity of the eradication of the color was followed spectroscopically by measuring the variation of the optical density for the particular absorption maximum with time of irradiation.

The influence of the polarity of the solvent on the velocity of the eradication process was investigated. For this purpose three different solvent mixtures were used; ethanol–methanol, ethanol–toluene and methylcyclohexane–petroleum ether. Also, the influence of acid and base added to the solvent mixtures was followed carefully.

Results

A spectrophotometric picture of the cycle in the four compounds studied is given in Figs. 1 to 4.

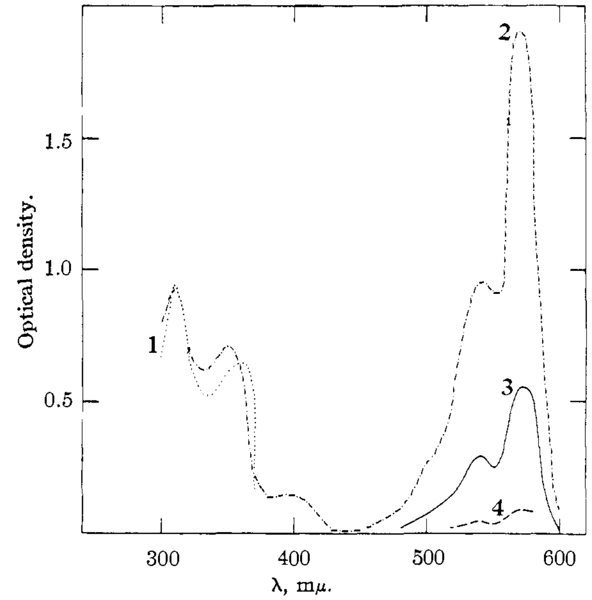


Fig. 1.—Compound I, 10 mg./l. (ethanol–toluene 1:1): 1 (......), before irradiation at 193°K.; 2 (-·-·-·), after irradiation with 365 mμ for 1 second; 3 (———), after irradiation with 436 mμ for 6 second; 4 (---------), after irradiation with 436 mμ for 16 seconds.

Curve 1 in each of the four figures shows that the original colorless solutions of the compounds do not absorb any visible light at the low temperatures used, and begin to absorb in the near ultraviolet.

When irradiated for a few seconds with the 365 mμ triplet, the colored form produced, in each case, has an intense absorption spectrum in the visible region with distinct maxima. The colored form of each compound is represented by curve 2 in the corresponding figure.

The reversion of the color formed is shown by curves 3 and 4 in Fig. 1 for the case of the indolinospiropyran (I) and by curve 3 in Figs. 2–4, for the other compounds investigated.

The eradication power of each of the monochro-

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(3) Y. Hirshberg, *Compt. rend.*, **231**, 903 (1950).

(4) E. Fischer and Y. Hirshberg, *J. Chem. Soc.*, **4522** (1952); Y. Hirshberg and E. Fischer, *ibid.*, 629 (1953); *J. Chem. Phys.*, **21**, 1619 (1953); *J. Chem. Soc.*, 297, 3129 (1954);

(5) Y. Hirshberg, E. H. Frei and E. Fischer, *ibid.*, 2184 (1953).

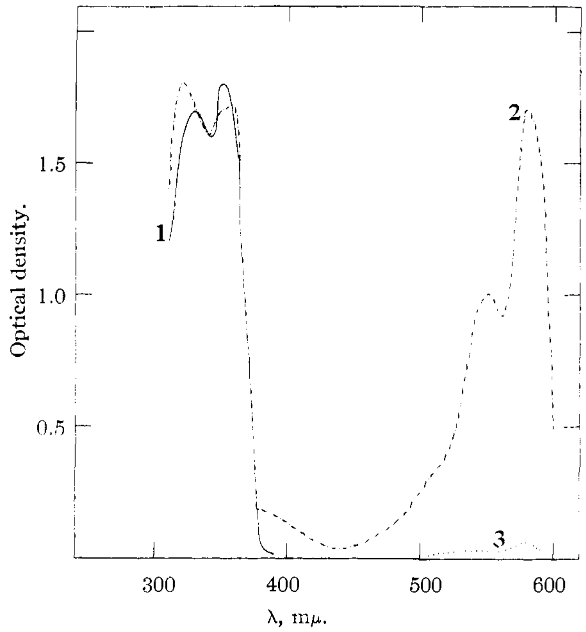


Fig. 2.—Compound II, 40 mg./l. (ethanol-toluene 1:1): 1 (———), before irradiation at 173°K.; 2 (-·-·-·), after irradiation with 365 mμ for 3 seconds; 3 (......), after irradiation with 546 mμ for 20 seconds.

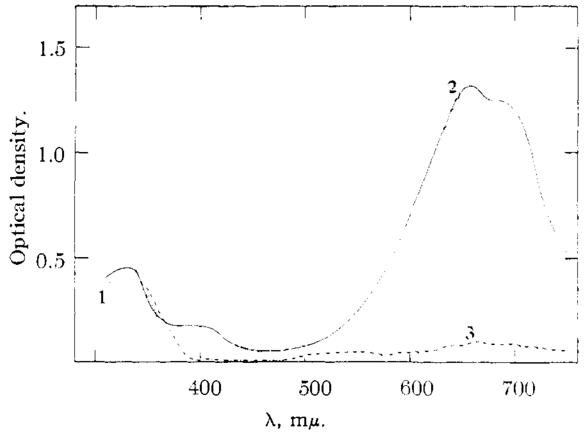


Fig. 3.—Compound III, 4 mg./l. (ethanol-methanol 1:1): 1 (......), before irradiation at 173°K.; 2 (———), after irradiation with 365 mμ for 2 seconds; 3 (-·-·-·), after irradiation with 546 mμ for 50 seconds.

matic visible groups is expressed by the half-life time of the colored modification during the particular eradication process. The half-times are uncorrected for intensity variation of arc with wave length, and without filter correction. They have been measured for each compound in different solvent mixtures, either neutral or having acid or base added in amounts here expressed as fractions of the molar concentrations of the dissolved compounds. The most important experimental data are summarized in Tables I–IV.

Discussion

1. **Compound I in Neutral Media.**—The violet-red colored form of the indolinospiropyran (I) formed by ultraviolet irradiation in a neutral

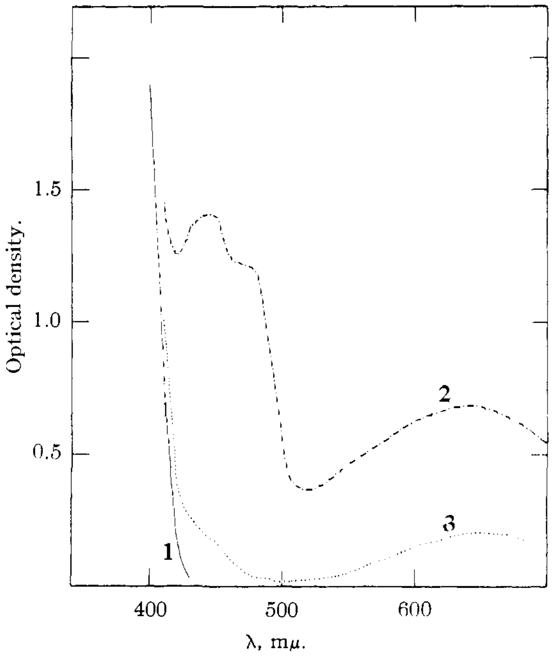


Fig. 4.—Compound IV, 30 mg./l. (toluene-ethanol 2:8): 1 (———), before irradiation at 203°K.; 2 (-·-·-·), after irradiation at 365 mμ for 30 seconds; 3 (......), after irradiation with 578 mμ for 50 seconds.

ethanol–methanol mixture has two distinct absorption maxima in the visible region, one at 570 mμ and the other at 530 mμ. During the successive eradication of the color by each of the four monochromatic visible groups (isolated from A-H6) surprising results were found. The 436 mμ group, which is least absorbed by the color (see curve 2, Fig. 1) was the most active for eradication, while the 578 mμ group, which corresponds to the absorption maximum of the color, was the least active for eradication (see 1 in Table I).

These results, although surprising photochemically, may be explained by the assumption of a particular mechanism for the eradication process of this color. The assumption is that the instantaneous quantitative reversion of the colored form into the colorless one will take place only when the colored species are brought by irradiation energy to a specific excited level.

While the 436 mμ group is little absorbed by the color, each quantum of this wave length absorbed is sufficient to bring one molecule of the colored form to the specific excited level, from which they return instantaneously to the ground level of the colorless form.

Although the 578 mμ or even the 546 mμ group are strongly absorbed by the color, their energies are not sufficient to bring the colored molecules to the above described excited level. Therefore, when irradiated by the 578 mμ or by the 546 mμ group, the colored molecules are brought to certain lower excited levels. Some of the excited colored molecules at these levels may, by collision between themselves, reach the specific higher level and return from there to the ground level of the colorless species. Most of the molecules, however, lose their excitation energy by collision with solvent

TABLE I

THE INFLUENCE OF MEDIA ON THE REVERSIBLE FORMATION AND ERADICATION OF COLOR BY IRRADIATION AT 193°K.

Indolinospiropyran (I), 10^{-7} mole in 10 cc.

		Color formed on irradiation[a]			Half-life time of color (sec.) On eradication by irradiation with			
No.	Solvents[b]	Color formed	Absorp. max., mμ	Optical density	578 mμ	546 mμ	436 mμ	405 mμ
1	Et + Me	Violet red	570	1.500	345	90	13	210
2	+0.2 equiv. HCl	Violet red	570	1.500	366	60	8	60
3	+0.5 equiv. HCl	Rose red	570	1.300	450	36	3	36
4	+0.75 equiv. HCl	Rose	570	0.650	480	19	1	13
5	+1.0 equiv. HCl	*Yellow*	*480*	1.500	5200	4	2	26
6	+1.0 equiv. ac.ac	Rose red	570	1.100	420	56	4	68
7	+2.0 equiv. ac.ac	Rose	570	0.630	980	41	2	31
8	+10 equiv. Py.	Violet red	570	1.700	664	132	23	
9	+0.5 equiv. TEA	Violet red	570	1.700	324	88	26	348
10	+1.5 equiv. TEA	Violet red	570	1.800	234	84	318	
11	Et + Tol	Violet red	570	1.800	528	174	2430	
12	+0.2 equiv. HCl	Violet red	570	1.600	398	147	171	
13	+0.5 equiv. HCl	*Orange*	*490*	1.450	444	18	8	42
14	+1.0 equiv. HCl	*Yellow*	*480*	1.300	5400	4	2	28
15	mch + pe	Violet red	570	1.800	2460	600	3600	
16	+15 equiv. HCl	Violet red	570	1.600	3285	432	624	

[a] 5 seconds with 365 mμ. [b] Et, ethanol; Me, methanol; equiv., equivalent to the compound dissolved; ac.ac., acetic acid; Py, pyridine; TEA, triethylamine; tol, toluene; mch, methylcyclohexane; pe, petroleum ether.

TABLE II

THE INFLUENCE OF MEDIA ON THE REVERSIBLE FORMATION AND ERADICATION OF COLOR BY IRRADIATION AT 188°K.

5-Methoxyindolinospiropyran (II), 5×10^{-7} mole in 10 cc.

		Color formed on irradiation[a]			Half-life time of color (sec.) On eradication by irradiation with			
No.	Solvents[b]	Color formed	Absorp. max., mμ	Optical density	578 mμ	546 mμ	436 mμ	405 mμ
1	Et + Me	Red violet	580	1.400	10	6	8	63
2	+0.05 equiv. HCl	Rose violet	580	1.200	7	5	6	50
3	+0.10 equiv. HCl	Rose	580	0.900	7	3	2	20
			490	.450	44	11	7	67
5	+0.2 equiv. HCl	Orange	580	.350	6	1	1	4
			490	.700	70	7	7	65
7	+0.3 equiv. HCl	Yellow	490	1.000	18000	7	*ca.* 50% formation and 50% eradication of color	
8	Et + Tol.	Red violet	580	1.700	12	7	31	
9	+3 equiv. TEA	Red violet	580	1.800	14	8	2100	
10	mch + pe.	Red violet	580	1.700	15	15	650	840
11	+5 equiv. ac.ac.	Rose violet	580	1.000	26	10	48	306

[a] 7 seconds with 365 mμ. [b] See *b* of Table I.

molecules and return to the ground level of the colored species.

A schematic representation of the energy transitions during formation and eradication of color is shown in Fig. 5.

The mechanism of the transitions may be represented as

Formation of color:

$$\mathrm{NC} + h\nu_1 \xrightarrow{1} [\mathrm{NC}^*] \xrightarrow{2} \mathrm{C}$$

NC—colorless species, ground level

[NC]*—colorless species excited level

C—colored species, ground level

C^*_n—colored species, excited levels

Eradication of color:

$$\text{(a)}\quad \mathrm{C} + h\nu_2 \overset{3}{\rightleftarrows} \mathrm{C}^*_1 \xrightarrow{4} \mathrm{NC}$$
$$\text{(b)}\quad \mathrm{C} + h\nu_3 \overset{5}{\rightleftarrows} \mathrm{C}^*_2 \xrightarrow{6} \mathrm{NC}$$
$$\text{(c)}\quad \mathrm{C} + h\nu_4 \overset{7}{\rightleftarrows} \mathrm{C}^*_3 \xrightarrow{8} \mathrm{NC}$$
$$\text{(d)}\quad \mathrm{C} + h\nu_5 \xrightarrow{9} \mathrm{C}^*_4 \xrightarrow{10} \mathrm{NC}$$

ν_n—One of 4 visible band passes transmitted by the filter combinations

ν_1—365 mμ

It is obvious that in that case, irradiation of the color at 436 mμ brings about course (d) of the eradication mechanism and therefore the fastest reversion from the colored form to the colorless one occurs.

The polarity of the solvent influences strongly

TABLE III

THE INFLUENCE OF MEDIA ON THE REVERSIBLE FORMATION AND ERADICATION OF COLOR BY IRRADIATION AT 163°K.
N-Methylacridinospiropyran (III), 2×10^{-7} mole in 10 cc.

		Color formed on irradiation[a]			Half life-time of color (sec.) On eradication by irradiation with			
No.	Solvents[b]	Color formed	Absorp. max., mμ	Optical density	578 mμ	546 mμ	436 mμ	Red light
1	Et + Me	Green blue	660	1.600	189	28	230	2700
2	+0.4 equiv. HCl	Green blue	650	1.300	72	20	110	
3	+0.6 equiv. HCl	Green blue	650	1.300	31	7	81	2348
4	+0.8 equiv. HCl	Green blue	650	1.250	20	4	35	2800
5	+1.0 equiv. HCl	Green blue	650	1.200	Disappears slowly spontaneously			
6	+1.5 equiv. HCl	Rose	540	0.730	35	11	138	
7	+0.5 equiv. TEA	Green blue	660	1.450	318	144	570	
8	+1.0 equiv. TEA	Green blue	660	1.500	5340	1500	8760	
9	+3.0 equiv. TEA	Green blue	660	1.500		3690		
10	Et + Tol	Blue green	670	1.600	40	21	190	
11	+0.2 equiv. HCl	Blue green	670	1.450	22	9	122	
12	+0.4 equiv. HCl	Blue green	670	1.400	7	2	52	
13	mch + pe.	Blue green	670	1.600		9000		
14	+1.0 equiv. HCl	Blue green	670	1.500		6000		
15	+5.0 equiv. ac.ac.	Rose	550	0.760		420		

[a] 2 seconds with 365 mμ. [b] See *b* of Table I.

TABLE IV

THE INFLUENCE OF MEDIA ON THE REVERSIBLE FORMATION AND ERADICATION OF COLOR BY IRRADIATION AT 203°K.
4,4'-Dimethylbianthrone (IV), 10^{-6} mole in 10 cc.

		Color formed on irradiation[a]			Half life-time of color (sec.) On eradication by irradiation with			
No.	Solvents[b]	Color formed	Absorp. maximum in mμ	Optical density	578 mμ	546 mμ	436 mμ	Red light
1	9 cc. Tol + 1 cc. Et	Green	640	0.950	24	18	160	31
2	2 cc. Tol + 8 cc. Et	Green	640	.820	17	22	122	30
3	+10 equiv. HCl	Green	640	.830	18	18	92	26
4	+10 equiv. ac.ac.	Green	640	.820	19	20	95	26
5	+10 equiv. TEA	Green	640	.850	45	120	135	120

[a] 2 seconds with 365 mμ. [b] See *b* of Table I.

the formation and the eradication of the color in spiropyran (I). When methanol is substituted by toluene in the solvent mixture, the formation of the color by ultraviolet irradiation is enhanced while the eradication of the color by irradiation with visible light is strongly hindered (compare 1 and 11 in Table I).

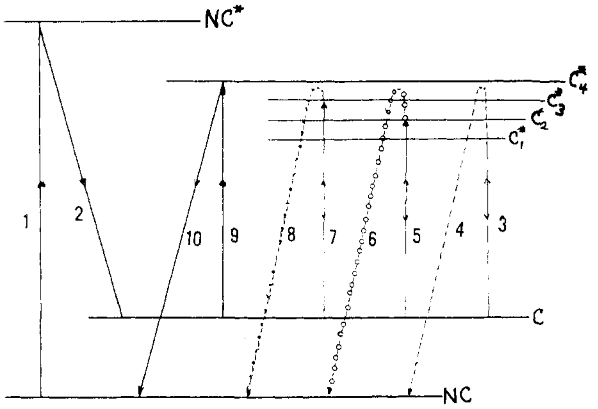


Fig. 5.—Schematic representation of energy transition during formation and eradication of color.

A still stronger hindrance of the eradication of the color is found in the case where the neutral non-polar solvent mixture methylcyclohexane–petroleum ether is used instead of the ethanol–methanol mixture (compare 1 and 15 in Table I).

The Influence of Acid and Base in the Case of I.—Addition of small quantities of acid (corresponding to fractions of the quantity of the spiropyran (I) dissolved) to the solvent mixtures, hinders the eradication of the color by irradiation with the 578 mμ group, while the eradication power of the other three visible groups is strongly enhanced. When the quantity of acid added reaches half (or more) of that of the spiropyran dissolved, irradiation with the 365 mμ triplet causes the formation of a strong yellow-orange color instead of violet-red. Also the yellow-orange color, which has an absorption maximum at 480–490 mμ, can be reversibly eradicated by visible light (see 5, 13 and 14 in Table I). Only the 578 mμ group is inactive, because this light is not absorbed at all by this color. The changes in the color formation with gradual addition of acid to the solution are presented by Fig. 6.

In non-polar solvents addition of acid in quantities up to ten times that of the spiropyran dissolved does not affect either the formation or the eradication of the color. This fact suggests strongly that the influence of acid on the formation and eradication of color is linked with the degree of dissociation of the acid in the solvent.

The presence of a weak base such as ammonia or pyridine, even in the polar solvents, has very little influence on the color formation and its eradication. One or more equivalents of a strong base like triethylamine (TEA) decreases the eradication power of the 436 mμ group very strongly (compare 1 with 8, 9 and 10 in Table I).

The Influence of the Methoxy Group Introduced into the Aromatic Nucleus of I.—The experimental data presented in Table II indicate that compound (II) is less basic than (I).

The colored modification of compound II showed absorption similar to that of compound I, with a bathochromic shift of 10 mμ in the absorption maxima (see curve 2 in Fig, 2). Solutions of II in neutral ethanol–methanol mixtures had to be irradiated for a longer time with ultraviolet light to get the same intensity of color as in the corresponding solutions of I.

The reversion of the colored form into the colorless one, when irradiated with visible light, is very much enhanced in the case of compound II as compared with that of (I).

In the case of II the colored form was eradicated with almost the same velocity when irradiated with 578 or 546 mμ or 436 mμ (see 1 in Table II). The substitution of methanol by toluene in the above-mentioned solvent mixture increased the velocity of color formation, but did not decrease very much the eradication power of any of the above visible groups (compare 1 and 8 in Table II). Even in the non-polar solvent mixture methylcyclohexane–petroleum ether the velocity of color disappearance when irradiated by 578 or by 546 mμ was still appreciable (see 10 in Table II).

Also, the presence of a strong base, like triethylamine, in an ethanol–toluene solution of II, did not diminish the eradication strength of the two above-mentioned visible light groups (compare 10 of Table I with 9 of Table II).

Addition of even 0.1 equivalent of HCl to the ethanol–methanol solution of compound II brought about a strong change in the color formation. Although the absorption maximum at 580 mμ was still strong for the rose-orange color formed, the 490 mμ maximum appeared instead of that at 540 mμ (see 3 in Table II). In the presence of 0.3 equivalent of the acid the color formed by ultraviolet irradiation was orange-yellow with a single absorption maximum at 490 mμ. This color could be completely and reversibly eradicated by irradiation with 546 mμ only. When 436 or 405 mμ was used, the eradication stopped at about 50% of the color. The cause has been found to be the fact that with the above solvent conditions these two visible groups are also very active in the formation of the color in compound II (see 7 in Table II).

The experimental results described indicate that the methoxy group attached to the aromatic nucleus has a pronounced influence on the nature of the indolinospiropyran (I). The methoxy group, while causing a shift from base to acid character, also enhances the polarity strength of indolinospiropyran. This may explain why the colored form of the 5-methoxyindolinospiropyran (II) can easily be reversed into its colorless one, by less excitation energy than in the case of I.

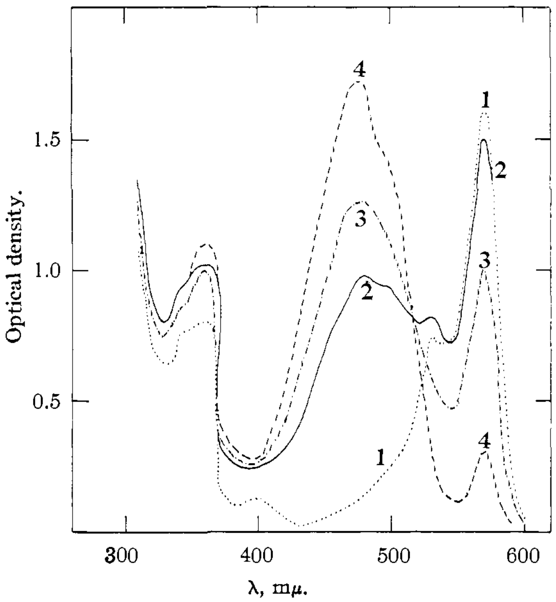


Fig. 6.—The influence of acid on the color formation of spiropyran (I) when irradiated with ultraviolet light at 193°K.: 1, in ethanol–methanol mixture—neutral; 2, in ethanol–methanol mixture, 0.32 equiv. HCl; 3, in ethanol–methanol mixture, 0.4 equiv. HCl; 4, in ethanol–methanol mixture, 0.6 equiv. HCl.

An important observation which should be mentioned was made during this study with both indolinospiropyrans. When in solutions of either of these compounds in polar solvents, a certain amount of acid is added, the original colorless solution turns yellow even before ultraviolet irradiation. This color disappears completely when irradiated at the appropriate low temperature with 436 mμ in the case of I and with 546 mμ in the case of II. After the eradication of the yellow color by the visible light, ultraviolet irradiation causes the formation of the orange-yellow color as described above.

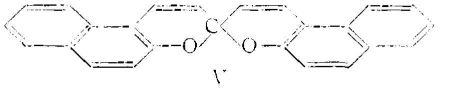
The Behavior of Compound III.—Neutral colorless solutions of N-methylacridinospiropyran (III), when irradiated at between 168 and 153°K. with 365 mμ develop green blue or dark blue colors. Their absorption spectrum is shown in Fig. 3 (curve 2), the absorption maximum being either 660 or 650 mμ. The most active visible light for the eradication is also, in this case, not the one which is most absorbed by the color, like the red group or the 578 mμ, but the 546 mμ which is the least absorbed of the three (see 1 in Table IV). The 436 mμ group corresponds to transitions which are outside the main absorption of the colored form and have to be discussed separately. The above fact suggests that also in case of III the colored modification has to be brought by irradiation energy to a certain excited level, from which it can return quickly to the ground level of the colorless modifications.

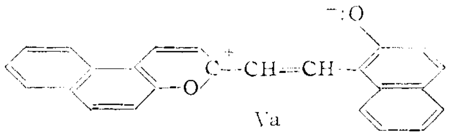
The important experimental data for III are summarized in Table III. They show that III is of a more basic character than I. Less ultraviolet irradiation is needed to get a given intensity of color with III than with I. More acid has to be added to the solvent mixtures in order to increase the eradication strength of the visible light used for this purpose (compare 2, 3 and 4 in Table III with the corresponding numbers in Table I). Even in the presence of one equivalent of HCl, irradiation with 365 mμ still causes the formation of the same color (although it disappears spontaneously) as in a neutral solution, whereas in I or II such solvent conditions bring about a cardinal change in the color formed (compare 6 in Table III with 5 in Table I).

When the amount of HCl added to an originally colorless solution of III reaches 1.5 times that of the compound dissolved, the solution turns rose. This color, which has an absorption maximum at 540 mμ, is eradicable at low temperature by irradiation with one of the four visible groups isolated from the mercury arc. Irradiation with 365 mμ causes the formation of a mixture of two colors: the blue one, which disappears spontaneously after ultraviolet irradiation has been discontinued, and the rose color, which is stable, and can be eradicated by irradiation with visible light as mentioned before (see 5 and 6 in Table III).

Even smaller quantities of triethylamine present in a solution of III hinder more strongly the eradication of its colored form than in the case of I (compare 7 in Table III with 9 in Table I). In the non-polar solvent mixture, the colored modification of III disappears only on prolonged irradiation with the most active visible light, even in the presence of one equivalent of HCl.

The Chemical Course of the Cycle in the Spiropyrans.—W. Dilthey and H. Wubken[6] have concluded that the thermochromic effect found in the case of di-β-naphthospiropyran (V) is due to the ionic dissociation of the molecule, the colored form being represented as a heteropolar molecule (Va).


V


Va

This has been later supported by the work of Dickinson and Heilbron.[7]

A thorough investigation into the possibility of intramolecular ionization in the series of spiropyrans, including the compounds I, II and III described in this paper, has been reported by Wizinger and Wenning.[8]

Since it has been proved[2] that in those compounds which exhibit both thermochromism and photochromism the colors formed are spectroscopically identical, it seems plausible to assume that when solutions of spiropyrans are irradiated by ultraviolet light at low temperatures, they undergo an intramolecular ionization process. In thermochromism, because of thermal equilibrium, only a small amount of the colorless form can undergo ring opening, whereas ultraviolet irradiation at low temperatures brings about a considerable transformation from the colorless to the colored, open form.

On the basis of the experimental results described, it seems that the chemical course of the whole cycle studied may schematically be represented as shown in the Chart.

At the appropriate low temperatures, when the colorless form of I, II and III (structure A) is irradiated by ultraviolet light, the spiropyranic C–O bond is opened and the colored hybrid molecule is formed (structure B). In inert non-polar solvents IB and IIIB are very stable; excitation of these molecules by visible light is not enough to bring about the reclosure of the spiropyranic ring. Therefore, the reversion process from the colored forms to the colorless ones by irradiation with visible light in non-polar solvents is very slow (see 15 in Table I and 13 in Table IV). In the case of IIB, the methoxy group in this position brings about a more active ionic colored form which is less stable and needs lower excitation energy for the reclosure of the spiropyranic ring; therefore, IIB, even in methylcyclohexane–petroleum ether mixtures, is readily reconverted, on absorption of visible light, into its colorless form IIA (see 10 in Table III).

In a polar solvent the colored molecules IB, IIB and IIIB are partly transformed into the quasi-complex colored salts, structures C. The colored complexes are also stable at the appropriate low temperatures. Because of the mobility of the highest energy electron in the cation, however, irradiation with visible light, which can bring it to a suitable excited level, causes the destruction of the complex and at the same time the reclosure of the spiropyranic ring with a much better yield than in structures B. Addition of acid to these solutions shifts the equilibrium toward C (Fig. 6), and by increasing the concentration of the latter, increases the speed of eradication at the appropriate wave length.

The changes in the eradication strength of the individual visible light groups are also connected with the changes in the color produced when different amounts of acid are present in the solutions, as previously described.

A strong base, like triethylamine, when present in equivalent amount to the spiropyran dissolved, hinders the salt complex formation between the colored molecule and the polar solvent; hence the reversion process, on irradiation with visible light in such media, is slow.

The Case of Compound IV.—The bianthrone derivative, compound IV, is insoluble in methylcyclohexane, very slightly soluble in either ethanol or methanol. The reversible formation and eradication of the colored modification of this compound was followed with solutions in toluene–ethanol mixtures, either neutral or containing acid or base in known amounts. The spectroscopic picture of the appearance and disappearance of the colored form of IV on irradiation at low temperature is shown in Fig. 4. Table IV contains a summary of the experimental data on the eradication strength of the various visible light groups when IV was dissolved in different media. It is easily seen that the velocity of the eradication of the color on irradiation by the three long wave length visible groups is quite the same in either neutral or acid media. No changes in

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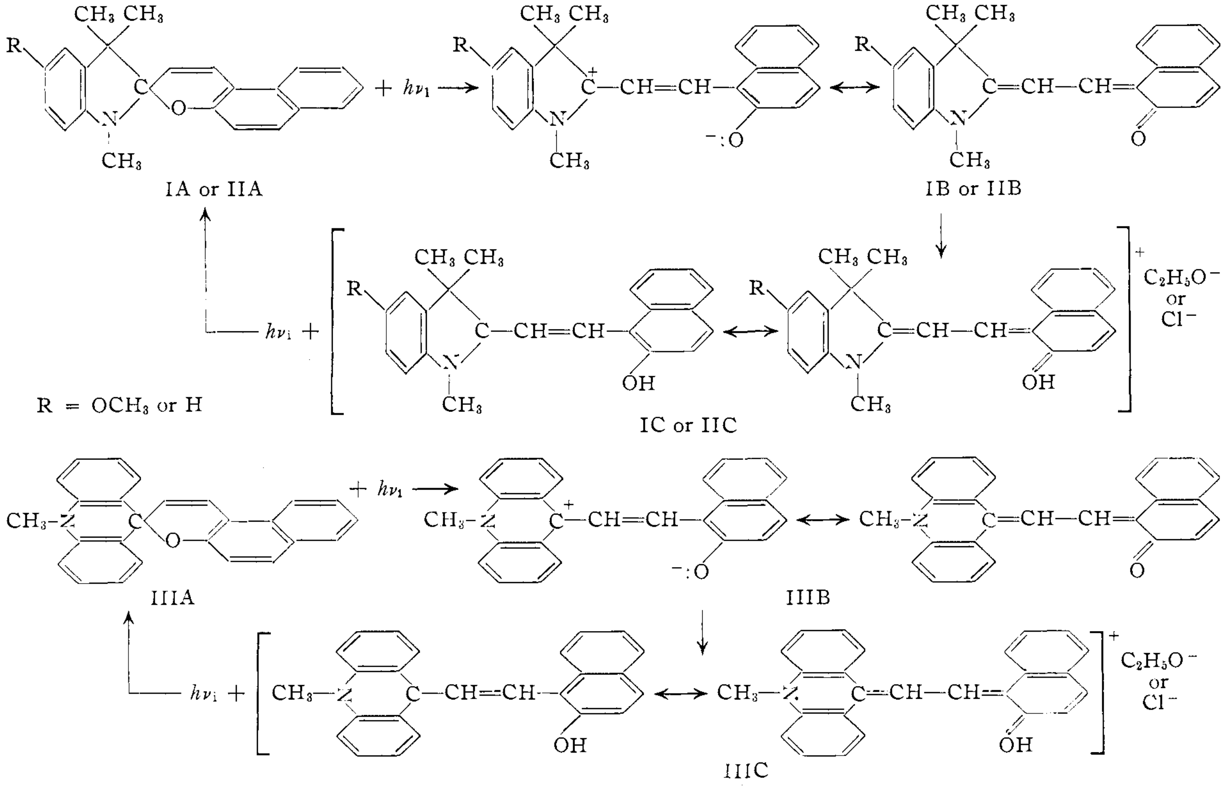
(6) W. Dilthey and H. Wubken, *J. prakt. Chem.*, **114**, 179 (1926).

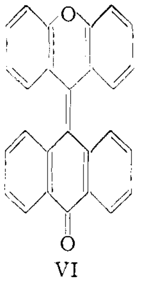
(7) R. Dickinson and I. M. Heilbron, *J. Chem. Soc.*, 1699 (1927).

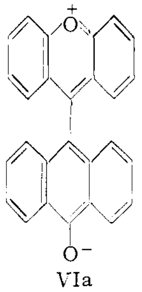
(8) R. Wizinger and H. Wenning, *Helv. Chim. Acta*, **23**, 247 (1940).



the color formation have been found, even in the presence of big amounts of acid (see 3 and 4 in Table IV). Hence the chemical mechanism of the appearance and disappearance of the color on irradiation at low temperature in this case differs from that described for the spiropyrans.

In a previous study on photochromism in the bianthrone series[2] it has been found that the colored modification of xanthylideneanthrone (VI), formed on irradiation with ultraviolet light at low temperature, has an increased dipole moment as compared with the colorless one. A plausible assumption might be that in IV, VI and related compounds the colored form is a steric isomer, the structure of which contains a higher contribution of the bipolar mesomer VIa or its analogs, whereas in the colorless isomer the contribution of mesomer VI predominates. While the spiropyrans described above all form bases of varying strength, this is not the case for the bianthrones. This explains why the irradiation characteristics of IV seem to be independent of the acidity of the solution.


VI


VIa

Use of the Phenomenon as a Memory.—In a "Computer" the "high-speed memory" is characterized by the following features. A certain very short signal (microseconds) is stored in the "memory" and this "information" will remain stable till a signal of another type, also of a very short duration, restores the former state. The cycle has to be reversible and reproducible indefinitely, and should be performable in a very short time.

All the reversible color changes caused by irradiation, which have previously been reported, have qualities differing essentially from those of the "memory" described above. In all these cases a very short irradiation may bring about the formation of a color. However, it has not proved possible to develop a cycle which can be reperformed in a very short time, since the bleaching takes place only under special conditions and is either slow or prevents the repetition of the cycle within a specified time. Thus in the reversible color changes induced by irradiation at room temperature,[1] it requires a specified time, large relative to times required for a "memory," for the bleaching to occur in the dark. In those cases where reversible colors are formed when rigid solutions are irradiated with ultraviolet light,[2] the colors disappear only when the solutions lose their rigidity; in order to repeat the cycle the solutions have first to be brought back to rigidity, thus introducing a considerable time lag.

The phenomenon discussed in this paper is the first reversible photochemical process which has essentially the same features as the "high-speed memory." The ultraviolet light signal produces a stable color, and, under the same conditions, a signal of visible light eradicates the color. By using appropriate wave lengths and large enough intensities the whole cycle can be performed in a very short time. The application of the latter is purely a technical problem. The possibility that it might prove of some practical use should be kept in mind. Meanwhile, we can consider the phenomenon described as the first photochemical memory model. As a matter of fact the search for such a reversible photochemical effect was originally undertaken at the suggestion of Dr. E. H. Frei of the Electronics Department, Weizmann Institute of Science, with the intention of building such a memory.

Experimental

Spectrophotometric Technique.—An attachment to the Beckman model D.U. quartz spectrophotometer was built, permitting the use of Dewar-type cells as described previously.[2]

Temperature Control.—The technique of work at low temperatures has been described in a former paper.[2]

Solvents.—Great care was taken to exclude traces of acid from all the solvents used. Methanol was distilled from KOH, ethanol was refluxed over CaO, and toluene, methylcyclohexane and petroleum ether were refluxed over and stirred with fused sodium before distillation.

Materials.—The syntheses of the four compounds studied are described in previous publications.[2]

Monochromatic Light.—The following combinations of Corning filters were used for the isolation of the individual monochromatic groups: for 365 mμ, 7380 + 5860; for 405 mμ, 3060 + 5970; for 436 mμ, 3389 + 5113; for 546 mμ, 3484 + 5120; for 578 mμ 3480.

The author is deeply indebted to Mr. M. Kaganowitch for the syntheses of the compounds investigated and to Mrs. Nelly Castel for her devoted technical assistance.

REHOVOTH, ISRAEL

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY AND THE INSTITUTO DE QUIMICA DE LA UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO]

Terpenoids. XXII.[1] Triterpenes from Some Mexican and South American Plants[2]

BY CARL DJERASSI, A. BOWERS, S. BURSTEIN, H. ESTRADA, J. GROSSMAN, J. HERRÁN, A. J. LEMIN, A. MANJARREZ AND S. C. PAKRASHI

RECEIVED OCTOBER 8, 1955

An examination of the triterpene content of ten plants from Mexico, Venezuela, Peru and Chile has resulted in the isolation of the following triterpenes: β-amyrin, maniladiol, erythrodiol, longispinogenin, oleanolic acid, gypsogenin, stellatogenin, betulin and betulinic acid.

The isolation[1,3] of a series of new triterpenes from certain giant cacti of the sub-tribe *Cereanae*, notably the genus *Lemaireocereus*, has encouraged us to continue the examination of related cacti and our results with seven species of the genera *Lemaireocereus*, *Trichocereus* and *Escontria* are reported herewith. In connection with the collection of these cacti, we also had the opportunity to obtain three plants (*Byrsonima spicata*, *B. crassifolia* and *Luffa operculata*) belonging to other families but which were investigated because there existed some evidence for believing that they may contain triterpenes.

The genus *Byrsonima* belongs to the *Malpighiaceae* family and only very few of its 500 species have been examined chemically.[4] It is interesting to note that extracts of the bark of the Mexican[5] *Byrsonima crassifolia* and the Peruvian[6] *B. spicata* (Cav.) Rich. have been used by the indigenous population for the expulsion of the placenta and the promotion of bleeding in females. Heyl[7] has reported the isolation from the bark of *B. crassifolia* of "byrsonimol" ($C_{29}H_{52}O$) with constants which are strongly reminiscent of β-amyrin (I) ($C_{30}H_{50}O$). Indeed, examination in these laboratories of bark samples of both *B. crassifolia* and *B. spicata* led to appreciable amounts of a single triterpene, identified as β-amyrin by comparison with authentic material.

The fruits of *Luffa operculata* (fam. *Cucurbitaceae*) form soapy solution in water and are referred to by the natives of Northern Peru[6] as "jaboncillo" (Sp. *jabon*, soap), which would indicate the presence of saponins. Mendoza and collaborators[8] have recorded the presence of a saponin in a related species of the cucumber family, *Luffa cylindrica* (Linn.) without however identifying the sapogenin.

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(1) Paper XXI, C. Djerassi, J. A. Henry, A. J. Lemin and T. Rios, *Chemistry & Industry*, 1520 (1955).

(2) This represents part of a joint research program, financed by the Rockefeller Foundation, on Latin American plant products between Wayne University and the National University of Mexico. We are also indebted to the Division of Research Grants of the U. S. Public Health Service for financial assistance (Grant No. G-3863).

(3) *Inter al.*, (a) C. Djerassi, L. E. Geller and A. J. Lemin, THIS JOURNAL, **75**, 2254 (1953); (b) C. Djerassi, E. Farkas, A. J. Lemin, J. C. Collins and F. Walls, *ibid.*, **76**, 2969 (1954); (c) C. Djerassi, L. E. Geller and A. J. Lemin, *ibid.*, **76**, 4089 (1954); (d) C. Djerassi and A. E. Lippman, *ibid.*, **76**, 5780 (1954); (e) C. Djerassi, L. H. Liu, E. Farkas, A. E. Lippman, A. J. Lemin, L. E. Geller, R. N. McDonald and B. J. Taylor, *ibid.*, **77**, 1200 (1955); (f) C. Djerassi and A. E. Lippman, *ibid.*, **77**, 1825 (1955); (g) C. Djerassi, G. H. Thomas and H. Monsimer, *ibid.*, **77**, 3579 (1955); (h) C. Djerassi, E. Farkas, L. H. Liu and G. H. Thomas, *ibid.*, **77**, 5330 (1955).

(4) *Cf.* C. Wehmer, "Die Pflanzenstoffe," G. Fischer, Jena, 1931, Vol. II, pp. 663–665.

(5) Its use has already been mentioned in the sixteenth century by Francisco Hernandez in his "Historia de las Plantas de Nueva Espana" (*cf.* Vol. I, p. 51 of 1942 edit., Imprenta Universitaria, Mexico, D.F.). See also survey on "Plant Materials Used by Primitive Peoples to Affect Fertility" by H. de Laszlo and P. S. Henshaw, *Science*, **119**, 626 (1954).

(6) Private communication from Dr. Ramon Ferreyra (Museo de Historia Natural "Javier Prado," Universidad Nacional Mayor de San Marcos, Lima, Peru) to whom we are greatly indebted for his continued assistance in supplying us with Peruvian plant materials and for the botanical identification.

(7) G. Heyl quoted in Elsevier's "Encyclopedia of Organic Chemistry," Amsterdam, 1940, Vol. 14, p. 596.

(8) A. S. Mendoza, P. Cruz and A. C. Santos, *Rev. Filip. Farm.*, **32**, No. 2, 49 (1941); A. S. Mendoza and A. C. Santos, *ibid.*, **32**, No. 7, 214 (1941). The presence of a saponin has also been mentioned in *Luffa acutangula* (K. S. Grewal and B. D. Kochhar, *Ind. J. Med. Res.*, **31**, 63 (1943)) and possibly *L. aegyptiaca* (S. Rangaswami and K. Sambumurthy, *Ind. J. Pharm.* **16**, 225 (1954)).