Table I
Ruthenium-Catalyzed Hydrogen–Deuterium Exchange in Alcohols[a]

Alcohol	Isotopic composition, %		
	d_0	d_1	d_2
Ethanol-d[b]	42	43	15
1-Butanol-d[b]	55	35	10
2-Propanol-d[b]	>98	<2	
1-Decanol[c]	7	35	58
1-Decanol	0	5	95
1-Dodecanol	0	6	94
1-Octanol	0	3	97
Cyclododecanol	95	5	

[a] The percentage of deuterium indicated represents the isotopic distribution at the C-1 carbon atom. Unless noted otherwise, reactions were carried out using procedures similar to that described for the deuteration of 1-decanol; the reaction temperature was 200°. The molar ratio of deuterium oxide to alcohol used was 50:1. [b] The alcohol was heated directly with the ruthenium catalyst in the absence of deuterium oxide. [c] The molar ratio of deuterium oxide to alcohol used was 5:1.

um introduced into the alcohol was dependent upon the molar ratio of deuterium oxide to alcohol employed.

The advantages of this procedure for isotopic labeling of primary alcohols in the C-1 position lie in its simplicity, its low cost, its avoidance of reactive oxidants and reductants, and its ability to be carried out under neutral pH.

Experimental Section[5]

General Methods. Unless stated otherwise, all reagents were obtained commercially and were used without further purification. Deuterated alcohols (Aldrich Chemical Co.) were greater than 99% pure. Tetrahydrofuran was dried by distillation from calcium hydride under a nitrogen atmosphere. Commercial catalysts were obtained from the following sources: $(Ph_3P)_3RuCl_2$, $(Ph_3P)_3RhCl$, and $(Ph_3P)_2IrCOCl$ (Strem Chemical Co.); K_2PtCl_4 (Alfa Inorganics); Pd/C and Raney nickel (K & K Laboratories).

General Procedure for Hydrogen–Deuterium Exchange in Deuterated Alcohols. Procedures similar to that described for the hydrogen–deuterium exchange in 1-butanol-*d* were followed for all deuterated alcohols. A mixture of 2 mg (0.002 mmol) of tris(triphenylphosphine)ruthenium dichloride and 150 μl (1.6 mmol) of 1-butanol-*d* was sealed under a nitrogen atmosphere in a 4-in. 5-mm Pyrex glass tube. The tube was placed in an oil bath, maintained at 200° for 1 hr, withdrawn, and cooled. The purity of the alcohol was determined by glpc using both a UC-W98 on Chromosorb W column and a Carbowax on Chromosorb W column. Alcohols were collected for mass spectral analysis by glpc using a F & M Model 720 thermal conductivity instrument. Isotopic compositions were determined from $(M - H_2O)^+$ peaks and were corrected for contributions from ^{13}C.[6]

1-Decanol-*1,1-d*$_2$. A mixture of 100 mg (0.1 mmol) of tris(triphenylphosphine)ruthenium dichloride, 1.58 g (10.0 mmol) of 1-decanol, and 10.0 g (0.5 mol) of 99.7% deuterium oxide was sealed under a nitrogen atmosphere in a 14-in. 12-mm Pyrex glass tube. The tube was placed in an oil bath, maintained at 200° for 0.5 hr, withdrawn, and cooled to room temperature. The contents of the tube was poured into 50 ml of ether and the organic phase was dried (Na_2SO_4), concentrated, and distilled (short-path distillation), giving 1.47 g (93%) of 1-decanol, bp 123-125° (20 mm). Mass spectral analysis indicated that the recovered alcohol was a mixture of 95% d_2, 5% d_1, and 0% d_0 material.

Acknowledgment. We are grateful to the Marquette University Committee on Research and Chemistry Department for their financial support.

Registry No. Tris(triphenylphosphine)ruthenium chloride, 15529-49-4; 1-decanol, 112-30-1; 1-decanol-*1,1-d*$_2$, 42006-99-5.

References and Notes

(1) A. Murray and D. L. Williams, "Organic Synthesis with Isotopes," Interscience, New York, N. Y., 1958, p 1341.

(2) We have found that temperatures in excess of 180° are necessary for rapid exchange to occur. Thus, when 1-butanol-*d* was heated in the presence of the ruthenium catalyst for 15 hr at 140°, the ^1H nmr spectrum of the resulting alcohol showed no evidence of hydrogen–deuterium exchange.

(3) The ^1H nmr spectrum of the resulting isotopic mixture of alcohols confirmed that only the C-1 carbon atom had become deuterated.

(4) The purity of the alcohol was measured by glpc using both a UC-W98 on Chromosorb W column and a Carbowax on Chromosorb W column.

(5) Boiling points are uncorrected. Mass spectra were recorded on a Consolidated Electrodynamics Corp. mass spectrometer, Type 21-103 C. All ^1H nmr spectra were recorded using a Varian A-60 spectrometer. The alcohols were analyzed by glpc on a Beckman GC-2A flame ionization instrument.

(6) Biemann has established that aliphatic alcohols, under electron impact, lose water exclusively *via* 1,3, 1,4, and 1,5 eliminations: W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, **86**, 2375 (1964).

The Chemistry of Flavandiones.[1] Reaction with Base[2]

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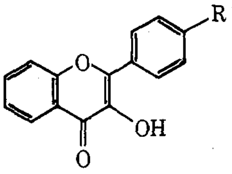
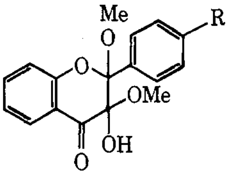
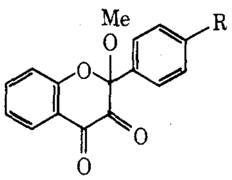
Flavolon (1) is oxidized by 1 mol of periodic acid. From the reaction in methanol, the methyl 3-hemiketal 2 of 2-methoxy-3,4-flavandione (3) can be isolated.[3] Solutions of 2 are always yellow, indicating that some 3 is always present. We have found that the hemiketal 2 undergoes a normal benzilic acid rearrangement. In aqueous methanol, the product is the hydroxy acid 4; in anhydrous methanol, the methyl ester 5. These products are readily accounted for in terms of the ionic reaction mechanism usually formulated for the benzilic acid rearrangement.[4] This result was not entirely predictable. Compound 2 is a mixed ketal of an *o*-hydroxydiphenylpropanetrione, and the reactions of 1,2,3-triketones with base are more complex.[5,6]



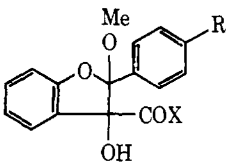
1, R = H
9, R = CH_3



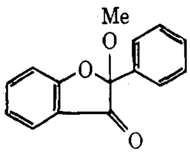
2, R = H
10, R = CH_3



3



4, R = H; X = OH
5, R = H; X = OCH_3
11, R = CH_3; X = OH
12, R = CH_3; X = OCH_3



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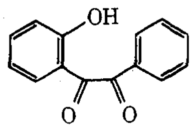

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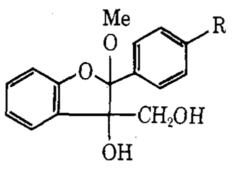

8, R = H
13, R = CH_3

The ester 5 is obtained by the reaction of 2 with a solution of sodium methoxide in anhydrous methanol or by passing a methanol solution of 2 through the hydroxide form of an anion exchange resin. The assigned structure is supported by spectra and analyses. The saponification of 5 yielded **4** from which **5** could be regenerated with diazomethane.

When the rearrangement of **2** was carried out in aqueous methanol, the product was the free acid **4**. However, this product, while a pleasant-looking solid, failed to give satisfactory elemental analyses and equivalent weights. Unless care was taken, it separated from the solution as a firm gel. Furthermore, the nmr spectrum was not characteristic for a carboxylic acid (see Experimental Section). However, its reversible conversion into the methyl ester **5** leaves little doubt that it is some form of the acid **4**. Cleavage with 1 mol of lead tetraacetate converted **4** to 2-methoxy-2-phenyl-3(2*H*)-benzofuranone (**6**). The hydrolysis of **6** afforded the known 2-hydroxybenzil **7**.[7] Both the acid **4** and its methyl ester **5** were reduced with lithium aluminum hydride to 2,3-dihydro-3-hydroxy-3-hydroxymethyl-2-methoxy-2-phenylbenzofuran (**8**). The structure of **8** is supported by spectra and elemental analyses.

The study was extended to the hemiketal **10**, prepared from 4′-methylflavonol (**9**). Compounds **11**, **12**, and **13** were prepared.

Experimental Section

All ir spectra were taken as Nujol mulls on a Perkin-Elmer Infracord, Model 137 (NaCl prism). All nmr spectra were obtained in $CDCl_3$ using a Varian A-60A spectrometer. All melting points were uncorrected. Analyses were carried out by Schwarzkopf Analytical Laboratory. The hydroxide form of the anion exchange resin was prepared by stirring 1 lb of Dowex 1X8 resin (20–50 mesh, chloride form) with 1 l. of cold 10% sodium hydroxide and washing with water until neutral.

2-Methoxy-4′-methyl-3,4-flavandione Methyl 3-Hemiketal (10). This is a new compound prepared in the usual way[3] from **9** and HIO_4 in MeOH. The yield of **10** was 50%: mp 152–153° dec; ir (mull) 2.90 (OH), 5.85 μ (C=O); nmr ($CDCl_3$) δ 2.44 (s, 3, CCH_3), 3.02, 3.08 (s, 6, OCH_3), 4.70 (s, 1, OH), 7.0–8.1 (m, 8, aryl H).

Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77; OCH_3, 19.75. Found: C, 68.74; H, 6.06; OCH_3, 21.64.

2,3-Dihydro-3-hydroxy-2-methoxy-2-phenylbenzofuran-3-carboxylic Acid (4). The hemiketal **2**[3] (5.0 g, 1.67 mmol), suspended in 50 ml of MeOH, was stirred with 5.0 g of KOH in 50 ml of H_2O. Compound **2** quickly dissolved, yielding a clear yellow solution. After standing overnight, the solution was poured into 200 ml of H_2O containing 10 ml of concentrated HCl. The cloudy solution was extracted with 200- and 100-ml portions of Et_2O. This ether extract was washed with saturated brine and allowed to stand over $CaSO_4$. Evaporation of the Et_2O afforded about 5 g of a foamy solid. This product was purified by dissolving it in 30 ml of warm $CHCl_3$ and adding 250 ml of hot petroleum ether (bp 60–68°). On standing, the clear solution set to a loose gel which was easily broken up and filtered, yielding 3.6 g (1.31 mmol, 78%) of **4** as a white solid, mp 113–115° dec. Work-up of the filtrate afforded an additional 0.4 g of product, total yield 84%. The product is particularly low in per cent C and does not titrate readily. It dissolves slowly in $NaHCO_3$ and quickly in NaOH. It is stable for several days in NaOH. The solid itself slowly acquires a yellow color. The following spectra data are on a fresh batch of the acid: ir (mull) 2.9, 3.2 (OH), 5.8 μ (C=O); nmr ($CDCl_3$) δ 3.25 (s, 3, OCH_3), 6.9–7.7 (m, 11+, aryl H + 2 OH). The actual ratio of the integrals for the aryl region and OCH_3 was 11.7:3. After D_2O, this ratio fell to 9.6:3, indicating that the two hydroxyl bands were hidden under the aryl signals. The excess OH signal may have been due to H_2O.

Satisfactory elemental analyses could not be obtained on the acid **4**. When heated to its melting point in a stream of N_2, **4** yielded methanol and 0.96 mol of CO_2.[8]

Methylation of 4 to 5. A 30% excess of CH_2N_2 in Et_2O was mixed with 500 mg of **4** in Et_2O. Evaporation yielded a crude product from which 370 mg (70%) of the methyl ester **5**, mp 117–120°, could be obtained, identified by comparison with **5** prepared as detailed below.

Saponification of 5 to 4. The ester **5** was hydrolyzed with 2 g of KOH in 8 ml of H_2O and 10 ml of MeOH. Tlc indicated that all the ester had reacted in 10 min. After 30 min, the solution was diluted with 50 ml of H_2O and acidified. Extraction with ether afforded 370 mg (84%) of **4** as a foamy solid. The crude product was recrystallized from $CHCl_3$-hexane (1:2) affording **4**, mp 110–111° dec.

2-Methoxy-2-phenyl-3(2*H*)-benzofuranone (6). A mixture of 2.03 g (4.58 mmol) of Pb $(OAc)_4$ and 100 ml of AcOH was stirred and to this 1.35 g (4.72 mmol) of the hydroxy acid **4** was added. It dissolved, yielding a pale yellow solution. After 12 hr, the AcOH was removed on a film evaporator. The resulting oil was taken up in 200 ml of Et_2O and washed with 200 ml of water. The water layer was shaken with 50 ml of Et_2O. The combined ether layers were dried with brine and $CaSO_4$ and upon evaporation yielded 1.1 g of an oil (100%) which soon solidified. Recrystallization was effected with 20 ml of petroleum ether, 0.80 g (73%) of **6**, mp 66.5–68°, being obtained: ir (mull) 5.80 μ (C=O); nmr ($CDCl_3$) δ 7–8 (m, 9, aryl H), 3.41 (s, 3, OCH_3).

Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.98; H, 5.03. Found: C, 75.08; H, 5.28.

The hydroxy acid **4** was oxidized at room temperature with a 0.04 *M* solution of $Pb(OAc)_4$ in AcOH, 2.2 mol of the oxidant being present. The excess Pb^{IV} was determined iodometrically.[9] These results were obtained [given as time (hours), moles of Pb^{IV} consumed/mole of **4**]: 0.5, 0.37; 1.25, 0.76; 2.5, 0.88; 3.5, 0.91; 4.5, 0.93; 13, 0.95.

2-Hydroxybenzil (7). The hydrolysis of **6** was effected by prolonged refluxing of **6** (600 mg) in a mixture of dioxane (8 ml), H_2O (8 ml), and concentrated H_2SO_4 (1 ml). After 2 days, water (100 ml) was added and the cloudy mixture was extracted with ether. **7** was removed by 2% sodium hydroxide and recovered by acidification and ether extraction. Evaporation of the ether left 400 mg (71%) of a yellow oil which soon solidified. A recrystallization from petroleum ether yielded pale yellow crystals, mp 73–75° (lit. mp 74°),[7] ir, broad weak band at 2.2–2.4 (chelated OH), 5.9 μ (C=O).

Methyl 2,3-Dihydro-3-hydroxy-2-methoxy-2-phenylbenzofuran-3-carboxylate (5). A. ***Via* Sodium Methoxide.** A solution of 1.5 g of Na in 75 ml of MeOH was refluxed for 1 hr with 1.5 g of the hemiketal **2**. The reaction mixture was poured into about 500 ml of an ice–water mixture. After acidification, the solution was extracted with two 50-ml portions of Et_2O. The combined Et_2O layers were washed with water and saturated brine before drying with $CaSO_4$. Evaporation of the Et_2O yielded 1.2 g of a mixture of oil and crystals. Recrystallization was effected with 75 ml of petroleum ether, 0.83 g (55%) of white crystals of **5**, mp 121–122°, being obtained. An additional 0.1 g (7%) of **5** could be obtained from the petroleum ether filtrate.

B. ***Via* Anion Exchange Method.** A solution of 3 g of the hemiketal **2** in 400 ml of anhydrous MeOH was slowly passed down a column of 100 ml of Dowex 1 × 8 (50–100 mesh, OH form). The rate must be very slow; in this particular run it was 1 drop every 10 sec. Once the solution of **2** was through the column, the resin was washed with 100 ml of MeOH. The effluent plus the washings were evaporated to about 2.5 g of a white solid. Recrystallization was effected with a mixture of 12 ml of CCl_4 and 15 ml of hexane, 2.03 g (67%) of **5** being obtained, mp 121–122°. The analytical sample melted at 122–123° (petroleum ether): ir (mull) 2.85 (OH), 5.70 μ (C=O); nmr ($CDCl_3$) δ 3.11, 3.27 (s, 6, OCH_3, $COOCH_3$), 4.2 (s, 1, OH), 7–8 (m, 0.9, aryl H).

Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37; OCH_3, 20.67. Found: C, 67.88; H, 5.63; OCH_3, 20.90.

2,3-Dihydro-3-hydroxy-3-hydroxymethyl-2-methoxy-2-phenylbenzofuran (8). A. From the Acid 4. A solution of 1.0 g of **4** in 100 ml of Et_2O was added slowly (2 hr) to a stirred suspension of 0.30 g of $LiAlH_4$ in 50 ml of Et_2O, the solution being warmed enough to reflux gently. The refluxing was continued for another 3 hr. After the solution stood overnight, the $LiAlH_4$ was decomposed by successive additions of 0.3 ml of H_2O, 0.3 ml of 15% NaOH, and 0.9 ml of H_2O.[10] The resulting slurry was readily filtered and evaporation of the ether afforded 0.8 g (84%) of a tough oil. Recrystallization from 5 ml of CCl_4-5 ml of hexane yielded 0.45 g (47%) of **8**, mp 115–116°. The analytical sample melted at 119–120°.

B. From the Ester 5. The same procedure on the ester **5** yielded **8** in 56% yield: ir (Nujol) 2.85 μ (OH); nmr ($CDCl_3$) δ 1.66 (broad s, 1, OH), 3.24 (s, 5, OCH_3 and $-OCH_2-$), 3.78 (broad s, 1, OH), 6.9–7.0 (m, 9, aryl H). The signals of OCH_2- and $-OCH_3$ at δ 3.24 were readily resolved by the use of the chemical shift reagent, $Eu(dpm)_3$.[11] At a concentration of 25 mg of **8** and 6.5 mg of $Eu(dpm)_3$ in 1 g of $CDCl_3$, the OCH_3 was a sharp singlet at δ 3.18 and the $-OCH_2-$ was a broader signal at δ 3.25.

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.52; H, 5.75.

2,3-Dihydro-3-hydroxy-2-methoxy-2-*p*-tolylbenzofuran-3-carboxylic Acid (11). The procedure followed that for **4**. Crystallization of the crude product from **10** was effected by dissolving it in CH_2Cl_2 (10 ml/g **11**) and adding 5 vol. of hot petroleum ether (bp 60–68°). From 5 g of **10**, 2.9 g (60%) of the acid **11** was obtained. An additional 0.7 g (14%) could be isolated from the mother liquor: mp 112–113° dec; ir (mull) 2.90, 3.20 (OH), 5.80 μ (C=O); nmr ($CDCl_3$) δ 2.35 (s, 3, CCH_3), 3.25 (s, 3, OCH_3), 7–7.7 (m, 10, aryl H + 2 OH). The actual ratio of integrals for the aryl region to the two methyl signals was 9.8:6 before D_2O and 8.2:6 after D_2O.

On melting under N_2, **11** yielded 0.93 mol of CO_2.[8] Methylation of **11** with a slight excess of CH_2N_2 in ether afforded the ester **12**, identified by comparison with **12** prepared as described below. However, as was the case with **4**, satisfactory analyses could not be obtained on **11**.

Methyl 1,2,3-Dihydro-3-hydroxy-2-methoxy-2-*p*-tolylbenzofuran-3-carboxylate (12). The procedure followed the sodium methoxide preparation for **5**. From 1 g of the hemiketal **10**, 0.8 g of a soft white solid was obtained. Recrystallization was effected with a mixture of 10 ml of CCl_4–40 ml of petroleum ether, yielding 0.52 g (52%) of white crystals of **12**, mp 144–146°. The analytical sample (from CCl_4) melted at 145.5–146.5°: ir (mull) 2.85 (OH), 5.75 μ (C=O); nmr ($CDCl_3$) δ 2.37 (s, 3, CCH_3), 3.17, 3.25 (s, 6, OCH_3, $COOCH_3$), 4.1 (broad, 1, OH), 6.8–7.7 (m, 8, aryl H).

Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77, OCH_3, 19.75. Found: C, 68.26; H, 5.74; OCH_3, 19.01, 19.07, 19.66.

2,3-Dihydro-3-hydroxy-3-hydroxymethyl-2-methoxy-2-*p*-tolylbenzofuran (13). Following the procedure for **8**, a 1.0 g sample of the acid **11** was reduced with $LiAlH_4$. The crude product was obtained in 62% yield. Purification was effected from CCl_4–hexane (1:1), the analytical sample of **13** melting at 94–95°, ir (mull) 2.85 μ (OH).

Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34; OCH_3, 10.84. Found: C, 71.31; H, 6.40; OCH_3, 10.70.

Registry No. **2**, 1603-46-9; **4**, 42856-76-8; **5**, 42856-77-9; **6**, 42856-78-0; **8**, 42856-79-1; **9**, 19275-68-4; **10**, 42856-81-5; **11**, 42856-82-6; **12**, 42856-83-7; **13**, 42856-84-8.

References and Notes

(1) For the preceding paper in this series, see *J. Org. Chem.*, **37**, 2774 (1972).

(2) Supported in part by the National Institute of General Medical Sciences, National Institutes of Health, U. S. Public Service (Grant No. 11830) and a grant to Bucknell University from the Dreyfus Foundation.

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(4) J. March, "Advanced Organic Chemistry: Reactions, Mechanism and Structure," 1st ed, McGraw-Hill, New York, N. Y., 1968, p 803.

(5) J. D. Roberts, D. R. Smith, and C. C. Lee, *J. Amer. Chem. Soc.*, **73**, 618 (1951).

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(7) Y. Asahina and J. Asano, *Ber.*, **62B**, 171 (1929).

(8) We are indebted to Dr. Eric H. Meier, Stanford University, for these determinations. The methanol was condensed in a Dry Ice trap and the CO_2 was then absorbed with a weighed tube of Ascarite.

(9) A. S. Perlin in "Oxidation," Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, p 198.

(10) Procedure of C. K. Steinhardt as described in L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 584.

(11) J. K. M. Saunders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971).

Citrus Bitter Principles. XII.[1] Photochemistry of Limonin

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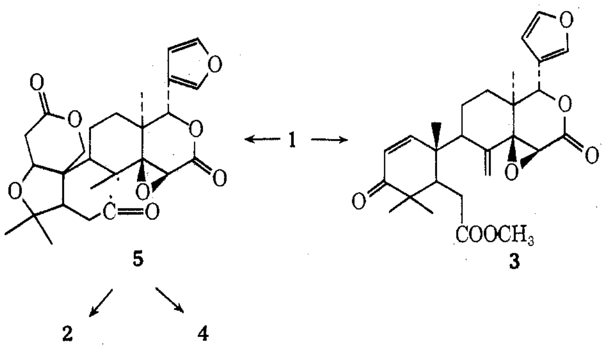
Received December 15, 1972

Limonin, a C_{26} triterpene occurring in some species of the Rutaceae, sometimes is responsible for bitterness in processed citrus products.[3] Specific reactions of limonin (**1**) are of interest as the basis of possible debittering methods. As part of such a study this paper describes photolysis studies of limonin.

Because of the complex and polyfunctional nature of limonin (**1**), prediction of the structure of possible limonin photoproducts was difficult. Irradiation of **1** in dioxane or methylene chloride with a high-pressure mercury-vapor lamp using a Pyrex filter gave low yields of two crystalline photoproducts. Only two products were obtained crystalline but tlc indicated the presence of further minor limonoid products, some of which were acidic but which could not be obtained crystalline.

The nonpolar photoproduct, called photolimonin I (**2**), possessed typical limonoid properties. It had the usual furan bands[4] in its ir spectrum and gave a positive Ehrlich's test,[5] indicating the presence of an intact furan ring. The nmr spectrum of photolimonin I, summarized in Table I, showed the usual furan resonances and signals assignable to H-1, H-19, H-15, and H-17.[6] The chemical shifts and multiplicity of these resonances indicated that the A, A′, and D rings were intact and unchanged from those in limonin. The nmr spectrum showed only *three* *C*-methyl resonances, whereas the starting limonin (**1**) has four *C*-methyl groups. A special feature of the nmr spectrum was an aldehyde resonance[7,8] at δ 9.78 and singlets at δ 5.37 and 5.44 which are assignable to an exocyclic methylene group. These results are best interpretable in terms of structure **2** and are compared in Table I with the nmr data of andirobin (**3**), a limonoid, having a similarly cleaved B ring, isolated from *Carapa guayanensis* Aubl. (Meliaceae).[9-11] The aldehyde resonance was a broadened singlet which could not be resolved into the expected triplet. However, irradiation of δ 2.80 gave a much sharper aldehyde resonance. Small, 1 Hz and less, coupling constants are not unusual in such systems.[11-13]



Photolimonin I showed a very low-amplitude negative Cotton effect ($a = -3.7$), consistent with the flexible conformations of the aldehyde group and its distance from an asymmetric center.[13,14]

A second photoproduct, photolimonin II (**4**), was obtained crystalline in low yield from the more polar chromatographic fractions. Photolimonin II showed physical properties (solubility, melting point, R_f on tlc) very similar to those of limonin (**1**) and gave an nmr spectrum (Table I) very similar to that of **1** with some differences in the chemical shifts. Nmr studies of limonoids[6] have shown that H-15 falls in the deshielding region of the 7-keto group, causing its resonance to occur relatively far downfield. In **4** the sharp singlet for H-15 falls further upfield out of the shielding region of the 7-keto group. Moreover, the C-19 methylene group now falls in the deshielding region of the epoxy group, causing its resonance to occur further downfield than it does in limonin. The decreased crowding of H-19 in photolimonin II also may contribute to its downfield position relative to limonin.