lization 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.
(3) M. A. Smith, R. A. Webb, and L. Cline, *J. Org. Chem.*, **30**, 995 (1965).
(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).
(6) G. A. Russell, and S. A. Wiener, *J. Amer. Chem. Soc.*, **89**, 6623 (1967).
(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

David L. Dreyer* and Jean F. Rigod

Fruit and Vegetable Chemistry Laboratory,[2] Pasadena, California 91106, and Department of Chemistry, California State University, San Francisco, San Francisco, California 94132

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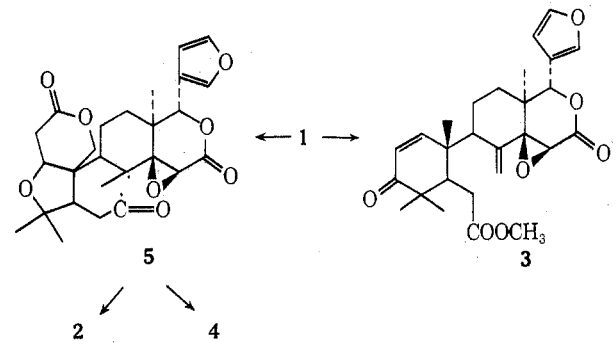
Limonin, a C_{26} triterpene occurring in some species of the Rutaceae, sometimes is responsible for bitterness in processed citrus products.[3] Specific reactions of limonin (**1**) are of interest as the basis of possible debittering methods. As part of such a study this paper describes photolysis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



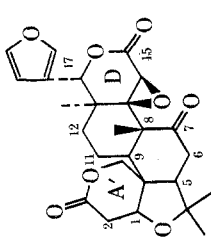
5 **3**

2 **4**

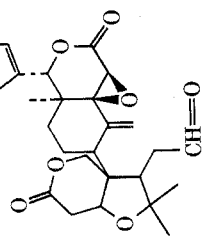
Photolimonin I showed a very low-amplitude negative Cotton effect ($a = -3.7$), consistent with the flexible conformations of the aldehyde group and its distance from an asymmetric center.[13,14]

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.

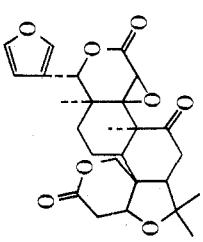
Table I
Nmr Data on Limonin Photoproducts in Deuteriochloroform



1



2



4

Compd	α-Furan	β-Furan	H-17	H-19	H-1	H-15	H-2	C-Methyls		Other	
Limonin (1)	7.36 (d) (J = 1 Hz)	6.30 (t) (J = 1 Hz)	5.45	4.42 4.75	4.03	4.03		1.30	1.17 1.08	1.17	
Photolimonin II (4)	7.44 (d) (J = 1 Hz)	6.37 (t) (J = 1 Hz)	5.51	4.90	3.97 (t) (J = 3 Hz)	3.78	2.95 (d) (J = 3 Hz)	2.48	1.27 1.13	1.27	
Photolimonin I (2)	7.44	6.37 (t)	5.51	4.35	4.33[a]	3.98	2.80	1.37	1.12	1.00	–CH=O >C=CH$_2$ 9.78 5.44 5.37
Andirobin (3)[b]	7.46	6.38	5.53			4.08		1.12	1.12 0.95	0.99	>C=CH$_2$ 5.44 5.33

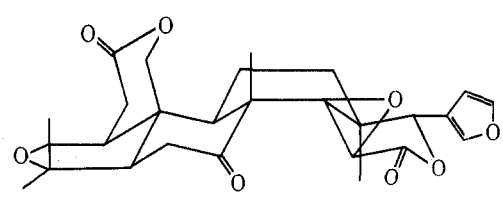
[a] Multiplicity obscured by H-19. [b] Data taken from ref 9.

The ORD curve of 4 exhibited a negative Cotton effect (a = −19.4) similar to, but not identical with, that of limonin.[15] These data are consistent with the identification of photolimonin II as 4, a C-8 stereoisomer of 1 in which the 8-methyl is α instead of β as in limonin. The sign of the Cotton effect for the 7-keto group of limonin is difficult to predict from the octant rule, since most of the D ring falls in a front octant. In photolimonin II most of the D ring falls in an upper right, back (negative) octant. Thus a negative Cotton effect is predicted.

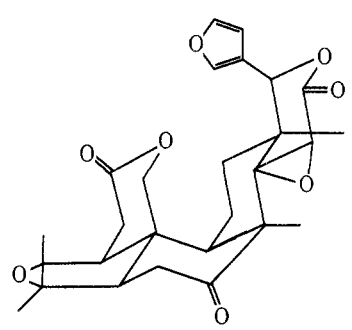
The two photoproducts isolated in this study are those which would result from 7,8-bond cleavage of **1**. Both photolimonins are the classical products expected from photolysis of saturated ketones.[13,16] The formation of 4 results from recombination of the diradical **5** on the α side of the planar C-8. This suggests that 1 and 4 might exist in a photochemical equilibrium. In an attempt to demonstrate the presence of a photochemical equilibrium between limonin (1) and photolimonin II (4), compound 4 was reirradiated. However, it was not possible to detect the formation of 1 among the reaction products even with a tlc system which could resolve compounds 1 and 4.

The nonbonded interactions in both limonin and photolimonin II appear to be of about the same magnitude. The boat C ring in limonin (I) is converted into a chair conformation in 4; however, a new axial 1,3-dimethyl interaction involving 8- and 13-methyls has been created.

The conversion of limonin to its C-8 stereoisomer (4) results in a significant conformational change. Limonin (**1a**) is a fairly planar, extended molecule while photolimonin II (**4a**) is a much more compact ball-shaped system. This structural change results in the loss of biological activity. In contrast to the extreme bitterness of limonin, photolimonin II is completely tasteless while photolimonin I is only slightly bitter.



1a



4a

The close structural similarity between photolimonin I (2) and andirobin (3) provides further laboratory analogy for the conversion of limonoids of the 7-deacetyl-7-oxogedunin type to the andirobin series.[9,10,17] Finally, the photolysis of the 7-keto group has not involved the β,γ-epoxy group.[18]

Experimental Section[19]

Photolimonin I (2). A saturated solution of limonin in methylene chloride (dioxane was used in some runs) was irradiated with a high-pressure mercury-vapor lamp in an immersion cell using a Pyrex filter. The solution was irradiated under nitrogen, with

stirring, for 12 hr. Solvent was removed in a rotary evaporator and the residue was recrystallized from methylene chloride–ethanol to give several crops of limonin. Solvent was removed from the mother liquors and the residue was chromatographed on acid-washed alumina. The content of the fractions was monitored by tlc using a 1:1 chloroform–ethyl acetate solvent system with Ehrlich's reagent to detect limonoids as described previously.[5] Those fractions containing a new nonpolar limonoid spot were combined, solvent was removed, and the residue was crystallized from methanol: mp 222–224°; ir (Nujol) ν 1758, 1718 (carbonyl), 1503, 879 (β-substituted furan), 904 cm^{-1} (exocyclic methylene); λ_{max} (EtOH) 215 mμ (ϵ 5200), 280 (16); R_f on tlc[10] 1.3 that of limonin; ORD in dioxane (c 0.15) at 22° $[\alpha]_{600}$ +27°, $[\alpha]_{370}$ +53°, $[\alpha]_{318}$ −107°, $[\alpha]_{281}$ +270°, $[\alpha]_{256}$ −340°, $[\alpha]_{246}$ +200° (last reading).

Anal. Calcd for $C_{26}H_{30}O_8$: C, 66.35; H, 6.42. Found: C, 65.8; H, 6.41.

Photolimonin II (4). Further work-up of the more polar fractions from the column by concentration gave several crops of impure limonin. Finally, solvent was removed and the residue was filtered through a short column of acid-washed alumina with chloroform to remove polar impurities. Solvent was removed from the eluents and the residue was crystallized from ethanol and then from chloroform–ethanol: mp 299–300° dec; ir (Nujol) ν 1753, 1698 (carbonyl), 1504, 879 cm^{-1} (β-substituted furan); λ_{max} (EtOH) 209, 283 mμ; R_f on tlc identical with that of limonin. Limonin and 4 could be resolved on silicic acid using a 1:1 benzene–nitromethane solvent system: ORD in dioxane (c 0.505) at 22° $[\alpha]_{600}$ −59.5°, $[\alpha]_{323}$ −1290°, $[\alpha]_{319}$ −1250°, $[\alpha]_{314}$ −1330°, $[\alpha]_{302}$ −690° (sh), $[\alpha]_{279}$ +615°, $[\alpha]_{260}$ −400° (last reading).

Anal. Calcd for $C_{26}H_{30}O_8$: C, 66.35; H, 6.42. Found: C, 65.8; H, 6.40.

Acknowledgment. The author is indebted to L. M. White for the analytical data, to Professor H. Mitsuhashi, Hokkaido University, for the ORD data, and to Dr. R. M. Horowitz for helpful discussions.

Registry No. 1, 1180-71-8; 2, 42867-82-3; 4, 42867-83-4.

References and Notes

(1) Part XI: D. L. Dreyer, M. V. Pickering, and P. Cohen, *Phytochemistry*, **11**, 705 (1972).
(2) Western Region, Agricultural Research Service, U. S. Department of Agriculture.
(3) J. F. Kefford and B. V. Chandler, *Advan. Food Res., Suppl. 2*, 159 (1970); T. W. Goodwin and L. J. Goad, "The Biochemistry of Fruit and Their Products," Vol. 1, A. C. Hulme, Ed., Academic Press, New York, N. Y., 1970, p 339.
(4) T. Kubota, *Tetrahedron*, **4**, 68 (1958).
(5) D. L. Dreyer, *J. Org. Chem.*, **30**, 749 (1965).
(6) D. L. Dreyer, *Tetrahedron*, **21**, 75 (1965).
(7) R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **44**, 45 (1966).
(8) G. J. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, **87**, 2864 (1965).
(9) W. D. Ollis, A. D. Ward, H. Meirelles De Oliveira, and R. Zelnik, *Tetrahedron*, **26**, 1637 (1970).
(10) See also nmr data on methyl angolensate and related compounds: C. W. L. Bevan, J. W. Powell, D. A. H. Taylor, T. G. Halsall, P. Tolf, and M. Welford, *J. Chem. Soc. C*, 163 (1967); *Chem. Ind. (London)*, 1751 (1964); D. E. U. Ekong and E. O. Olagbemi, *ibid.*, 944 (1966); E. K. Adesogan and D. A. H. Taylor, *Chem. Commun.*, 899 (1969); D. P. Chakraborty, K. C. Das, and C. F. Hammer, *Tetrahedron Lett.*, 5015 (1968).
(11) W. R. Chan, K. E. Magnus, and B. S. Mootoo, *J. Chem. Soc. C*, 171 (1967).
(12) J. K. Paisky and L. Weiler, *Tetrahedron Lett.*, 261 (1972); A. R. Battersby, A. R. Burnett, and P. G. Parsons, *Chem. Commun.*, 1282 (1968); *J. Chem. Soc. C*, 1187 (1969).
(13) P. Bladon, W. McMeekin, and I. A. Williams, *J. Chem. Soc.*, 5727 (1963).
(14) C. Djerassi and L. E. Geller, *J. Amer. Chem. Soc.*, **81**, 2789 (1959).
(15) D. L. Dreyer, *Tetrahedron*, **24**, 3273 (1968).
(16) G. Quinkert, B. Wegemund, F. Homburg, and G. Cimbollek, *Chem. Ber.*, **97**, 958 (1964); G. Quinkert, *Pure Appl. Chem.*, **9**, 607 (1964); *Angew. Chem., Int. Ed. Engl.*, **4**, 211 (1965); H. Wehrli and K. Schaffner, *Helv. Chim. Acta*, **45**, 385 (1962); J. Iriarte, K. Schaffner, and O. Jeger, *ibid.*, **47**, 1255 (1964).
(17) J. D. Connolly, R. Henderson, R. McCrindle, K. H. Overton, and N. S. Bhacca, *J. Chem. Soc.*, 6935 (1965).
(18) R. J. Chambers and B. A. Marples, *Chem. Commun.*, 1122 (1972).
(19) Nmr spectra were taken at 60 MHz and values are given in δ relative to internal tetramethylsilane. The relative areas of peaks were consistent with the assignments.

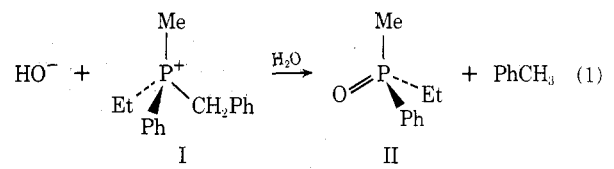
Phenylsilane Reduction of Phosphine Oxides with Complete Stereospecificity

Kenneth L. Marsi

Department of Chemistry, California State University, Long Beach, Long Beach, California 90840

August 27, 1973

The resolution of racemic benzylethylmethylphenylphosphonium iodide into its enantiomers (I = R) by McEwen, *et al.*,[1] in 1959 made possible the first stereochemical studies of nucleophilic substitution reactions at phosphorus.[2] Since substitution of benzyl by hydroxyl occurs stereospecifically with inversion giving rise to optically pure phosphine oxide (II) from optically pure phosphonium salt (eq 1), the reaction provides access to optically active oxides for stereochemical studies.[3] Although attempts to prepare optically active phosphines by hydride reduction of optically active phosphine oxides produced only racemic mixtures,[4] Horner, a short time later, announced that cathodic reduction of optically active salts such as I yielded the corresponding phosphines with retention and high optical purity.[5] More recently, optically active phosphines have been successfully obtained from optically active oxides by amine-moderated reductions with trichlorosilane, which affords predominant retention or inversion of configuration depending upon the choice of amine.[6] One geometric isomer of 3-methyl-1-phenylphospholane 1-oxide (III) has been reduced with predominant inversion of configuration by use of hexachlorodisilane.[7]



In 1969 the use of phenylsilane to reduce one isomer of 1,3-dimethylphospholane 1-oxide (IV) with *complete* retention of configuration was noted by us.[8] Subsequently, other examples of the conversion of racemic cis and trans isomers of cyclic phosphine oxides to the corresponding phosphines with complete retention of configuration at phosphorus were demonstrated in our laboratories.[9-11] Since the synthetic utility of phenylsilane was not elaborated upon in previous publications[8-11] and since we have now shown that acyclic optically active phosphine oxides are subject to phenylsilane reduction giving rise to optically active phosphines, also with *complete* retention of configuration, we wish at this time to make more extensive comment on this very useful reagent. In fact, we believe it to be the reducing agent of choice when stereochemically pure phosphines are required from stereochemically pure phosphine oxides. This method of reduction is especially important because optically active phosphine oxides are now more generally and conveniently available than optically active phosphonium salts as a result of Mislow's procedure involving conversion of diastereomerically pure menthyl phosphinate esters to optically active phosphine oxides with Grignard reagents.[12] Too, the interest in phosphine–metal complexes in homogeneous catalysis and the possibilities of asymmetric synthesis using chiral phosphines in such complexes[13] add a further dimension of importance to this reductive technique. Yields surpass those of any other reductive method, averaging over 90%, and as far as we have been able to determine (Table I) the reaction is 100% stereospecific for the variety of oxides studied.