ported.[3] The light petroleum extracts were concentrated, and the crude pisatin, which separated on cooling, was purified by repeated recrystallization from light petroleum, aqueous ethanol and finally from light petroleum; yield about 4.5 g., m.p. 72°.

Properties of Pisatin.—In aqueous solution pisatin is stable to heating to 98° (30 minutes) and autoclaving (15 pounds, 20 minutes), its ultraviolet spectrum and biological activity being unchanged. Physical constants are $[\alpha]^{20}_{364}$ mμ +940°, $[\alpha]^{20}_{436}$ mμ +570°, $[\alpha]^{20}_{578}$ mμ +280° (*c* 0.11 in ethanol); λ_{max} in ethanol: 213 mμ (log ε 4.75), 280 mμ (log ε 3.62), 286 mμ (log ε 3.68) and 309 mμ (log ε 3.86); λ_{max} values in ethanol were unchanged by the addition of 0.05 *M* sodium hydroxide. Solubility in 1 ml. at 23° was: water 0.03 mg., light petroleum 0.5 mg., oleyl alcohol 6 mg., carbon disulfide 15 mg., carbon tetrachloride 25 mg., ethanol > 42 mg. and dioxane > 130 mg. Distribution coefficients between light petroleum and water, and water–methanol mixture were: water (2.3:1), 20% methanol (1.7:1), 50% methanol (0.2:1) and 80% methanol (0.02:1); between cyclohexane and water (3.6:1) and oleyl alcohol and water (>100:1).

Anal. Calcd. for $C_{17}H_{14}O_6$: C, 64.96; H, 4.49; O, 30.55; OCH_3, 9.87; active H, 0.32; mol. wt., 314. Found in sample dried below 40° *in vacuo:* C, 64.95; H, 4.61; O, 31.1; OCH_3, 9.76; active H, 0.44; mol. wt., 291.

Anhydropisatin.—Pisatin (350 mg.) was dissolved in acetone (450 ml.), diluted to 500 ml. with water, and concentrated hydrochloric acid (2.5 ml.) added. After standing overnight in the dark, at room temperature, the white precipitate was collected by centrifuging, washed with acetone and then recrystallized from ethanol, yielding anhydropisatin in colorless needles; yield 220 mg., m.p. 179–180° alone or mixed with an authentic specimen of O-methylanhydrosophorol. No optical rotation was observed over the wave length range 405 to 578 mμ (*c* 0.04 in ethanol); λ_{max} in ethanol: 215 mμ (log ε 4.49), 234 mμ (log ε 4.30), 244 mμ (log ε 4.2), 257 mμ (log ε 4.1), 291 mμ (log ε 3.8), 339 mμ (log ε 4.58) and 358 mμ (log ε 4.60). Solubility in 1 ml. at 23° was; water 0.0 mg., carbon disulfide 6.5 mg., carbon tetrachloride 9 mg., ethanol 10 mg., dioxane 733 mg.

Anal. Calcd. for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08; O, 27.00; OCH_3, 10.47; mol. wt., 296. Found in sample dried below 70° *in vacuo:* C, 68.87; H, 4.10; O, 26.8; OCH_3, 10.31; mol. wt., 285.

Irradiation of Anhydropisatin.—Anhydropisatin (100 mg.) was dissolved in ethanol, and the resulting solution allowed to stand in diffuse daylight for 1 hour. The solution was concentrated and, on standing, colorless crystals separated and were subsequently recrystallized from aqueous ethanol; yield 30 mg., m.p. 104°. This substance gave positive color tests for phenols and had a *pK* of 9.1 in 10% ethanol; λ_{max} in ethanol: 214 mμ (log ε 4.67), 269 mμ (log ε 4.18) and 319 mμ (log ε 4.39). The anion had λ_{max} 325 mμ, and was intensely blue-fluorescent in solution.

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found in sample dried below 40° *in vacuo:* C, 66.21; H, 5.35.

Irradiation of Pisatin.—Pisatin (30 mg.) in aqueous solution was irradiated with 253.7 mμ light until deep yellow. The solution was shaken with benzene, which was then washed with water. The resulting isoflavylium compound was re-extracted into a small volume of concentrated hydrochloric acid, diluted with water, and then re-extracted into benzene. This process was repeated six times. The isoflavylium compound was finally taken into ether, and dried over sodium sulfate. It was then saturated with hydrogen chloride, and a dark red globule separated out from the ether. This was dried *in vacuo*, yielding a deposit of the isoflavylium chloride (8 mg.).

Acknowledgments.—The authors thank Professor A. J. Birch, University of Manchester, for providing a sample of pterocarpin and Professor H. Suginome, Hökkaido University, for a sample of O-methylanhydrosophorol. Thanks are also tendered to Drs. E. Spinner and D. D. Perrin, Department of Medical Chemistry, Australian National University for providing and assisting with the interpretation of the infrared spectra, and for determining dissociation constants, respectively.

[CONTRIBUTION FROM THE DEPARTMENT OF MEDICAL CHEMISTRY, AUSTRALIAN NATIONAL UNIVERSITY, AND THE DIVISION OF PLANT INDUSTRY, C.S.I.R.O., CANBERRA, AUSTRALIA]

The N.m.r. Spectrum of Pisatin

BY D. D. PERRIN AND DAWN R. PERRIN

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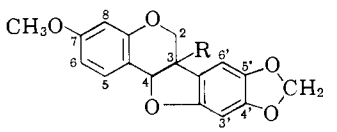
From an analysis of its nuclear magnetic resonance spectrum in carbon tetrachloride, pisatin is assigned the structure Ia. Examination of the aromatic portions of their n.m.r. spectra indicates that in pisatin and pterocarpin the methylenedioxy group is located across positions 4′ and 5′, and hence that pisatin is 3-hydroxypterocarpin.[1]

Pisatin, an antifungal substance of molecular formula $C_{17}H_{14}O_6$, has been isolated from fungal-infected pods of *Pisum sativum*.[2] At an early stage in the investigation, infrared spectra and chemical evidence, including a positive Labat test, showed pisatin to have a methoxyl group, a methylenedioxy group and an alcoholic (non-phenolic) hydroxyl group,[3] but otherwise provided little information about its structure. Subsequently, detailed analysis of n.m.r. spectra, as discussed below, suggested that pisatin is Ia. Examination of the n.m.r. spectrum of pterocarpin (a benzofurobenzopyran derivative found in the heartwood of *Pterocarpus santalinus* L.[4]) strongly supported this conclusion, which was also reached independently from examination of other chemical evidence.[3]



Ia, R = OH
b, R = H

Experimental

The n.m.r. spectra, for which we are indebted to Dr. N. Hayakawa of the Japan Atomic Energy Research Institute, were obtained using a Varian Associates V-4300-C high reso-

(1) J. B. Bredenberg and J. N. Shoolery, *Tetrahedron Letters*, **9**, 285 (1961), have also concluded from n.m.r. spectra that the methylenedioxy group in pterocarpin is located across positions 4′ and 5′, so that pterocarpin has the structure Ib.

(2) I. A. M. Cruickshank and D. R. Perrin, *Nature*, **187**, 799 (1960); *Australian J. Biol. Sci.*, **14**, 336 (1961).

(3) D. R. Perrin and W. Bottomley, *J. Am. Chem. Soc.*, **84**, 1919 (1962).

(4) A. McGookin, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 787 (1940).

lution n.m.r. spectrometer with a hydrogen precession frequency of 56.4 mc. Pisatin and pterocarpin were run as dilute solutions in carbon tetrachloride, and anhydropisatin was run in dioxane solution. Toluene in an external capillary was used for calibration, and chemical shifts were converted to the scale, zero for benzene as external reference. On this scale the ring proton peak of toluene is +0.09 p.p.m. and the methyl proton peak is 5.00 p.p.m.[5] For comparison of the present results with literature values the external benzene standard was equated with the following: τ-value (tetramethylsilane scale), 3.51[6]; water as external reference at 23°, −1.70[6]; chloroform as external reference or solvent, 0.85[5]; benzene as internal reference, 0.77,[6] p.p.m. No corrections were applied for bulk magnetic susceptibility effects, which might be expected on theoretical grounds[7] to decrease chemical shifts in chloroform solutions by 0.11 p.p.m. and increase them in dioxane by 0.20: in the present instance these corrections would not affect the interpretation of the spectra. Initial assignments of the n.m.r. peaks shown in Fig. 1 were based on correlation tables[8] and comparison with other published spectra.

Results and Discussion

By direct measurement of the areas under the peaks it was confirmed that pisatin contained fourteen hydrogens, a number of which could be assigned unequivocally. The sharp peak at 2.77 p.p.m., with an area corresponding to three hydrogens, was due to the methoxyl group. Its chemical shift was less than for a methoxyl group in an aliphatic molecule (around 3.1 p.p.m.[8]) but accorded with that for methoxyl groups attached to aromatic rings (around 2.7 p.p.m.[8]; *cf.* aspidospermine, 2.59[9]; aspidocarpine, 2.67[10]; chakranine and its Hofmann degradation products, 2.62 to 2.98[11]). The multiple-banded spectrum with peaks between −0.79 and +0.26 p.p.m. had an area equivalent to five hydrogens which were attributed to aromatic systems. Except that the peaks at −0.79 and −0.64 p.p.m. (one hydrogen) were observed to correspond to a spin-spin separation of 9 c.p.s., which is characteristic of *ortho*-coupling of hydrogens on a benzene ring,[12] no further interpretation of this region was attempted at this stage. The twin peaks at 0.55 and 0.64 p.p.m. (two hydrogens) had to be assigned to the methylenedioxy group. The observed splitting of 0.09 p.p.m. indicated unequal shielding of these two hydrogens by the aromatic ring to which this group was attached and implied molecular asymmetry about the plane of this ring (*cf.* dicentrine and bulbocapnine, where methylenedioxy groups have quartets of lines at 0.38, 0.40, 0.52, 0.55 p.p.m. and 0.37, 0.38, 0.54, 0.57 p.p.m., respectively[13]). Failure to observe similar fine-splitting in pisatin could have been due to insufficient resolution. The peak at 3.90 p.p.m. (one hydrogen) was assigned to the hydroxylic hydrogen because of the typical broadening and

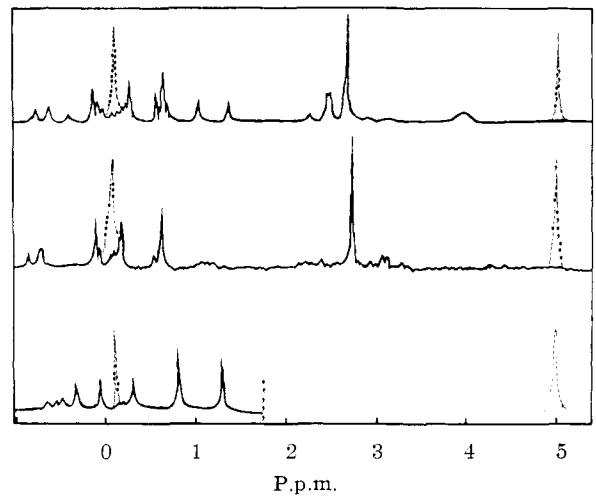
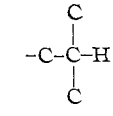


Fig. 1.—N.m.r. spectra of pisatin (top), pterocarpin, in carbon tetrachloride (middle), (3) anhydropisatin in dioxane (bottom curve). External toluene reference, benzene scale.

absence of fine structure. This value was much higher than for primary and secondary aliphatic alcohols and was also somewhat greater than the range (1.1 to 2.9 p.p.m.) given by Chamberlain[8] for "aromatic alcohols (not phenols)." It was, however, comparable with the tertiary alcoholic hydrogen in hydroxylunacridine (3.65 p.p.m.[14]).

The above tentative assignments suggested that pisatin contained two benzene rings which (i) were not fused, (ii) did not lie in the same plane, (iii) had a methoxyl group and a methylenedioxy group attached to one or other ring and (iv) were substituted in four other positions. The remaining fragment of pisatin was $(C_3H_3O_2)(OH)$. The peak at 2.54 p.p.m. (two hydrogens) and the twin peaks at 1.03 and 1.40 p.p.m. (one hydrogen) remained unassigned at this point but imposed formidable restrictions on possible structures. Thus, their shapes indicated the absence of the moiety, $-\overset{|}{C}H-\overset{|}{C}H-$. Similarly, the absence of any peaks in the 4–6 p.p.m. region showed that this fragment did not contain any paraffinic hydrogens, or the grouping



in which up to two of the carbons could belong to aromatic rings.

Of the very few structures that could be built from the above fragments, only linkage of the benzene rings in a chromano-coumarane system with the hydroxyl on carbon-3, as in Ia, fulfilled the conditions outlined and at the same time provided a consistent interpretation of the remainder of the n.m.r. spectrum. The previously-unassigned, weakly-split peak at 2.54 p.p.m., together with the small peak at 2.32 p.p.m., was assigned to the two hydrogens on carbon-2. This carbon atom forms part of a non-planar ring which

(5) P. Higham and R. E. Richards, *Proc. Chem. Soc.*, 128 (1959).
(6) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).
(7) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 81.
(8) N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).
(9) H. Conroy, P. R. Brook, M. K. Rout and N. Silverman, *J. Am. Chem. Soc.*, **80**, 5178 (1958).
(10) S. McLean, K. Palmer and L. Marion, *Can. J. Chem.*, **38**, 1547 (1960).
(11) A. R. Katritzky, R. A. Y. Jones and S. S. Bhatnagar, *J. Chem. Soc.*, 1950 (1960).
(12) Reference 7, p. 193.
(13) S. Goodwin, J. N. Shoolery and L. F. Johnson, *Proc. Chem. Soc.*, 305 (1958).
(14) S. Goodwin, J. N. Shoolery and E. C. Horning, *J. Am. Chem. Soc.*, **81**, 3736 (1959).

can be compared with, say, xylopyranose tetraacetate in which there is the same sequence, –O–CH_2–C(H)–O–, in a puckered six-membered ring. (This is only an approximation because in pisatin four of the atoms in this ring need to be planar, namely the two benzene carbons and their adjacent oxygen and carbon atoms). The slight nonequivalence of the electronic environments of these two hydrogens in pisatin, and the absence of a hydrogen on carbon-3, leads to their n.m.r. peaks forming part of an AB system[15] in which $J_{AB} > (\delta_B - \delta_A)$. There should be another small peak near 2.76 p.p.m., but this region is masked by the methoxyl peak. Mathematical analysis[15,16] of this system gave $J_{AB} \sim 11.8$ c.p.s. for the spin–spin coupling of the two hydrogens on carbon-2 and $\delta_B - \delta_A \sim 0.09$ p.p.m. This J-value is in good agreement with comparable coupling constants (*cf.* 12 c.p.s. for the two hydrogens on carbon-5 of xylopyranose tetraacetate[17] and 12.4 c.p.s. for CH_3D and CH_2DCCl_3.[18]). The chemical shifts, 2.50, 2.59 p.p.m., for these two hydrogens in pisatin are about 0.2 p.p.m. less than in the sugar acetates[17]: this reduced shielding is to be expected because in pisatin the adjacent oxygen is joined to a benzene ring, whereas in the sugar acetates it forms part of a saturated ring system. They are also not very much less than for aromatic methoxyl peaks.

The remaining peaks, at 1.03 and 1.40 p.p.m. (one hydrogen), had to be assigned to the hydrogen on carbon-4. In the absence of a hydrogen on carbon-3 the splitting of the signal into two peaks seemed surprising, especially as the separation would require a spin–spin coupling of as much as 21 c.p.s. if it were due to interaction with another hydrogen atom. It is suggested, on the contrary, that the shape of the signal indicates hindered internal rotation, which gives rise to two conformations of roughly comparable energy. Atomic models (Courtauld and Leybold) of the proposed structure of pisatin show that the unstrained configuration, in which the –OH and –H on carbons 3 and 4 are *cis* to each other, can exist in two conformations which are interconvertible by simultaneous rotation about the four single bonds of the dihydrofuran ring. This rotation, which is similar to the suggested "flip" of the fused cyclopentane–cyclohexane system in B-norcoprostane derivatives,[19] makes it possible for the hydrogen on carbon-4 to be either quasi-equatorial or quasi-axial with respect to the pyran ring (while at the same time it is quasi-axial or quasi-equatorial with respect to the dihydrofuran ring). The internal rotation about C–C bonds in *cis*-decalin[20] is also comparable. In the first of these forms the pisatin molecule is very roughly linear, whereas in the second case it is sharply V-shaped, but in both conformations the planes of the benzene rings are more or less perpendicular to each other.

If this effect operates, the signal due to the hydrogen on carbon-4 would be as found, namely two peaks which show no further splitting. The difference of 0.37 p.p.m. in the chemical shifts of the peaks should also be comparable with differences for hydrogen on carbon-1 of anomeric forms of sugar acetates: values found range from 0.30 p.p.m. for mannopyranose pentaacetates to 0.69 p.p.m. for arabinose tetraacetates (ribopyranose tetraacetate, 0.06 p.p.m., is anomalous).[17] The absolute values of these chemical shifts in the sugars are about 0.5 p.p.m. less than in pisatin. The α-hydrogens of the dihydrofurano rings in lunine and lunacrine, with peaks at 1.64 p.p.m.,[21] are also roughly comparable. It is possible that the splitting of the methylenedioxy peak in pisatin may be due substantially to the existence of the two postulated conformations rather than to the effect of dissymmetry about the plane of the benzene ring which was discussed above. The only other chemical shifts that might be expected to be significantly affected by the postulated equilibrium in pisatin are those of the methylene group on carbon 2, but, on the other hand, inspection of an atomic model shows that the relative positions of these hydrogens are not very much changed by the rotation. The methoxyl peak might perhaps be expected to be a doublet, but any such splitting should be very small because the methoxyl group is attached to a position remote from the "hinge" of pisatin.

The aromatic region of the n.m.r. spectrum of pisatin was analyzed as shown in Fig. 2. Eight of the peaks were identified as forming a simple ABC system in which $J_{xy} << \delta_x - \delta_y$. The spin–spin coupling constants, $J_{AB} = 3.1$ c.p.s., $J_{BC} = 8.7$ c.p.s., indicate 1,2,4-substitution in a benzene ring, with H_B and H_C *meta* and *para*, respectively, to H_A. (Typical coupling constants are: *o*, 5–9 c.p.s.; *m*, 1–3 c.p.s.; *p*, 1 c.p.s.[12]). The broadening of some of the bands is consistent with the additional coupling due to $J_{AC} \sim 1$ c.p.s. Because the two peaks at -0.16 and $+0.26$ p.p.m. (one hydrogen each) show no splitting they must be located *para* to each other on the remaining benzene ring.

These requirements still allow four possible assignments of the methoxyl and the methylenedioxy groups in pisatin: one of these assignments is strongly favored on biogenetic grounds. All eleven known isoflavanoids, including isoflavanones and the chromanocoumaranes pterocarpin and homopterocarpin, have an oxygen substituent located on carbon-7 and carbon-6 is unsubstituted.[22] This leads to the conclusion that the methoxyl group in pisatin is located on carbon-7 and, hence, that pisatin has the structure Ia. The hydrogens labeled as A,B,C,D,E, in Fig. 2 must therefore be attached to carbons 8,6,5,6′ and

(15) Conventions and symbols are as introduced by H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

(16) E. L. Hahn and D. E. Maxwell, *Phys. Rev.*, **88**, 1070 (1952).

(17) R. Lemieux, R. K. Kullnig, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958).

(18) M. Karplus, D. H. Anderson, T. C. Farrar and W. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957).

(19) T. Goto and L. F. Fieser, *J. Am. Chem. Soc.*, **81**, 2276 (1959).

(20) W. G. Dauben and K. S. Pitzer, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, chap. 1.

(21) S. Goodwin, J. N. Shoolery and L. F. Johnson, *J. Am. Chem. Soc.*, **81**, 3065 (1959).

(22) H. Grisebach and W. D. Ollis, *Experientia*, **17**, 4 (1961).

TABLE I

COMPARISON OF THE AROMATIC REGIONS OF THE N.M.R. SPECTRA OF PISATIN AND PTEROCARPIN

Solutions in carbon tetrachloride; shifts in p.p.m. relative to benzene

Proton	Pisatin Peaks[a]	Pisatin Mean	Pterocarpin Peaks	Pterocarpin Mean
C	−0.79, −0.64	−0.72	−0.83, −0.71	−0.77
D	−0.16	− .16	−0.08	− .08
B	−0.12, −0.07 + .03, + .09	− .01	−0.04 +0.08, +0.11	+ .04
A	+ .15, + .20	+ .18	+0.17	+ .17
E	+0.26	+ .26	+0.21	+ .21
	J_{AB} = 8.7 c.p.s.		= 7 c.p.s.	
	J_{BC} = 3.1 c.p.s.		= 3 c.p.s.	

[a] The small peak at −0.42 p.p.m. in the pisatin spectrum is probably an impurity.

3′, respectively. These assignments are also consistent with expectations based on Hammett's σ-values, which place chemical shifts for aromatic protons relative to methoxyl groups (and, presumably, the other –OR groups in the molecule) in the sequence, $\sigma_m < \sigma_p < \sigma_o$.[23]

Pterocarpin had been assigned a structure differing from Ib only by having, "reasonably certainly," the methylenedioxy group attached to carbons 3′ and 4′.[24] Its n.m.r. spectrum was therefore obtained for comparison with that of pisatin. Although, because pterocarpin is not very soluble in carbon tetrachloride, much of the fine structure of its n.m.r. signals is lost, there is a striking similarity of the aromatic portions of the n.m.r. spectra of pisatin and pterocarpin (Fig. 1) as regards shifts, shapes and relative intensities. Because the chemical shift of a peak due to a hydrogen on a benzene ring depends critically on the position of the hydrogen with respect to electron-donating and -withdrawing substituents, and the extent to which the peak is split depends on the manner in which other hydrogens are disposed about the ring, it seemed probable that pisatin and pterocarpin had the same distribution of hydrogens around the aromatic rings. This should lead to pterocarpin having 10 peaks in the aromatic part of its spectrum. Eight of these were identified and analyzed as shown in Table I, where they are compared with results for pisatin. Their near-identity leads to the structure (Ib) for pterocarpin.[1,25]

The remaining portion of the pterocarpin spectrum shows the expected resemblance to pisatin: the methoxyl peaks occur in almost the same positions, as also do the methylenedioxy peaks. In pterocarpin the methylenedioxy peak shows only a slight splitting, which supports the suggestion of an equilibrium between two different conformations (one of which is somewhat more stable) rather than the unequal shielding of the type found in dicentrine and bulbocapnine. Peaks due to the four hydrogens on carbons 2, 3 and 4 could not be adequately resolved, partly on account of the low signal-to-noise ratio and partly because of the very much greater splitting of peaks (Thus, the hydrogens on carbons 2 and 3 form an ABC system which should give rise to 15 lines which are further split by the hydrogen on carbon 4).

(23) For discussion see ref. 7, pp. 262, 326.

(24) A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1440 (1940); and ref. 4.

(25) The spectrum obtained by Bredenberg and Shoolery (ref. 1) using a deuterated chloroform solution is very well resolved and all ten aromatic peaks are observed. Their spin–spin coupling constant of J_{AB} = 9 c.p.s. is more accurate than our figure of 7 c.p.s. and is close to the value of 8.7 c.p.s. we have obtained for pisatin. In addition, the signal due to the hydrogen on carbon 4 is identified as a doublet centered on 1.01 p.p.m. (*cf.* 1.03 and 1.40 p.p.m. in pisatin).

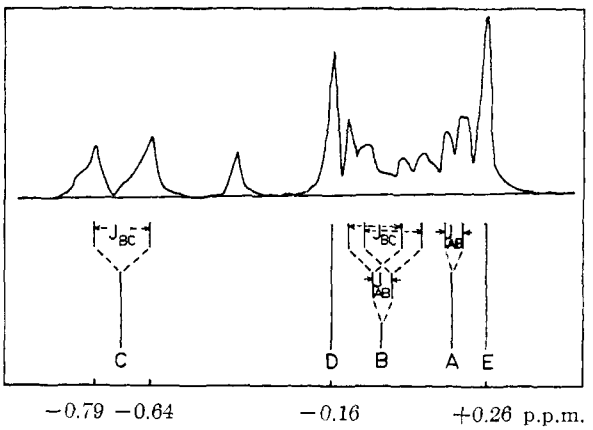
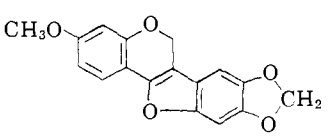


Fig. 2.—Analysis of the aromatic region of the n.m.r. spectrum of pisatin in carbon tetrachloride. The peak at −0.42 p.p.m. is probably an impurity.

In acid solutions, pisatin readily loses a molecule of water to give anhydropisatin, $C_{17}H_{12}O_5$, which is believed to have the structure II.[3] Anhydropisatin is only sparingly soluble in carbon tetrachloride but is more soluble in dioxane. Its n.m.r. spectrum in dioxane (Fig. 1) is consistent with the proposed structure. The twelve hydrogens in the molecule are accounted for by a methoxyl group[3] (peak masked by solvent), the two sharp peaks at 1.26 and 0.79 p.p.m. (2 hydrogens each), and the series of peaks between +0.27 and −0.69 p.p.m. (five aromatic hydrogens). The peak at 0.79 p.p.m. (or 0.59 p.p.m. if the bulk susceptibility correction is applied) is obviously due to the methylenedioxy group. The peak at 1.26 p.p.m. is assigned to the pair of hydrogens on carbon 2. Relative to pisatin this represents a shift of the signal by almost 1 p.p.m. toward lower fields and is to be expected because of the increase in conjugation and the fact that this group is now attached directly to the aromatic ring system. Unlike pisatin, neither of these peaks shows any splitting. This is because dehydration to give anhydropisatin has made both the ring A and the whole molecule very nearly planar, thereby, in both cases, rendering the two hydrogens equivalent.



II

Acknowledgments.—We wish to thank Professor A. J. Birch, University of Manchester, for the generous gift of the pterocarpin used in this work, and Mr. Y. Inoue of the Department of Medical Chemistry, Australian National University, for very helpful discussion.