Anal. Calcd. for $C_{44}H_{34}O_8$: C, 76.5; H, 4.36. Found: C, 76.4; H, 5.00.

4,4'-Di-O-methyl-5,5'-di-C-benzylellagic Acid.—A solution of 4,4'-di-O-methyl-3,3'-di-O-benzyl-5,5'-di-C-benzylellagic acid (0.5 g.) in ethyl acetate (200 ml.) was hydrogenated at room temperature and pressure in the presence of a palladium–charcoal catalyst. The filtered ethyl acetate solution was evaporated and the crystalline residue was recrystallized from tetrahydrofuran–methanol. 4,4'-Di-O-methyl-5,5'-di-C-benzylellagic acid was obtained as colorless needles, m.p. 360°.

Anal. Calcd. for $C_{30}H_{22}O_8$: C, 70.6; H, 4.35; 2 MeO–, 12.2. Found: C, 70.6; H, 4.32; MeO–, 11.8.

The diacetate of this product was prepared by heating it with acetic anhydride and sodium acetate for 30 minutes. After adding water the acetate was collected and recrystallized from dioxane–methanol. It separated in colorless felted needles, m.p. 325°.

Anal. Calcd. for $C_{34}H_{26}O_{10}$: C, 68.7; H, 4.41. Found: C, 68.7; H, 4.49.

Action of Sodium Methoxide on Di-O-methylellagorubin.—Di-O-methylellagorubin (1.6 g.) was refluxed with a solution of sodium (2.0 g.) in anhydrous methanol (100 ml.) for 15 minutes. The dimethyl ether gradually passed into solution and yellow sodium salt began to crystallize out. The mixture was cooled, acidified with hydrochloric acid and diluted with water. The solid product was collected and recrystallized successively from methanol and benzene–hexane (1.4 g.). It separated in almost colorless needles, m.p. 159°, which did not give a color with methanolic ferric chloride but dissolved in aqueous sodium bicarbonate to give an intensely yellow solution. Heated with aqueous sodium hydroxide for 1 hour it was recovered unchanged on acidification.

Anal. Calcd. for: $C_{46}H_{42}O_{10}$: C, 73.2; H, 5.61; 4 MeO–, 16.4. Found: C, 73.2; H, 5.76; MeO–, 16.3.

Acid Hydrolysis of the Methanol Addition Product.—The above product (0.2 g.) was heated with methanol (4.0 ml.) and concentrated hydrochloric acid (1.0 ml.) for 10 minutes. Water was added and the crystalline product was collected and recrystallized from tetrahydrofuran–methanol. 3,3'-Di-O-methyl-5,5'-di-C-benzylellagic acid, m.p. and mixed m.p. 317–318°, was thus obtained.

Anal. Calcd. for $C_{30}H_{22}O_8$: C, 70.6; H, 4.35; MeO–, 12.2. Found: C, 70.6; H, 4.49; MeO–, 11.9.

Catalytic Hydrogenation of the Methanol Addition Product.—A solution of the di-O-methylellagorubin–methanol addition product (0.26 g.) in methanol (15.0 ml.) was hydrogenated at room temperature and pressure in the presence of 30% palladium–charcoal catalyst until the hydrogen uptake was complete. The catalyst was filtered. Evaporation of the filtrate gave a crystallized residue which was recrystallized from ethyl acetate–hexane. The product separated in colorless blades, m.p. 216–217°.

Anal. Calcd. for $C_{32}H_{30}O_{10}$: C, 66.8; H, 5.27; 4 MeO–, 21.6. Found: C, 66.8; H, 5.26; MeO–, 21.5.

A solution of the above hydrogenation product (50 mg.) in methanol (10.0 ml.) and concentrated hydrochloric acid (2.0 ml.) was heated on a steam-bath for 15 minutes. Water was added. The solid product was collected and recrystallized from tetrahydrofuran–methanol. 3,3'-Di-O-methyl-5,5'-di-C-benzylellagic acid thereby separated in slightly yellow needles, m.p. 317–318°.

Anal. Calcd. for $C_{30}H_{22}O_8$: C, 70.6; H, 4.35; 2 MeO–, 12.2. Found: C, 70.6; H, 4.42; MeO–, 12.2.

A solution of the hydrogenation product (60 mg.) in a 1% methanolic potassium hydroxide solution (5.0 ml.) was allowed to stand at room temperature for 10 minutes. It was acidified (HCl) and diluted with water. The yellow needles were collected and recrystallized from tetrahydrofuran–methanol. 3,3'-Di-O-methyl-5,5'-di-C-benzylellagic acid, m.p. and mixed m.p. 317–318°, was thus obtained.

Action of Sodium Methoxide on Di-O-benzylellagorubin.—Di-O-benzylellagorubin (0.2 g.) was refluxed with a solution of sodium (0.4 g.) in methanol (10.0 ml.) for 20 minutes. The mixture was cooled, acidified, diluted with water and filtered. The solid was recrystallized from benzene–hexane and from methanol. The methanol addition product separated in colorless rectangular flakes, m.p. 179–180°. It was recovered unchanged on treatment with warm aqueous sodium hydroxide.

Anal. Calcd. for $C_{58}H_{50}O_{10}$: C, 76.8; H, 5.56. Found: C, 76.8; H, 5.60.

Acknowledgments.—The author is indebted to Dr. T. A. Geissman and Dr. R. M. Horowitz for many helpful discussions and to L. M. White for the elementary analyses.

PASADENA, CALIF.

[CONTRIBUTION FROM WESTERN REGIONAL RESEARCH LABORATORY, A LABORATORY OF THE WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Plant Polyphenols. VIII. The Structure of Ellagorubin. Part A. Infrared Spectra. Part B. High Resolution Nuclear Magnetic Resonance Spectra

BY FRED STITT,[1a] EDITH GONG,[1a] K. J. PALMER[1b] AND J. N. SHOOLERY[1b,c]

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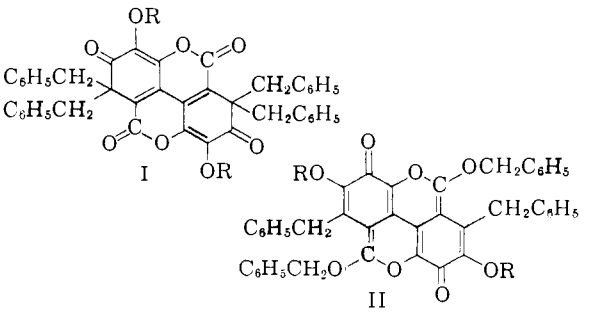
It is shown that both infrared and nuclear magnetic resonance spectra of ellagorubin are compatible with structure I (R = H) proposed by Jurd, but not with II (R = H) proposed by other investigators. The n.m.r. spectra for ellagorubin, two of its derivatives, and two derivatives of ellagic acid are analyzed. Infrared data in the carbonyl stretching region are discussed for these same compounds as well as for ellagic acid and nine other derivatives.

In the preceding paper of this series,[2] chemical evidence in conjunction with ultraviolet spectra indicate that ellagorubin has the structure I (R = H) rather than II (R = H) as proposed by Schmidt, Voigt and Bernauer.[3] Both infrared and nuclear magnetic resonance (n.m.r.) spectra are shown in this paper to be compatible with structure I (R = H) and incompatible with structure II (R = H) for ellagorubin.



(1) (a) Part A. (b) Part B. (c) Varian Associates, Palo Alto, Calif.

(2) Part VII, L. Jurd, THIS JOURNAL, **81**, 4610 (1959).

(3) O. T. Schmidt, H. Voigt and K. Bernauer, *Chem. Ber.*, **88**, 91 (1955).

TABLE I

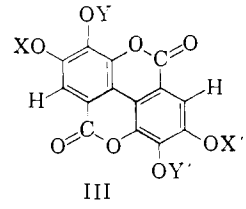
WAVE LENGTHS OF STRONG INFRARED BANDS BETWEEN 5.00 AND 6.15 μ OF ELLAGIC ACID, ELLAGORUBIN AND SOME OF THEIR DERIVATIVES[a]

Compound	Structure No.	X	X′	Y	Y′	Acetate carbonyl, μ	Lactone carbonyl, μ	Other bands, μ
Ellagic acid	III	H	H	H	H		5.90	
Ellagic acid tetraacetate	III	Ac	Ac	Ac	Ac	5.58, 5.62	5.72	
O-Tetrabenzylellagic acid	III	Bz	Bz	Bz	Bz		5.71	
5,5′-Di-C-benzylellagic acid	IV	H	H	H	H		5.84	
3,3′-Di-O-methyl-5,5′-di-C-benzylellagic acid	IV	H	H	Me	Me		5.75	
O-Tetramethyl-5,5′-di-C-benzylellagic acid	IV	Me	Me	Me	Me		5.78	
5,5′-Di-C-benzylellagic acid 4-monoacetate	IV	Ac	H	H	H	5.64	5.81	
5,5′-Di-C-benzylellagic acid tetraacetate	IV	Ac	Ac	Ac	Ac	5.57, 5.63	5.71	
3,3′-Di-O-methyl-5,5′-di-C-benzylellagic acid diacetate	IV	Ac	Ac	Me	Me	5.66	5.72	
3,3′,4-Tri-O-benzyl-5,5′-di-C-benzylellagic acid	IV	H	Bz	Bz	Bz		5.77	
O-Tetrabenzyl-5,5′-di-C-benzylellagic acid	IV	Bz	Bz	Bz	Bz		5.77	
3,3′,4-Tri-O-benzyl-5,5′-di-C-benzylellagic acid acetate	IV	Ac	Bz	Bz	Bz	5.66	5.77	
Ellagorubin	I		R = H				5.83	5.97
O-Dimethylellagorubin	I		R = Me				5.75	6.05
Ellagorubin diacetate	I		R = Ac			5.61	5.73	5.99, 6.10

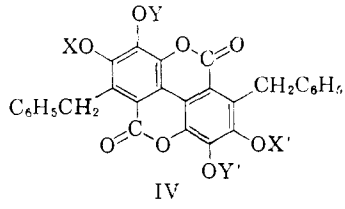
[a] A Beckman IR-3 spectrophotometer with NaCl optics was used to record the spectra of approximately 1-mg. samples in the form of KBr pressed disks, 12 mm. in diameter.

Part A: Infrared Spectra

The infrared spectra of ellagic acid (III, X,X′,Y,-Y′ = H) and eleven of its derivatives were examined to provide background information on related compounds of known structure. The positions of all bands in the region from 5.00 to 6.15 μ



III



IV

are shown for these compounds in Table I. Except for the acetate derivatives, only one carbonyl stretching band is observed. An additional band at lower wave length appears in the spectra of the diacetate derivatives, where the acetate groups are symmetrically substituted on the two aromatic rings of III. Interaction of adjacent acetate groups in the tetraacetate derivatives produces a second acetate carbonyl band of still higher frequency. Since no more than a single lactone carbonyl stretching frequency is observed for any of these ellagic acid derivatives, it is concluded that each pair of symmetrically placed carbonyl groups of structures I and II would likewise give rise to only a single carbonyl stretching band. This is in accord with the selection rules for isolated molecules having a center of symmetry.

Our infrared spectra for ellagorubin and its dimethyl ether agree satisfactorily with those of Schmidt, Voigt and Bernauer[3] when allowance is made for the higher resolution obtained with our instrument. However, the structure they have proposed for ellagorubin (II, R = H) appears to be incompatible with the infrared spectra. If structure II were correct a single band would be expected in the carbonyl stretching region. Furthermore this band probably would appear in the region from about 6.00 to 6.10 μ where the carbonyl stretching frequencies for both α,β-α',β'-unsaturated ketones and quinones with the carbonyl groups in different rings are usually found.[4] Instead we observed two strong sharp bands at 5.83 and 5.97 μ for ellagorubin (Table I). The presence of these two bands is accounted for readily by structure I. The 5.83 μ band arises from the α,β-unsaturated lactone carbonyl and the 5.97 μ band is due to the α,β-γ,δ-unsaturated ketone carbonyl. Both of these assignments are compatible with the observed range of these groups in other compounds.[4]

The positions of the lactone carbonyl bands (5.71 to 5.90 μ) in ellagic acid and its derivatives (Table I) probably reflect intramolecular effects of substituents and, in a few cases, intermolecular hydrogen bonding. The shift from 5.90 μ in ellagic acid to 5.84 μ on introduction of benzyl groups in the 5,5′-positions suggests that presence of these bulky substituents results in molecular packing in the crystalline lattice such that the lactone carbonyl groups are unable to form as strong intermolecular hydrogen bonds as in ellagic acid. This hypothesis is supported by the nature of the spectra in the 3.0 μ region.[5] When two or more OH groups of ellagic acid or 5,5′-di-C-benzylellagic acid are converted to acetate groups, the lactone carbonyl band is observed at 5.71–5.72 μ; if converted to methyl ether or benzyl ether groups, the band position is 5.75–5.78 μ. The only observed exception to these ranges is O-tetrabenzylellagic acid (5.71 μ).

The effects of substituents on the position of the lactone carbonyl band appear to be the same for ellagorubin as for 5,5′-di-C-benzylellagic acid. For ellagorubin, its dimethyl ether and its diacetate, the lactone carbonyl band positions are 5.83, 5.75 and 5.73 μ, respectively; the figures for 5,5′-di-C-

(4) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, Chap. IX.

(5) Intermolecular hydrogen bonding is indicated by broad OH stretching bands with maxima above 3.0 μ observed for ellagic acid and the two derivatives of Table I containing three or more OH groups. This band is very broad in ellagic acid and peaks near 3.27 μ, whereas it is narrower and peaks near 3.03 μ in both 5,5′-di-C-benzylellagic acid and 5,5′-di-C-benzylellagic acid 4-monoacetate. Ellagic acid derivatives of Table I containing one or more OH groups each show a sharp OH stretching band in the range 2.83 to 2.93 μ.

benzylellagic acid and its corresponding tetra derivatives are 5.84, 5.78 and 5.71 μ.

Part B: High Resolution Nuclear Magnetic Resonance Spectra

High resolution nuclear magnetic resonance (n.m.r.) spectra were obtained on (A), O-tetramethyl-5,5′-di-C-benzylellagic acid (structure IV, X, X′, Y, Y′ = Me); (B), O-tetrabenzyl-5,5′-di-C-benzylellagic acid (structure IV, X, X′, Y, Y′ = $-CH_2C_6H_5$); (C), ellagorubin diacetate; (D) ellagorubin dimethyl ether; and (E), ellagorubin.

The purpose of the present investigation was to determine whether high resolution n.m.r. spectra can distinguish between structure II (R = H) proposed by Schmidt, *et al.*,[3] for ellagorubin and structure I (R = H) suggested by Jurd[2] on the basis of chemical and ultraviolet absorption data and supported by infrared spectra. To provide background material the n.m.r. spectra of two ellagic acid derivatives (A) and (B), as well as ellagorubin and two of its derivatives (C) and (D) were obtained. On the basis of this evidence it appears that ellagorubin must have two benzyl groups bonded at both 5 and 5′ and consequently the correct structure for this compound must be I (R = H).

A discussion of the n.m.r. spectra can be conveniently introduced by first considering the spectrum obtained from A which is reproduced in Fig. 1A. The spectra are drawn so that the magnetic field increases from left to right. The numbers at the bottom of the figures express the shift in cycles per second (c.p.s.) from pure benzene.

The spectrum of A consists of four prominent peaks. The peak at −47 c.p.s. is due to the hydrogens on the benzene rings while the other three peaks are due to the methylene and methyl hydrogens. The peak due to the phenyl hydrogens is shifted to a lower frequency than for pure benzene because of the comparative isolation of the phenyl groups in A.[6] Since the two phenyl groups are equivalent, only a single peak is observed.

The peak at 97 c.p.s. is assigned to the two methylene groups and the two peaks at 131 and 154 c.p.s. consequently must arise from the methoxy groups. This assignment of peaks is confirmed by an examination of the spectrum from B reproduced in Fig. 1B. The peak at 98 c.p.s. has the same shape as the peak at 97 c.p.s. in Fig. 1A. Since both A and B have methylene groups at the 5,5′-positions this n.m.r. peak must arise from these hydrogens. In addition, the two peaks at 56 and 85 c.p.s. must be due to the methylene groups attached to the ether oxygen atoms. Since there are four such groups occurring as two symmetrical pairs two n.m.r. peaks are expected and two occur.

It is interesting to note that the two peaks at 56 and 85 c.p.s. in Fig. 1B have nearly the same separation as the two peaks at 131 and 154 c.p.s. in agreement with the fact that the methyl ether and benzyl ether groups occupy similar positions in the respective molecules. The shift of the peaks for the methylene groups to lower frequencies than those for the methyl ether groups is due partly to the electron-withdrawing power of the adjacent benzene rings,[7] and partly to the magnetic anisotropy of the benzene ring.[8]

One other point which confirms the above assignment is the shape of the absorption lines. The peaks at 131 and 154 c.p.s. in Fig. 1A and 56 and 85 c.p.s. in Fig. 1B are narrower and higher than the peak at 97–98 c.p.s. Since there are two narrow peaks and one broad one and there are two sets of groups which contain an ether oxygen and one which does not, it is logical to assume that the broad peak at 97–98 c.p.s. is due to the methylene hydrogens in $C-CH_2-C_6H_5$, whereas the methylene hydrogens in benzyl ether and the methyl hydrogens in methyl ether give rise to the narrow peaks. The side chains containing oxygen presumably produce narrower peaks because the additional atom increases the rotational freedom of the side chain.

The absorption line due to the phenyl hydrogens in B appears as a doublet since two of the benzene rings are connected through methylene groups whereas the other four are connected through methylene ether groups to the heterocyclic framework. The integrated intensity of the two peaks in the doublet should be in the ratio 2:1 and this appears to be so.

The n.m.r. spectrum of C is reproduced in Fig. 1C. In addition to the absorption of the phenyl hydrogens, three absorption peaks occur at 167, 238 and 287 c.p.s. The latter peak is due to a small amount of hydroxyl.[9] The occurrence of the other two sharp peaks with large positive shifts is compatible only with structure I (R = Ac) because if ellagorubin diacetate had structure II (R = Ac) three peaks with positive shifts would occur. Consequently, the n.m.r. spectrum conclusively demonstrates that ellagorubin must have four symmetrically positioned benzyl groups.

The ratio of the integrated intensities of the peaks due to methylene and acetate hydrogens should be 8:6. The peak at 167 c.p.s. has the largest integrated intensity; consequently this peak is assigned to the methylene hydrogens of the benzyl groups and the peak at 238 c.p.s. is assigned to the hydrogens on the acetate groups. This latter assignment is in agreement with the approximate chemical shift to be expected for the acetate hydrogens.[10]

The occurrence of the methylene peak at 167 c.p.s. as compared to the methylene peak in ethyl benzene at 231 c.p.s.[11] is thought to be due to additional magnetic interaction between the methylene hydrogens and the benzene ring of the adjacent benzyl group. Since benzene rings are magnetically anisotropic, they display a magnetic moment when placed in a magnetic field. As a result protons forced into close proximity to

(6) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

(7) B. P. Dailey and J. N. Shoolery, THIS JOURNAL, **77**, 3977 (1955).

(8) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

(9) A weak band at 2.9 μ in the infrared spectrum also suggests some residual OH in this material.

(10) A large number of steroidal 21-acetates in $CDCl_3$ have been examined and the resonance found at +254 c.p.s. relative to benzene in a coaxial cell; unpublished work, Varian Associates.

(11) The value 231 c.p.s. was obtained from a 10% solution of ethylbenzene in chloroform.

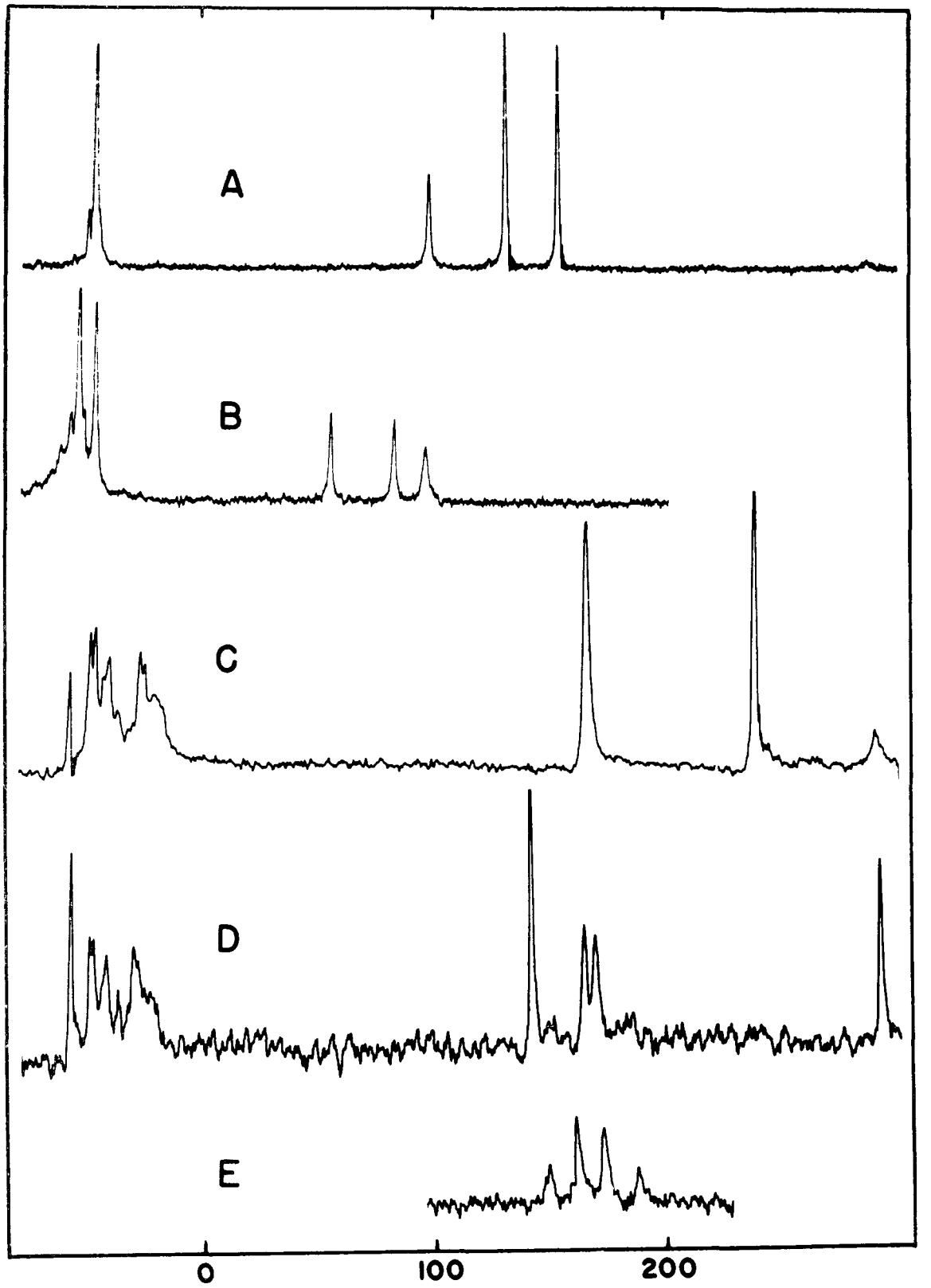


Fig. 1.—N.m.r. spectra at 60 megacycles/sec. of (A) O-tetramethyl-5,5′-di-C-benzylellagic acid; (B) O-tetrabenzyl-5,5′-di-C-benzylellagic acid; (C), ellagorubin diacetate, (D), ellagorubin dimethyl ether, (E), ellagorubin. Magnetic field increases from left to right. Scale indicates shift in cycles/sec. from benzene.

benzene rings undergo an appreciable shift in average resonance frequency. In ellagorubin the magnetic interaction between the methylene hydrogens and the benzene rings is apparently un-

usually strong because two benzyl groups are bonded to the same carbon atom.

Evidence that a similar magnetic interaction is also occurring between the benzene rings of the benzyl groups attached to the same carbon atom is suggested by the comparatively broad absorption band centered at −33 c.p.s. (Fig. 1C) as compared to the sharp peaks observed in this region for the ellagic acid derivatives (Fig. 1A and B).

The n.m.r. spectrum of ellagorubin dimethyl ether is reproduced in Fig. 1D. The absorption band centered at −39.5 c.p.s. is broad and similar in appearance to the same band in curve 1C. (The sharp peak just to the left of this broad band at −57.5 c.p.s. is due to a small amount of residual $CHCl_3$ in the deuterated solvent.) The peak at 142 c.p.s. arises from the methyl ether groups. The two peaks centered at 167 c.p.s. appear to be the intense inner pair of two symmetrical doublets, and from their position must be due to the methylene hydrogens of the benzyl groups. The four lines making up the two doublets appear more clearly in the n.m.r. spectrum of ellagorubin. This spectrum was obtained by dissolving the latter in pyridine. (A spectrum of ellagorubin could not be obtained in $CDCl_3$ because it was too insoluble.) Although the pyridine solution turned dark, an excellent trace of the four peaks was obtained. The section of the spectrum in the region of interest is shown in Fig. 1E. This characteristic set of four peaks has been observed for compounds which contain two magnetically non-equivalent hydrogens bonded to the same carbon atom.[12] The non-equivalence probably occurs because of unequal residence times in the various rotational conformations even though the potential barrier is not high enough to prevent rapid internal rotation,[12b] but if the shifts of each proton depend differently upon the angular orientation of the benzyl group to the heterocyclic system, non-equivalence could arise even if the rotational conformations were equally populated. The separation of the peaks in Fig. 1E gives a spin–spin coupling, J, of 14 c.p.s., and a relative chemical shift, δ_{rel}, for the two non-equivalent hydrogens of 23 c.p.s. at 60 megacycles.

It is interesting that the n.m.r. spectrum of ellagorubin diacetate (C) has only a single sharp peak in the region where the dimethyl ether derivative shows four peaks. As a result it must be concluded that all methylene hydrogens in the diacetate are much more nearly equivalent. It would therefore appear that substitution of an acetate group for a methoxy group produces a change in either the residual times of the benzyl rotational conformations or a change in the dependence of the chemical shift of the methylene protons as a function of the angular orientation.

The peak at 292 c.p.s. in the spectrum of ellagorubin diacetate suggests the presence of methyl groups attached to an aliphatic carbon atom. Since none of the proposed structures for ellagorubin contains such a group, the peak at 292 c.p.s. must be due to the presence of an impurity, perhaps a small amount of solvent.

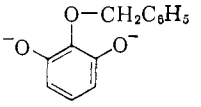
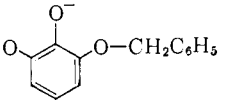
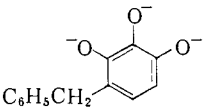
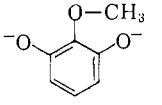
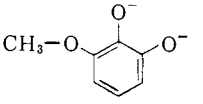
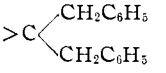
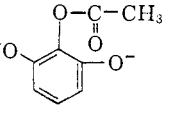
(12) (a) J. J. Drysdale and W. D. Phillips, THIS JOURNAL, **79**, 319 (1957); (b) P. M. Nair and J. D. Roberts, *ibid.*, **79**, 4565 (1957).

The four peaks in the spectrum of ellagorubin dissolved in pyridine presumably occur because this solvent complexes with the conjugated hexadienone system as indicated by the appearance of the dark color. In the addition complex the benzyl groups may be prevented from rotating freely or the chemical shift may become a function of the angular orientation of the benzyl group and consequently the methylene hydrogens are non-equivalent. It would be interesting to obtain the n.m.r. spectrum of ellagorubin in a solvent with which it does not react in order to see whether or not only a single peak would occur for the methylene protons as is observed for the diacetate derivative dissolved in chloroform.

The n.m.r. results on the five compounds discussed above are summarized in Table II.

TABLE II

PROTON RESONANCE SHIFT FOR METHYL AND METHYLENE HYDROGENS AT 60 MEGACYCLES PER SECOND

Group	Shift, c.p.s., from benzene	Compound
	56	B
	85	B
	97 98	A B
	131 142	A D
	154	A
	167	C
	238	C

Experimental

High resolution n.m.r. spectra were obtained at 60 megacycles per second in a magnetic field of approximately 14,100 gauss. The compounds were studied in dilute solutions in deuterated chloroform, concentrations ranging from approximately 0.1 to 0.4 M depending upon the solubility. The zero of reference in each spectrum was taken as the resonance position of pure benzene contained in a precision external annular cell.[13] The shift values of the sharp peaks in the spectrum of each compound were determined by the audiofrequency side band method[14] in cycles

(13) Wilmad Glass Co., Landisville, N. J.

(14) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

per second and could be reproduced to within 1 c.p.s. The sign of the shift is chosen to be positive when the resonance falls at a higher applied field than the reference. With this definition the frequency of a resonance unsplit by spin–spin coupling is proportional to the total shielding, relative to benzene, at the proton group being studied. For comparison with work done at other field strengths it will often be desirable to convert the position of a peak (or center of a spin–spin multiplet) to field-independent units. The position of any point in the spectrum in the generally accepted dimensionless units, δ, can be determined by dividing by 60 the frequency obtained from linear interpolation between measured peaks. This corresponds to the definition $\delta = 10^6 \times (H - H \text{ ref.})/H \text{ ref.}$ The deuterated chloroform[15] used as solvent was found by n.m.r. assay to be 99.5% pure $CDCl_3$.

The instrument employed for these measurements was a Varian Associates V-4300-C high resolution n.m.r. spectrometer with associated 12-inch magnet system equipped with a V-K3506 flux stabilizer.[16] Samples were placed in precision ground Pyrex tubes with 5 mm. o.d. and 4 mm. i.d. and rotated at several hundred r.p.m. by a small air turbine during the recording of the spectra. Audiofrequency side bands for calibration purposes were generated with a Hewlett–Packard 200-CD audio oscillator[16] and measured with a Hewlett–Packard 521-C frequency counter.[16]

Acknowledgment.—We are indebted to L. Jurd for suggesting this problem and for the samples used in this investigation. The n.m.r. spectra were obtained by Mr. L. F. Johnson of Varian Associates.

(15) Merck, Ltd., Montreal, Can.

(16) Mention of manufacturers or of trade names of products or equipment does not imply that they are recommended by the Department of Agriculture over others not mentioned.

ALBANY, CALIF.

[CONTRIBUTION FROM THE FRUIT AND VEGETABLE CHEMISTRY LABORATORY, A LABORATORY OF THE WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Plant Polyphenols. IX. Structure of the Yellow Product from the Benzylation of Ellagic Acid[1]

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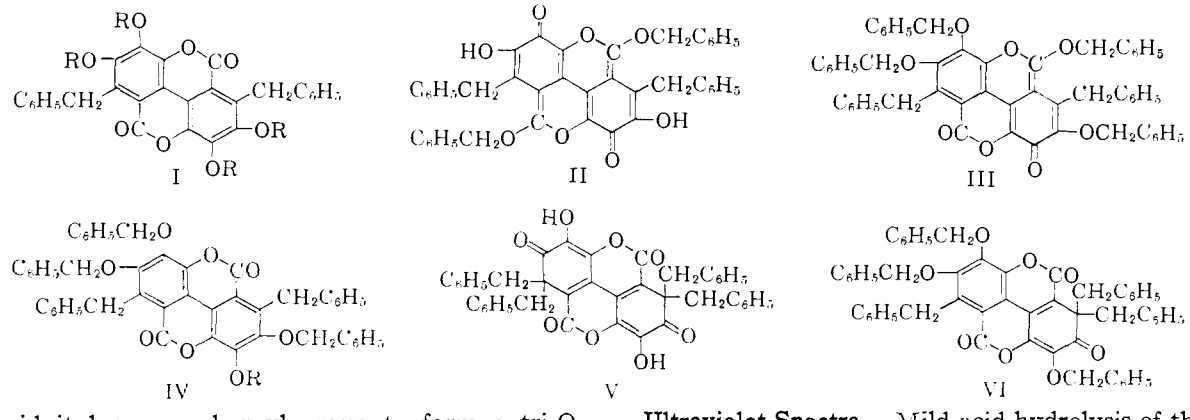
Ultraviolet, infrared and nuclear magnetic resonance spectral measurements on the yellow compound formed in the benzylation of ellagic acid establish its structure as VI.

During experiments on the benzylation of ellagic acid in aqueous alkali a small quantity of a yellow compound, m.p. 176–177°, was obtained in addition to the chief products, ellagorubin and 5,5′-di-C-benzyl-tetra-O-benzylellagic acid (I, R = $C_6H_5CH_2$–). The yellow compound, $C_{56}H_{42}O_8$, is isomeric with I (R = $C_6H_5CH_2$–), does not contain a free hydroxyl group, and gives 5,5′-di-C-benzylellagic acid (I, R = H) on catalytic hydrogenation. When treated with acetic anhydride and sulfuric acid it loses one benzyl group to form a tri-O-benzyl-5,5′-di-C-benzylellagic acid monoacetate, m.p. 225–226°. Since ellagorubin contains two labile benzyl groups it was concluded that in the yellow compound one of its rings is aromatic as in I (R = $C_6H_5CH_2$–) and the other is quinoidal as in ellagorubin. On the basis of Schmidt's formula II for ellagorubin,[4] structure III was proposed for the yellow compound and structure IV (R = CH_3CO–) for the ellagic acid monoacetate derived from it.[5] As it has since been shown that ellagorubin has structure V[6] it follows that the structure assigned to the yellow compound must be corrected to VI. Structure VI has now been confirmed by further ultraviolet, infrared and nuclear magnetic resonance spectral measurements.



Ultraviolet Spectra.—Mild acid hydrolysis of the yellow compound produces a tri-O-benzyl-5,5′-di-C-benzylellagic acid, m.p. 249°. Acetylation of this gives the monoacetate, m.p. 225–226°, previously obtained[5] by reaction of the yellow compound with acetic anhydride and sulfuric acid.

(1) Financial support for part of this work was provided by the Diamond Walnut Growers, Inc., Stockton, Calif.

(2) Agricultural Research Service, Albany, Calif.

(3) Varian Associates, Palo Alto, Calif.

(4) O. T. Schmidt, H. Voigt and K. Bernauer, *Chem. Ber.*, **88**, 91 (1955).

(5) L. Jurd, THIS JOURNAL, **79**, 6043 (1957).

(6) (a) Part VII, L. Jurd, *ibid.*, **81**, 4610 (1959); (b) part VIII, F. Stitt, E. Gong, K. J. Palmer and J. N. Shoolery, *ibid.*, **81**, 4615 (1959).