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]

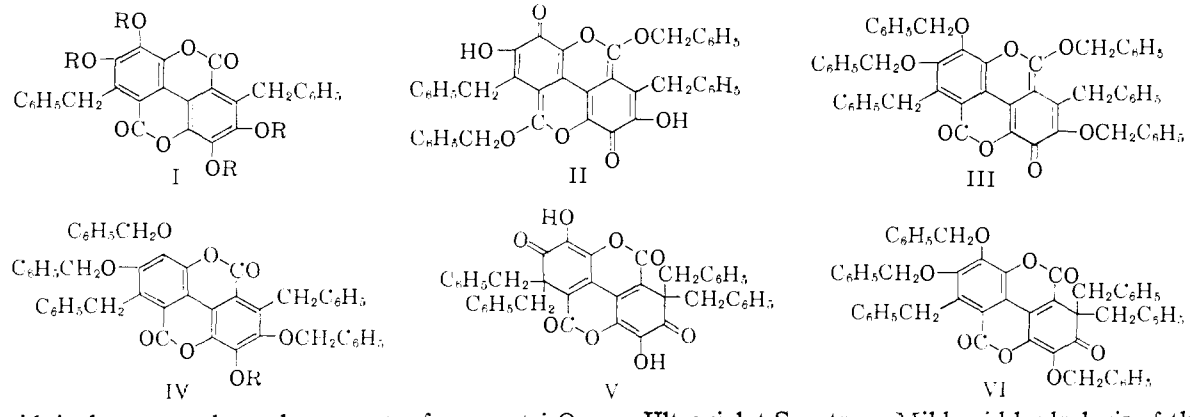
Plant Polyphenols. IX. Structure of the Yellow Product from the Benzylation of Ellagic Acid[1]

BY LEONARD JURD, K. J. PALMER,[2] FRED STITT[2] AND J. N. SHOOLERY[3]

RECEIVED JANUARY 20, 1959

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).

The spectra of the tri-O-benzyl-5,5′-di-C-benzylellagic acid and its acetate were then compared with those of synthetic 3,3′,4-tri-O-methylellagic acid (VII)[7] and its acetate. Thus the monoacetate of the tri-O-benzyl-5,5′-di-C-benzylellagic acid, λ_{max} 378, 364, 252 mμ, has λ_{max} 366, 352, 250 mμ, while the monoacetate of 3,3′,4-tri-O-methylellagic acid, λ_{max} 369, 355, 249 mμ, has λ_{max} 357, 344, 247 mμ. Acetylation of each of these phenols, therefore, results in identical hypsochromic shifts, *viz.*, 12,12 (11), 2 mμ of their respective bands (Fig. 1).

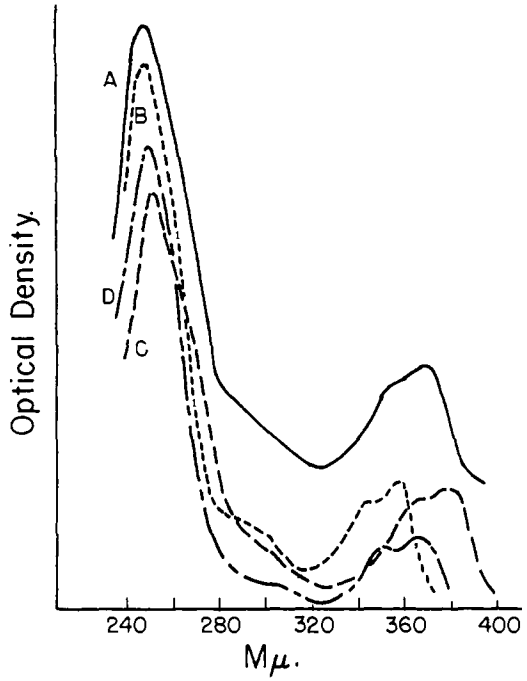


Fig. 1.—Ultraviolet absorption spectra in ethanol of: (A) ———, 3,3′,4-tri-O-methylellagic acid; (B) — — —, 3,3′,4-tri-O-methylellagic acid monoacetate; (C) — - —, tri-O-benzyl-5,5′-di-C-benzylellagic acid; (D) —··—, tri-O-benzyl-5,5′-di-C-benzylellagic acid monoacetate.

It has been noted previously[6] that whereas the strongly acidic hydroxyl groups in the 3,3′-positions of ellagic acid are ionized by both sodium acetate and sodium ethylate, hydroxyls located in the 4,4′-positions are sufficiently acidic to be ionized only by sodium ethylate. In agreement with this, sodium acetate does not appreciably alter the ultraviolet spectrum of either 3,3′,4-tri-O-methylellagic acid or the tri-O-benzyl-5,5′-di-C-benzylellagic acid, whereas sodium ethylate produces a bathochromic shift of the main band to 411 and 430 mμ, respectively (Fig. 2). The intense yellow color of these tri-O-alkylellagic acids in sodium ethylate provides strong support for the previous suggestion[6] that the yellow color of solutions of 3,3′-di-O-alkylellagic acids (VIII) in sodium ethylate is due to the formation of a highly conjugated resonance form IX. It is apparent that alkylation of one of the 4,4′-hydroxyls to yield VII can still result in the formation of the same highly conjugated form X.

(7) Part VI, L. Jurd, THIS JOURNAL, **81**, 4606 (1959).

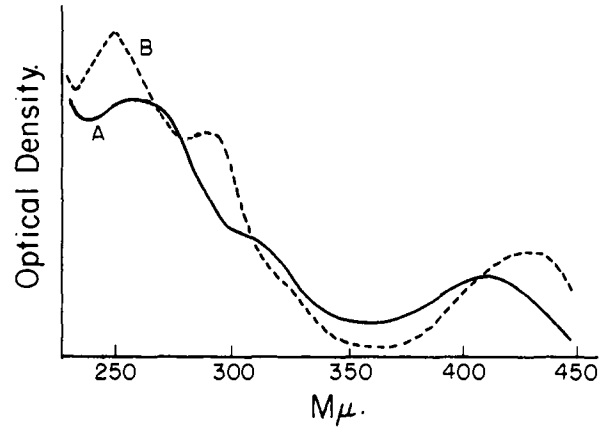
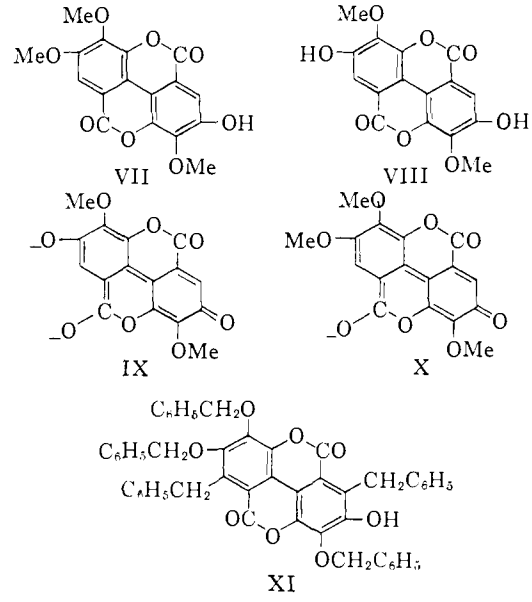


Fig. 2.—Ultraviolet absorption spectra in 0.002 *M* sodium ethylate of : (A) ———, 3,3′,4-tri-O-methylellagic acid; (B) — — —, tri-O-benzyl-5,5′-di-C-benzylellagic acid.

On the basis of these ultraviolet spectra the tri-O-benzyl-5,5′-di-C-benzylellagic acid has the constitution XI. It follows that the structure of the yellow compound is VI.



Infrared Spectrum.—The yellow compound shows four bands in the 5.2 to 6.2 μ region: 5.68, 5.81, 6.03 and 6.11 μ with approximate peak absorbances of 0.45, 0.70, 0.38 and 0.31, respectively. With respect to carbonyl groups, structure III contains one lactone and one quinoidal carbonyl while structure VI contains two lactone and one dienone groups. Assignment of the 6.03 μ band presents no difficulty on the basis of either structure as arising from the quinoidal or dienone carbonyl group,[8] but the 5.68 and 5.81 μ bands indicate the presence of two lactone groups rather than one. For ellagorubin and ellagic acid derivatives, only a single lactone carbonyl stretching band is observed[6b] although each contains two lactone rings. However, the molecular structures of these compounds have a center of symmetry so that the

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

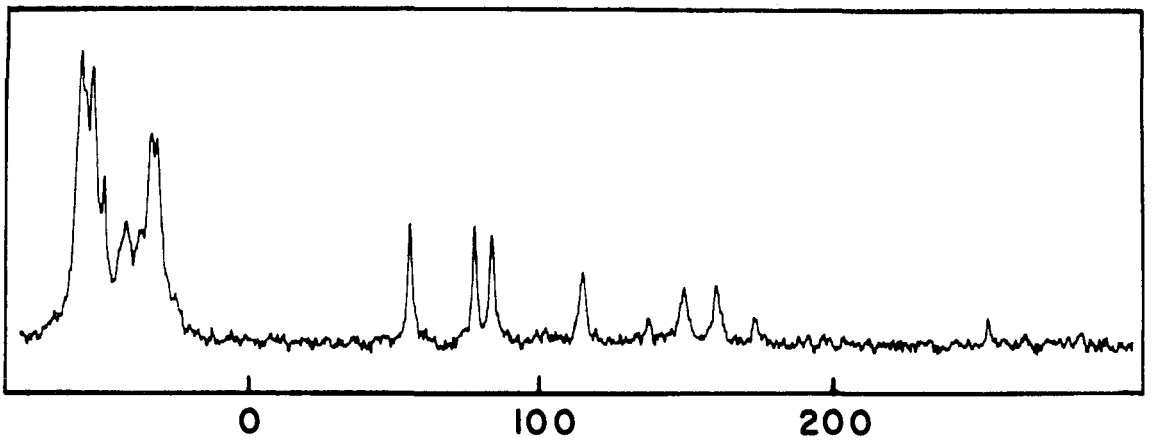


Fig. 3.—N.m.r. spectrum at 60 megacycles/sec. of yellow intermediate formed when ellagic acid is benzylated. Magnetic field increases from left to right. Scale indicates shift in cycles/sec. from benzene.

two lactone carbonyl groups have the same intramolecular environment and their equivalence is apparently retained in the crystalline state. The non-equivalence of the two lactone carbonyls of structure VI thus accounts for the 5.68 and 5.81 μ bands. The most closely related compounds earlier examined[6b] showed lactone carbonyl bands at 5.71 μ for O-tetrabenzylellagic acid and 5.77 μ for O-tetrabenzyl-5,5′-di-C-benzylellagic acid. It is concluded that the infrared spectrum of the yellow compound formed on alkaline benzylation of ellagorubin is compatible with structure VI, but not with structure III.

N.m.r. Spectrum.—The n.m.r. spectra obtained for certain ellagic acid and ellagorubin derivatives[6b] contain certain features which make the distinction between structures III and VI, the two structures proposed for the yellow product formed on benzylation of ellagic acid, rather straightforward. The reproduction of the spectrum, shown in Fig. 3, has the magnetic field increasing from left to right; the numbers at the bottom of the figure give the shift in cycles per second (c.p.s.) from pure benzene.

The n.m.r. spectrum of the yellow compound consists of a series of peaks centered at a shift of −46 c.p.s., due to the hydrogens on the phenyl groups, three sharp peaks at shifts of 55, 77 and 83 c.p.s., a single peak shifted 114 c.p.s. and a group of four peaks at 137, 149, 160 and 173 c.p.s. In addition to the absorption in the region of −46 c.p.s., due to the hydrogens on the benzene rings, a compound with structure III should have six absorption lines. Since eight lines are observed, structure III is incompatible with the n.m.r. spectrum of the yellow compound. Additional evidence in support of this conclusion is the fact that if one ignores the two small peaks at shifts of 137 and 173 c.p.s., in order to obtain six peaks, it is evident that the remaining six consist of three narrow and three relatively broad peaks. In part VIII of this series[6b] it has been shown that for compounds of the type under discussion narrow peaks arise from benzyl ether linkages whereas relatively broad peaks arise when the benzyl groups are bonded directly to the heterocyclic framework. Consequently, a compound with structure III would exhibit four narrow and two relatively broad peaks, rather than three of each.

Upon comparison of the n.m.r. spectrum of the yellow compound with the spectra obtained from the ellagic acid and ellagorubin derivatives,[6b] it is evident both from the shape and position of the absorption lines that the peaks occurring at 55 and 83 c.p.s. arise from benzyl ether groups on a benzene ring and the relatively broad line at 114 c.p.s. is due to the methylene hydrogens of a benzyl group bonded to a benzene ring. These three groups occur in both structure III and structure VI.

This leaves the narrow line at 77 c.p.s. and the symmetrical quartet of lines between 137 and 172 c.p.s. to be accounted for. Structure VI does this very nicely. The line at 77 c.p.s. has the shape and position expected for a benzyl ether group attached to a double bonded carbon atom, and accordingly can be assigned to the benzyl group at the 3-position of the dienone ring. The quartet of lines is similar to that found for ellagorubin when dissolved in pyridine and is now recognized as being characteristic for two magnetically non-equivalent hydrogens bonded to the same carbon atom. It has been suggested that the non-equivalence of the methylene hydrogens arises from the fact that various rotational conformations can have unequal residence times even though the potential energy barrier is not high enough to prevent rapid internal rotation of the groups relative to one another.[9] In molecules of the type CH_2R–CXYZ it is even possible for the CH_2 protons to be non-equivalent with equal residence times in the rotational conformations if the chemical shifts of these protons are different functions of the angular orientations. Since the methylene groups of the two benzyl side chains are equivalent, only one set of four lines is observed.

From the separation of this set of four peaks the spin–spin coupling, J, and the relative chemical shift, δ_{rel}, for the two non-equivalent hydrogens can be calculated. These values are J = 12 c.p.s. and δ_{rel} = 20 c.p.s. at 60 megacycles found for ellagorubin dissolved in pyridine.[6b] The spin–

(9) P. M. Nair and J. D. Roberts, THIS JOURNAL, **79**, 4565 (1957).

spin coupling of 12–14 c.p.s. also agrees closely with that recently found for two non-equivalent methylene hydrogens in certain steroids.[10]

The group assignments of the n.m.r. lines from the yellow compound are summarized in Table I. It is evident from the above discussion of the n.m.r. data that the latter are in complete accord with the conclusion that the structure of the yellow compound formed when ellagic acid is benzylated is VI and not III.

Experimental

Acid Hydrolysis of the Yellow Compound.—A solution of the yellow compound (60 mg.) in glacial acetic acid (2.0 ml.) was cooled and treated with 4 drops of concentrated sulfuric acid. After standing for 20 minutes a considerable quantity of colorless crystalline material had separated. Excess of water was added, the solid was collected and recrystallized from acetone–methanol. 3,3′,4-Tri-O-benzyl-5,5′-di-C-benzylellagic acid separated in colorless needles, m.p. 249°, which did not give a ferric chloride reaction.

Anal. Calcd. for $C_{49}H_{38}O_8$: C, 78.15; H, 4.82. Found: C, 78.2; H, 4.99.

The infrared spectrum was obtained on the solid material in the form of a KBr pressed disk using a Beckman IR-3 spectrophotometer[11] with NaCl optics.

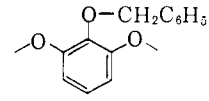
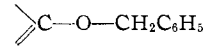
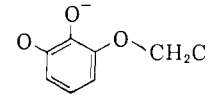
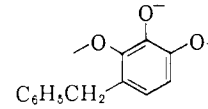
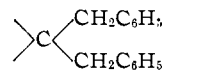
The high resolution n.m.r. spectrum was obtained at Varian Associates with their 60 megacycle spectrometer.[11]

(10) J. N. Shoolery and M. T. Rogers, THIS JOURNAL, **81**, in press (1959).

(11) 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.

TABLE I

PROTON RESONANCE SHIFT AT 60 MEGACYCLES PER SECOND IN YELLOW COMPOUND FOR METHYLENE HYDROGENS

Group	Shift, c.p.s. from benzene
	55
	77
	83
	114
	137, 149, 160, 172

The yellow compound was dissolved in deuterated chloroform to a concentration of about 0.2 *M*. The experimental procedure was the same as that described in part VIII.

Acknowledgment.—We wish to thank Edith Gong for obtaining the infrared spectral data, Mr. L. F. Johnson for obtaining the n.m.r. spectrum, and L. M. White for the elementary analyses.

PASADENA, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Composition of Pyrodextrins. II. Thermal Polymerization of Levoglucosan[1]

BY M. L. WOLFROM, A. THOMPSON[2] AND R. B. WARD[2]

RECEIVED FEBRUARY 27, 1959

A fragmentation study of a polymer made by heating 1,6-anhydro-β-D-glucopyranose reveals that this anhydro moiety is capable of polymerizing when heated to produce the usual glucosidic linkages found in a pyrodextrin. Thus, in the dextrination of starch at high temperatures, the reaction may be a depolymerization destroying an α-D-(1 → 4)-linkage and forming a terminal anhydro group, followed by repolymerization to produce other glucosidic linkages.

It has been shown,[3] by isolative procedures, that during the production of pyrodextrins by roasting starch, without added acid catalyst, the normal α-D-(1 → 4)-linkages tend to disappear and α- and β-D-(1 → 6)-, and smaller quantities of β-D-(1 → 2)-linkages, are formed together with some 1,6-anhydro-β-D-glucopyranose end groups. This is in general agreement with the findings of other workers[4] employing other methods on pyrodextrins formed under acid catalysis. The fact that the reaction proceeds very rapidly at 200° and in the substantial absence of water or acid indicates that hydrolysis and reversion may not be significant factors under these conditions. It has been postulated that the initial step in the pyrolysis of cellulose,[5] is chain rupture with the formation of a 1,6-anhydro end group. Since an end product of the pyrolysis of starch and cellulose is 1,6-anhydro-β-D-glucopyranose, it is logical to assume such an intermediate step. The isolation of 1,6-anhydro-β-D-glucopyranose[3] from the hydrolyzate of a pyrodextrin formed at high temperature also lends support to this conception. We suggest that such an anhydro end group may also act as an intermediate in reforming the polymer and in producing other linkages in the molecule. The primary hydroxyl on carbon six of a nearby D-glucose unit may be the preferred point of reaction.

Pictet[6] obtained a polymer by heating 1,6-anhydro-β-D-glucopyranose at a temperature of 235–240°. We wish to report herein a fragmentation study of this polymer in which gentiobiose, isomaltose, maltose, cellobiose, sophorose and 1,6-anhydro-β-D-glucopyranose were isolated and

(1) Presented before the Chemistry Section of the Ohio Academy of Science at the Columbus, Ohio, Meeting, April 17–18, 1959.

(2) Research Associate (A. T.) and Postdoctoral Fellow (R. B. W.) of the Corn Industries Research Foundation.

(3) A. Thompson and M. L. Wolfrom, THIS JOURNAL, **80**, 6618 (1958).

(4) G. M. Christensen and F. Smith, *ibid.*, **79**, 4492 (1957); J. D. Geerdes, Bertha A. Lewis and F. Smith, *ibid.*, **79**, 4209 (1957); Bernadine Brinhall, *Ind. Eng. Chem.*, **36**, 72 (1944).

(5) W. A. Parks, R. M. Esteve, Jr., M. H. Gollis, R. Guercia and A. Petrarca, *Abstracts Papers Am. Chem. Soc.*, **127**, 6E (1955).

(6) A. Pictet, *Helv. Chim. Acta*, **1**, 226 (1918).