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Chemical Studies on the Heartwood of *Cassia garrettiana* CRAIB. II.[1] Nonanthraquinonic Constituents

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Nonanthraquinonic constituents isolated from the heartwood of *Cassia garrettiana* CRAIB. (Leguminosae) together with several anthraquinones were shown to be betulic acid, rhamnocitrin, rhamnetin, protocatechuic aldehyde, quercetin, 3,3′-dihydroxybibenzyl, 3,3′,4-trihydroxybibenzyl, 3,3′,4,5′-tetrahydroxybibenzyl, 3,3′,4,5′-tetrahydroxystilbene, and 2,3,5,7-tetrahydroxy-9,10-dihydrophenanthrene (which was isolated and identified as tetraacetate).

Keywords——*Cassia garrettiana* CRAIB.; rhamnocitrin; rhamnetin; protocatechuic aldehyde, quercetin; 3,3′-dihydroxybibenzyl; 3,3′,4-trihydroxybibenzyl; 3,3′,4,5′-tetrahydroxybibenzyl; 3,3′,4,5′-tetrahydroxystilbene; 2,3,5,7-tetrahydroxy-9,10-dihydrophenanthrene

In the previous paper[1] it has been reported that the heartwood of *Cassia garrettiana* CRAIB. (Leguminosae), one of the Thei drugs "Sa mae sarn", afforded five anthraquinones together with ten kinds of nonanthraquinonic constituents, and that the anthraquinones, tentatively named compound I—III, XIV, and XV were shown to be chrysophanol, chrysophanol benzanthrone with the structure of 4-methyl-6,8-dihydroxy-7*H*-benz[*de*]anthracene-7-one, chrysophanol dianthrone, a new anthrone C-glycoside named cassialoin whose structure was established as 10-hydroxy-10-D-glucosylchrysophanol-9-anthrone, and (−)-11-deoxyaloin, respectively. This paper is concerned with the identification and the structure elucidation of the nonanthraquinonic constituents, tentatively named compound IV—XIII.

Out of these compounds, IV, VI, VII, IX, and X were identified as betulic acid, rhamnocitrin, rhamnetin, protocatechuic aldehyde, and quercetin, respectively, on the basis of the physical and chemical properties and of the spectral evidence described in the experimental.

Compound V, mp 138—140°, colorless needles, whose analytical data are consistent with the molecular formula $C_{14}H_{14}O_2$, gives a blue coloration with Gibbs′ reagent. The infrared (IR) spectrum of V shows the presence of hydroxyl group and aromatic ring, and gives no absorption band corresponding to carbonyl group.

The proton magnetic resonance (PMR) spectrum of V exhibits the signals due to two benzylic methylene goups (δ 2.73), eight aromatic protons (δ 6.52—7.03), and two hydroxyl groups (δ 9.15). In the aromatic region of this spectrum two protons are observed as a triplet (δ 7.03, J=8.5 Hz) and the remainders appear as a broad signal (δ 6.5—6.6) with three splits. The shape of these signals is very similar to that reported for *m*-cresol.[3] On the basis of this spectral evidence and the analytical data, V is suggested to be 3,3′-dihydroxybibenzyl, and this was confirmed by comparing V with an authentic sample of 3,3′-dihydroxybibenzyl prepared by applying the procedure appearing in the literature.[4]

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[1] Part I: K. Hata, K. Baba, and M. Kozawa, *Chem. Pharm. Bull.* (Tokyo), **26**, 3792 (1978).
[2] Location: *Kawai 2-Chome, Matsubara, Osaka.*
[3] C.J. Pouchert and J.R. Campbell (eds.), "The Aldrich Library of NMR Spectra," Vol. 4, Aldrich Chemical Company, Inc., Milwaukee, 1974, p. 112.
[4] R.M. Letcher, L.R.M. Nhamo, and I.T. Gumiro, *J. Chem. Soc. Perkin I*, **1972**, 206.

Compound VIII, mp 120—121°, colorless needles, whose analytical data are in agreement with the molecular formula $C_{14}H_{14}O_3$, gives a purple coloration with Gibbs' reagent. The IR spectrum of VIII shows the presence of hydroxyl group and aromatic ring. The PMR spectrum is fairly similar to that of V except that in the aromatic region one proton appears as a triplet at δ 7.03, and that signals due to three hydroxyl groups are observed as two singlets. On the basis of this spectral evidence and the analytical data, VIII was shown to be trihydroxybibenzyl. Although the positions of the hydroxyl groups can not be deduced clearly from the PMR data, VIII can be presumed to be 3,3′,4- or 3,3′,5-trihydroxybibenzyl from the fact that V, as mentioned above, was established as 3,3′-dihydroxybibenzyl, and that XI, as described subsequently, was proved to be 3,3′,4,5′-tetrahydroxybibenzyl. In order to confirm this presumption, synthesis of the former was initially undertaken and the resulting product was proved to be identical with VIII. Thus, VIII was established as 3,3′,4-trihydroxybibenzyl.

Compound XI, mp 161—162°, off-white needles, whose analytical data are in accord with the molecular formula $C_{14}H_{14}O_4$, gives a deep green coloration with dilute aqueous sodium hydroxide solution. The PMR spectrum of XI shows the signals due to two benzylic methylene groups (δ 2.60), four hydroxyl groups (δ 8.60 and 8.90), and six aromatic protons (δ 6.03—6.58). The signals in the aromatic region, whose detailed data are shown in the experimental, are indicative of the presence of 1,3,5- and 1,3,4-trisubstituted benzene rings. This spectral data together with the analytical data indicate that XI can be assigned to 3,3′,4,5′-tetrahydroxybibenzyl, and this was confirmed by comparing XI with an authentic sample of 3,3′,4,5′-tetrahydroxybibenzyl prepared by hydrogenation of compound XII which was proved as 3,3′,4,5′-tetrahydroxystilbene as described subsequently.

Compound XII, mp 231—232°, pale red needles, was assigned the molecular formula $C_{14}H_{12}O_4$ from the fact that it gave tetraacetate with the molecular formula $C_{22}H_{20}O_8$ which was confirmed on the basis of the analytical, mass and PMR spectral data. XII exhibits blue-violet fluorescence under ultraviolet (UV) light and gives a gray-blue coloration with Gibbs′ reagent, which rapidly fads to brown. The UV spectrum of XII shows absorption maxima at 215 and 325 nm. The PMR spectrum of XII, whose detailed data are shown in the experimental, shows the signals due to eight protons in the aromatic region (δ 6.10—6.95) as well as four hydroxyl groups (δ 9.06), and shows the absence of benzylic methylene group. On the basis of this PMR data and the fact that XII is fluorescent under UV light, XII is suggested to be 3,3′,4,5′-tetrahydroxystilbene. Chemical confirmation for this supposition was found in the observation that oxidation of permethylated XII with potassium permanganate led to the formation of 3,4- and 3,5-dimethoxybenzoic acid which were isolated and identified as their methyl ester.

Compound XIII was isolated as an acetate, because it could be hardly freed from contamination with XII for all means of purification by column chromatography. XIII-acetate, mp 188—188.5°, colorless needles, was assigned the molecular formula $C_{22}H_{20}O_8$ on the basis of the analytical and mass spectral data. It gives a deep green coloration with dilute aqueous sodium hydroxide solution. The PMR spectrum of the acetate shows the signals due to four O-acetyl groups (δ 2.29), two benzylic methylene groups (δ 2.79) and four aromatic protons appearing as a pair of doublets (δ 6.87 and 6.95, J=*ca.* 2 Hz) and two singlets (δ 7.08 and 7.81). This PMR data together with the molecular formula indicate that XIII-acetate is 2,3,5,7-tetraacetoxy-9,10-dihydrophenanthrene, which has been previously reported to be formed by intra-molecular oxidative coupling of 3,3′,4,5′-tetrahydroxybibenzyl, prepared synthetically, with ferric chloride followed by reductive acetylation.[5] However, the melting point of this synthetic product has been reported to be 200—201°, being about 10° higher than that of XIII-acetate.

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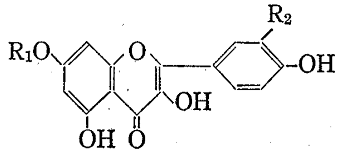
[5] H. Erdtman and A. Ronlan, *Acta Chem. Scand.*, 23, 249 (1969).

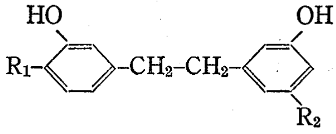
Therefore, in order to confirm the identity of XIII-acetate, synthesis of 2,3,5,7-tetraacetoxy-9,10-dihydrophenanthrene was undertaken by employing the same procedure as that reported, and the resulting product, mp 189—190°, was proved to be identical with XIII-acetate. Accordingly, the discrepancy observed between the melting points of both compounds might be considered to have arised from the conditions of measurement. The PMR spectrum of crude XIII shows the absence of any peaks due to acetyl group, excluding the possibility that XIII might occur naturally as an acetyl derivative. Thus, XIII was identified as 2,3,5,7-tetrahydroxy-9,10-dihydrophenanthrene. An attempt to obtain XIII in the pure state from XIII-acetate was unsuccessful, because of the insufficiency of the material.

It has been also known that 3,3′,4,5′-tetrahydroxybibenzyl dissolves in aqueous alkali resulting in a deep green solution which on acidification gives XIII together with an amorphos polymer as well as the starting material.[5] In the present studies, as mentioned above, XI was observed to give a deep green solution with aqueous alkali, while V and VIII were found to give a yellow solution with aqueous alkali, from which on acidification only the starting materials were recovered.

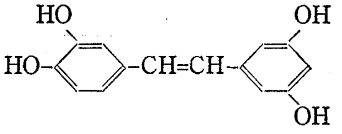
The compounds V, VIII, XI, and XIII do not seem to have been previously encountered as the natural products, although following bibenzyls (BB) and 9,10-dihydrophenanthrenes (DHP) have been found to occur naturally: 3,5-dihydroxy-BB, 3-hydroxy-5-methoxy-BB (the heartwood of *Pinus* spp.)[6]; 2-hydroxy-3,4-dimethoxy-BB named pellepiphyllin (*Pellia epiphylla* CORDA, a species of liverwort)[7]; 2,4-dimethoxy-7-hydroxy-DHP named orchinol (Orchidaceous plants infected with a species of mold)[8]; 3,4′-dihydroxy-4,5-dimethoxy-BB, 2,5-dihydroxy-3,7-dimethoxy-DHP, 4,6,7-trihydroxy-2,3-dimethoxy-DHP, 2,6-dihydroxy-3,4,7-trimethoxy-DHP (the heartwood of *Combretum* spp.)[4]



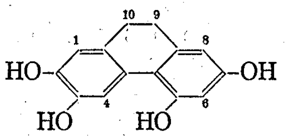
VI: $R_1=CH_3$, $R_2=H$
VII: $R_1=CH_3$, $R_2=OH$
X: $R_1=H$, $R_2=OH$



V: $R_1=R_2=H$
VIII: $R_1=OH$, $R_2=H$
XI: $R_1=R_2=OH$



XII



XIII

Fig. 1

Experimental

Betulic Acid (IV)——Recrystallized from MeOH to colorless needles, mp 317—318°, $[\alpha]_D^{18}$ +8° (c=1.0, pyridine) [lit. mp 320°, $[\alpha]_D$ +12°].[9] Mass Spectrum m/e: 456 [M^+]. It gives a red-violet coloration with

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[6] G. Lindstedt and A. Misiorny, *Acta Chem. Scand.*, **5**, 121; 129 (1951) [*C.A.*, **45**, 8011*h*; 8012*d* (1951)]; M. Sogo and K. Hata, *Tech. Bull. Kagawa Agr. Coll.* (Japan), **5**, 15 (1953—1954) [*C.A.*, **48**, 12922*b* (1954)].

[7] B. Vera and H. Vlastimil, *Collect. Czech. Chem. Commun.*, **35**, 1926 (1970) [*C.A.*, **73**, 5574*j* (1970)].

[8] E. Hardegger, H.R. Biland, and H. Corrodi, *Helv. Chim. Acta*, **46**, 1354 (1963).

[9] T.K. Devon and A.I. Scott, "Handbook of Naturally Occurring Compounds," Vol. II, Academic Press, New York and London, 1972, p. 310.

Ac_2O and H_2SO_4. The IR and PMR[10] spectra are identical with those reported for betulic acid.[11] Yield 0.04%.

3,3′-Dihydroxybibenzyl (V)——Recrystallized from hexane-EtOAc to colorless needles, mp 138—140°. It gives a blue coloration with Gibbs' reagent and ammonia aq. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3300 (OH), 1610, 1590 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 2.73 (4H, singlet, $PhC\underline{H}_2C\underline{H}_2Ph$), 6.52—6.62 (6H, broad signal with three splits, aromatic H×6), 7.03 (2H, triplet, $J=8.5$ Hz, aromatic H×2), 9.15 (2H, singlet, $O\underline{H}\times 2$). *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.41; H, 6.81. The melting point showed no depression on admixture with an authentic sample of 3,3′-dihydroxybibenzyl prepared by synthesis. The IR and PMR spectra are superimposable to those of the authentic sample. Yield 0.004%.

Synthesis of V——1) Formation of α-(3-Hydroxyphenyl)-3-hydroxycinnamic Acid (Vi-1): A mixture of 3-hydroxyphenylacetic acid (1.5 g), 3-hydroxybenzaldehyde (1.5 g), triethylamine (5 ml) and Ac_2O (10 ml) was refluxed for 5 hr under a stream of nitrogen. The reaction mixture was evaporated under reduced pressure, and the residue was stirred with 10% NH_4OH (80 ml) for several min. After the mixture had been allowed to stand overnight, it was extracted with $CHCl_3$, and the aqueous layer was acidified with dil-HCl and extracted with EtOAc. The EtOAc layer was washed with water, dried and evaporated to dryness. The residue (2.5 g) was purified by column chromatography on silica gel using hexane–EtOAc (1:1) as the eluent, and recrystallized from hexane–EtOAc to give colorless crystalline powder, mp 210—213°, yield 1.7 g. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3350, 3000—2500 (OH), 1670 (COOH), 1600, 1580 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 6.5—7.4 (8H, multiplet, aromatic H×8), 7.66 (1H, singlet, $C{=}C\underline{H}$), 9.5 (3H, broad singlet, $O\underline{H}\times 3$).

2) Decarboxylation of Vi-1 to 3,3′-Dihydroxystilbene (Vi-2): A mixture of Vi-1 (500 mg), copper chromite (300 mg) and quinoline (10 ml) was refluxed for half an hour under a stream of nitrogen. The reaction mixture was poured into 10% HCl (50 ml) and was extracted with EtOAc. The EtOAc layer was washed with water, dried and evaporated to dryness. The residue was purified by column chromatography on silica gel using hexane–EtOAc (5:1) as the eluent, and recrystallized from hexane to give colorless needles, mp 111—112°, yield 300 mg. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3400—3100 (OH), 1610, 1580 (aromatic ring). PMR (in acetone-d_6) δ_{ppm}: 6.55 (2H, singlet, $C\underline{H}{=}C\underline{H}$), 6.65—6.90 (6H, multiplet, aromatic H×6), 7.10 (2H, triplet, $J=8.5$ Hz, aromatic H×2), 8.30 (2H, broad singlet, $O\underline{H}\times 2$).

3) Hydrogenation of Vi-2 to V: To a solution of Vi-2 (200 mg) in EtOH (30 ml) was added palladium catalyst (PdO 20 mg) and the mixture was stirred in the presence of hydrogen until consumption of hydrogen was interrupted. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was recrystallized from hexane–EtOAc to give colorless needles, mp 139—140°, yield 180 mg. The spectral data are identical with those of V.

Rhamnocitrin (VI)——Recrystallized from hexane–EtOAc to yellow crystalline powder, mp 218—219° [lit. mp 222°].[12a] It is positive towards Mg–HCl reaction. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3250 (OH), 1660 (C=O), 1610, 1590 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 3.87 (3H, singlet, $OC\underline{H}_3$), 6.33, 6.70 (1H each, doublet, $J=$ *ca.* 2 Hz, aromatic H×2), 6.96, 8.10 (2H each, doublet, $J=8.5$ Hz, aromatic H×4), 9.47, 10.03, 12.48 (1H each, singlet, $O\underline{H}\times 3$). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 265 (4.17), 368 (4.27), UV $\lambda_{\max}^{\mathrm{EtOH(AlCl_3)}}$ nm: 266, 427.5, UV $\lambda_{\max}^{\mathrm{EtOH(NaOAc)}}$ nm: 265, 376, UV $\lambda_{\max}^{\mathrm{EtOH(NaOEt)}}$ nm: 422. Yield 0.003%.

Rhamnetin (VII)——Recrystallized from hexane–EtOAc to yellow crystalline powder, mp 290° [lit. mp 295°].[12b] It is positive towards Mg–HCl reaction. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3500—3300 (OH), 1680 (C=O), 1630, 1600 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 3.87 (3H, singlet, $OC\underline{H}_3$), 6.32, 6.63 (1H each, doublet, $J=$ *ca.* 2 Hz, aromatic H×2), 6.93 (1H, doublet, $J=8.5$ Hz, aromatic H), 7.62 (1H, doublet×doubelt, $J=8.5\times$ *ca.* 2 Hz, aromatic H), 7.73 (1H, doublet, $J=$ *ca.* 2 Hz, aromatic H), 9.43 (3H, broad singlet, $O\underline{H}\times 3$), 12.55 (1H, singlet, $O\underline{H}$). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 257 (4.38), 374 (4.39), UV $\lambda_{\max}^{\mathrm{EtOH(AlCl_3)}}$ nm: 270, 437, UV $\lambda_{\max}^{\mathrm{EtOH(NaOAc)}}$ nm: 257, 377, UV $\lambda_{\max}^{\mathrm{EtOH(NaOEt)}}$ nm: 421.5. Yield 0.01%.

3,3′,4-Trihydroxybibenzyl (VIII)——Recrystallized from hexane–EtOAc to off-white needles, mp 120—121°. It gives a purple coloration with Gibbs' reagent and ammonia aq. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3490, 3300 (OH), 1620, 1600 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 2.67 (4H, singlet, $PhC\underline{H}_2C\underline{H}_2Ph$), 6.36—6.66 (6H, multiplet, aromatic H×6), 7.03 (1H, triplet, $J=8.5$ Hz, aromatic H), 8.60 (2H, broad singlet, $O\underline{H}\times 2$), 9.16 (1H, singlet, $O\underline{H}$). *Anal.* Calcd. for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 72.99; H, 5.94. The melting point showed no depression on admixture with an authentic sample of 3,3′,4-trihydroxybibenzyl prepared by synthesis. The IR and PMR spectra are superimposable to those of the authentic sample. Yield 0.005%.

Synthesis of VIII——1) Formation of α-(3,4-Dihydroxyphenyl)-3-hydroxycinnamic Acid (VIIIi-1): A mixture of 3-hydroxybenzaldehyde (1 g), 3,4-dihydroxyphenylacetic acid (1 g), Ac_2O (5 ml) and triethylamine

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10) The PMR spectra were measured by means of Hitachi R40 Spectrometer using TMS as the internal standard.

11) C.J. Pouchert(ed.), "The Aldrich Library of Infrared Spectra," 2nd Ed., Aldrich Chemical Co., Inc., Milwaukee, 1975, p. 1282; C.J. Pouchert and J.R. Campbell(eds.), "The Aldrich Library of NMR Spectra," Vol. 10, Aldrich Chemical Co., Inc., Milwaukee, 1974, p. 108.

12) *a)* T.K. Devon and A.I. Scott, "Handbook of Naturally Occurring Compounds," Vol. I, Academic Press Inc., New York and London, 1975, p. 130; *b) Idem, ibid.*, p. 143.

(3 ml) was refluxed for 5 hr under a stream of nitrogen, and the reaction mixture was treated by use of a similar procedure to that employed in preparing Vi-1. The crude product (*ca.* 1 g) was purified by column chromatography on silica gel using hexane–EtOAc (1: 1) as the eluent, and recrystallized from hexane-EtOAc to give off-white crystalline powder, mp 225° (dec.), yield 300 mg. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3350, 3000—2500 (OH), 1670 (COOH), 1610, 1585 (aromatic ring). PMR (in acetone-d_6) δ_{ppm}: 6.35—6.70 (6H, multiplet, aromatic H×6), 7.03 (1H, triplet, J=8.5 Hz, aromatic H), 7.53 (1H, singlet, C=C$\underline{\text{H}}$), 9.35 (4H, broad singlet, O$\underline{\text{H}}$×4).

2) Decarboxylation of VIIIi-1 to 3,3′,4-Trihydroxystilbene (VIIIi-2): A mixture of VIIIi-1 (250 mg), copper chromite (100 mg) and quinoline (5 ml) was refluxed for 40 min under a stream of nitrogen, and the reaction mixture was treated by use of a similar procedure to that employed in preparing Vi-2. The crude product was purified by column chromatography on silica gel using hexane–EtOAc (2: 1) as the eluent, and recrystallized from hexane–EtOAc to give colorless crystalline powder, mp 172—173°. It exhibits an intense blue-violet fluorescence under filtered UV light. Yield 150 mg. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3350—3100 (OH), 1610, 1590 (aromatic ring). PMR (in acetone-d_6) δ_{ppm}: 6.55—7.10 (9H, multiplet, aromatic H×7 and C$\underline{\text{H}}$=C$\underline{\text{H}}$), 7.90 (3H, broad singlet, O$\underline{\text{H}}$×3).

3) Hydrogenation of VIIIi-2 to VIII: To a solution of VIIIi-2 (120 mg) in EtOH (30 ml) was added palladium catalyst (PdO 10 mg) and the mixture was stirred in the presence of hydrogen until consumption of hydrogen was interrupted. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was recrystallized from hexane–EtOAc to give off-white needles, mp 120—121°, yield 100 mg. The spectral data are identical with those of VIII.

Protocatechuic Aldehyde (IX)——Recrystallized from hexane EtOAc to pale yellow needles, mp 151—153° (dec.). It is positive towards 2,4-dinitrophenylhydrazine test solution, and gives a yellow-green coloration with Gibbs' reagent and ammonia aq. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3240 (OH), 1680 (C=O), 1600 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 6.93 (1H, doublet, J=8.5 Hz, aromatic H), 7.29 (1H, doublet×doublet, J=8.5×*ca.* 2 Hz, aromatic H), 7.35 (1H, doublet, J=*ca.* 2 Hz, aromatic H), 9.70 (1H, singlet, C$\underline{\text{H}}$O), 9.53, 10.10 (1H each, broad singlet, O$\underline{\text{H}}$×2). The IR and PMR spectra are superimposable to those of an authentic sample of protocatechuic aldehyde. Yield 0.03%.

Quercetin (X)——Recrystallized from hexane–EtOAc to yellow crystalline powder, mp *ca.* 312° (dec.). It is positive towards Mg–HCl reaction. The melting point of the pentaacetate (mp 194°) shows no depression on admixture with an authentic sample of quercetin pentaacetate (mp 194°). The spectral data of X and X-pentaacetate are identical with those of authentic samples of quercetin and its pentaacetate, respectively. Yield 0.02%.

3,3′,4,5′-Tetrahydroxybibenzyl (XI)——Recrystallized from hexane–EtOAc to off-white crystalline powder, mp 161—162°. It dissolves in 5% NaOH aq. with a deep green coloration. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3300 (OH), 1620, 1600 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 2.60 (4H, singlet, PhC$\underline{\text{H}}_2$C$\underline{\text{H}}_2$Ph), 6.03 (3H, broad singlet, aromatic H×3), 6.43 (1H, doublet×doublet, J=8.5×*ca.* 2 Hz, aromatic H), 6.55 (1H, doublet, J=*ca.* 2 Hz, aromatic H), 6.58 (1H, doublet, J=8.5 Hz, aromatic H), 8.60, 8.90 (2H each, broad singlet, O$\underline{\text{H}}$×4). *Anal.* Calcd. for $C_{14}H_{14}O_4$: C, 68.28 H, 5.73. Found: C, 68.17 H, 5.77. The melting point showed no depression on admixture with an authentic sample of 3,3′,4,5′-tetrahydroxybibenzyl prepared by hydrogenation of 3,3′,4,5′-tetrahydroxystilbene (XII). The spectral data are identical with those of the authentic sample. Yield 0.035%.

3,3′,4,5′-Tetrahydroxystilbene (XII)——Recrystallized from hexane–EtOAc to pale red needles, mp 231—232°. It gives a gray-blue coloration with Gibbs' reagent and ammonia aq., which turns rapidly to brown, and it exhibits blue-violet fluorescence under filtered UV light. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 215, 325. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3300 (OH), 1600, 1510 (aromatic ring). PMR (in DMSO-d_6) δ_{ppm}: 6.10 (1H, doublet, J=*ca.* 2 Hz, aromatic H), 6.37 (2H, doublet, J=*ca.* 2 Hz, aromatic H×2), 6.64 (1H, doublet, J=8.5 Hz, aromatic H), 6.70, 6.83 (1H each, doublet, J=16 Hz, C$\underline{\text{H}}$=C$\underline{\text{H}}$), 6.87 (1H, doublet×doublet, J=8.5×*ca.* 2 Hz, aromatic H), 6.95 (1H, broad singlet, aromatic H), 9.06 (4H, broad singlet, O$\underline{\text{H}}$×4). Yield 1.30%.

XII-Tetraacetate——A solution of XII (4.2 g) in a mixture of Ac_2O (25 ml) and pyridine (2 ml) was allowed to stand at room temperature overnight. After the reaction mixture had been treated in the usual way, the product was recrystallized from EtOH to give colorless needles, mp 124—125°, yield 3.5 g. PMR (in $CDCl_3$) δ_{ppm}: 2.30 (12H, singlet, OCOC$\underline{\text{H}}_3$×4), 6.80—7.40 (8H, aromatic H×6 and C$\underline{\text{H}}$=C$\underline{\text{H}}$). *Anal.* Calcd. for $C_{22}H_{20}O_8$ (tetraacetoxystilbene): C, 64.07; H, 4.89. Found: C, 64.08; H, 5.08. Mass Spectrum *m/e*: 412 [M$^+$].

Oxydation of XII-Tetramethyl Ether with $KMnO_4$——To a solution of XII (3 g) in a mixture of anhydrous acetone (200 ml) and Me_2SO_4 (5 g) was added K_2CO_3 (35 g) and the mixture was refluxed for 3 hr. The reaction mixture was filtered and the filtrate was poured into water (100 ml), evaporated under reduced pressure to remove the greater part of acetone and the residual liquor was made alkaline with 20% NaOH aq., stirred for half an hour and extracted with ether. The ethereal solution was washed with water, dried and evaporated to give pale brown oil (3 g). PMR (in $CDCl_3$) δ_{ppm}: 3.63 (6H, singlet, OC$\underline{\text{H}}_3$×2), 3.88, 3.93 (3H each, singlet, OC$\underline{\text{H}}_3$×2), 6.33—7.17 (8H, aromatic H×6 and C$\underline{\text{H}}$=C$\underline{\text{H}}$).

To a solution of the brown oil (XII-tetramethyl ether) (2.8 g) in acetone (50 ml) was added a solution of $KMnO_4$ (6.5 g) in 50% acetone (300 ml) dropwise with stirring. The reaction mixture was allowed to stand for 3 hr, and to this mixture was added Na_2SO_3 aq. to decompose an excess of $KMnO_4$. The mixture was filtered, evaporated under reduced pressure to remove the greater part of acetone, and the residual liquor was extracted with ether. The aqueous layer was acidified with 20% H_2SO_4 and extracted with ether, and the ethereal solution was washed with water, dried and evaporated to dryness. The residue was methylated with diazomethane in ethereal solution and the product was purified by column chromatography on silica gel using hexane–EtOAc (9: 1) as the eluent to give two products, tentatively named A and B. A: Colorless needles of mp 42—43°. The melting point showed no depression on admixture with an authentic sample of methyl 3,5-dimethoxybenzoate. The IR spectrum is identical with that of the authentic sample. Yield 300 mg. B: Colorless needles of mp 54—55°. The melting point showed no depression on admixture with an authentic sample of methyl 3,4-dimethoxybenzoate. The IR spectrum is identical with that of the authentic sample. Yield 500 mg.

Hydrogenation of XII to XI——To a solution of XII (500 mg) in EtOH (50 ml) was added palladium catalyst (PdO 50 mg) and the mixture was stirred in the presence of hydrogen until consumption of hydrogen was interrupted. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was recrystallized from benzene–HOAc (3: 1) to give off-white crystalline powder, mp 161—162°, yield 450 mg. *Anal.* Calcd. for $C_{14}H_{14}O_4$: C, 68.28: H, 5.73. Found: C, 68.55; H, 5.64. The melting point showed no depression on admixture with XI. The spectral data are identical with those of XI.

2,3,5,7-Tetraacetoxy-9,10-dihydrophenanthrene (XIII-Acetate)——The mother liquor which had been seperated from crude XII was evaporated to dryness and the residue (1.5 g) was acetylated with Ac_2O and NaOAc in the usual way. The product of viscid oil was crystallized on mixing up with ether, and was recrystallized from hexane–EtOAc to colorless needles, mp 188—188.5°. It dissolves in 5% NaOH aq. with a deep green coloration. IR ν_{max}^{Nujol} cm^{-1}: 1760 (C=O), 1610, 1580 (aromatic ring). PMR (in $CDCl_3$) δ_{ppm}: 2.29 (12H, singlet, $OCOC\underline{H}_3 \times 4$), 2.79 (4H, singlet, $PhC\underline{H}_2C\underline{H}_2Ph$), 6.87, 6.95 (1H each, doublet, $J=ca.$ 2 Hz, aromatic $H \times 2$), 7.08, 7.81 (1H each, singlet, aromatic $H \times 2$). *Anal.* Calcd. for $C_{22}H_{20}O_8$: C, 64.07; H, 4.89. Found: C, 64.32; H, 4.96. Mass Spectrum *m/e*: 412 [M^+]. Yield 0.02%. The melting point showed no depression on admixture with an authentic sample of 2,3,5,7-tetraacetoxy-9,10-dihydrophenanthrene prepared by synthesis. The spectral data are identical with those of the authentic sample.

Synthesis of XIII-Acetate——To a solution of XI (450 mg) in water (100 ml) was added 2.4% $FeCl_3$ aq. (23 ml) dropwise over about 3 min. The dark brown precipitate was collected by centrifugation, suspended in water (25 ml) and centrifuged again. This operation was repeated twice, and finally the precipitate was suspended in 2 N H_2SO_4 (20 ml) and centrifuged. The precipitate was heated with powdered zinc (5 g) in 60% HOAc (25 ml) for 50 min in a boiling water bath. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure to dryness. The residue was acetylated with Ac_2O and NaOAc in the usual way, and the product was purified by column chromatography on silica gel using hexane–EtOAc (1: 1) and recrystallized from hexane–EtOAc to give colorless crystalline powder, mp 189—190°, yield 230 mg. *Anal.* Calcd. for $C_{22}H_{20}O_8$: C, 64.07; H, 4.89. Found: C, 63.93; H, 4.79. The spectarl data are identical with those of XIII-acetate.

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