CHAPTER III

Experimental

Melting points are uncorrected. The petroleum ether used throughout the investigation had b.p. 60-80°. All optical rotations were determined in chloroform solution unless stated otherwise. NMR spectra were determined on HA-100 spectrometers, using chloroform-d solutions containing tetramethylsilane as reference. The IR spectra were recorded in Perkin-Elmer 337 and 221 spectrophotometer. UV absorption spectra were taken in Zeiss VSU-1 spectrophotometer. The mass spectra were determined with an MS-9 mass spectrometer, using direct sample introduction into the ion source.

Isolation of the neutral benzene soluble material

Dried and powdered stem bark of *Sapium baccatum* Roxb. (2 kg.) was extracted with benzene in a Soxhlet apparatus for twenty hours. on cooling the benzene extract a yellow insoluble solid precipitated out which was collected by filtration and was kept aside. From the clear filtrate benzene was distilled off and the residual gummy solid (30 gm.) was taken up in ether (2 lit.). A cloudy precipitate remained in the ether extract was separated out by filtration. The clear ether solution was washed with 10% sodium hydroxide solution (4 x 200 ml). The ether layer was washed with cold water till the washings were neutral, dried over anhydrous sodium sulphate and evaporated, when the neutral material (10.6 gm) was obtained as a yellow gummy solid.

Chromatography of the above gummy solid

The above gummy material (10.6 gm) dissolved in benzene (18 ml) was placed on a column of alumina (400 gm) deactivated with 16 ml of 10% aqueous acetic acid. The chromatogram was developed with petroleum ether and eluted with the following solvents (Table II).

Table II

Eluent	Fractions 50 ml each	Residue on evaporation (gm)	Melting point in $^{\circ}C$
Petroleum ether (100 ml)	1-2	Oil (1.2 gm)	-
Petroleum ether (350 ml)	3-6	Solid (2.45 gm)	230-6°
Petroleum ether:benzene (4:1) (150 ml)	10-12	Oil (0.5 gm)	-
Petroleum ether:benzene (3:2) (300 ml)	13-18	Solid with pet. (1.14 gm)	70-5°
Petroleum ether:benzene (3:2) (250 ml)	19-23	Solid (0.4 gm)	262-8°
Petroleum ether:benzene (1:1) (250 ml)	24-28	Solid (0.8 gm)	128-32°
Petroleum ether:benzene (2:3) (200 ml)	29-32	Oil (0.3 gm)	-
Petroleum ether:benzene (1:4) (200 ml)	33-36	Oil (0.4 gm)	-
Benzene (250 ml)	37-41	Oil (0.2 gm)	-
Benzene:ether (4:1) (200 ml)	42-45	Oil (0.3 gm)	-
" " (3:2) (300 ml)	46-51	Solid (0.3 gm)	210-15°

Further elution with more polar solvents did not afford any solid material

Examination of Fractions 3-6 (Table II) : Isolation of taraxerone

The solid fractions 3-6 (Table II) were combined (2.5 gm), m.p. 230-6° and was rechromatographed over a column of active alumina (100 gm). The solid dissolved in benzene (6 ml) was placed on the column. The chromatogram was developed in petroleum ether and was eluted with the following solvents (Table III).

Table III

Chromatography of the above material (2.45 gm)

Eluent	Fractions 50 ml each	Residue on evaporation	Melting point
Petroleum ether	1-4	Trace oil, soluble in petroleum ether	-
Petroleum ether: benzene (4:1) (400 ml)	5-12	Crystalline solid (2.02 gm)	235-7°

Further elution with more polar solvents did not afford any material

The fractions 5-12 (Table III) were combined (2.08 gm) and crystallised from a mixture of chloroform and methanol. After three crystallisations it afforded shining crystals (1.3 gm) m.p. 238-40° $(\alpha)_D$ + 10.8°. Its melting point was not depressed when mixed with an authentic sample of taraxerone. It also showed identical IR throughout the region when compared with that of an authentic specimen of taraxerone.

Found: C, 84.64; H, 11.02%

Calc. for $C_{30}H_{48}O$: C, 84.84, H, 11.39%

UV (95% ethanol) : λ_{max} 286 mμ, ϵ = 82.3

IR (KBr disc) : ν_{max} 1705 (carbonyl), 822 (trisubstituted double bond).

Color reaction tests

(a) Tetranitromethane displayed a yellow color.

(b) Liebermann-Burchardt: The compound developed a violet coloration with a mixture of acetic anhydride and conc. sulphuric acid.

(c) Zimmermann color test was positive.

Lithium aluminium hydride reduction of taraxerone 159 : Preparation of taraxerol 160

To the ketone (200 mg) dissolved in dry ether (25 ml) was added lithium aluminium hydride (25 mg) and the mixture was refluxed on the water bath for four hours. The reaction mixture was then cooled and to this 15 ml of moist ether was added followed by a saturated solution of sodium sulphate (15 ml). The mixture was extracted with ether, washed to neutral with water and dried (Na_2SO_4). Removal of the ether gave a solid mass (190 mg) which was chromatographed over alumina. A column of alumina (10 gm. deactivated with 0.4 ml of 10% aqueous acetic acid) was developed with petroleum ether and the above residue dissolved in benzene (4 ml) was added to it. The following solvents were used for elution (Table IV).

Table IV

Eluent	Fractions 50 ml each	Residue
Petroleum ether	1-2	Nil
Petroleum ether: benzene (4:1)	3-4	Nil
Petroleum ether: benzene (3:2)	5-10	Crystalline solid 180 mg m.p. 268-70°

Further elution with more polar solvents did not yield any material

Fractions 5-10 (Table IV) were combined and the solid (180 mg) was crystallised from chloroform and methanol mixture when a solid of constant m.p. 271-3°, $(\alpha)_D$ + 3.7° was obtained. Its melting point was not depressed when mixed with an authentic specimen of taraxerol.

Found: C, 84.14; H, 11.39%

Calc. for $C_{30}H_{50}O$: C, 84.50; H, 11.73%.

Preparation of 2,4-Dinitrophenylhydrazone derivative of taraxerone

2,4-Dinitrophenylhydrazine (300 mg) dissolved in rectified spirit (5 ml) and a few drops of conc. H_2SO_4 was added to the solution of taraxerone (200 mg) in chloroform (1 ml). The reaction was shaken and on concentration gave orange red crystals. The crude DNPH on crystallisation from chloroform and methanol yielded pure 2,4-DNP derivative of taraxerone, m.p. 258-60°.

Found: C, 71.32; H, 8.27, N, 9.43%

Calc. for $C_{36}H_{52}O_2N_2$:C, 71.52; H, 8.61; N, 9.27%

Isomerisation of taraxerone[21] : Preparation of β-amyrone 107

To a suspension of taraxerone (600 mg) in glacial acetic acid (140 ml) maintained at 90° was added conc. hydrochloric acid (4 ml) and the reaction mixture was heated on a water bath for twenty minutes during which the solid dissolved in the solvent. The reaction mixture was then cooled and diluted with water. A solid came out which was taken up in ether. The ether layer was washed with water till neutral. On removing solvent a solid came out (520 mg). The solid on crystallisation from chloroform and methanol mixture afforded fine needle shaped crystals m.p. 174-6°, $(\alpha)_D$ + 105.6°, which was found to be identical with an authentic sample of β-amyrone 107 (m.m.p. and rotation).

Examination of fraction 13-18 (Table I) : Isolation of 1-hexacosanol

The solid materials from fractions 13-18 (Table I) were combined (1.14 gm) and was chromatographed over a column of alumina (50 gm) deactivated with 2 ml of 10% aqueous acetic acid. The solid dissolved in benzene (5 ml) was placed on the column. The chromatogram was developed in petroleum ether and was eluted with the following solvents (Table V).

Table V

Chromatograph of the above solid m.p. 60-65° (1.4 gm)

Eluent	Fractions 50 ml each	Residue on evaporation	m.p.
Petroleum ether	1-2	Trace oil	-
Petroleum ether: benzene (4:1)	3-4	Nil	-
Petroleum ether: benzene (3:2)	5-9	Solid with petroleum ether (0.83 gm)	75-6°

Further elution with more poler solvents did not afford any solid material

The above solid of m.p. 75-76° (0.83 gm) from the fractions 5-9 (Table V) were collected and crystallised from petroleum ether. After three crystallisations it gave crystals having m.p. 78-9°, $(\alpha)_D \pm 0^\circ$. Analysis of the compound corresponded to the molecular formula $C_{26}H_{54}O$. This has been identified as 1-hexacosanol[22].

Found: C, 81.32, H, 13.86%

Calc. for $C_{26}H_{54}O$: C, 81.67; H, 14.13%

IR (chloroform) : ν_{max} 3350 broad (-OH group) cm^{-1}

UV : No absorption above 220 mμ.

Preparation of 1-hexacosanol acetate

To the alcohol (180 mg) dissolved in pyridine (3 ml) was added acetic anhydride (3 ml) and the solution was allowed to stand at room temperature for fifteen hours. The solution was then poured in ice cold water when a gummy solid separated out. It was taken up in ether. The ether layer after washing with water was dried (Na_2SO_4). The solvent was then removed when a gummy residue (138 mg) was obtained, which after crystallisations from a mixture of methanol and acetone afforded pure 1-hexacosanol acetate m.p. 68-69°, $(\alpha)_D \pm 0°$. Its melting point was not depressed when mixed with an authentic specimen of 1-hexacosanol acetate. Its infrared spectrum was also indistinguishable from that of an authentic specimen of 1-hexacosanol acetate.

Found: C, 78.84; H, 13.62%

Calc. for $C_{28}H_{56}O_2$: C, 79.24; H, 13.26%.

Examination of Fractions 19-23 (Table II) : Isolation of taraxerol

The solid material m.p. 265-8°, from fractions 19-23 (Table I) were combined (400 mg). The mixture after several crystallisation from a mixture of chloroform and methanol afforded taraxerol, m.p. 278-80°, $(\alpha)_D$ + 3.7°. Its m.p. was not depressed when mixed with an authentic specimen of taraxerol.

Found: C, 84.72; H, 11.68%

Calc. for $C_{30}H_{50}O$:C, 84.50; H, 11.74%.

Preparation of taraxeryl acetate 161

To the alcohol (200 mg) dissolved in pyridine (5 ml) was added acetic anhydride (5 ml) and the solution was heated on a water bath for five hours. The solution was cooled and then poured into ice cold water when a crystalline solid separated out. The solid was collected, washed with water till the washings were neutral and then dried. The crude acetate m.p. 275-80° after several crystallisations from a mixture of chloroform-methanol afforded pure taraxeryl acetate (120 mg) m.p. 295-7°, $(\alpha)_D$ + 9.16°. The solid was found to be identical with an authentic sample of taraxeryl acetate (m.m.p. and IR comparison).

Found: C, 81.72; H, 11.52%

Calc. for $C_{32}H_{52}O_2$: C, 82.05; H, 11.11%.

Oxidation of taraxerol : Preparation of taraxerone 159

A solution of taraxerol (200 mg) dissolved in pyridine (5 ml) was added to a chromium trioxide-pyridine complex prepared from pyridine (2 ml) and chromium trioxide (200 mg) and the mixture was kept at room temperature for fourteen hours. The crude product (0.18 gm) obtained by working up in the usual manner was chromatographed over a column of active alumina (5 gm). The chromatogram was developed with petroleum ether and the product dissolved in benzene (5 ml) was poured on the column and then eluted with the following solvents (Table V).

Table VI

Eluent	Fractions 50 ml each	Residue on evaporation
Petroleum ether	1-2	Nil
Petroleum ether: benzene (4:1)	3-6	Solid m.p. 236-8° (0.12 gm)

Further elution with more polar solvents did not yield any material.

Fractions 3-6 (Table VI) (120 mg) on recrystallisation from chloroform and methanol furnished needle shaped crystals m.p. 238-40°, $(\alpha)_D$ + 10.8°, identical with an authentic sample of taraxerone (m.m.p. and IR).

Found: C, 84.69; H, 11.08%

Calc. for $C_{30}H_{50}O$:C, 84.90; H, 11.32%.

Examination of fractions 24-28 (Table III) : Isolation of β-sitosterol 71

The solid material m.p. 128-32°, from fractions 24-28 (Table II) were combined (0.8 gm) which after several crystallisations from methanol and finally from acetone afforded β-sitosterol, m.p. 136-7°, $(\alpha)_D$ - 36°. Its melting point was not depressed when mixed with an authentic specimen of β-sitosterol.

Found: C, 83.34; H, 11.62%

Calc. for $C_{29}H_{50}O$:C, 83.98; H, 12.15%.

Preparation of β-sitosterol acetate 72

β-sitosterol (0.5 gm) was acetylated with pyridine (5 ml) and acetic anhydride (5 ml) in the usual manner. The product isolated in the usual way with ether was crystallised from chloroform and methanol mixture when crystals of the acetate, m.p. 126-7°, $(\alpha)_D$-40° were obtained. The latter was identified as β-sitosterol acetate by comparing it with an authentic specimen of β-sitosterol acetate (m.m.p. and IR comparison).

Found : C, 81.15; H, 11.35%

Calc. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48%.

Examination of Fractions 46-51 (Table II) : Isolation of a new nor-triterpene alcohol

Fractions 45-51 (Table II) were combined (300 mg) and its solution in benzene (5 ml) was placed on a column of alumina (30 gm. deactivated with 1.2 ml of 10% aqueous acetic acid). The chromatogram was developed with petroleum ether and eluted with the following solvents (Table VII).

Table VII

Eluent	Fractions 50 ml each	Residue
Petroleum ether: benzene (1:1)	1-4	Nil
Petroleum ether: benzene (1:3)	5-7	Nil
Benzene	8-12	Oil
Benzene:ether (4:1)	13-15	Oil
Benzene:ether (3:2)	16-21	Solid (0.2 gm) m.p. 220-2°

Further elution with more polar solvents did not yield any material

Fractions 16-12 (Table VII) were combined and on crystallisation several times from methanol yielded fine needle shaped crystals, m.p. 228-9°, $(\alpha)_D$ - 9.09°.

Found: C, 75.92; H, 10.14%

$C_{29}H_{46}O_4$ requires: C, 75.98; H, 10.05%

UV spectra (ethanol) : No absorption in the range 220-300 mμ.

IR spectra[23,24] (KBr disc) : ν_{max} 3360 (-OH, broad) 2070 ($-CH_2-$ broad) 1467, 1453 (-CH=CH-, doublet); 1398, 1369 (gem-dimethyl sharp), 890, 875 (-CH=CH-) cm^{-1},

Mass spectra[23] : m/e 426, 440, 458 (M^+)

NMR spectra (Fig. 20) : Signals at 0.88, 0.91, 0.95, 1.04, 1.18, (21H, 7 tert. $-CH_3$), 2.16, 2.2, 2.28, 2.32 (quartet of doublets, 2 C-OH groups); 3.22, 3.3 (3H, 2H-C-OH: 4.00 (quartet of doublets, $-CH_2-$) and 6.42, 6.52, 6.72, 6.80 (AB quartet, CH=CH) ppm.

Preparation of the acetate of nor-triterpene $C_{29}H_{46}O_4$

The compound (0.2 gm) was acetylated with pyridine (2 ml) and acetic anhydride (2 ml) in the usual way. The solid obtained was dissolved in benzene (5 ml) and was placed on a column of alumina acid). The chromatogram was developed with petroleum ether and eluted with the following solvents (Table VII).

Table VIII

Eluent	Fractions 50 ml each	Residue
Petroleum ether	1-3	Nil
Petroleum ether: benzene (9:1)	4-6	Nil
Petroleum ether: benzene (4:1)	7-12	Solid (0.13 gm) m.p. 200-5°

Further elution with polar solvents did not yield any material

The solids from fractions 7-12 (Table VIII) were combined which on crystallisation from chloroform and methanol mixture afforded fine needle shaped crystals, m.p. 213-5°, $(\alpha)_D$ + 47.5°.

Found: C, 72.79; H, 9.07%

$C_{33}H_{50}O_6$ requires: C, 73.06; H, 9.22%

UV spectra (ethanol): no absorption in the range 220-300 mμ.

IR spectra ($CHCl_3$)[23,24]: ν_{max} 1737 (O-$COCH_3$); 1467, 1453 (-CH=CH-, doublet), 1389, 1369 (gem dimethyl, sharp); 1245-50 (-O-$COCH_3$); 895-872 (-CH=CH-). No hydroxyl absorption.

Mass spectra : peaks at 422, 482, 510, 524, 542 (M^+).

NMR spectra : signals at 0.885, 0.93 (6-H), 0.96, 0.98, 1.01, 1.025 (21-H, 7 tert-CH_3); 1.99, 2.055 (6H, 2-O$COCH_3$), 4.70, 4.8 (2H, 2H-O$COCH_3$); 6.40, 6.49, 6.675, 6.75 (AB quartet, -CH=CH=) ppm (fig. 21).

Perbenzoic acid titration of the above diacetate m.p. 213-15°

To the above acetate (0.150 gm) dissolved in chloroform in a 25 ml volumetric flask, a solution of perbenzoic acid (5 ml) was added and the volume made upto to 25 ml with chloroform. A similar blank solution of perbenzoic acid (5 ml) was prepared in a 25 ml volumetric flask. On titrating the above two solutions with a standard N/100 sodium thiosulphate solution no difference in titre value was observed even after 24 hours.

Potassium iodide-acetic acid titration on the diacetate m.p.213-15°

The acetate, m.p. 213-15° (0.0445 gm) was dissolved in acetic acid (5 ml) in a 25 ml volumetric flask and a saturated solution of potassium iodide in glacial acetic acid was added and then the volume

made upto 25 ml. A similar blank solution of potassium iodide in glacial acetic acid was prepared in a 25 ml volumetric flask. The above solution were titrated against sodium thiosulphate solution (0.02969N). The difference in the titre value was 2.4 ml of thiosulphate solution for 10 ml of each solution. Calculation revealed that two equivalent atoms of iodine were liberated by the compound, showing that one atom of iodine is liberated by one atom of oxygen, indicating that a peroxide linkage of the type C-O-O-C in the molecule that may be present.

Hydrogenation of the acetate m.p. 213-15°

The acetate m.p. 213-15° (200 mg) dissolved in ethanol (30 ml) was hydrogenated in presence of 10% palladium-on-charcoal catalyst at ordinary temperature and pressure. On working up the reaction mixture in the usual manner afforded fine needle shaped crystals m.p. 262-3°.

UV spectra (ethanol) : No absorption in the range 220-300 mμ

IR spectra ($CHCl_3$) : ν_{max} 3590 cm^{-1} (-OH), 1738 ($-OCHCH_3$), 1372, 1388 (gem dimethyl), 1230 ($-OCHCH_3$ broad), 895 (-CH=CH-) cm^{-1}.

NMR spectra (100 Mc/s) : Signals at 0.86, 0.885, 0.885, 0.905 (6H), 2-O-$COCH_3$), 4.68, 4.78 (1H, $\underline{H}$-C_3-$OCOCH_3$), 5.1 (quartet of a doublet 1H, $\underline{H}$-C_2-OCOCHO, 3.4, 3.48 (1H, H-C-O$\underline{H}$) 5-9 (multiplet 1H, vinyl proton), 1.895 (hydroxyl proton C-O$\underline{H}$ ppm (Fig. 23).

Acetylation of the above acetate m.p. 262-63° (200 mg) was acetylated by heating with acetic anhydride and pyridine. The reaction mixture on working up in the usual manner afforded crystals m.p. 170°. The acetate showed an absorption in its hydroxyl region in its IR spectra.

Found: C, 73.24; H, 869%

$C_{35}H_{52}O_7$ requires C, 73.64, H, 8.90%.

UV spectra (in 95% ethanol) : No absorption in the range 220-300 mμ.

IR spectra ($CHCl_3$) : max 3600 (-OH- group), 1730 ($-OCOCH_3$), 1370, 1386 (gem dimethyl), 1230 ($-OCOCH_3$).

NMR spectra (100 Mc/S): signals at 0.88, 0.9 (6H), 0.98, 0.985, 1.025, 1.08, (21H, seven tert. methyl group), 1.98, 2.04, 2.12 (9H, 3-O-$COC\underline{H}_3$), 5.08 (quartet of a doublet 1H, $\underline{H}$-C_2-$OCOCH_3$), 3.4 ($C\underline{H}$-O-$COCH_3$), 5.62 (multiplet 1H, vinyl proton) ppm (Fig. 24).

<u>Lithium aluminium hydride reduction of the original alcohol m.p. 228-29°</u>

To a solution of the original alcohol, m.p. 228-29° (300 mg) in dioxan (15 ml) was added lithium aluminium hydride (0.2 gm) and the mixture refluxed on the water bath for an hour. Excess of LAH was destroyed with ethyl acetate (100 ml) and the organic layer was washed with water, and dried (Na_2SO_4). Evaporation of the solvent furnished a crystalline solid which on crystallisation from methanol gave crystals, m.p. 302--3°

Acetylation of this compound by acetic anhydride-pyridine method and working up in the usual manner furnished an acetate, m.p. 301°

This acetate was found to a different one from that of an acetate m.p. 170° prepared by hydrogenation of the original diacetate and subsequent acetylation.

Further work on this new nor triterpenoid is in progress.

Purification and crystallisation of 3,3'-di-O-methyl ellagic acid 164

The crude benzene insoluble solid (500 mg) having m.p. 250-80° was dissolved in 10% aqueous sodium hydroxide solution (100 ml) and extracted with ether to remove any neutral material that might be present. The alkaline layer was filtered and the clear filtrate was acidified with cold 10% hydrochloric acid (150 ml) and kept in a frigidaire for three days. The precipitated solid was separated by filtration, washed with water and dried. The solid was crystallised several times from dimethyl formamide to afford fine yellow crystals of 3,3'-di-O-methyl ellagic acid 164 m.p. 322-24°. The solid was found to be identical with an authentic sample of 3,3'-di-O-methyl ellagic acid.

Found: C, 58.15; H, 3.36; MeO-, 17.93%

Calc. for $C_{16}H_{10}O_8$: C, 58.18; H, 3.27; 2MeO-, 18.8%

UV spectra (ethanol) : λ_{max} 250, 270, 358 (inflexion) and 372 mμ.

Sample + CH_3COONa : λ_{max} 250, 269, 258 (inflexion) and 372 mμ

IR spectra : Peaks at 3395-3180, 2990, 1735, 1722, 1610, 1590, 1495, 1365, 1280, 1210, 1120, 1110, 1070, 990, 985, 920, 870, 790 and 753 cm^{-1}.

Mass spectra : m/e 330 (M^+), 315 ($M^+ - CH_3$), 300 ($M^+ - 2CH_3$).

Solubility:

It was very sparingly soluble in acetone, chloroform, ether, ethyl acetate, ethanol and methanol but was soluble in dioxan and dimethyl formamide.

Colour reactions

It dissolved readily in aqueous sodium hydroxide, sodium carbonate solutions with the development of a yellow color. Ferric chloride solution-brown color, conc. H_2SO_4 - yellow color, Greiss-mayer reagent - no color.

Acetylation of 3,3'-di-O-methyl ellagic acid : Preparation of 3,3'-di-O-methyl 4,4'-diacetate

To 3,3'-di-O-methyl ellagic acid (400 mg) dissolved in pyridine (8 ml) was added acetic anhydride (8 ml) and the mixture was heated on a water bath for 16 hours. On cooling to room temperature needle shaped crystals of acetate separated out which was collected. On crystallisation of the acetate from dioxan colorless crystals (310 mg) m.p. 300-302° (decomp.) was obtained. The solid was found to be identical with an authentic sample of 3,3'-di-O-methyl ellagic acid 4,4'-diacetate (m.m.p.).

Found: C, 57.90; H, 4.06, CH_3CO-, 18.5%

Calc. for $C_{20}H_{14}O_{10}$: C, 57.0; H, 3.41; $2CH_3CO$-, 20.8%

UV spectra (Ethanol) : λmax 247, 357, 370 mμ

Acetylation of 3,3'-di-O-methyl ellagic acid by CH_3COONa and Ac_2O method : Preparation of 3-3'-di-O-methyl ellagic acid 4,4'-diacetate

To 3,3'-di-O-methyl ellagic acid (500 mg) in acetic anhydride (10 ml), anhydrous sodium acetate (5 gm) was added and the mixture was refluxed for half an hour. The mixture was then cooled and poured in ice cold water. An oil first came out which solidified within few minutes. The solids were collected, dried and crystallised from dioxan. After three crystallisations it afforded colorless crystals m.p. 302-4° (decomp.) which was found to be identical with the above diacetate and also with an authentic sample of 3,3'-di-O-Methyl ellagic acid 4,4'-diacetate (m.m.p.).

Found: C, 57.93; H, 4.08; CH_3CO-, 18.92%

Calc. for $C_{20}H_{14}O_{18}$: C, 57.9, H, 3.41; 2 CH_3CO-, 20.8%

The acetate was found to be insoluble in cold aqueous sodium hydroxide but on heating it slowly went into solution with the development of yellow coloration. Ferric chloride did not produce any coloration but with conc. H_2SO_4 it developed a yellow coloration.

Methylation of 3,3'-di-O-methyl ellagic acid : Preparation of tetra-o-methyl ellagic acid 165

A mixture of 3,3'-di-O-methyl ellagic acid 164 (300 mg), dry acetone (250 ml), anhydrous potassium carbonate (5.0 gm) and dimethyl sulphate (1.2 ml) was refluxed for six hours. The reaction mixture was filtered. The filtrate on evaporation did not yield any residue. The residue left on the Buchner funnel was treated with water and methanol when a solid separated out. The latter on crystallisation from dimethylformamide yielded yellow crystals m.p. 337-38° which showed no depression in melting point when mixed with an authentic sample of tetra-o-methyl ellagic acid. IR spectra of the two compound were also identical.

Found: C, 60.11, H, 4.05, CH_3O - 31.0%

Calc. for $C_{18}H_{14}O_8$: C, 60.33, H, 3.91; $4CH_3O$-, 35.0%

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