

CHAPTER-II

EXPERIMENTAL

The melting points are uncorrected. The UV spectra were taken in Ziess VSU-1 spectrophotometer in ethanol solutions unless stated otherwise. The IR spectra were recorded in Perkin-Elmer spectrometer 337.

Extraction: The details of the extraction of the bark of Sapium sebiferum Roxb. and separation of the benzene insoluble solid C has already been described in Part-I, Chapter-IV , p.19.

Purification and crystallisation of 3,4-di-O-methyl ellagic acid 1

The benzene insoluble solid (0.6 g.) which had the melting point 280-300° 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 seven days. The precipitated solid was separated by filtration, washed with water and dried. The solid was crystallised several times from dimethylformamide to afford fine yellow crystals of 3,4-di-O-methyl ellagic acid 1, m.p. > 360°.

Found	:	C, 58.15; H, 3.36; MeO-, 17.93%.
Calculated for $C_{16}H_{10}O_8$:	C, 58.18; H, 3.27; 2MeO-, 18.8%.
UV spectra (Ethanol)	:	peaks at 259 (ϵ , 35,582), 350 (inflexion) 410 m μ (ϵ , 10,187).

IR Spectra (KBr disc) : peaks at 3395-3180, 2990, 1735, 1715, 1685, 1617, 1608, 1595, 1495, 1435, 1365-1345, 1280, 1210, 1170, 1110, 1070, 990, 985, 920, 870, 790 and 753 cm^{-1} .

Mass spectra : 330 (M^+), 315 ($\text{M}^+ - \text{CH}_3$), 300 ($\text{M}^+ - 2\text{CH}_3$).

Solubility: It was very sparingly soluble in acetone, chloroform, ether ethyl acetate, ethanol and methanol but was soluble in dioxan and dimethylformamide.

Colour reactions: It dissolved readily in aqueous sodium hydroxide, sodium carbonate solutions with the development of a yellow colour which turned violet on heating. Ferric chloride gave - brown colour; lead acetate - yellow precipitate; conc. H_2SO_4 - yellow colour; Griessmayer reagent - no colour.

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

To 3,4-di-O-methyl ellagic acid (0.4 g.) dissolved in pyridine (8 ml.) was added acetic anhydride (8 ml.) and the mixture was heated over water bath for 24 hours. Fine needle shaped crystals of acetate separated out which was collected. On crystallisation of the acetate from DMF white crystals (0.3 g.) of the acetate m.p. $302-4^\circ$ was obtained.

Found : C, 57.90; H, 3.66; $\text{CH}_3\text{CO}-$, 18.5%.

Calculated for $\text{C}_{20}\text{H}_{14}\text{O}_{10}$: C, 57.95; H, 3.41; $2\text{CH}_3\text{CO}-$, 20.9%.

UV spectra (Ethanol) : peaks at 255, 378, 405 $\text{m}\mu$.

The acetate produced a yellow colour on the surface when aqueous sodium hydroxide solution was added but did not dissolve in it. On heating it slowly went into solution with the development of a violet colour. Ferric chloride produced no change in colour. Lead tetraacetate also gave no colour, but with conc. H_2SO_4 it developed a yellow colour.

Methylation of 1 : Preparation of tetra-O-methyl ellagic acid 5

3,4-di-O-methyl ellagic acid 1 (0.2 g.) was heated under reflux in dry acetone (200 ml.) with anhydrous potassium carbonate (4.0 g.) and dimethyl sulphate (1 ml.) for 6 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 crystalline solid separated out. The latter on crystallisation from dimethylformamide yielded yellow crystals, m.p. $337-8^{\circ}$ which showed no depression in melting point when mixed with an authentic sample of tetra-O-methyl ellagic acid kindly supplied by Prof.T.R. Seshadri. IR spectra of the two compounds were also identical.

Found : C,60.11; H,4.05; CH_3O- ,30%.

Calculated for $C_{18}H_{14}O_8$: C,60.33; H,3.91; CH_3O- ,35%.

Benzylation of 1 : Preparation of 3,4-di-O-methyl-3',4'-di-O-benzyl ellagic acid

3,4-di-O-methyl ellagic acid (0.5 g.) was refluxed in acetone (30 ml.) with anhydrous potassium carbonate (2.5 g.), potassium iodide (2.5 g.) and benzyl chloride (2.5 ml.) for 12 hours. The orange colour of the mixture turned light yellow during the reaction. The reaction mixture was filtered

on the Buchner funnel and the solid was washed with water and dried. The residual solid on crystallisation from DMF yielded fine yellow needle shaped crystals, m.p. 284-5°.

Found	:	C,70.24; H,4.13%.
Calculated for C ₃₀ H ₂₂ O ₈	:	C,70.06; H,4.35%.
UV spectra (Ethanol)	:	peaks at 250, 348 (inflexion), 360 m μ .

The compound was insoluble in sodium hydroxide solution and did not give any colour with ferric chloride solution. Conc.H₂SO₄ gave yellow colour but lead acetate did not give any colour.

Preparation of diphenyl methylene acetal derivative 6 with dichlorodiphenyl methane

To 3,4-di-O-methyl ellagic acid 1 (0.6 g.) taken in a 5 ml. round bottomed flask was added α,α -dichlorodiphenyl methane (0.8 g.) and the mixture heated to 170-180° for 5 minutes. The reaction mixture was extracted with hot benzene and dried. The solid product was crystallised from DMF when yellow crystal of m.p. above 360° was obtained. A depression in melting point (m.m.p. 310°) was observed when mixed with the original compound 1.

Found	:	C,70.22; H,3.38%.
Calculated for C ₂₉ H ₁₈ O ₈	:	C,70.44; H,3.69%.
UV spectra (Ethanol)	:	peaks at 257, 350, 362 m μ .

It was insoluble in aqueous sodium hydroxide solution and gave no colour with ferric chloride solution. Conc.H₂SO₄ produced a yellow colour but lead acetate did not deposit any yellow precipitate.

REFERENCES

1. A.C.Jain in "Advancing Frontiers in Chemistry of Natural Products", Hindusthan Publishing Corporation, India, 1965, 190.
2. J.Shinoda and C.P.Kun, J.Pharm.Soc.,Japan, 1930, 502; 1931, 4870.
3. L.R.Row and G.S.R.Subba Rao, Tetrahedron, 1962, 357.
4. V.M.Chari, S.Neelakantan, T.R.Seshadri, Ind.J.Chem., 1968, 231.
5. B.F.Cain, New Zealand, J.Sci., 1963, 364.
6. T.R.Seshadri and K.Vasistha, Curr.Sci., 1963, 499; 1964, 334.
7. Y.Takino, H.Imagawa, Y.Aoki and T.Ozawa, Agri.Biol.Chem.,Japan, 1963, 562.
8. D.E.Hathway, Biochem.J., 1957, 445.
9. B.P.Moore, Aust.J.Chem., 1964, 901.
10. L.Jurd, J.Amer.Chem.Soc., 1959, 4606.
11. O.T.Schmid in "Recent Developments in the Chemistry of Natural Phenolic Compounds", Pergamon Press, 1961, 139.
12. F.M.Dean in "Progress in Chemistry of Natural Products" Ed.L. Zechmeister, Wien-Springer-Verlag, 1952, Vol.9, 282.