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STUDIES IN THE CHEMICAL CONSTITUENTS OF FLOWERS OF *MANGIFERA INDICA*

Part -II. Isolation and Characterization of Some Alkylgallates from Blossoms of *Mangifera indica*

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Six new alkylgallates, methylgallate, *n*-propylgallate, *n*- pentylgallate, *n*-octylgallate, 4-phenyl-*n*-butylgallate, 6-phenyl- n-hexylgallate and dihydrogallic acid have been isolated from the blossoms of *Mangifera indica*. The identity of these compounds has been established by comparison with synthetic alkylgallates, mass spectrometry and thin layer chromatography.

Key words: *Mangifera indica*, Blossoms, Alkylgallates.

Mangifera indica belongs to the Family Anacardiaceae, a fairly large ever green tree distributed in tropical and sub-tropical parts of South Asia [2], Africa and Latin America. Mangoes are grouped under two broad categories seedling type (wild and cultivated) and horticultural clonene, propagated by budding or grafting. In continuation with our studies in the chemical constituents of flowers of *Mangifera indica* [3], some alkylgallates which are its main phenolic constituents were studied and reported in a preliminary publication [4]. This communication describes the isolation and identification of various alkylgallates from the blossoms of *Mangifera indica*.

TABLE 1.

S. No.	Solvent	Fraction No.	Colour	Molecular mass (M^+, *m/z*)	Solvent used for crystallization	M.P. °C	Molecular formula	Structure identified
1.	Ethyl acetate	1-3	Light green	–	–	–	–	–
2.	Ethyl acetate	4	Light green	282	–	–	$C_{15}H_{22}O_5$	*n*-Octyl gallate
3.	Ethyl acetate	4B	Light green	198	Hexane	148-150	$C_9H_{10}O_5$	Ethyl gallate
4.	Ethyl acetate	5	Light green	330	–	–	$C_{19}H_{22}O_5$	6-Phenyl-*n*-hexyl gallate
5.	Ethyl acetate	6	Light green	212	Methanol	142-143	$C_{10}H_{12}O_5$	*n*-Propyl gallate
6.	Ethyl acetate	7	Light green	198	Hexane	–	$C_9H_{10}O_5$	Ethyl gallate
7.	Ethyl acetate	7A	Light green	240	–	–	$C_{12}H_{16}O_5$	*n*-Pentyl gallate
8.	Ethyl acetate	8	Light green	302	Methanol	159-162	$C_{17}H_{18}O_5$	4-Phenyl-*n*-butyl gallate
9.	Ethyl acetate	9-10	Light green	–	–	–	–	–
10.	Ethyl acetate	11	Light green	464	Methanol	–	–	2,2,5.6,7,23,23 Heptamethyl 3-one 17-ol,19 tetraecosene
11.	Ethyl acetate	11A	Light green	212	Methanol	142-143	$C_{16}H_{12}O_5$	*n*-Propyl gallate
12.	Ethyl acetate	12	Light green	284	Methanol	–	–	Unidentified
13.	Ethyl acetate	13	Greenish	212	Methanol	142-143	$C_{10}H_{12}O_5$	*n*-Propyl gallate
14.	Ethyl acetate	14-15	Greenish	–	–	–	–	–
15.	Ethyl acetate	16-17	Greenish	198	Hexane	148-150	$C_9H_{10}O_5$	Ethyl gallate
16.	Ethyl acetate	18-21	Greenish	–	–	–	–	–
17.	Ethyl acetate	22	Greenish	198	–	148-150	$C_9H_{10}O_5$	Ethyl gallate
18.	Ethyl acetate	23	Greenish	200	Methanol	150-152	$C_9H_{12}O_5$	Dihydrogallic acid
19.	Ethyl acetate	24-26	Greenish	–	–	–	–	–

Fragmentation of prominent ions follow normal course.

Phenolic and polyphenolic compounds have already been reported from different parts of this plant [5-20], but only two phenolic compounds i.e. gallic acid and ethyl gallate have been reported from the flowers of this plant [5-7]. For this study ethanolic extract of flowers of *Mangifera indica* was employed. The naturally shed flowers (1 kg), of *Mangifera indica* collected from suburbs of Karachi during the season of February and March, were separated out from their floral axis and extracted three time with (5 L) ethanol. The solvent was evaporated under reduced pressure and a gummy mass 150 gm thus obtained. This gummy mass dissolved in *n*-hexane and soluble fraction was separated out, *n*-hexane soluble portion was concentrated on rotary evaporator, under reduced pressure, yielding a crystalline compound which was identified as ethyl gallate, whereas *n*-hexane insoluble fraction (7.50 gm) was treated with hot ethyl acetate. The ethyl acetate soluble fraction was studied with the help of column and thin layer chromatography for its chemical constituents.

For column chromatography aluminium oxide (acidic) obtained from E. Merck Darmstadt (90) (70-230 mesh ASTM) was used as the adsorbent and (40 gm Al_2O_3 per gm of the extract) eluted from ethyl acetate and subsequently from a mixture of ethyl acetate and methanol. Forty fractions were collected near about (15 ml) in a 50 ml conical flask. First 26 fractions were collected from ethyl acetate, 9 were collected by using the mixture of ethyl acetate and methanol (50:50) and 5 were collected of ethyl acetate and methanol (25:75). All the samples were evaporated to dryness under reduced pressure. The residue was dissolved in a small quantity of methanol and kept overnight. The results of this experiment is presented in Table 1.

TABLE 2. PHENOLIC CONSTITUENTS OF FLOWERS OF *MANGIFERA INDICA*.

S. No.	Formula	M.P. °C	Solvent used for crystallization	Molecular mass *m/z*	Prominent peaks *m/z*	Identified AS	Lit. M.P[21] °C
1.	$C_8H_8O_5$	–	Methanol	184	–	Methyl gallate	160-162
2.	$C_9H_{10}O_5$	148-150	Hexane	198	198,183 170,153,125	Ethyl gallate	152-154
3.	$C_{10}H_{12}O_5$	142-143	Methanol	212	212,198,183 109,153,125	*n*-Propyl gallate	142-143
4.	$C_{12}H_{16}O_5$	Oily	–	240	240,212,198, 153,125	*n*-Pentyl gallate	–
5.	$C_{15}H_{22}O_5$	Oily	–	282	282,198,153 125,33,71	*n*-Octyl gallate	–
6.	$C_{17}H_{18}O_5$	158-162	Methanol	302	302,198,130 170,153,125	4-Phenyl-*n*- butyl gallate	–
7.	$C_{19}H_{22}O_5$	Oily	–	330	330,255,239, 198,157	6-Phenyl-*n*- hexyl gallate	–
8.	$C_9H_{12}O_5$	150-152	Methanol	200	200,198,183 170,154,153	Dihydrogallic acid	–
9.	–	Oily	–	284	Unidentified	–	–

R_f = Values with different solvent system and coating materlal are given in the Table 3.

TABLE 3. R_f VALUES OF GALLIC ACID AND ALKYL GALLATES.

S. No.	Solvent system	Gallic acid	Methyl gallate	Ethyl gallate	*n*-Propyl gallate	*n*-Pentyl gallate	*n*-Octyl gallate	4-Phenyl *n*-butyl gallate	6-Phenyl hexyl gallate
1.	Carbon tetrachloride: ethanol (3:2)	0.13	0.39	0.46	0.50	0.58	0.65	0.60	0.63
2.	Benzene: methanol: acetic acid (25:4:1)	0.05	0.23	0.29	0.40	0.55	0.62	0.59	0.61
3.	Carbon tetrachloride: isopropanol: formic acid (40:6:2)	0.06	0.25	0.34	0.39	0.52	0.59	0.58	0.60

The identification of various alkylgallates were done by comparison of their melting points, MS and R_f values of various alkylgallates synthesised during the present study. The results of column chromatography are given in Table 2.

These results were confirmed by thin layer chromatograpy in comparison with synthetic alkyl gallates in three different solvent [22] systems on silica gel (Obtained from E. Merck No. PF 254). It may be noted that gallic acid and methyl gallate were detected by TLC only and could not be isolated by column chromatography. The results of TLC is given in Table 3.

Gallic acid and its esters separated considerably better in solvent 1,2,3. The distribution and sharpness were better than when using carbon tetrachloride-ethanol (7:3), which had been recommended by Davidek [23].

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