

## CONSTITUENTS OF ACER PENTAPOMICUM

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**Abstract.** Gallic acid and its methyl and ethyl esters have been isolated from the leaves of *A. pentapomicum* and identified by IR and NMR spectroscopy and mass spectrometry of the ester triacetates.

The chemical constituents of several species of *Aceracea* have been reported in a recent chemotaxonomic study.<sup>1</sup> More recently a number of cyclopropylamino compounds have been isolated from many species of *Acer* and their distribution pattern studied against a recent classification of the genus.<sup>2</sup> Nothing is known, however, of the constituents of *A. pentapomicum*, a small deciduous tree commonly found in the Kaghan valley and in the Jhelum district of the Punjab.

### Discussion

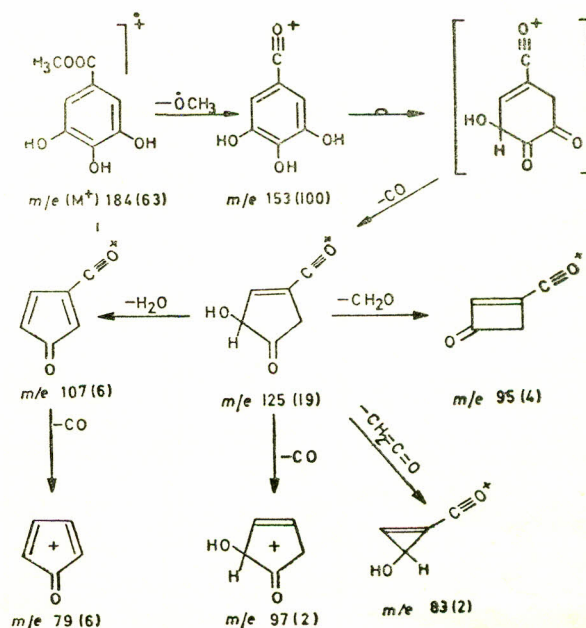
Silica gel column chromatography of an ethanolic extract of the dried, powdered defatted leaves, on elution with a benzene-ethyl acetate mixture yielded three compounds which were examined by IR, NMR spectroscopy and high resolution mass spectrometry. All three compounds exhibited hydroxyl (*ca* 3300), carbonyl (*ca* 1690) and ester carbonyl (*ca* 1740) and aromatic (*ca* 1605  $\text{cm}^{-1}$ ) peaks in the IR. The first product eluted from the column was converted into its more soluble acetate for NMR examination and showed an aromatic two-proton singlet, a methoxy three-proton singlet and a nine-proton singlet indicating an aromatic methyl ester, triacetate. The IR spectrum showed phenolic ester (*ca* 1785), ester carbonyl (*ca* 1740) and aromatic (*ca* 1605  $\text{cm}^{-1}$ ) peaks. The absence of a significant peak at  $m/e$  152 ( $M^+ - \text{CH}_3\text{OH}$ ) in the mass of the parent ester indicated no hydroxyl function in the *ortho* position since the base peak (B) in methyl *o*-hydroxybenzoates arises from the elimination of methanol.<sup>3</sup> The ester was, therefore, methyl 3,4,5-trihydroxybenzoate (I). The mass cracking pattern (relative abundance in parenthesis) is similar to that of gallic acid and its derivatives,<sup>4</sup> and is interpreted in scheme 1. Stepwise elimination of ketene from the triacetate ( $M^+$ , 310) giving peaks at  $m/e$  268, 226 and 184 (B), preceded a fragmentation pattern similar to that of the parent ester. The second substance eluted from the column was similarly shown to be the ethyl ester (II) from its mass and the NMR spectrum of the triacetate. The mass cracking pattern of this ester proceeded via two paths, the major involving elimination of an ethoxyl radical and the other elimination of ethylene by a McLafferty rearrangement (scheme 2). The

mass of the triacetate again showed stepwise elimination of ketene giving the molecular ion of the ester (II) as the base peak. The third substance was gallic acid (III) from its m.p., IR and mass.<sup>4</sup> Finally, elution with ethanol gave sucrose which was identified by m.p. and mixed m.p. with authentic sucrose, and m.p. of its octaacetate.

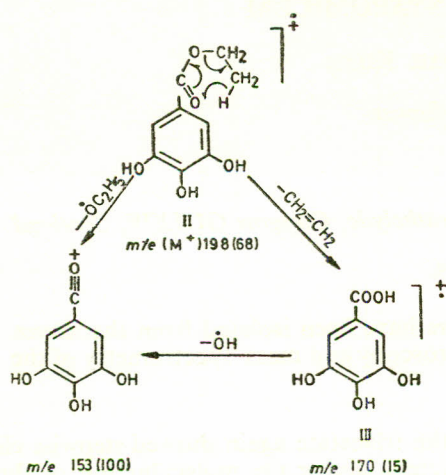
### Experimental

The solvent was removed from the ethanolic extract of the dry, powdered defatted leaves and the oily residue applied to a silica gel column. Elution with benzene gave a small amount of non-crystallisable material and elution was continued by gradually diluting benzene with ethyl acetate. When the mixture was 70 : 30, methyl 3,4,5-trihydroxybenzoate, m.p. 202° (from benzene-ethyl acetate) (charcoal) was obtained. (Found : C, 52.2 ; H, 4.5%. Calcd.

Scheme 1



Scheme 2



for  $C_8H_8O_5$ : C, 52.2; H, 4.25%. IR  $\nu_{max}$  (KCl), 3300, 1695, 1600, 1200  $cm^{-1}$ . The triacetate prepared from acetic anhydride in pyridine had m.p. 168° (from benzene). (Found: C, 54.7; H, 4.5%. Calcd. for  $C_{14}H_{14}O_8$ : C, 54.2; H, 4.5%). IR  $\nu_{max}$  (KCl) 1785, 1740, 1605, 1190  $cm^{-1}$ . Mass  $m/e$  310 ( $M^+$ ), 268 ( $M^+ - C_2H_2O$ ), 226 ( $M^+ - 2 C_2H_2O$ ), 184 ( $M^+ - 3 C_2H_2O$ ). NMR  $\tau$   $CDCl_3$  2.2 (2H, s, Ar), 6.1 (3H, s,  $OCH_3$ ), 7.75 (9H, s,  $CH_3CO$ ).

The proportion of ethyl acetate was increased to 50 : 50 when ethyl 3,4,5-trihydroxybenzoate, m.p. 162° (from benzene-ethyl acetate) was eluted. (Found: C, 55.7; H, 5.35%. Calcd. for  $C_9H_{10}O_5$ : C, 56.2; H, 5.05%). IR  $\nu_{max}$  (KCl) 3300, 1710, 1600, 1200  $cm^{-1}$ . The triacetate had m.p. 138° (from benzene). (Found: C, 55.9; H, 4.9%. Calcd. for  $C_{15}H_{16}O_8$ : C, 55.55; H, 4.9%). IR  $\nu_{max}$  (KCl) 1780, 1740, 1600, 1200  $cm^{-1}$  (broad). Mass  $m/e$  324 ( $M^+$ ), 282 ( $M^+ - C_2H_2O$ ), 240 ( $M^+ - 2 C_2H_2O$ ), 198 ( $M^+ - 3 C_2H_2O$ ). NMR  $\tau$   $CDCl_3$  2.17 (2H, s, Ar), 5.6 (2H, q,  $J$  6Hz,  $OCH_2$ ), 7.7 (9H, s,  $COCH_3$ ), 8.6 (3H, t,  $J$  6Hz,  $CH_2CH_2$ ).

Continued elution with this mixture gave gallic acid, m.p. 235° (dec.) (from benzene-ethyl acetate); mass  $m/e$  170 ( $M^+$ ), 153 ( $M^+ - OH$ ), 125 ( $M^+ - COOH$ ). IR  $\nu_{max}$  (KCl), 3450, 2700-2200, 1670, 1600  $cm^{-1}$ .

The column was finally eluted with ethanol and gave sucrose (m.p. 180°). The octaacetate<sup>5</sup> had m.p. 87°.

### References

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