

DICOTYLEDONAE

ANACARDIACEAE

POLYPHENOLS OF *MANGIFERA INDICA*

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Abstract—The isolation of β -glucogallin and a gallotannins from the unripe mango fruit and mango seed pulp respectively is described. The identity of the gallotannin with the Chinese gallotannin has been established.

EARLIER, the polyphenolic components present in bark,¹ pannicles² and fruit³ of mango (*Mangifera indica*) were described. Also, it was reported³ that on a preliminary examination the gallotannin present in the fruit of *Mangifera indica* was identical with that present in the mango pannicles and that it was based on a β -penta-*O*-galloylglucose core to which chains of at least 3 extra galloyl groups were attached. The present communication describes the isolation of β -glucogallin from the mature green mango fruit and the isolation and identification of a gallotannin present in mango (*M. indica*; Rumani seedling variety) seed pulp.

Isolation of β -Glucogallin from Unripe Mango Fruit

The ether and ethyl acetate soluble fractions from the acetone extract of the unripe mango fruit extract were examined and the results reported earlier.³ The residue left after the removal of ether and ethyl acetate soluble portions has now been examined; this fraction on concentration and subsequent cellulose-column chromatography, afforded β -glucogallin as a white crystalline solid. The compound gave one molecule each of gallic acid and glucose on hydrolysis. The analytical values IR and NMR spectra and melting points of the compound (202–204° as determined by the Koffler melting point apparatus; *lit.* natural 212°,⁴ synthetic 207°⁵ and 214°⁶) and its acetate (123–125°; *lit.* 125°⁶ and 126°⁴) agreed with those of β -glucogallin.

Isolation of Gallotannin from Mango Seed Pulp

The isolation of a gallotannin from the pannicles² as well as mature and unripe fruit³ of mango were reported earlier. Examination of the seed pulp of unripe mango fruit has now revealed the presence of a gallotannin which occurs to an extent of 8–10%. The gallotannin was found to be almost identical with that present in pannicles² and fruit.³ Methylation of the gallotannin by diazomethane gave a mixture of four components by thin layer chromatography, of which one was major. Of the three minor components, one was identified as

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¹ M. A. EL ANSARI, S. RAJADURAI and Y. NAYUDAMMA, *Leath. Sci.* **14**, 247 (1967).

² M. A. EL ANSARI, K. K. REDDY, K. N. S. SASTRY and Y. NAYUDAMMA, *Leath. Sci.* **15**, 295 (1968).

³ *Idem. ibid.*, **16**, 13 (1969).

⁴ E. GILSON, *Compt. Rend.* **136**, 385 (1903); *Chem. Zeatr.* **1**, 1799 (1903).

⁵ O. T. SCHMIDT and H. SCHMADEL, *Ann. Chem.* **649**, 149 (1961).

⁶ O. T. SCHMIDT and H. REUSS, *Ann. Chem.* **649**, 137 (1961).

methyl-3,4,5-tri-*O*-methyl gallate which must have probably formed as a result of decomposition of the original gallotannin by traces of base present in the diazomethane.⁷ The major component (M) which is taken to represent the bulk of the gallotannin did not have any hydroxyl absorption in the IR spectrum.

It was established⁷ that the NMR spectrum of the methylated derivative would provide a more reliable average composition for the gallotannin than analysis of the glucose content. The NMR spectrum of compound (M) (Fig. 1) indicated the identity of the mango gallotannin with Chinese gallotannin.

It is interesting to note the presence of such toxic substances as gallotannin^{8,9} in an edible fruit like mango. Even though the gallotannin is present to a small or negligible extent in well-ripe fruit, the content in unripe fruit is quite significant.

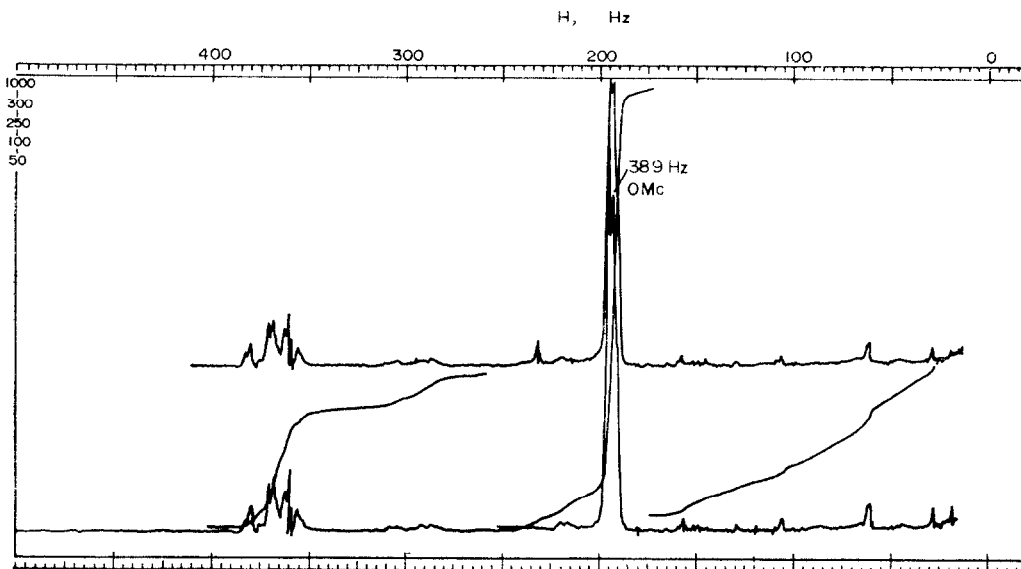


FIG. 1.

EXPERIMENTAL

Collection of the plant materials. Mango fruits, collected from a 15-yr-old tree on the grounds of Central Leather Research Institute (Madras) were used.

Preparation of extracts. Mature green (unripe) fruits were taken and separated into flesh (reported as fruit portion in our earlier communication³) and seed. The extraction of the flesh with acetone and the subsequent fractionation of the acetone extract into Et₂O soluble, EtOAc soluble and the residual portions were carried out as described earlier.³

Isolation of β -glucogallin from unripe mango fruit The residue left after the removal of Et₂O and EtOAc soluble portions of the unripe mango fruit was evaporated to a small volume (110 ml) *in vacuo* and the concentrate (20 ml) on cellulose column chromatography with H₂O as eluant gave β -glucogallin as colourless prisms, m p 202–204° (*lit.* 214°,⁶ 207°⁵) (Found. C, 40.70; H, 4.8. Calc. for C₁₀H₁₅O₁₀ · C, 40.68; H, 5.09%), *R_f* in 6% HOAc, 0.92; acetate (alcohol) colourless needles, m p. 123–125° (*lit.* 125°⁶ and 126°⁴) [α]_D²⁰ –25.6 (c, 0.1 in tetrachloroethane). The NMR spectrum of the compound was determined in CDCl₃ at 60 Mc using a Varian A 60 machine.

⁷ G. BRITTON, P. W. CRABTREE, E. HASLAM and J. E. STANGROOM, *J. Chem. Soc. C*, **783** (1966).

⁸ J. Z. KREZANOSKI, *Radiology*, **87**, 655 (1966).

⁹ J. SINGH and E. M. BOYD, *J. Can. Ass. Radiol.* **17**, 124 (1966).

Isolation of gallotannin from the seed pulp. The seed pulp was extracted as above and the EtOAc soluble fraction was redissolved in minimum quantity of solvent and precipitated with excess of CHCl_3 ($\times 2$) to yield gallotannin as a white amorphous powder m.p. and mixed m.p. (with the gallotannin isolated from mango pannicles²) 219–225° (with darkening at 205°).

Gallotannin methyl ether. The methylation of gallotannin was carried out as described earlier.^{2,3} TLC of the fully methylated gallotannin was carried out on silica-gel using CHCl_3 –EtOAc (5:1 v/v⁷) as the developing solvent system. The TLC plates, examined under UV light, indicated the presence of 4 spots, of which one was major. The bands corresponding to the 4 spots were cut out and eluted separately with acetone. Chromatography of each fraction on silica-gel was repeated separately and the elution done in a similar way. The major substance (M) on a final purification through EtOAc–light petroleum ether (40–60°) was obtained as an amorphous white powder, m.p. 125° (with slight sintering at 120°) (Found: C, 58.42; H, 5.35%. Calc. for $\text{C}_{74}\text{H}_{78}\text{O}_{34}$: C, 58.80; H, 5.17%) ν_{max} 1730 cm^{-1} and $[\alpha]_{\text{D}}^{20} +18.4^\circ$ (c, 2.6 in CHCl_3), R_f , 0.78 (in CHCl_3 –EtOAc, 5:1, v/v). One of the remaining 3 minor components (m 1) (R_f , 0.93) was identified as methyl tri-*O*-methylgallate by co-chromatography. The NMR spectrum of compound (M) was determined in CDCl_3 at 60 Mc using a Varian A 60 machine.

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COMPOSITAE

SESQUITERPENE LACTONES FROM THE GENUS *AMBROSIA*

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Abstract—The sesquiterpene lactone constituents of 25 new plant collections from the Southwestern United States, Mexico (including Baja Calif.) and Jamaica, representing 16 different taxa belonging to the genus *Ambrosia*, are described.

IN CONNECTION with our continuing chemosystematic investigation of the genus *Ambrosia*,¹ we wish to report here the sesquiterpene lactone chemistry of 25 new plant collections which represent 16 different *Ambrosia* taxa from the Southwestern United States, Mexico (including Baja Calif.) and Jamaica. No new compounds were encountered in the present investigations. However, the finding of isoalantolactone (VI) in *A. camphorata* from Baja California

¹ See T. J. MABRY, Chap. 13 in *Phytochemical Phylogeny* (edited by J. B. HARBORNE), pp. 269–300, Academic Press, London (1970) for a recent review of the sesquiterpene lactone chemistry of the genus *Ambrosia*.