Phytochemistry, 1975, Vol. 14, pp. 847–848. Pergamon Press. Printed in England.

ALUMINIUM AND MAGNESIUM HYDROXY CITRATES IN *ADINANDRA BRASSII* HEARTWOOD

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(*Received* 31 *July* 1974)

Key Word Index—*Adinandra brassii*; Theaseae; aluminium and magnesium hydroxy citrates; heartwood deposit.

A white amorphous material (200 g) was deposited in the heartwood of 1 m length of trunk of an *Adinandra brassii* tree. This tree was growing near Kiunga in the Western District of Papua, New Guinea, on ridges described as leached aluminosilicates tending towards bauxite. The heartwood deposit was present in longitudinal cracks in the timber and was observed after milling procedures.

Preliminary tests on the recovered material mp > 350° and IR spectrum (KBr) 3400, 1600, 1400 etc cm^{-1}, indicated the presence of an organometallic compound or mixture. It was soluble with slight effervescence in dilute $NaHCO_3$ which on standing at 100° deposited a gelatinous ppt containing both Al and Mg. Intensive testing for cations, Table 1, revealed the presence of only the above two cations in significant quantities, while the anions Cl^-, PO_4^{3-}, SO_4^{2-} and NO_3^- were not detected. Treatment of an aq. soln with NH_4OH–NH_4Cl to pH 6·5 failed to precipitate any insoluble hydroxides.

Ion exchange chromatography on Dowex 50 W cation exchange resin [1] afforded semi-crystalline citric acid; matching IR with a published spectrum [2], *p*-bromophenacyl ester mp 149·5°, dimethyl ester mp 117° and MS of this ester. The qualitative data indicated a mixture of Mg and Al citrates of fairly high purity; however the quantitative results outlined below revealed a more complex composition. Ion exchange chromatography on Dowex 50 W (H^+ form) provided an aq. fraction titratable with 0·1 M NaOH to phenolphthalein and containing 9·09 milli-equivalents of anhydrous citric acid.* The titrated solution was acidified with H_2SO_4 and the citric acid oxidized with KBr–$KMnO_4$ to pentabromoacetone [3]. The yield from this reaction, 99%, showed that citrate ions were the only organic anions present in the heartwood deposit.

Authentic citric acid similarly oxidized gave a 99·4% yield of pentabromoacetone. The ion exchange column was eluted with 4 M HCl and this solution was used for the estimation of Mg by atomic absorption spectroscopy, found 1·45 milli-equivalents* and Al gravimetrically as Al_2O_3 [4], found 13·77 milli-equivalents.* Al and Mg were also determined by the same procedure (i.e. gravimetric and AAS) on a H_2SO_4–HNO_3 digest. A mixed acid digest was necessary to destroy the citrate moiety as digestion with HNO_3 followed by NH_4OH treatment in the presence of NH_4Cl

Table 1. Elements sought in the heartwood deposit

Element	Level of detection (%)
Na	0·06
Zn, Si, K, Cu, Fe, Mn, Ni	<0·01
As, Ba, Ca, P, Sb	not detected <0·02
Bi, Cd, Co, Li, Pb, Sn, Sr, Ti, V, Zr	not detected <0·001
Ag, Be, Cr, Mo	not detected <0·0001

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* Milliequivalents of ion/g.

failed to precipitate any insoluble hydroxides. The H_2SO_4–HNO_3 procedure resulted in identical Al and Mg values to those obtained for the ion exchange method reported above. The sum of the cation milli-equivalents exceeded that for the citrate ion by 6·13 m-equiv/g and this imbalance could only be accounted for by the presence of hydroxyl ions in the molecules. Furthermore, the milliequivalents of Al found required more than 1 atom of Al per citrate anion indicating that compounds such as $Al_2(OH)_4$ citrate(H), Mg(OH) Al(OH) citrate and $Al_2(OH)_3$ citrate might be present.

The observation of slight effervescence during dissolution in $NaHCO_3$ solution infers the presence of some free-COOH groups. The IR spectrum in nujol mull and KBr discs was compared with those of Na_3 citrate, Na_2H citrate and citric acid similarly recorded. Citric acid (KBr disc) has a strong absorption band (C=O stretch) at 1700–1740 cm^{-1} which was not present in the spectra of either trisodium citrate or of our material. The latter two had strong absorption bands (broad) at 1590 with a shoulder at 1660 cm^{-1}.

Na_2H citrate showed absorption maxima at 1715 and 1585 cm^{-1}. Na_2H citrate and Na_3 citrate and our material showed strong absorption bands at 1440 and 1395, 1440 and 1390 and 1465 and 1400 cm^{-1} respectively. The absorption bands near 1600 and 1400 cm^{-1} are characteristic of the ionized carboxyl group present in salts of organic acids [5]. The results would support an almost completely ionic structure; the slight effervescence observed during solution in $NaHCO_3$ must therefore represent only a small percentage of free-COOH groups.

EXPERIMENTAL

Isolation. White amorphous heartwood deposit was removed from the wood and ground in an agate mortar to pass a 200 μm screen. Wood free powder was washed on a sintered glass crucible with hot EtOH and Et_2O and dried at 110° for 1 hr. IR: ν_{max}^{KBr} 3400, 1660 (sh), 1600, 1465, 1400, 1308, 1275, 1108, 1025, 975, 930, 903, 845, 710, 660 cm^{-1}.

Ion exchange chromatography. 0·5 g Dissolved in dist. H_2O was applied to a 19 mm × 15 cm column of Dowex 50 W X-4 (H^+ form). Elution of citric acid was complete within a vol. of 150 ml, rotavapor concn gave the solid acid. IR: ν_{max}^{KBr} 3490, 3280, 2630, 2550, 1740, 1700, 1425, 1385, 1355, 1320, 1308, 1290, 1240, 1215, 1195, 1175, 1140, 1080, 1050, 930, 905, 880, 820, 780, 685 cm^{-1}. The dimethyl ester (prepd. via. BF_3-MeOH) had mp 116–118° IR: ν_{max}^{Nujol} 3450, 1740, 1310, 1250, 1210, 1180, 1125, 1075, 1060, 1010, 985, 850 cm^{-1}. MS: *m/e* 221 (M^+ + H, 1%), 203 (0·2), 189 (3·5), 185 (1), 176 (2), 175 (21), 172 (1·5), 171 (18·5), 161 (1·5), 157 (2), 153 (4), 147 (2), 145 (1), 144 (9·5), 143 (100), 140 (2), 139 (23), 129 (5), 116 (26), 115 (6), 111 (14), 102 (6·5), 101 (96), 87 (10), 84 (14), 74 (28), 69 (33), 59 (69·5), 43 (92·5). The *p*-bromophenacyl ester was recrystallized from EtOH–H_2O as needles, mp 149·5°.

The cations. These were recovered from the ion exchange column by elution with 200 ml of 4 M HCl. Standards and samples used for AAS determination of Mg were adjusted to contain 1500 ppm of Sr^{2+}.

Acknowledgements—The authors thank Mr. D. J. Hamilton of Dept. of Primary Industries, Brisbane for the MS determination and Mr. R. J. Finlayson of the University of New South Wales for detection of the elements listed in Table 1. Permission by the Department of Agriculture, Stock and Fisheries to publish these results is acknowledged. The heartwood deposit was brought to our notice by the Papua New Guinea Department of Forests. The plant was identified by Mr. P. J. Eddowes of the above Department and is identified by registration no. 48439.

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