Apparent Organobromine Compounds in Higher Plants by Neutron-Activation Analysis

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In a broad search (1) for organochlorine compounds in plant parts never exposed to pesticides an occasional occurrence in plants of apparent organobromine compounds was demonstratable by neutron-activation analysis (2). Finely ground plant parts were dehydrated with chloride- and bromide-free isopropyl alcohol then coextracted with chloride- and bromide-free n-hexane; the hexane extract was washed free of isopropyl alcohol and of inorganic halides with chloride- and bromide-free distilled water, concentrated about 50-to-1, then thermal-neutron activated and scanned, after a suitable decay interval, for 37-minute Cl^{38} and for both 18-minute Br^{80} and 36-hour Br^{82} by gamma-ray spectrometry (2). In Table I are presented typical results from plants and some of their parts grown on virgin land never exposed to a pesticide. Some of these data represent crops and harvests over several years (1).

Bulletin of Environmental Contamination & Toxicology,
Vol. 1, No. 4, 1966, published by Springer-Verlag New York Inc.

Table I.

Apparent organochlorine and organobromine residues in plant parts.

Plant	Plant part	Chlorine p.p.m.[a,b]	Bromine p.p.m.[a,c]
<u>Atriplex lentiformis</u>	Leaves and stems	2.4, 3.3	4.40±0.03 4.90±0.03
<u>Schinus Molle</u>	Tops	1.7, 1.4	1.10±0.02
<u>Suaeda</u> sp.	Whole plants	5.5, 3.3	0.30±0.01
Beets	Tops	0.3	0.15±0.02
Broccoli	Heads	Nil	0.13±0.01
Chard	Foliage	0.2	0.20±0.01
Corn, sweet	Leaves	0.2, 0.3	0.51±0.02
Cucumber	Seeds[d]	1.7, 1.4[e]	9.91±0.05
Barley	Whole plants	---	0.34±0.02 0.26±0.02
Lima beans	Whole plants	0.9	0.20±0.01
Onions	Whole plants	0.1	0.18±0.01 0.27±0.05
Peppers	Whole plants	0.4	0.18±0.01
Radishes	Tops	Nil	0.10±0.01
Zucchini	Fruits	0.2, 0.3	0.13±0.01
Several crops	Edible parts	---	~1[f]

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[a] Duplicate values are from separate samples and usually separate crops. Gamma radiation measurements at 1.65 Mev for Cl and 0.55 Mev for Br. The hexane, isopropyl alcohol, and water used in preparing samples for analysis were free of chlorides and bromides, within the limits of detection by neutron-activation analysis, after 50-to-1 concentration.

[b] Reference (1).

[c] Reproducibility from counting statistics.

[d] Commercial source.

[e] 555, 605, and 672 p.p.m. Cl by combustion chloride analysis (15) because of the high interference of Br^- in the direct potentiometric determination of Cl^-.

[f] Reference (3).

Neutron-activation analysis for bromine is highly specific and reproducible (2) so there can be little doubt that this element was actually present in the amounts indicated. Whether it was actually organically bound bromine is another matter in view of the recently demonstrated (1) solubility in hexane, and carry-over through repeated water washes of hexane solutions, of chloride ion as a phosphatidyl choline complex. Despite the lack in Table I of any relationship between chloride and bromide values for specific samples, bromide ion may also complex with these omnipresent lecithin-type substances to give false positives in organobromine-determining pesticide and other residue analyses involving added or metabolized organobromine compounds. Thus, one should be immediately suspicious of all "organobromine" data below about 0.5 p.p.m. (cf. Table I). On the other hand, except possibly for some Senecio spp. there are apparently no naturally occurring organochlorine compounds elaborated by higher plants (4), but there are claimed some plant-elaborated organobromine and organofluorine compounds and numerous organoiodine compounds, as illustrated in Table II.

The only really positive organohalides in higher plants would be the fluorine compounds in the two Dichapetalum spp. The report of bromoacetic acid in wine is rather old and somewhat doubtful because this chemical has sometimes been used as a wine "preservative". The organoiodine compound(s) reported in wheat do not seem to have been very well characterized as yet, and even with jaconine some authors feel that the iodine present is an artifact of the isolation. Thus, there are organochlorine and organobromine compounds from the microorganisms and bromine and iodine compounds from the more complex thallophytes as the only really positively identified naturally occurring organohalogen compounds, plus possibly jaconine.

Table II.

Examples of organohalogen compounds as plant elaborates.

Halogen	Compound	Plant	Illustrative reference
Bromine	Br-antibiotics[a/]	Microorganisms	5
	Bromophenols	Algae	6
	Bromophenols	Seaweed	7
	Bromoacetic acid	Wine (grapes?)	14
Chlorine	Jaconine	Senecio jacobaea	8
	Several	Microorganisms	4,5
Fluorine	Fluoroacetic acid	2 Dichapetalum spp.	9
Iodine	Iodo-tyrosins	Marine algae	10,11
	Triodoacetaldehyde	Seaweed	12
	Organic iodine	Wheat	13

[a/] Organochlorine-antibiotic producing organisms grown in nutrient media from which chloride was excluded and bromide was available.

It is suggested that future work to isolate and measure by any technique organohalogen compounds in plant parts incorporate a step whereby the organic extract is washed several times also with 10% nitric acid solution (1) to destroy any lecithin-halide-ion type complexes that may be present in solution. Depending upon the measuring technique [(e.g., direct potentiometric analysis after combustion (15)], traces of bromine from either organic or inorganic bromides could result in a large error in chloride analysis, as with the cucumber seeds in Table I (cf. footnote *e*); however, the present data do not *consistently* demonstrate such a probability.

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Paper No. 1661, University of California Citrus Research Center and Agricultural Experiment Station, Riverside, California. Supported in part by U. S. Public Health Service Grant No. EF-0029 from the National Institutes of Health.