Table 1. Amino acid composition of Viscotoxin A*ox2*. The results are expressed as number of residues per molecule.

Amino acid	Found	Nearest integer	Amino acid composition of Viscotoxin A*ox3* [4]
Lysine	3.01 [a]	3	4
Arginine	2.75 [a]	3	3
Cysteic acid	6.25 [a]	6	6
Aspartic acid	4.07 [a]	4	4
Threonine	3.98 [b]	4	5
Serine	6.93 [b]	7	5
Glutamic acid	0.83 [a]	1	—
Proline	3.08 [a]	3	5
Glycine	5.10 [a]	5	4
Alanine	1.99 [a]	2	3
Valine	0.34 [b]	1	—
Isoleucine	2.83 [b]	3	3
Leucine	1.11 [b]	1	2
Tyrosine	1.87 [b]	2	2
Phenylalanine	0.82 [a]	1	—

[a] Mean value of 2 determinations.
[b] Value extrapolated to zero time or maximum value as calculated from analysis of samples hydrolyzed for 24 h and 72 h.

the total number of amino acid residues is 46 in both substances.

Acknowledgements. This work was supported by a grant (B69-13X-2084-03A) from the *Swedish Medical Research Council.*

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Received February 6, 1970.

Ageratone and Dihydroageratone, New Benzofuran Derivatives from *Ageratum houstonianum* Mill.

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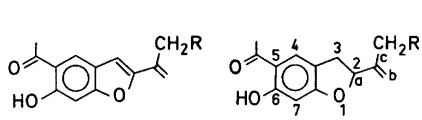
The genera *Ageratum* and *Eupatorium* which are botanically closely related have also been shown to be chemically related since both *Ageratum* [1,2] and *Eupatorium* [3] species contain chromenes.

Benzofuran derivatives such as euparin (*1*) [4] and hydroxytremetone (*2*) [5] are also present in *Eupatorium* species. We now wish to report the isolation of two new acetates, ageratone (*3*) and dihydroageratone (*4*) from the roots of *Ageratum houstonianum* Mill. Their structural relationship to euparin (*1*) and hydroxytremetone (*2*) further confirms the chemical relationship between the two genera.

Ageratone (2-acetoxyisopropenyl-5-acetyl-6-hydroxybenzofuran) (*3*) (m.p. 122—124°C). The IR spectrum (KBr) indicates the presence of an acetate ester (1735 cm^{-1}) and a hydrogen-bonded aromatic carbonyl group (1632 cm^{-1}). This is confirmed by



1 R = H
3 R = OAc

2 R = H
4 R = OAc

the NMR spectrum (Table 1) which has two sharp three proton singlets at τ 7.88 (acetate methyl) and 7.32 (aromatic acetyl methyl). The hydrogen bonded hydroxyl proton resonates as a sharp singlet at τ −2.15.

Moreover, the NMR spectrum reveals the presence of two aromatic protons at τ 2.18 and 3.31, two well separated methylene protons at τ 3.90 and 4.37 and the furanoid proton at τ 2.93. Finally the methylene protons of the acetate carrying carbon atom resonate as a two proton

Table 1. NMR spectra of euparin (*1*), ageratone (*3*), hydroxytremetone (*2*), and dihydroageratone (*4*). For numbering, see figure.

	2a	2b		2c		3	4	5	6	7
Euparin (*1*)	—	4.30	4.88	7.93		3.12	2.23	7.40	−2.43	3.56
Ageratone (*3*)	—	3.90	4.37	5.03	7.88	2.93	2.18	7.32	−2.15	3.31
Hydroxytremetone (*2*)	4.7	4.9	5.1	8.25		6.9	2.52	7.48	−2.97	3.63
Dihydroageratone (*4*)	4.7	4.6	4.7	5.32	7.94	6.8	2.49	7.48	−3.03	3.62

singlet at τ 5.03. These data are in good agreement with the NMR spectrum of euparin (*1*) (see Table 1).

The UV spectrum of ageratone (*3*) [λ_{max} (EtOH) 240 nm (ε 4700), 325 nm (10 000)] is markedly different from the UV spectrum of euparin. We ascribe this to differences around the bond connecting the isopropenyl group to the furan nucleus.

The mass spectrum of ageratone is dominated by peaks at *m/e* 274 (M^+), *m/e* 259 $(M-15)^+$ and *m/e* 43 ($CH_3C{\equiv}O^+$). There is no loss of acetic acid, but loss of ketene occurs to some extent. The elemental composition of ageratone as $C_{15}H_{14}O_5$ is determined by accurate measurement of the molecular ion peak (found: 274.0841 as calculated).

Dihydroageratone (2-acetoxyisopropenyl-5-acetyl-6-hydroxy-2,3-dihydrobenzofuran) (*4*). The IR spectrum ($CHCl_3$) of the oily acetate *4* indicates the acetoxy group (1740 cm^{-1}) and a hydrogen-bonded aromatic carbonyl (1640 cm^{-1}). The NMR spectrum reveals the presence of a primary acetate grouping (2-H singlet at τ 5.32 and 3-H singlet at τ 7.94). Furthermore, both the UV spectrum [λ_{max} (EtOH) 222 nm (ε 16 400), 237 nm (ε 20 300), 278 nm (ε 18 700), 325 nm (12 800)] and the rest of the NMR spectrum are in good agreement with the spectral data for hydroxytremetone (*2*) (see Table 1 and a following communication).[6]

The acetyl methyl group and the hydroxyl proton resonate as sharp singlets at τ 7.48 and −3.03, respectively, the two aromatic protons at τ 2.49 and 3.63 and the methylene protons at τ 4.6 and 4.7, as in the NMR spectrum of hydroxytremetone (*2*) not so well spread. Finally the hydrogens of the dihydrofuran nucleus give rise to multiplets centered at τ 6.8 (2 H C-3) and 4.7 (1 H C-2).

The mass spectrum of dihydroageratone (*4*) shows loss of acetic acid from the molecular ion which has not been observed in the mass spectrum of ageratone (*3*). Transitions like $276^+ \rightarrow 203^+ + 73$ ($\cdot CH_2OAc$) and $276^+ \rightarrow 176^+ + 100$ ($CH_2{=}CH{-}CH_2OAc$) also support the suggested structure. The molecular composition as $C_{15}H_{16}O_5$ was determined by accurate measurement of the molecular ion peak (found: 276.0991, calc. 276.0998).

Acknowledgement. One of us (S.C.) is grateful to *Direktoratet for utviklingshjelp* (*NORAD*) for a fellowship.

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Received February 3, 1970.