Tetrahedron Letters No.27, pp. 2573-2575, 1967. Pergamon Press Ltd. Printed in Great Britain.

ESSENTIAL OIL OF AGERATUM CONYZOIDES - ISOLATION AND STRUCTURE OF TWO NEW CONSTITUENTS

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(Received 10 April 1967)

The isolation and structure of ageratochromene (I) from the essential oil of *Ageratum houstonianum* has been reported (1). Moudgill (2) isolated a compound of molecular formula $C_{12}H_{16}O_2$ from the essential oil of *Ageratum conyzoides* (Appa grass) of Indian origin. No structure was proposed for this compound. Joly (3) has reported that the oil of *Ageratum conyzoides* from French Upper Ubangi consists largely of a phenolic ester. We now wish to report the isolation and structure of two more constituents from the essential oil of *Ageratum conyzoides* collected in Kerala, India.

Following a rigorous column chromatography (basic alumina - highly active) and preparative layer chromatography (silica gel G), two new constituents,[*] designated A[†] and B (20% and less than .5% respectively), were isolated from the essential oil (obtained in .157% yield from the semi-dried plant).

Structure of compound A: b.p. 142-144°/15 mm; n_D^{25} 1.5578; empirical formula $C_{12}H_{14}O_2$; UV: $\lambda_{max.}^{EtOH}$ 280 (ϵ 6644) and 304 mμ (ϵ 5844); IR (neat): 1647 (C=C stretch), 1616, 1570, 1502 (aromatic), 1372, 1387 (CH_3 bending), 1039, 1031 (OCH_3), and 756 cm^{-1} (Ph-C out of plane vibration); NMR ($CDCl_3$); peaks at 83 (6H), 221.5 (3H), doublet at 323.8 (1H) and multiplets between 368.5-413 cps (4H). The physical data suggested a 6-demethoxyageratochromene (II) structure. The IR spectrum of an authentic sample of 7-methoxy-2,2-dimethylchromene (4) was found identical with that of the natural product. Further, refluxing compound A with 2,4-dinitrophenylhydrazine in n-butanol in the presence of conc. sulphuric acid gave a 2,4-dinitrophenylhydrazone, m.p. 219-220°, undepressed in m.p. with an authentic sample (4) thereby confirming the assignment (II).

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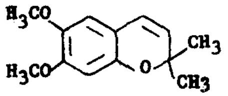
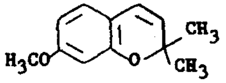
[*] Further attempts to isolate the other components in a pure form are being made.

[†] All new compounds gave acceptable elemental analyses. NMR spectra were recorded using a Varian A-60 spectrometer with TMS as internal standard.

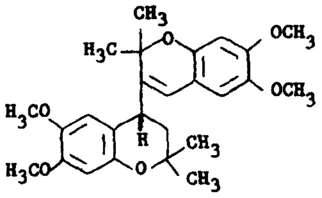
Structure of compound B: m.p. 154-154.5°; mol. wt. (mass spectrometry)* 440; $[\alpha]_D^{24}$ -7.1° (0.7% in $CHCl_3$); UV; $\lambda_{max.}^{EtOH}$ 293 (ϵ 8,232) and 323 (ϵ 9,086); IR (Nujol): 1658 (C=C stretch), 1618, 1595, 1508, 1460 (aromatic), 1370, 1381 (CH_3 bending), 1242, 1038 (OMe), 865 (out of plane bending H of phenyl) and 755 cm^{-1} (Ph-C out of plane vibration).



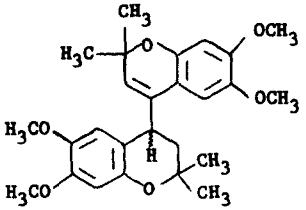
I



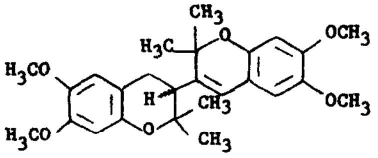
II



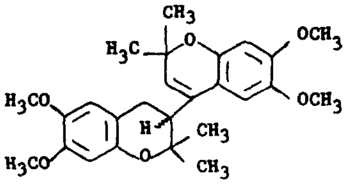
III



IV



V



VI

Ageratochromene (I) shows $\lambda_{max.}$ at 278 and 322 mμ while its dihydro derivative shows $\lambda_{max.}$ at 293 mμ. The 293 and 323 mμ absorption bands of compound B suggest the presence of a styrene as well as an alkyl benzene fragment (5). The mass spectral fragmentation* (ions at 221 and 219) with the UV data suggest that compound B is probably a dimer of ageratochromene (I). Four alternate structures (III to VI) can be written for the dimer. The NMR spectrum ($CDCl_3$) of compound B shows 4 distinct CH_3 singlets (76.4, 85.9, 90.9 and 95.4 cps), multiplet centered at 111.4 (2H), 208 (1H) cps and peaks at 223.5, 227 and 231 cps (12H). In the vinyl proton region, spectrum shows sharp singlets at 360 (1H), 383.5, 386 (3H) and 397.5 cps (1H). Structures (V) and (VI) do not represent the dimer as the NMR spectrum does not show two benzylic protons (6). The β-proton of a substituted styrene invariably gives signals in the NMR spectrum between 300 to 350 cps (6). The spectrum of compound B does not show any proton in this region, and this rules out structure (IV) for the dimer. Hence, structure (III) is tentatively assigned compound B, a dimer of ageratochromene (I). Further work on the stereochemistry and also its synthesis is in progress and will be reported elsewhere.

ACKNOWLEDGMENT: We wish to thank Prof. George R. Pettit and Prof. D. K. Banerjee for helpful discussions. We also thank the Indian Institute of Science, Bangalore, for the award of a predoctoral research fellowship to one of us (MT).

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*We wish to thank Dr. J. S. Shannon, Division of Coal Research, C.S.I.R.O., Chatswood. N.S.W., Australia, for this determination

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