

Structure of a Dimer of Ageratochromene

By T. R. Kasturi* and E. M. Abraham, Department of Organic Chemistry, Indian Institute of Science, Bangalore-560012, India

Peter Brown, Department of Chemistry, Arizona State University, Tempe, Arizona, 85281, U.S.A.

A solid obtained in the dimerisation of ageratochromene (6,7-dimethoxy-2,2-dimethyl-1-benzopyran) (II) in the presence of acid has been shown to be 5,6,6a,6b,7,12b-hexahydro-1,2,10,11-tetramethoxy-5,5,7,7-tetramethylcyclopenta[1,2-*c*:5,4,3-*d'**e'*]bis[1]benzopyran (IV) by a study of its n.m.r. and mass spectra.

We have recently reported^{1,2} the isolation of a dimer (I) of ageratochromene from the essential oil of *Ageratum conyzoides*, and its synthesis by dimerisation of ageratochromene (II). From the dimerisation reaction in methanolic hydrochloric acid, we isolated² two more solids in addition to the expected dimer (I). The same materials are obtained, in higher yield when the dimerisation is carried out in acetic acid-sulphuric acid. We now discuss the structure of one of these solids.

The u.v. spectrum of this compound showed λ_{\max} 218 (ϵ 11,730) and 291 nm (5380), indicating the presence of a chroman unit. The presence of an aromatic ring (1620 cm^{-1}) and a *gem*-dimethyl group³ (doublet at 1370

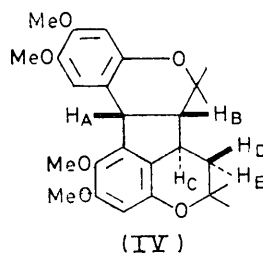
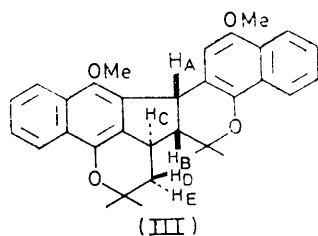
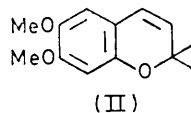
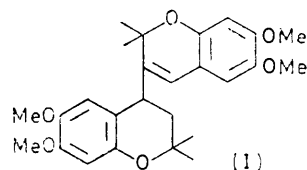
no coupling to any other protons; their separations at 60 and 100 MHz are in the expected ratio of 6:10. These methyl signals must arise from two *gem*-dimethyl groups.

Cotterill *et al.*⁴ have used spin-decoupling and deuteration experiments to prove the structure of isolapachenole (III).⁵ A comparison of the n.m.r. data for our compound with those for isolapachenole (Table) showed that

N.m.r. assignments for the dimer (IV) and isolapachenole (III)⁵

Dimer (IV)		Isolapachenole (III)	
δ	Assignment	δ	Assignment
1.27, 1.35, 1.42, 1.5	4 \times Me	1.25, 1.4, 1.48, 1.6	4 \times Me
1.3—1.6	H _E	1.3—1.6	H _E
2.05—2.4	H _B and H _D	2.16—2.42	H _B and H _D
3.0—3.35	H _C	3.05—3.4	H _C
3.78, 3.81	3 \times OMe	3.95, 4.05	2 \times OMe
3.9	1-OMe*		
4.45	H _A	4.7	H _A
6.25, 6.37, 7.3	ArH	7.2—7.6, 7.9—8.3	ArH

* A molecular model reveals that this methoxy-group is likely to be more deshielded than the others.



and 1380 cm^{-1}) was indicated by its i.r. spectrum. The n.m.r. spectrum showed the presence of only three aromatic protons (sharp singlets at δ 6.25, 6.37, and 7.3) and no olefinic protons (see Figure).

The 60 and 100 MHz spectra of this solid showed a doublet at δ 4.45 (1H) with the same separation (7 Hz) in each case; this must arise from a single nucleus, probably a doubly benzylic proton. The separations of the three singlets (12H) at δ 3.78, 3.81, and 3.90 in the 60 and 100 MHz spectra are in the ratio 6:10; hence these signals must be due to four methoxy-groups. The four methyl signals at δ 1.27, 1.35, 1.43, and 1.5 are distinct and show

the former probably has a similar dimeric structure (IV); the n.m.r. signals were assigned as indicated in the Table. The stereochemistry of compound (IV) may be as indicated on the basis of Cotterill's work.⁴

The mass spectrum (Scheme 1), especially the fragments at m/e 287 and 231, supports the structure assigned. However the spectra of compounds (I) and (IV) show significant differences. The base peak in the case of (I) is due to the loss of a methyl group, with formation of a benzopyrylium cation⁶ (m/e 425), whereas this fragment is of low abundance in the case of (IV). The cleavage of the central bond in (I) to give the fragments of m/e 219 and 221 supports the assigned structure, whereas there is no such cleavage in the case of the dimer (IV).

The formation of the dimer (IV) from ageratochromene (II) could take place as indicated in Scheme 2. Initial protonation of the styrene double bond produces a stable benzylic carbonium ion (V), which attacks the styrene double bond in a second molecule of ageratochromene (II) to give another carbonium ion (VI). This could

¹ T. R. Kasturi, E. M. Abraham, and M. Thomas, *Indian J. Chem.*, 1973, **11**, 91.

² T. R. Kasturi, and M. Thomas, *Tetrahedron Letters*, 1967, 2573.

³ K. Nakanishi, 'Infrared Absorption Spectroscopy—Practical,' Holden-Day, San Francisco, 1962, p. 20.

⁴ W. D. Cotterill, R. Livingstone, K. D. Bartle, and D. W. Jones, *Tetrahedron*, 1968, **24**, 1981.

⁵ R. Livingstone and M. C. Whiting, *J. Chem. Soc.*, 1955, 3631.

⁶ C. S. Barnes and J. L. Occolowitz, *Austral. J. Chem.*, 1964, **17**, 975.

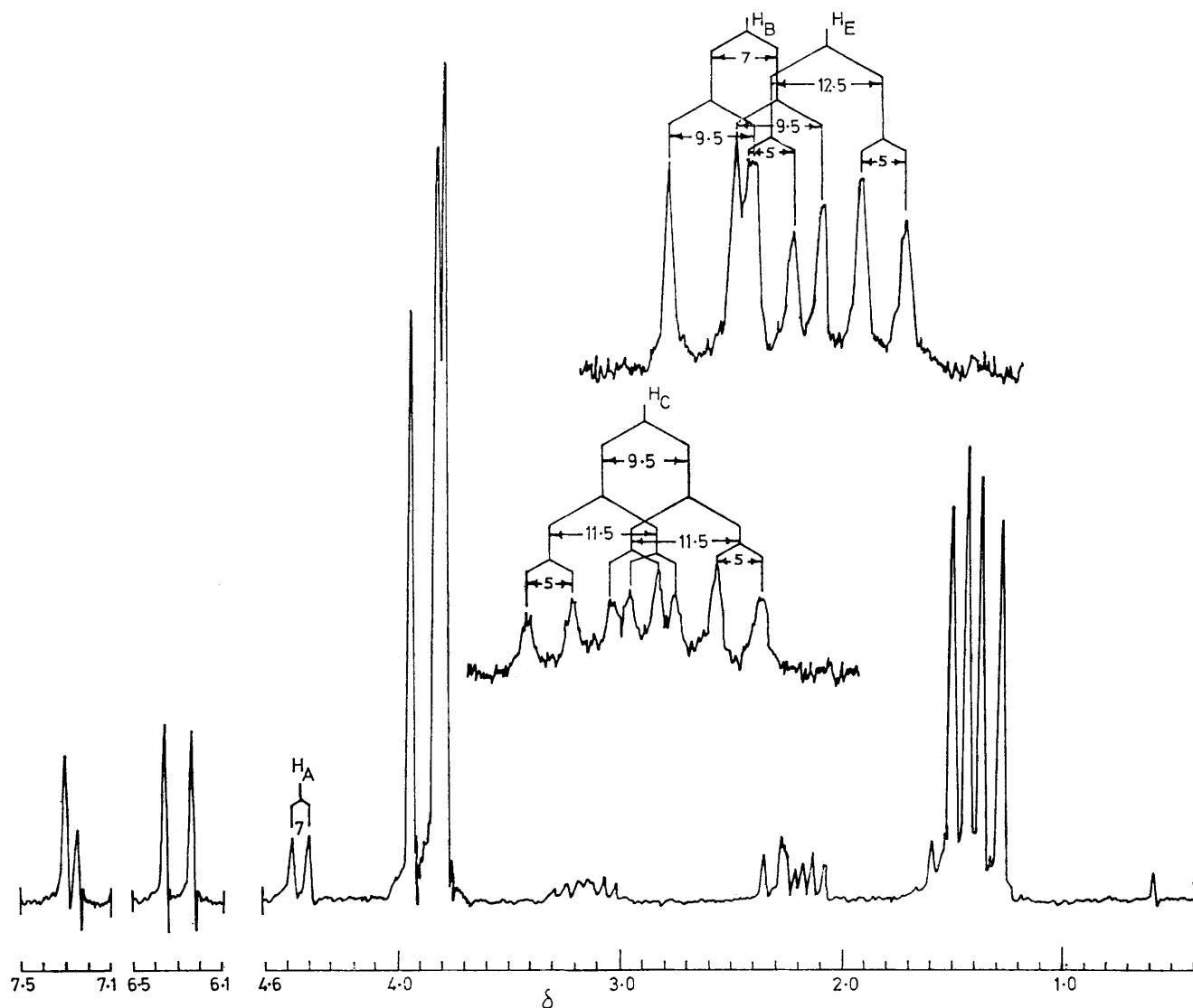
either lose a proton to give the dimer (I) or undergo Friedel-Crafts-type cyclisation⁵ to give the dimer (IV). This mechanism is supported by the fact that dimerisation of ageratochromene (II) with iodine* produces only the dimer (I).

EXPERIMENTAL

The u.v. spectrum was taken on a Unicam SP 700 spectrometer and the i.r. spectrum on a Perkin-Elmer 237

solvent and Me_4Si as internal standard. Low resolution mass spectra were recorded by Mr. E. Kelly on a Varian Atlas CH-4 mass spectrometer (70 eV) with a built-in direct inlet system. High resolution measurements were made by Mr. R. Scott on a Varian Atlas SM1B double-focusing spectrometer (resolution *ca.* 10,000; PFK as mass standard).

Dimerisation of Ageratochromene (II).—(a) *In methanolic hydrochloric acid.*² To a solution of ageratochromene (II) (0.4 g) in methanol (5.0 ml) was added methanol (5.0 ml)



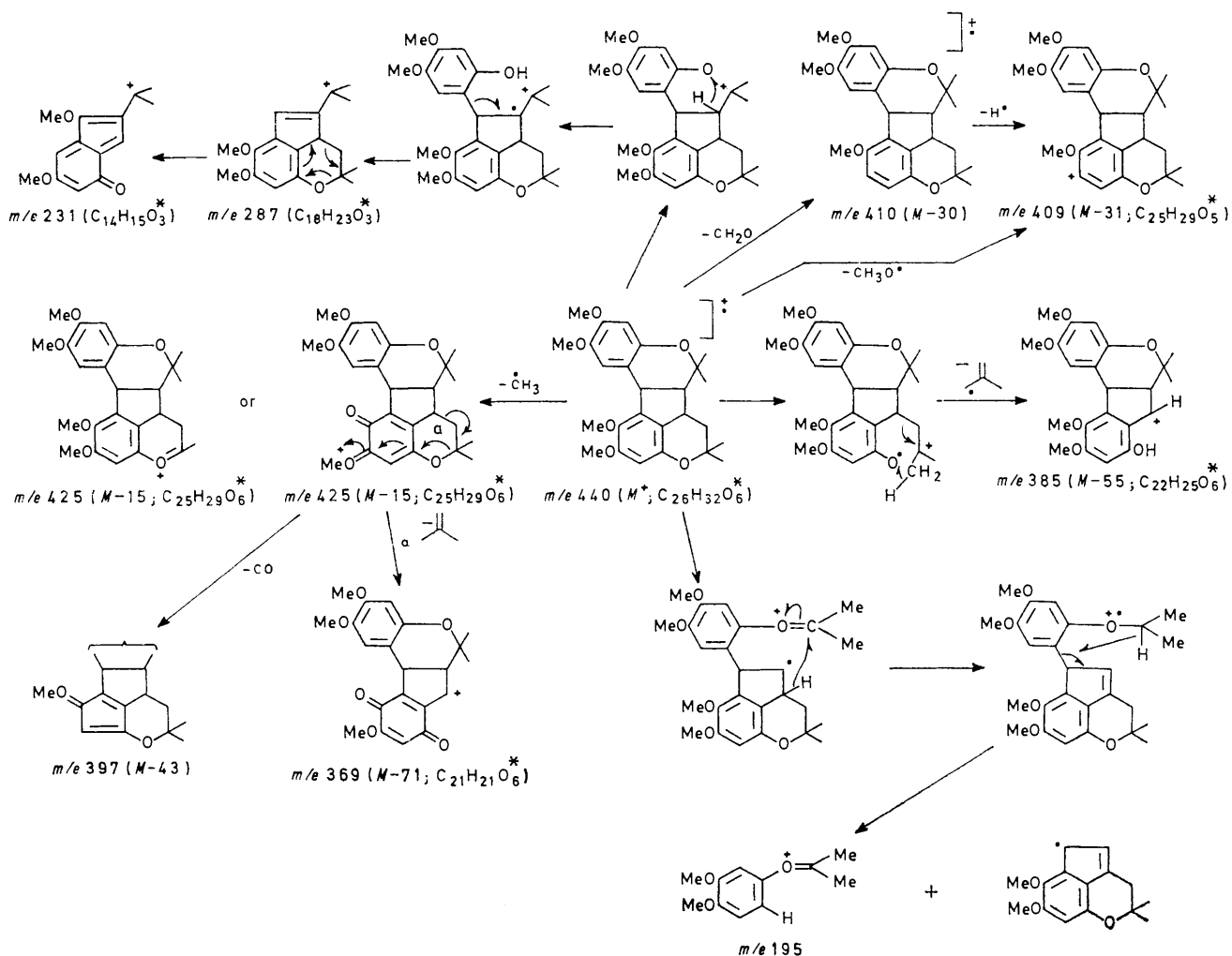
N.m.r. spectrum of the dimer (IV) (separations in Hz)

Infracord spectrometer. N.m.r. spectra were recorded on Varian A-60 and HA-100D spectrometers, with CDCl_3 as

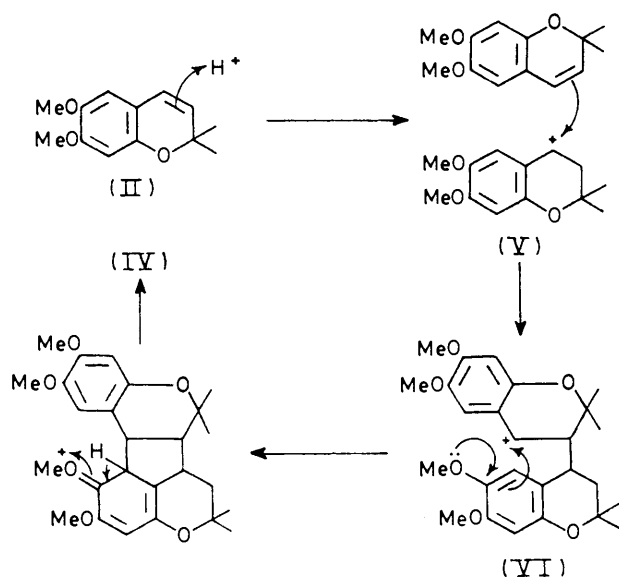
* Initially² the dimerisation was carried out with iodine in chloroform. Traces of acid in the chloroform were responsible for the formation of the dimer (IV) in addition to the dimer (I). However, when acid-free chloroform was used, only the dimer (I) was formed.

saturated with hydrogen chloride gas. The mixture was kept at room temperature for 15 h. The precipitate was filtered off, washed with water, dried, purified by preparative layer chromatography, and crystallised to give the *dimer* (IV) (0.04 g), m.p. 198–199° (R_f in CHCl_3 0.38) (Found: C, 70.6; H, 7.95. $\text{C}_{26}\text{H}_{32}\text{O}_8$ requires C, 71.0; H, 8.4%).

Purification of the residue yielded the dimer (I) (0.22 g;



SCHEME 1 Mass spectral fragmentation of the dimer (IV); compositions confirmed by high resolution measurements are indicated by an asterisk



SCHEME 2

m.p. 154°; R_F in $CHCl_3$ 0.3) and a more polar compound (0.02 g; R_F in $CHCl_3$ 0.28), m.p. 207°.

(b) *In acetic acid-sulphuric acid.* A solution of ageratochromene (II) (0.3 g) in glacial acetic acid (0.7 g) containing sulphuric acid (0.9 g) was left at room temperature for 20 h, then diluted with water and filtered. Preparative layer chromatography gave compound (IV), m.p. 198–199° (0.12 g), the dimer (I), m.p. 154° (0.05 g), and the polar compound, m.p. 207° (0.10 g).

(c) *With iodine in acid-free chloroform.* A solution of ageratochromene (II) (0.3 g) in acid-free chloroform (25 ml) containing iodine (0.3 g) was stirred at room temperature for 15 h, diluted with ether, washed successively with water, sodium thiosulphate solution, and water, dried (Na_2SO_4), and evaporated. The residue crystallised from methanol to give the dimer (I) (0.2 g), m.p. 154°, only.

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