Cyclopentadiene and cycloheptatriene provide an especially interesting test of the postulate. Cyclic delocalization *via* hyperconjugative π–σ interaction has been predicted for cyclopentadiene.[13] The exaltation observed supports this prediction although the smaller exaltation exhibited by 5,5-dimethylcyclopentadiene would imply that cyclic hyperconjugative delocalization may be less effective in the *gem*-dimethyl case. Cyclic delocalization through overlap of the indented 1–6 π-orbital lobes of the buckled ring has been invoked[14] to rationalize the structure and enhanced resonance energy of the cycloheptatriene system, a rationalization strongly supported by the sizeable exaltation exhibited by this system. Among the monocyclic hydrocarbons observed, cyclopentadiene and cycloheptatriene alone might reasonably have been expected to exhibit exaltation; they alone do so.

It is especially significant that the pseudo-aromatic compounds cyclooctatetraene, pentafulvene, heptalene, dibenzopentalene, and [16]annulene exhibit *small* exaltations which place them among the nonaromatic compounds. The above results confirm the absence of diamagnetic ring current in these systems and, consequently, their nonaromatic nature.

Observation of appreciable *negative* exaltations for [16]annulene and heptalene is consistent with the theory of induced *paramagnetic* ring currents.[15] However, the exaltations of pseudo-aromatic compounds establish that these $4n$ π-electron systems do not exhibit the strongly paramagnetic behavior predicted for bond-equivalent systems[8b] but demonstrate the quenching of orbital paramagnetism which accompanies bond alternation.[16,17] Magnetic susceptibility is clearly a sensitive indicator of the bond alternation in such systems.[17]

Experimental details and discussion of this work as well as investigations of additional carbocyclic and heterocyclic organic and inorganic systems will be presented in subsequent publications.

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(13) R. S. Mulliken, *J. Chem. Phys.*, 7, 339 (1939); C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 312; G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp 672–675.

(14) R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, 839 (1962); M. Trätteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

(15) See J. A. Pople and K. G. Untch, *ibid.*, **88**, 4811 (1966); H. C. Longuet-Higgins, Chemical Society International Symposium on Aromaticity, Sheffield, England, July 6–8, 1966; Special Publication No. 21, The Chemical Society, London, 1967, pp 109–111; F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967).

(16) G. Wagniere and M. Gouterman, *Mol. Phys.*, **5**, 621 (1962).

(17) T. Nakajima and S. Kohda, *Bull. Chem. Soc. Japan*, **39**, 805 (1966).

(18) National Science Foundation Fellow, 1962–1966.

Hyp J. Dauben, Jr., James D. Wilson,[18] John L. Laity
Department of Chemistry, University of Washington
Seattle, Washington 98105
Received September 25, 1967

The Structure of Thamnosin. A Novel Dimeric Coumarin System

Sir:

Thamnosin was first isolated from *Thamnosma montana* Torr. and Frem. and formulated as $C_{25}H_{26}O_5$.[1] Reinvestigation of the molecular formula by high-resolution mass spectrometry[2] forced a revision to $C_{30}H_{28}O_6$. Further investigations on this substance as indicated below have led to the structural assignment IV, a novel system not previously encounted in nature.

The presence of the coumarin chromophores (1725, 1610, and 1557 cm^{-1}), as well as trisubstituted and *trans*-disubstituted olefinic linkages (820 and 980 cm^{-1}, respectively), were immediately suggested from the infrared spectrum of thamnosin. The nmr spectrum of the latter[3] indicated the presence of a tertiary methyl group (8.78, probably allylic), a vinyl methyl (8.20), two methoxyl groups (6.29 and 6.27), an olefinic proton (4.75, multiplet), and a complex multiplet in the aromatic region (2.4–3.9, ten protons). An expansion of the latter region revealed the presence of a conjugated *trans*-disubstituted double bond (AB pattern at 3.98 and 3.82, J_{AB} = 16 cps).

Dihydrothamnosin, $C_{30}H_{30}O_6$, mp 226–228°, obtained by catalytic reduction (10% palladium on charcoal) showed a disappearance of the above-mentioned absorption for the disubstituted double bond. The chromophoric change created by the hydrogenation reaction as shown in the uv spectrum (λ_{max}^{MeOH} 227, 256, 298 (sh), and 333 mμ in thamnosin, λ_{max}^{MeOH} 224, 246 (sh), 254, 300 (sh), and 330 mμ in dihydrothamnosin) indicated that this olefinic system was linked to an aromatic chromophore, the latter most likely being a coumarin system. In fact, the virtual identity of the absorption maxima in the uv spectrum of the dihydro compound with that of suberosin (7-methoxy-6-isopent-2′-enylcoumarin)[4] dictated the presence of a 6-substituted 7-methoxycoumarin skeleton. Furthermore, the intensity of this absorption, being essentially *twice* that of suberosin, suggested that dihydrothamnosin consisted of two 7-methoxycoumarin moieties ($C_{10} \times 2$) and a C_{10}-alkyl residue linked to the 6 position of these molecules.

The nmr spectrum of dihydrothamnosin again showed sharp singlets for a tertiary methyl group (8.97), a vinyl methyl (8.26), two methoxyl resonances (6.25 and 6.22), an olefinic proton (4.83, multiplet), and a series of signals in the aromatic region (2.4–3.9) which now integrated for eight protons. The significant upfield shift of the tertiary methyl (8.78, thamnosin → 8.97, dihydrothamnosin) suggested that it was situated on a carbon atom adjacent to the reducible double bond.

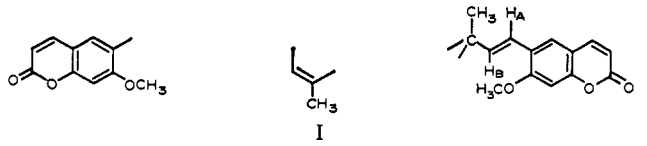
On the basis of the above evidence it was possible to postulate, as a working hypothesis, the following partial structure (I) for thamnosin.

(1) D. L. Dreyer, *Tetrahedron*, **22**, 2923 (1966).

(2) Mass spectra were determined on an AEI MS9 mass spectrometer. In all instances reported molecular formulas were established by this technique. Satisfactory elemental analyses were also obtained for all compounds.

(3) All nmr spectra were measured in deuteriochloroform (unless otherwise stated) with tetramethylsilane as the internal standard with a Varian HA-100 spectrometer. All signals are reported in τ units. In all instances the nmr data were highly informative due to the excellent separation of the signals which could be achieved with essentially all these compounds.

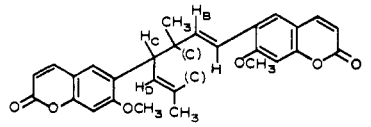
(4) F. E. King, J. R. Housley, and T. J. King, *J. Chem. Soc.*, 1392 (1954).



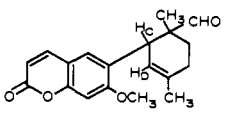
I

It is appropriate to note at this time that the mass spectrum of thamnosin was very striking, since there were virtually no peaks between the molecular ion (*m/e* 484, 8% abundance) and the base peak (*m/e* 242). This important result suggested that thamnosin was cleaved, under electron impact, into two equal halves, and therefore some structural symmetry must be present in this molecule. The nature of the C_{10}-alkyl residue mentioned above must accommodate this fragmentation pattern (see below).

Thamnosindiol, $C_{30}H_{30}O_8$, obtained by osmium tetroxide hydroxylation of thamnosin, possessed a uv spectrum identical with that of dihydrothamnosin, clearly indicating that the same double bond was involved in the hydrogenation and hydroxylation reactions. The nmr spectrum of the diol was highly informative and clearly indicated the presence of all 30 protons. Apart from the above-mentioned signals, one-proton doublets at 6.28 (H_C, J = 5 cps, see II) and 4.75 (H_D, J = 5 cps, see II) were of significance. Spin-decoupling experiments demonstrated that irradiation at the resonance frequency of the olefinic proton allowed the doublet at 6.28 to collapse into a singlet. This result, along with the chemical shift, indicated that H_C must be situated next to an aromatic system on the one hand and a fully substituted aliphatic carbon atom on the other. On the basis of the above, the partial structure of thamnosin could be expanded to II.



II

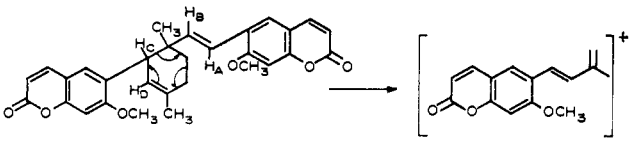


III

Periodic acid oxidation of thamnosindiol provided two aldehydic compounds designated as aldehyde I and aldehyde II. High-resolution mass spectra of these compounds established their molecular formulas as $C_{11}H_8O_4$ and $C_{19}H_{20}O_4$, respectively, and provided conclusive evidence that this reaction cleaves the diol into two compounds *without* any loss of carbon.

Aldehyde I, λ_{max}^{MeOH} 255, 308, and 329 mμ, nmr [$(CF_2Cl)_2C(OD)_2$] −0.23 (Ar–*CHO*), 6.01 (CH_3O), was tentatively assigned the structure 7-methoxycoumarin-6-carboxaldehyde and this was established by comparison (mixture melting point, tlc, superimposable uv and ir spectra) with an authentic sample.[5]

Aldehyde II resisted crystallization, but data were obtained on tlc-pure material: ir 1720 and 1615 cm^{-1} (coumarin, saturated aldehyde); uv λ_{max}^{MeOH} 229, 254 (sh), 296 (sh), and 328 mμ; nmr signals: 0.73 (1 H, singlet, CHO), 2.45 (1 H, doublet, J = 9.5 cps, H–C_4 of coumarin), 2.85 (1 H, singlet, H–C_5 of coumarin), 3.31 (1 H, singlet, H–C_8 of coumarin), 3.84 (1 H, doublet, J = 9.5 cps, H–C_3 of coumarin), 4.76 (1 H, multiplet, H_DC=C–), 5.84 (1 H, doublet, H_CC<), 6.2 (3 H, singlet, CH_3O–C_7 of coumarin), 8.21 (3 H, singlet, CH_3C=C–), 8.82 (3 H, singlet, CH_3C<). These data, when taken in conjunction with the above results (only C_2H_4 and one degree of unsaturation still remain unaccounted in thamnosin), establish structure III for aldehyde II and, in turn, IV for thamnosin.



IV V

The mass spectrum of thamnosin is now readily explained by the well-known retro-Diels–Alder fragmentation process as indicated in IV → V (*m/e* 242). It is to be noted that such a fragmentation would be expected to be extremely facile in this instance, since benzylic and allylic bonds are involved and a highly stabilized ion (V) results. In fact, on the basis of the mass spectrum, structure IV was strongly favored even before much of the above data had been accumulated.

Numerous confirmatory experiments (epoxidation, further reduction, ozonization, etc.) were conducted to support the above proposals, but these will be presented in our detailed paper. In brief, the most important experiment in this regard involved controlled ozonolysis of dihydrothamnosin followed by catalytic reduction of the ozonide to yield a *single* compound which from spectral data was shown to be a keto aldehyde. In particular, nmr signals for the aldehydic proton (0.02, 1 H, doublet, J = 2 cps), a methyl ketone (7.87, 3 H, singlet), and the proton H_C (see IV) which appeared as a doublet (5.76, J = 2 cps, >CH_CCHO) should be noted. Decoupling experiments established that the carbon atom bearing H_C in thamnosin could only be connected to an aromatic system, a tetrasubstituted carbon atom, and a trisubstituted double bond whose olefinic proton was in turn coupled with H_C. The formation of the keto aldehyde, therefore, conclusively established the presence of the trisubstituted double bond in a cyclohexene system as postulated in IV.

Thamnosin represents a novel system which to the best of our knowledge has not been previously encountered in any natural source. A biosynthetic study on this molecule could be very interesting and is anticipated.

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(5) We are very grateful to Dr. F. E. King, Forest Products Research Laboratory, Aylesbury, Bucks, England, for supplying us with an authentic sample.

(6) Enquiries about this work should be directed to this author.

James P. Kutney,[6] Tadanobu Inaba
Chemistry Department, University of British Columbia
Vancouver 8, Canada

David L. Dreyer
Fruit and Vegetable Chemistry Laboratory
U. S. Department of Agriculture
Pasadena, California

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A Benzohomotropylium Cation

Sir:

The inclusion of the homoallylic interaction in the homotropylium cation I allows for the explanation of two unusual and significant features displayed by this