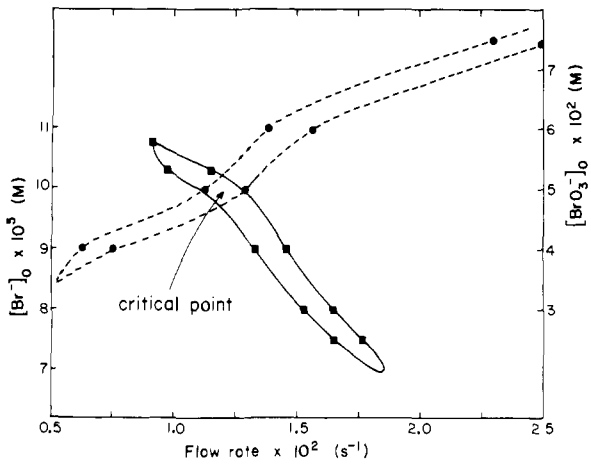

Figure 3. Phase diagram showing how region of oscillation shifts as constraints are varied in the region of the critical point. Solid line encloses region of oscillation as $[Br^-]_0$ and k_0 vary at fixed $[BrO_3^-]_0$ = 0.05 M. Dashed line encloses oscillatory region as $[BrO_3^-]_0$ and k_0 vary at $[Br^-]_0 = 1.0 \times 10^{-4}$ M. Other constraints as in Figure 1.

region about these points, small amplitude oscillations occur as shown in Figure 2.

If any of the constraints, $[BrO_3^-]_0$, $[Br^-]_0$, or flow rate k_0, is changed by as little as a few percent away from the critical point, oscillations cease and can be regained only by making a compensating change in one of the other constraints. The manner in which the oscillation region shifts with the constraints is shown in Figure 3.

The oscillator discovered here can function only in a flow reactor, since the necessary generation of bromide (process C in Noyes' scheme[5]), which occurs via the organic substrate in all previously found bromate oscillators, is replaced here by an input flow of bromide. The bromate–bromide–catalyst system is the simplest bromate oscillator yet found (or likely to be found). It may be called the minimal or basic bromate oscillator. As we show elsewhere,[12] it forms the cornerstone of a larger systematic classification of bromate oscillators, of which Noyes' five classes constitute one subsystem. It opens the way, with use of the cross-shaped diagram technique,[14] to developing a new class of bromate–bromide–catalyst–oxidizing substrate oscillators, which we shall discuss in a future publication. It is significant that though the range of bromate oscillators is considerably larger than contained in Noyes' classification,[5] the basic mechanistic description remains valid.

From a mechanistic point of view, the present system is probably the best understood chemical oscillator. The tiny region and small amplitude of oscillation agree beautifully with Bar-Eli's calculation.[10] The possibility of such behavior in the immediate region of a critical point has also been predicted from more general models.[15,16] Experimentally, however, this system constitutes perhaps the most difficult oscillator to work with, since very small differences in the constraints, even those involved in changing nominally identical input tubes in the flow system, can significantly shift the region of oscillation.

With the discovery of this basic bromate oscillator and of other oxyhalogen oscillators in flow systems, it appears that the development of a unified classification of not only bromate but chlorite and iodate oscillators as well is well within reach.

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Registry No. BrO_3^-, 15541-45-4; Br^-, 24959-67-9.

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A New Method for the Identification of the Origin of Natural Products. Quantitative ^2H NMR at the Natural Abundance Level Applied to the Characterization of Anetholes

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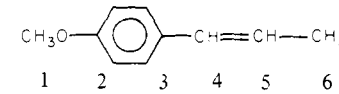
We have shown by high-field ^2H NMR spectrometry at the natural abundance level that very spectacular differences exist in the internal distribution of ^2H in organic molecules. This phenomenon has been exemplified in particular by the case of ethyl[1] and vinyl[2] derivatives. We show in this study of various anethole samples the potential of this new method as a very powerful tool for the characterization and identification of natural products from different origins.

It is known that significant variations exist in the overall deuterium content of organic molecules, and mass spectrometry has been successfully used to measure this total ^2H content in various species.[3] Unfortunately this technique requires relatively complicated and tedious preparation of the samples, and moreover it does not provide direct information about the internal distribution of ^2H. Although attempts have been made to obtain this information by means of complex chemical transformations of the sample,[4] to our knowledge no unambiguous conclusions have been drawn, and the interpretation of the variation in the overall ^2H contents in terms of chemical and biochemical mechanisms has usually remained speculative. It is therefore particularly interesting from both the analytical and mechanistic points of view to have a method at our disposal that is capable of providing direct access to the deuterium content of each specific molecular site.

The NMR spectra of ^2H at the natural abundance level obtained at 38.897 MHz with proton noise decoupling for various samples of trans anethole are composed of six lines characterized by the following chemical shift values.



	1	2	3	4	5	6
ppm/Me_4Si	3.75	6.80	7.23	6.28	6.08	1.83

As a result of the low natural abundance of ^2H (156×10^{-6}) with respect to ^1H, the probability of having bideuterated species is negligible, and the signals observed for the anethole samples correspond respectively to the six molecular species I–VI monodeuterated in sites 1–6. We shall define the intramolecular distribution of ^2H by means of the molar fractions $f(i)$ of molecules I–VI. These parameters can be derived from the area $S(i)$ of the individual deuterium signals on condition that suitable experimental parameters are selected.[5] Moreover in order to compare the ^2H content in a given site of a given anethole sample to that of the same site in another sample, we inserted coaxially into the measuring cell a tube containing a reference substance (CH_3CN).

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Table I. Isotopic Analysis of Anethole Samples from Different Origins[a]

origin	D/H, ppm	f(I)	f(II)	f(III)	f(IV)	f(V)	f(VI)	R(6)	R(2,3)	T_S
statistics		0.250	0.166	0.166	0.083	0.083	0.250	3	4	
fennel										
A	140.0	0.228	0.226	0.166	0.085	0.085	0.210	2.763	5.158	
B	143.0	0.231	0.230	0.163	0.079	0.081	0.216	2.805	5.104	2.650
mean	141.5	0.230	0.228	0.164	0.082	0.083	0.213	2.784	5.131	
CAT										
C	144.0	0.222	0.207	0.164	0.083	0.077	0.247	3.338	5.013	
D	141.5	0.227	0.212	0.156	0.079	0.073	0.253	3.343	4.863	
E	140.5	0.220	0.211	0.162	0.084	0.078	0.245	3.341	5.086	2.636
mean	142.0	0.223	0.210	0.161	0.082	0.076	0.248	3.340	4.962	
estragole F	151.5	0.223	0.186	0.148	0.115	0.075	0.254	3.417	4.493	3.058
synthesis G	136.0	0.250	0.176	0.170	0.053	0.081	0.270	3.240	4.152	2.495

[a] $f(i)$ are the molar fractions of the different deuterated molecules i and $R(i)$ the relative enrichment factors. Usually several spectra (three to eight) were recorded for each sample of anethole, and each spectrum was treated at least three times. The average values given for $f(i)$ and $R(i)$ are characterized by standard deviations of about 0.008 and 0.07, respectively. The D/H values have been obtained by mass spectrometry. They are referenced to the SLAP-SMOW scale.[6] The ^{2}H NMR spectra were obtained with a Bruker WM 250 spectrometer (5.87 T) using a 15-mm cell, an acquisition time of 6.8 s (sweep width 1200 Hz), and a 90° pulse (100 × 10^{-6} s); 2000–2500 scans were stored for each spectrum (T = 308 K). [b] SAT = star anise tree.

This external reference also enabled the relative overall ^{2}H contents of the various samples, $T_S = \sum_{i=0}^{6} S(i)/S(\text{ref})$, to be determined. The absolute values of these overall contents can be obtained by calibrating the results with respect to the international standard, SMOW.[6]

We investigated seven different samples of anetholes referenced A–G. Samples A and B were obtained from fennel (*Foeniculum vulgare* Miller) and samples C–E from star anise tree (*Illicium verum* Hooker). Anethole F was prepared by the isomerization of a sample of estragole extracted from turpentine, and anethole G was synthetized from anisole. Table I lists the values of the molar fractions $f(i)$ of the six monodeuterated species and those of the internal factors $R(i) = 3S(i)/S(CH_3O)$, which characterize the internal distribution referred to the CH_3O site.[1]

A statistical distribution of ^{2}H among the six molecular sites would correspond to probability factors, $R(i)$ statistics, equal to the number of hydrogens in each site. The values $f(i)$ statistics corresponding to the statistical distribution are also given in the table.

It may be emphasized first that a satisfactory agreement exists between the overall contents of ^{2}H as determined by mass and ^{2}H NMR spectrometry: D/H D/H = 68.4 + 27.2 T_S, with R = 0.99. In the present state of the experimental techniques, the NMR method is the less accurate but does not require tedious preparation of the samples, and the time consumption is reduced by a factor 1–5 for concentrated or liquid samples. The major interest of the NMR method, however, lies in its ability to provide information about the internal distribution. Indeed mass spectrometry is unable to make the distinction between anetholes obtained from fennel and those obtained from star anise tree since the D/H values are nearly equal for samples A–E. The quantitatively ^{2}H NMR method, on the contrary, succeeds in distinguishing these compounds. Thus we observe that methyl group 6 of the propenyl fragment is systematically enriched with respect to methoxy group 1 in the anetholes extracted from star anise tree, whereas the reverse situation is found in samples A and B obtained from fennel. This behavior is clearly shown by the $R(6)$ values. In fact a simple inspection of the spectra enables the immediate identification of each sample.[7] The synthetic anethole G is clearly distinguishable from the others, in particular by a strong ^{2}H depletion in the ethylenic site 4. Interestingly a noticeable enrichment of this ethylenic site 4 with respect to 5 is observed in the anethole F, which results from an isomerization of estragole, itself extracted from turpentine and characterized by a high deuterium content in the methylene group involved in the isomerization process. It is worth noting that the natural products exhibit a high aromatic ^{2}H enrichment, which is understandable if we bear in mind that the aromatic ring originates from photosynthesized carbohydrates having a high overall D/H content.[3c]

Registry No. *trans*-Anethole, 4180-23-8.

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(7) It should be noted that due to the limited number of samples investigated the quantitative conclusions given here may not necessarily extend to the whole population of anethole samples.

Total Synthesis of (±)-Mycorrhizin A and (±)-Dechloromycorrhizin A

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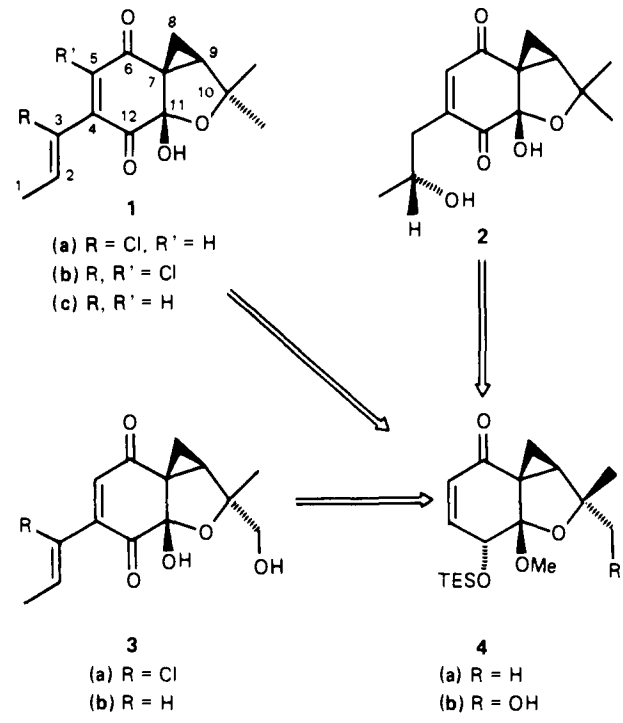
Mycorrhizin A (**1a**), an antibiotic first isolated by Wickberg



and Trofast[2] in 1977 from a sterile mycelium (ATCC No. 36554)

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