Absolute Configuration of (−)-Theaspirone

Sir:
In a previous communication the authors have described the structure of theaspirone, but the stereochemistry of (−)-theaspirone had not been elucidated.

This communication deals with the determination of the absolute configuration of (−)-theaspirone.

Recently, Nakatani et al. reported the configuration of C-2 in the synthetic one on the basis of the observation of NOE in NMR.

The authors determined the configuration at C-2 in (−)-theaspirone based on the observation of intermolecular NOE.

The change of the integrated intensity of H (C-2) was observed by saturation of CH₃ (C-6), while noticeable difference could not be found at CH₃ (C-2) as shown in Fig. 1.

Based on the comparison of our results with Nakatani’s data, the configuration of C-2 in (−)-theaspirone was determined as the structural formula(I).

The ORD, CD and UV spectra of (−)-theaspirone are shown in Fig. 2.

The ORD spectrum showed a negative Cotton effect arising from the $\pi \rightarrow \pi^*$ transition of the $\alpha,\beta$-unsaturated-ketone chromophore, and $n \rightarrow \pi^*$ transition showed a positive Cotton effect.

The CD spectrum arising from $\pi \rightarrow \pi^*$ transition was negative.

The sign of these data was the opposite of that assigned to the corresponding transition of the unsaturated-ketone chromophore in the ORD and CD spectra of (+)-abscisic acid (II) and (III), and was identical with the spectra of blumenol A (IV), B (V) and C (VI).

Cornforth et al. reported the absolute configuration in of (+)-abscisic acid (II) determined by applying the Mills empirical rule and ORD spectra.

Oritani et al. synthesized (+)- and (−)-abscisic acid from (+-) and (−)-α-ionone, and corrected the absolute configuration (II) which was determined by Cornforth et al. as the structural formula (III).

(−)-Theaspirone has $\alpha,\beta$-unsaturated ketone
and the relation of C-5 to carbonyl was the same for (+)-abscisic acid.

The authors determined the absolute configuration of C-5 in (-)-theaspirone as S-configuration on the basis of the comparison of ORD and CD spectra of (-)-theaspirone with Oritani's data.7)

From these results, the absolute configuration of (-)-theaspirone was determined to be 2-(R)-5-(S)-1-oxa-8-oxo-2, 6, 10, 10-tetramethylspiro-(4,5)-6-decene (I).

The authors would like to express their thanks to Professors T. Mitsui and H. Fukami, Kyûto University and to Professor T. Gotô, Nagoya University, for their helpful discussions in the course of this work. The authors are also indebted to Dr. T. Oritani, Tohoku University, for his kind supply of a copy of the ORD and CD spectra of (-)-abscisic acid.

REFERENCES


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Received June 15, 1972