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# MOLECULAR STRUCTURE OF 3β-ACETOXYATRACTYLON[1]

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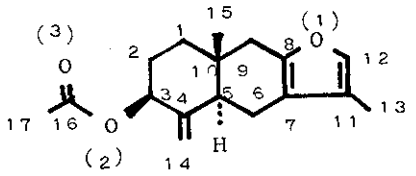
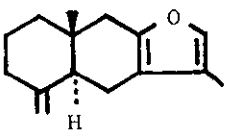
The structure of a sesquiterpene 3β-acetoxyatractylon (I) obtained from Atractylodes lancea was confirmed by means of an X-ray crystal structure analysis. The crystal is the orthorhombic, space group $P2_12_12_1$, and the structure was solved by MULTAN with final R-value 0.062.

Recently the structure of a new sesquiterpene, 3β-acetoxyatractylon (I) obtained from Atractylodes lancea has been elucidated by the aid of IR, NMR and Mass spectroscopy.[2] In this report, we present the three-dimensional molecular structure



I



II

and absolute configuration at C(3) of I confirmed by an X-ray crystal structure analysis.

Crystals of suitable quality for an X-ray analysis were obtained from a n-hexane solution as transparent prisms elongated along the c-axis. They belong to the orthorhombic, space group $P2_12_12_1$, with four molecules of an unit cell dimensions of a=10.679(3) Å, b=23.154(6) Å, c=6.105(2) Å; $\delta_{cal.}$=1.210 g/cm$^3$, $\delta_{obs.}$=1.22 g/cm$^3$. Reflection data were collected by means of a Rigaku automatic four-circle diffractometer with graphite monochromated Cu Kα radiation. A total of 1235 independent reflections with 2θ less than 140° were measured in the ω-2θ scanning mode, and of those 909 had |F| values greater than three times their standard deviations and were used in the structure analysis.

The crystal structure was solved by multi-solution method (MULTAN).[3] Phases of 240 reflections with $|E| \geq 1.3$ were determined and the resulting E map revealed all twenty non-hydrogen atoms. The structure was refined by the least-squares method of block-diagonal approximations including anisotropic temerature factors for non-hydrogen atoms. The hydrogen atoms except the ones in the methyl group of the molecule were obtained on the difference Fourier map. The final R-value was 0.062.[4,5]

The final carbon and oxygen atomic coordinates and their standard deviations are listed in Table I. The bond lengths and angles of the molecule are shown in Table II and III. They had been estimated with standard deviations in the range of 0.01-0.08 Å and 0.2-0.9°, respectively. The mean bond lengths and angles are in agreement with the normally accepted values. The torsional angles of the molecule are shown in Table IV. Based on the known absolute configuration of the relative compound, atractylon (II),[2] which showing a similar CD curve, the structure of I illustrates c-axis projection of the molecule. The absolute configuration of the asymmetric center at C(3) position was confirmed as S chirality.

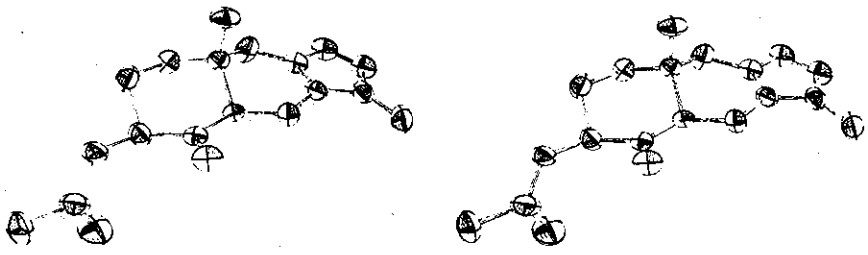


Figure 1. Stereoscopic view of β-acetoxyatractylon (I)

Table I. Fractional Atomic Coordinates (x $10^4$)

(Standard deviations are given in parentheses)

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| C(1) | 2178(6) | 4019(3) | 3594(14) | C(11) | 2877(7) | 1572(3) | 4143(15) |
| C(2) | 2645(7) | 4372(3) | 1685(15) | C(12) | 2137(7) | 1523(3) | 5931(17) |
| C(3) | 3959(6) | 4172(3) | 982(15) | C(13) | 3571(8) | 1119(3) | 2938(17) |
| C(4) | 3971(5) | 3532(3) | 432(13) | C(14) | 4431(7) | 3329(3) | -1406(14) |
| C(5) | 3445(6) | 3166(3) | 2301(12) | C(15) | 1136(6) | 3249(3) | 1324(15) |
| C(6) | 3462(6) | 2513(3) | 1765(13) | C(16) | 5530(6) | 4691(3) | -998(18) |
| C(7) | 2843(6) | 2187(3) | 3600(15) | C(17) | 5779(7) | 4997(3) | -3147(17) |
| C(8) | 2080(6) | 2444(3) | 5058(15) | O(1) | 1633(5) | 2045(2) | 6527(9) |
| C(9) | 1746(7) | 3063(3) | 5222(14) | O(2) | 4319(4) | 4508(2) | -911(2) |
| C(10) | 2111(6) | 3376(3) | 3036(14) | O(3) | 6266(4) | 4605(2) | 473(11) |

Table II. Bond Lengths (Å)

| | | | | | |
|---|---|---|---|---|---|
| C(1)-C(2) | 1.509 | C(1)-C(10) | 1.530 | C(16)-C(17) | 1.514 |
| C(2)-C(3) | 1.538 | C(5)-C(10) | 1.571 | C(3)-O(2) | 1.445 |
| C(3)-C(4) | 1.520 | C(9)-C(10) | 1.568 | O(2)-C(16) | 1.363 |
| C(4)-C(5) | 1.528 | C(7)-C(11) | 1.463 | C(16)-O(3) | 1.210 |
| C(5)-C(6) | 1.548 | C(11)-C(12) | 1.352 | C(8)-O(1) | 1.372 |
| C(6)-C(7) | 1.503 | C(11)-C(13) | 1.481 | C(12)-O(1) | 1.372 |
| C(7)-C(8) | 1.345 | C(4)-C(14) | 1.311 | | |
| C(8)-C(9) | 1.481 | C(10)-C(15) | 1.504 | | |

Table III. Bond Angles (°)

| | | | |
|---|---|---|---|
| C(1)-C(2)-C(3) | 111.2 | C(2)-C(3)-O(2) | 108.5 |
| C(2)-C(1)-C(10) | 111.4 | C(4)-C(3)-O(2) | 110.2 |
| C(2)-C(3)-C(4) | 111.3 | C(4)-C(5)-C(6) | 112.3 |
| C(4)-C(3)-C(2) | 110.5 | C(6)-C(5)-C(10) | 112.3 |
| C(3)-C(4)-C(5) | 112.3 | C(9)-C(10)-C(1) | 105.9 |
| C(4)-C(5)-C(10) | 112.3 | C(5)-C(10)-C(9) | 109.1 |
| C(1)-C(10)-C(5) | 108.7 | C(9)-C(10)-C(15) | 109.1 |
| C(5)-C(4)-C(14) | 125.6 | C(5)-C(10)-C(15) | 112.3 |
| C(3)-C(4)-C(14) | 123.1 | C(1)-C(10)-C(15) | 112.3 |

Table III. Bond Angles (°) (continued)

| | | | |
|---|---|---|---|
| C(5)-C(6)-C(7) | 109.2 | C(12)-C(11)-C(13) | 128.7 |
| C(6)-C(7)-C(12) | 122.8 | C(7)-C(11)-C(13) | 126.4 |
| C(6)-C(7)-C(11) | 129.8 | C(11)-C(12)-O(1) | 112.3 |
| C(11)-C(7)-C(12) | 107.2 | C(12)-O(1)-C(8) | 105.7 |
| O(1)-C(8)-C(7) | 110.3 | C(3)-O(2)-C(16) | 117.2 |
| O(1)-C(8)-C(9) | 122.3 | O(2)-C(16)-C(17) | 109.8 |
| C(7)-C(8)-C(9) | 128.1 | C(17)-C(16)-O(3) | 127.1 |
| C(10)-C(9)-C(8) | 108.7 | O(2)-C(16)-O(3) | 122.3 |
| C(7)-C(11)-C(12) | 104.6 | | |

Table IV. Torsional Angles (°)

| | | | |
|---|---|---|---|
| C(1)-C(2)-C(3)-C(4) | 56.3 | C(6)-C(5)-C(10)-C(1) | 178.5 |
| C(2)-C(3)-C(4)-C(5) | -53.7 | C(6)-C(5)-C(10)-C(15) | -57.2 |
| C(3)-C(4)-C(5)-C(6) | -179.6 | C(6)-C(7)-C(11)-C(12) | -179.1 |
| C(4)-C(5)-C(6)-C(7) | -175.7 | C(6)-C(7)-C(11)-C(13) | 0.4 |
| C(5)-C(6)-C(7)-C(8) | 18.6 | C(7)-C(11)-C(12)-O(1) | 1.0 |
| C(6)-C(7)-C(8)-C(9) | -2.6 | C(8)-C(7)-C(11)-C(13) | 178.2 |
| C(7)-C(8)-C(9)-C(10) | 15.8 | C(8)-C(9)-C(10)-C(15) | 78.5 |
| C(8)-C(9)-C(10)-C(1) | -160.6 | C(8)-C(9)-C(10)-C(5) | -43.7 |
| C(9)-C(10)-C(1)-C(2) | 174.4 | C(8)-C(7)-C(11)-C(12) | -1.3 |
| C(10)-C(1)-C(2)-C(3) | -59.3 | C(10)-C(5)-C(6)-C(7) | -48.7 |
| C(11)-C(7)-C(8)-C(9) | 179.4 | C(11)-C(12)-O(1)-C(8) | -0.4 |
| C(1)-C(2)-C(3)-O(2) | 177.2 | C(11)-C(7)-C(8)-O(1) | 1.1 |
| C(2)-C(3)-O(2)-C(16) | 139.4 | C(12)-O(1)-C(8)-C(7) | -0.5 |
| C(2)-C(3)-C(4)-C(14) | 128.9 | C(12)-O(1)-C(8)-C(9) | -178.9 |
| C(3)-C(4)-C(5)-C(10) | 53.5 | C(13)-C(11)-C(12)-O(1) | -178.4 |
| C(3)-O(2)-C(16)-O(3) | -3.5 | C(14)-C(4)-C(5)-C(10) | -129.2 |
| C(4)-C(5)-C(10)-C(9) | -169.3 | C(17)-C(16)-O(2)-C(3) | 175.8 |
| C(4)-C(5)-C(10)-C(1) | -54.4 | C(4)-C(3)-O(2)-C(16) | -99.0 |
| C(4)-C(5)-C(10)-C(15) | 70.0 | C(15)-C(10)-C(1)-C(2) | -66.6 |
| C(5)-C(6)-C(7)-C(11) | -163.8 | O(1)-C(8)-C(9)-C(10) | -166.1 |
| C(5)-C(10)-C(1)-C(2) | 57.5 | C(14)-C(4)-C(5)-C(6) | -2.2 |
| C(6)-C(7)-C(8)-O(1) | 179.5 | O(2)-C(3)-C(4)-C(5) | -173.1 |
| C(6)-C(5)-C(10)-C(9) | 63.6 | O(2)-C(3)-C(4)-C(14) | 9.5 |

## REFERENCES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(2) Y. Nishikawa, Y. Watanabe, T. Seto, and I. Yasuda, Yakugaku Zasshi, 1976, 96, 1089.

(3) G. Germain, P. Main, and M. M. Woolfson, Acta Cryst., 1971, A27, 368.

(4) Observed and calculated structure factors can be obtained from the authors upon request.

(5) The atomic scattering factors used in these calculations were taken from "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, 1968, p. 201.


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