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CONFORMATIONS OF RACEMIC 8α-METHOXY AND 8β-ACETOXY DERIVATIVES OF 1,1,4aβ-TRIMETHYL-2β-HYDROXY-1,2,3,4,4a,5,6,7,8,9-DECAHYDROPHENANTHRENE1) AS REVEALED BY X-RAY METHODS, AN EXAMPLE OF UNUSUALLY FLATTENED CONFORMATION OF CYCLOHEXENE RING

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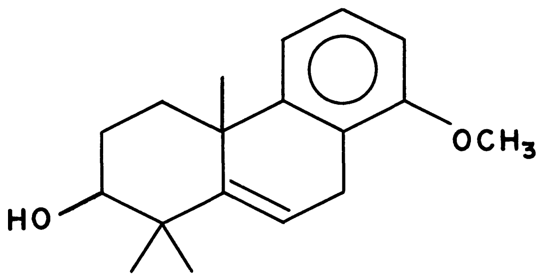
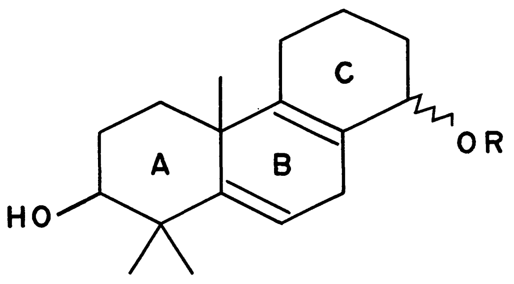
The conformations of the 8α-methoxy and 8β-acetoxy derivatives of 1,1,4aβ-trimethyl-2β-hydroxy-1,2,3,4,4a,5,6,7,8,9-decahydrophenanthrene have been studied by means of X-ray crystallographic analysis. As a result, it has been found that, in the former substance, the C ring of cyclohexene-type has an unusually flattened conformation and shows an unusual thermal behavior.

It has recently been found that the Birch reduction of I (racemate) with lithium in liquid ammonia and tert-butanol affords a tetrahydroanisole, II, against expectation.2) The methoxyl group in the unexpected product is quite easily replaced by an acetoxyl group in the acetolysis reaction.2) However, the configurations of the methoxyl and acetoxyl groups were difficult to determine by chemical means. In order to establish the configurations of these groups and to find the explanation of the high reactivity of II, the molecular structures of II and the acetolysis product, III, have been studied by means of X-ray crystallographic analysis.

The crystal data of II and III are summarized in Table 1. For either of the two crystals, the space group was assumed to be $P\bar{1}$ at the beginning of the



I



II R = CH_3

III R = $COCH_3$

Table 1. The crystal data

Compound	II	III
Formula	$C_{18}H_{28}O_2$	$C_{19}H_{28}O_3$
Mp	162-4°C	146-7°C
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a	10.502 Å	11.463 Å
b	11.706	11.509
c	7.488	7.430
α	71°33'	84°42'
β	91°46'	102°47'
γ	116°22'	115°40'
Z	2	2

study, which was confirmed later by successful refinement. The intensities of reflections with 2θ values up to 140° were collected on an automatic four-circle diffractometer with Cu $K\alpha$ radiation by using the 2θ-ω scan technique, and were corrected for the usual Lorentz and polarization factors. In all, 2276 and 2769 structure factors were obtained for II and III respectively.

Both structures were solved by the symbolic addition method,3) and refined by the block-diagonal-matrix least-squares method, anisotropic thermal motions being assumed for all the non-hydrogen atoms.4) After 26 and 28 hydrogen atoms were located in difference Fourier maps for II and III respectively, further least-squares refinement was repeated including these hydrogen atoms. The final R factors were 6.7 and 5.4% for II and III respectively. The atomic coordinates for II and III thus obtained are listed in Tables 2 and 3 respectively.

The molecular frameworks and conformations of II and III are shown in Figs. 1 and 2. It is found that the methoxyl group in II is located on the α-side (angular Me/OMe trans) of the molecule, while the acetoxyl group in III on the β-side. This shows that the configuration at the C(14) atom1) becomes inverted in the acetolysis. It should be noted that, notwithstanding inversion of the configuration, both the methoxyl and acetoxyl groups are axially bonded to the C rings with deformed half-chair forms. Seeing especially the methoxyl group takes the axial orientation although this conformation makes the C ring unstable (vide infra), the allylic axial methoxyl and acetoxyl on cyclohexenes seem to have an effect to stabilize the system, probably by allowing the transfer of some amount of π-electrons on the double bond into the overlapping antibonding orbital of the C-O bond.

The bond lengths and angles for II and III are given in Fig. 3. These values are all reasonable considering their standard deviations, except for the C(12)-C(13) bond in II. The C ring in II is found to show an unusual behavior. As will be seen in Fig. 4, the C(12) and C(13) atoms vibrate vigorously in the direction almost perpendicular to the mean plane of the C ring; the largest

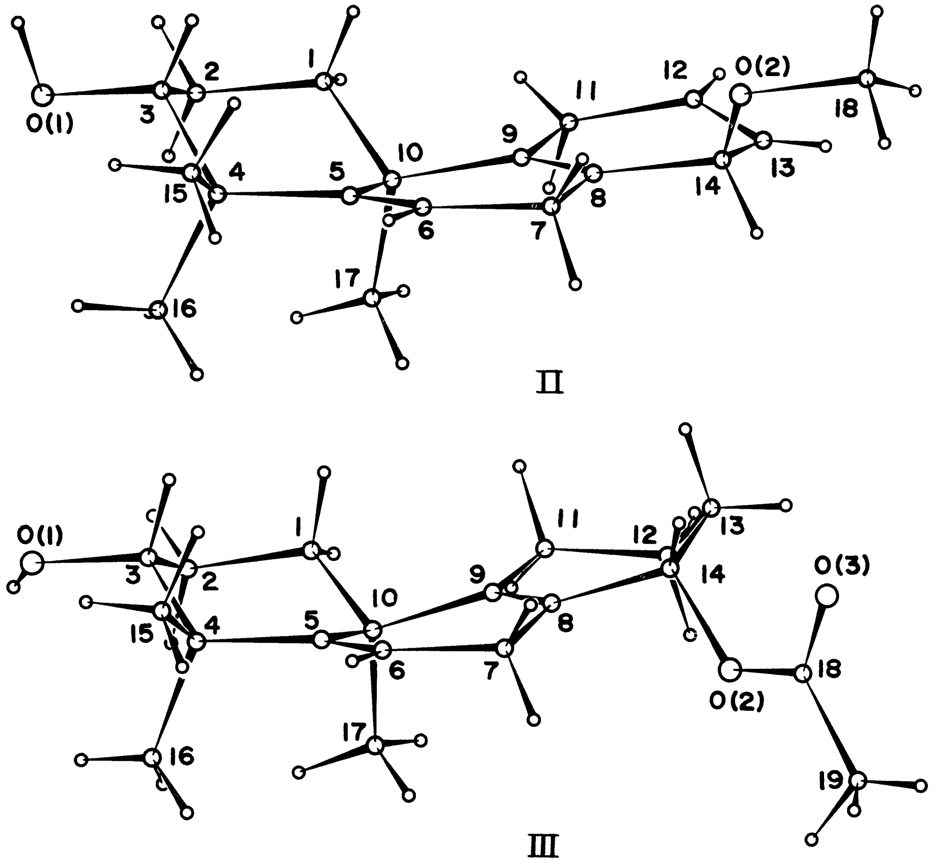


Fig. 1. The molecular frameworks and the numbering systems of the atoms. For II, the two hydrogen atoms that were not located in the difference Fourier map are not drawn. The α-side in the text corresponds to the β-side in these pictures.

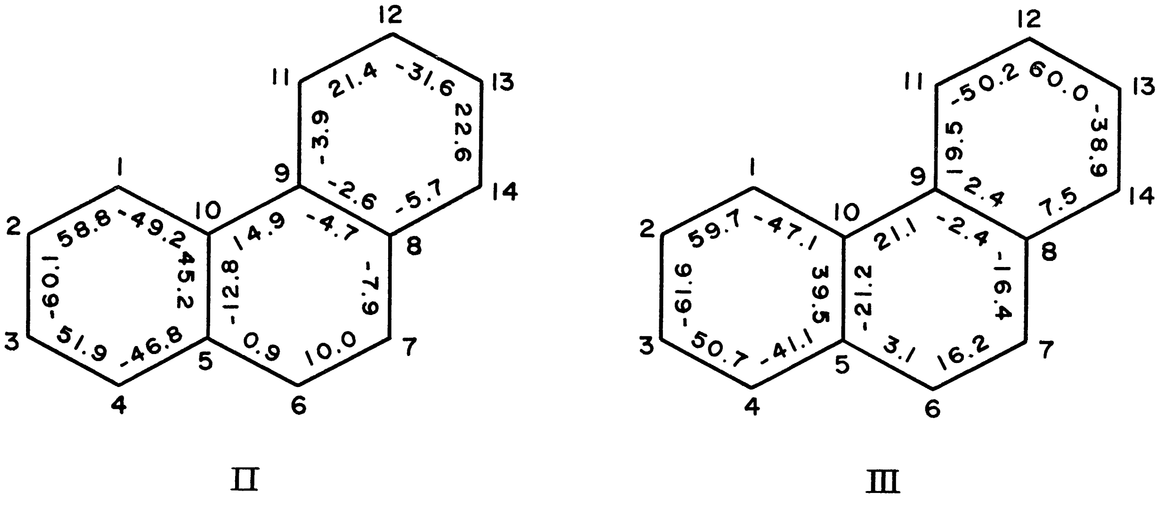
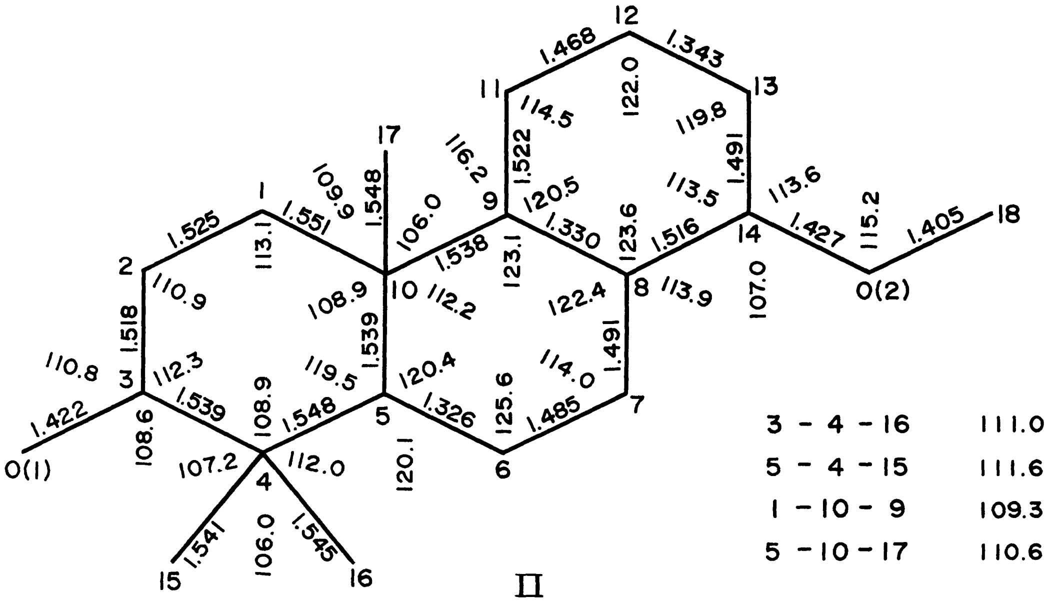
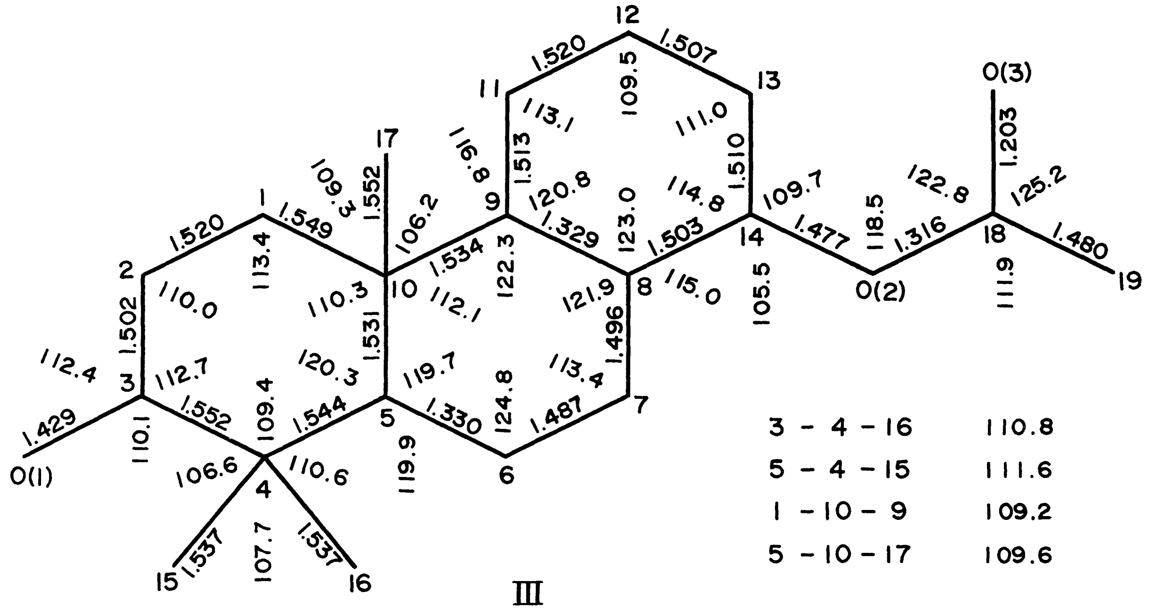


Fig. 2. The torsion angles (°) for II and III.



II



III

Fig. 3. The bond lengths (Å) and angles (°) for II and III. Their average standard deviations are, respectively, about 0.004 Å and 0.3° for II, and 0.003 Å and 0.2° for III.

values of the root-mean-square deviations are estimated to be about 0.52 and 0.59 Å respectively. On the other hand, the distance between the two atoms is calculated to be about 1.34 Å; this is still smaller than the unusual values found in other cyclohexene derivatives.[5, 6] In the present case, it seems to be unreasonable that the shortening of the C(12)-C(13) bond is explained by the conformational disorder, because, in one of the two possible half-chair conformations of the C ring, the methoxyl oxygen atom cannot form a stable hydrogen bond with the hydroxyl group in another adjacent molecule while, in the other conformation, the equatorial hydrogen atoms at the C(1) and C(11) atoms approach each other at a very small distance. Hence, this remarkable shortening is probably due to special thermal vibrations of the C(12) and C(13) atoms. The unusual behavior of the C ring seems to arise mainly from the steric repulsion between the β hydrogen atom at the C(1) atom and the α hydrogen at the C(11), although these two equatorial hydrogen atoms keep a distance of about 2.10 Å after all through deformation of the tricyclic system. This strong repulsion will not only deform the A and B rings, but also act so as to flatten the C ring of the half-chair form. It is in fact found that the C(12) and C(13) atoms are, respectively, only about o.14 and 0.18 Å displaced from the mean plane through the other four atoms in the ring. Such an unstable conformation of the C ring will enable the C(12) and C(13) atoms to vibrate vigorously even in the crystalline state. On the other hand, the C ring in III is found to be quite normal. This will be because, although in III the β hydrogen atom at the C(11) atom is placed close to the β hydrogen at the C(1), these two hydrogen atoms are about 2.23 Å distant from each other without great deformation of the C ring.

The above mentioned high reactivity of II in the acetolysis reaction could arise from the highly strained conformation of II. The steric effect would destabilize the reactant, II, to lower the activation energy and hence would promote the acetolysis of II.

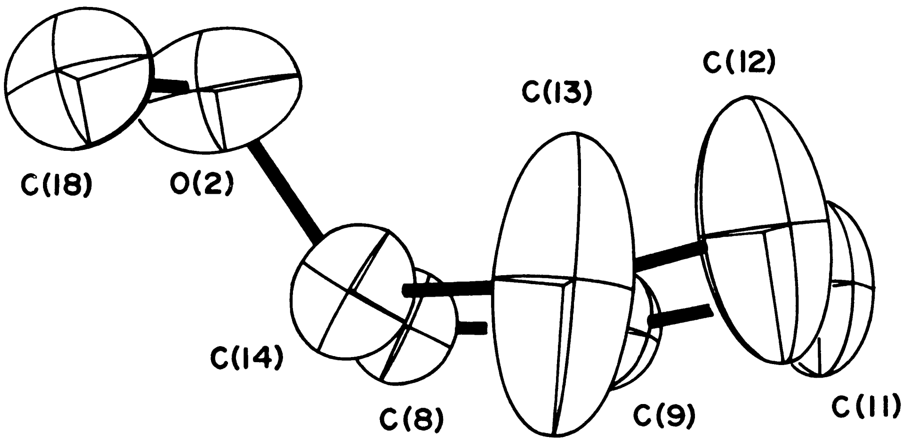


Fig. 4. The thermal behavior of the C ring in II. The thermal ellipsoids are scaled to enclose 50% probability.

Table 2. The final atomic coordinates for II

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
O(1)	0.7614	0.3884	0.2840	C(9)	0.2049	-0.0455	0.3124
O(2)	0.0054	-0.3306	0.6912	C(10)	0.3300	0.0987	0.2556
C(1)	0.4636	0.1006	0.1695	C(11)	0.1763	-0.1146	0.1637
C(2)	0.5988	0.2344	0.1338	C(12)	0.0560	-0.2519	0.2233
C(3)	0.6330	0.2656	0.3166	C(13)	-0.0480	-0.2948	0.3641
C(4)	0.5115	0.2772	0.4069	C(14)	-0.0139	-0.2411	0.5248
C(5)	0.3686	0.1494	0.4256	C(15)	0.5499	0.2903	0.6021
C(6)	0.2812	0.0833	0.5878	C(16)	0.5044	0.4088	0.2903
C(7)	0.1435	-0.0423	0.6264	C(17)	0.2804	0.1898	0.1032
C(8)	0.1192	-0.1056	0.4762	C(18)	-0.1218	-0.4389	0.8017

Table 3. The final atomic coordinates for III

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
O(1)	0.3613	0.3557	0.2033	C(9)	0.8460	0.3017	0.3046
O(2)	1.0612	0.2007	0.5789	C(10)	0.6967	0.2618	0.2483
O(3)	1.2079	0.2850	0.8346	C(11)	0.9247	0.3517	0.1533
C(1)	0.6709	0.3594	0.1058	C(12)	1.0544	0.3386	0.1981
C(2)	0.5281	0.3413	0.0640	C(13)	1.1289	0.3936	0.3873
C(3)	0.4895	0.3569	0.2376	C(14)	1.0496	0.3234	0.5326
C(4)	0.4981	0.2554	0.3863	C(15)	0.4770	0.2958	0.5637
C(5)	0.6346	0.2531	0.4144	C(16)	0.3870	0.1212	0.3303
C(6)	0.6964	0.2383	0.5829	C(17)	0.6361	0.1273	0.1556
C(7)	0.8281	0.2355	0.6272	C(18)	1.1403	0.1940	0.7335
C(8)	0.9040	0.2872	0.4757	C(19)	1.1409	0.0652	0.7594

References and Notes

1) In the text, the steroid numbering was adopted.

2) N. Hamanaka, T. Okuno, T. Nakajima, A. Furusaki, and T. Matsumoto, preceding paper.

3) J. Karle and I. L. Karle, Acta Crystallogr., 21, 849 (1966).

4) All the calculations necessary for the present study were carried out on a FACOM 230-60 computer at the Computer Center of Hokkaido University, using our programs.

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