

CONFORMATION OF RING A IN 3-OXOTRITERPENOIDS. DIPOLE MOMENTS AND CD SPECTRA*

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The A ring of 3-oxotriterpenoids allobetulone (*I*) and 3-oxo-lupane-28-nitrile (*IV*) exists by about 40% in the boat form as derived from comparison of their dipole moments with those of 2 α -methyl derivatives *II*, *V* (chair models) and 2 β -methyl compounds *III*, *VI* (boat models). The same result was obtained from the CD spectra of 3-oxotriterpenoids *I*–*VIII* and from isomerization of the 2 α - and 2 β -substituted ketones *XI* and *XII*, respectively.

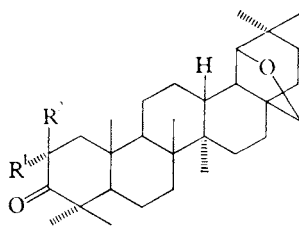
Conformation of the A ring in 4,4-dimethyl-3-oxo-5 α -steroids and 3-oxotriterpenoids has been studied by a wide variety of physical methods with quite contradictory results (see refs^{1,2} and references therein). In the case of 4,4-dimethyl-3-oxo-5 α -steroids most authors have already agreed that in solution the chair form highly predominates^{1–3}. However, for 3-oxotriterpenoids, which contain one axial 8 β -methyl group more than 4,4-dimethyl-5 α -steroids, interpretations of the existing physical data are still diametrically different: thus Witz, Herrmann, Lehn and Ourisson⁴ interpreted the CD spectra on the basis of deformed chair conformation whereas the same spectra served Tsuda and co-workers^{1,5} as a proof of high population of the twist-boat form**. Lehn, Levisalles and Ourisson⁶ originally interpreted the dipole moment of 3-oxolupane-28-nitrile (*IV*) by an equilibrium between the chair (70%) and boat (30%) forms but later⁷ they concluded that the A ring is conformationally homogeneous and exists in a deformed chair form. A similar conclusion (distorted chair) has been derived by Bose, Manhas and Malinowski⁸ from the dipole moments of allobetulone (*I*) and the ketone *IV*. In our previous communication we have shown² that the vicinal coupling constants between the protons on C₍₁₎ and C₍₂₎ indicate a chair–boat equilibrium, the chair form slightly predominating. Consistent with this result are also the solvent- and lanthanide-induced shifts² of the protons at C₍₂₎.

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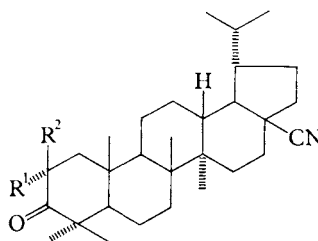
** In this work we consider only two fundamental conformational types of the A ring, chair and boat, without specifying their detailed geometry. A detailed geometric analysis and characterization of various forms of the A ring from X-ray diffraction data has been performed by Tsuda and Kiuchi¹. The twist-boat form assumed by us² is closer to the classical boat with C₍₃₎ and C₍₁₀₎ in the stem-stern position and corresponds to the twist form *T*₁, or rather to the *T*₁(B₃) form, according to the classification of the Japanese authors¹.

The above-mentioned conclusions from the dipole moments of ketones *I* and *IV*⁶⁻⁸ were obtained on the basis of a vector addition of the C=O and CN or C—O—C group moments, the angles between the vectors being estimated from Dreiding models. Although the calculation of the angles involved a certain deformation of the triterpenoid skeleton^{6,7}, the results may not correspond to the actual situation since the distances between both polar groups are considerable and since the molecular models give only an idealized picture of the actual geometry. Similarly, the interpretation of CD spectra^{1,3,5} is also based on inspection of molecular models and application of the octant rule.

For conformational study of the A ring in allobetulone (19 β ,28-epoxy-18 α H-oleanan-3-one (*I*)) and 3-oxolupane-28-nitrile (*IV*) we have chosen a different approach using 2 α -methyl-3-oxo derivatives *II* and *V* as chair models and 2 β -methyl-3-oxo compounds *III* and *VI* as boat standards. Now we present the results obtained from dipole moments of ketones *I*–*VI*, from CD spectra of ketones *I*–*VIII*, and from isomerizations of 2 α - and 2 β -substituted 3-oxotriterpenoids *XI* and *XII*. The preparation and configuration of model compounds *II*, *III*, *V* and *VI* have been already described^{9,10}. The chair conformation of the A ring in the 2 α -methyl derivatives *II* and *V*, and the boat form in the 2 β -isomers *III* and *VI* has been deduced from vicinal coupling constants in our previous work².



I, $R^1 = R^2 = H$
II, $R^1 = CH_3, R^2 = H$
III, $R^1 = H, R^2 = CH_3$



IV, $R^1 = R^2 = H$
V, $R^1 = CH_3, R^2 = H$
VI, $R^1 = H, R^2 = CH_3$

EXPERIMENTAL

Ketones *I*–*VI* (ref.^{9,10}) were recrystallized from benzene–light petroleum and dried over phosphorus pentoxide under diminished pressure at 100°C for 2 days. The electric dipole moments were determined at 25°C in benzene solutions (five solutions in the concentration range $1 \cdot 10^{-3}$ to $2 \cdot 10^{-2}$ mol \cdot l⁻¹) using the method of Halverstadt and Kumler¹¹. Relative permittivities (ϵ_{12}) were measured on an instrument with direct frequency reading (working frequency 1.3 MHz), densities (d_{12}) were determined in an Ostwald–Sprongler pycnometer. Molecular refractions (R_D) were calculated from the published¹² increments; no correction for atomic polarization was done. The results are given in Table I, the employed symbols are the same as in reference¹³. Within the experimental error limits, the found dipole moments of ketones *I* and *IV* agreed with

the published^{7,8} values. The CD spectra were taken in $1-3 \cdot 10^{-3}$ mol \cdot l⁻¹ dioxane solutions on a Roussel-Jouan 185 dichrographe.

RESULTS AND DISCUSSION

Dipole Moments

The low dipole moments of the 2α -methyl-3-oxo derivatives *II* and *V* (Table I) are compatible with the chair form of the A ring whereas the high values for the 2β -methyl derivatives *III* and *VI* correspond to the boat form; this confirms the conclusions made on the basis of vicinal coupling constants². The dipole moments of the unsubstituted ketones *I* and *IV* are between those of the 2α -methyl and 2β -methyl derivatives, indicating that both forms of the A ring contribute considerably to the conformational equilibrium. The population of the boat form was calculated from the equation

$$\% \text{ boat} = 100(\mu^2 - \mu_c^2)/(\mu_b^2 - \mu_c^2),$$

where μ is the experimentally found dipole moment of *I* or *IV* and μ_c and μ_b are the moments of the respective chair and boat forms of the A ring in the ketones *I* and *IV*.

The values of μ_c and μ_b can be approximated by the experimentally found dipole moments of the respective 2α -methyl (*II* and *V*) and 2β -methyl (*III* and *VI*) derivatives, under assumption that attachment of a methyl group to the C₍₂₎ carbon of 3-oxotriterpenoids *I* and *IV* has no effect on the dipole moments or geometry of both conformers and that the used models *II*, *III*, *V* and *VI* are conformationally

TABLE I
Dipole moments of ketones *I-VI* in benzene at 25°C

Ketone	α^a	β^a	P_2^0 cm ³ mol ⁻¹	R_D cm ³ mol ⁻¹	μ^b 10 ⁻³⁰ Cm
<i>I</i>	2.38	-0.215	320	129.9	10.2 ^c
<i>II</i>	1.18	-0.217	227	134.5	7.1
<i>III</i>	3.76	-0.245	444	134.5	13.0
<i>IV</i>	3.89	-0.210	442	130.1	13.0 ^d
<i>V</i>	1.75	-0.212	274	134.7	8.7
<i>VI</i>	6.65	-0.217	690	134.7	17.4

^a α and β are slopes of the plots ϵ_{12} vs w_2 and d_{12}^{-1} vs w_2 , respectively; $\epsilon_1 = 2.2731$, $d_1^{-1} = 1.1456$; the values were calculated by the least-squares method; ^b standard deviations 0.1 to 0.2 \cdot 10⁻³⁰ Cm; ^c reported⁸ $10.0 \pm 0.1 \cdot 10^{-30}$ Cm; ^d reported⁷ $13.1 \pm 0.1 \cdot 10^{-30}$ Cm.

homogeneous with respect to the A ring. The estimated populations of the boat form in the ketones *I* and *IV*, together with the employed characteristic values of μ , are summarized in Table II (*A*).

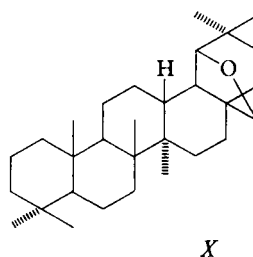
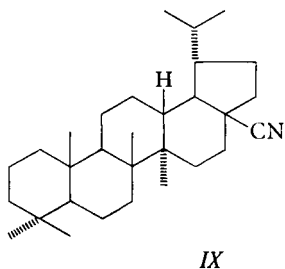
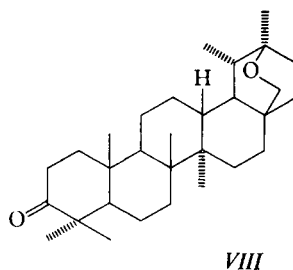
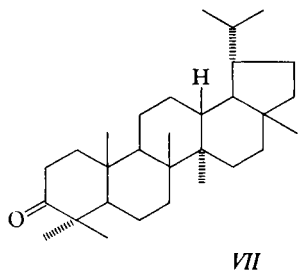


TABLE II

Characteristic values of dipole moments and angles between the dipoles for the chair and boat forms, and population of the boat form in ketones *I* and *IV*

Ketone	conformer	$10^{-30} \mu$ Cm		φ° ^a		% boat ^b	
		<i>A</i> ^c	<i>B</i> ^c	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
<i>I</i>	chair	7.1	7.4	138	134	45 ± 7	39 ± 7
	boat	13.0	13.4	65	59		
<i>IV</i>	chair	8.7	8.7	137	136	41 ± 5	39 ± 4
	boat	17.4	17.7	80	78		

^a Angle between dipoles C=O and C—O—C, or C=O and C≡N; ^b maximal errors are given under assumption of experimental errors $\pm 0.2 \cdot 10^{-30}$ Cm for all values of μ ; ^c *A* — uncorrected, *B* — corrected for the effect of the methyl group.

From the values of μ we estimated the angles φ between the vectors of dipole moments of polar groups in the A and E rings in the chair and boat forms of ketones *I* and *IV*. As group moments for the carbonyl group, ether ring and nitrile group we used, like other authors⁶⁻⁸, the dipole moments of structurally closest compounds: 3-lupanone⁷ (*VII*; $10.0 \cdot 10^{-30}$ Cm), 19 β ,28-epoxy-18 α -oleanane⁸ (*X*; $5.1 \cdot 10^{-30}$ Cm) and 28-lupanenitrile⁷ (*IX*; $12.6 \cdot 10^{-30}$ Cm). Since the parent hydrocarbon (lupane) has no dipole moment⁷, the moments of compounds *VII*, *IX* and *X* can be ascribed to the polar groups present in them. The interaction between dipoles in the A and E rings was neglected because of sufficiently long distance (~ 1 nm) between the polar groups. The φ values are included in Table II (*A*).

The thus-calculated population of the boat form and the angles φ suffer from a systematic error, caused by neglecting the effect of the methyl at C₍₂₎ on the dipole moments. We tried to assess this effect and calculate the corrected characteristic values (μ_c and μ_b) for both conformers in the ketones *I* and *IV*. The dipole moment of 2-methylcyclohexanone is by about $0.3-0.4 \cdot 10^{-30}$ Cm lower¹⁴ than those of cyclohexanone or various 3- and 4-alkylcyclohexanones. Also, 2 α -methyl-5 α -cholestan-3-one has a lower (by $0.33 \cdot 10^{-30}$ Cm) dipole moment¹⁵ than 5 α -cholestan-3-one¹⁶. We can therefore assume that a methyl at C₍₂₎ decreases the moment of a carbonyl group in position 3 at most by $0.4 \cdot 10^{-30}$ Cm (the possible small change in direction can be neglected). This decrease affects differently the total dipole moments of the chair (μ_c) and the boat (μ_b) in *I* and *IV*, depending on the angle φ and on the relative magnitude of the group moments. Therefore, the dipole moments were corrected for the effect of the methyl group by subtracting $0.4 \cdot 10^{-30}$ Cm from the dipole moment of 3-lupanone (*VII*) and taking the value of $9.6 \cdot 10^{-30}$ Cm for the carbonyl in 2-methyl-3-oxo derivatives. In the same way as above, we calculated the corrected values of angles φ from the dipole moments of 2-methyl derivatives *II*, *III*, *V* and *VI* and from them back (using the value of $10.0 \cdot 10^{-30}$ Cm for carbonyl in unsubstituted ketones) the dipole moments for both conformers (μ_c and μ_b) in the ketones *I* and *IV*. The corrected angles φ , dipole moments, and population of the boat form, are given in Table II (*B*).

As seen from Table II, corrections for the effect of the methyl group affect only little the φ values and population of the conformers. Since the correction for the methyl group is considered to be maximal, the correct values lie probably somewhere between these extremes. The mentioned results were obtained from dipole moments determined without correction for atomic polarization. However, with these types of compounds and low dipole moments, the atomic polarization may not be negligible. Dipole moments, calculated under assumption that the atomic polarization is about 5–15% of the molecular refraction, R_D , (ref.¹³), are lower for all the ketones *I*–*VI* (by $0.1-0.7 \cdot 10^{-30}$ Cm) but the boat populations differ only negligibly (less than 1%) from those given in Table II. Much greater errors in the population values are caused by inaccuracies in determination of the dipole moments (Table II).

Errors, arising from possible differences in geometry of conformers in the model compounds and the unsubstituted ketones, cannot be estimated. Further errors may arise by possible conformational inhomogeneity of the A ring in the model ketones *II*, *III*, *V* and *VI*, (*i.e.* the 2α -methyl ketones may contain a small amount of the boat whereas the 2β -isomers may exist to a small extent in the chair form). Even if we admitted up to 15% of the undesired form (which is not probable, judging from the vicinal coupling constants²) the maximal error in the final boat population in ketones *I* and *IV* would not exceed 10%. In actual fact, the errors are lower because the error due to neglecting the chair form in the 2β -methyl derivative is partly compensated by the presence of the boat form in the 2α -isomer and *vice versa*. We are therefore of the opinion that the value $40 \pm 10\%$ realistically describes the equilibrium population of the boat conformation in ketones *I* and *IV*.

It is worth notice that our approach using model compounds requires no knowledge of the angles φ . These angles were used only to estimate the effect of the methyl group in position 2 on the dipole moments of the individual conformers, in which case their accuracy is not important. We assume, however, that the angles φ , listed in Table II, are not far from the actual values. For the ketone *IV* our φ values differ considerably from those derived from Dreiding models for deformed chair (109°) and boat (35°) by Lehn, Levisalles and Ourisson⁷. On the basis of the chair-boat equilibrium we can also interpret the dipole moment of the ketone *IV*, measured by the same authors⁷ in *p*-xylene at 75°C . From their dipole moments of ketone *VII* ($12.5 \cdot 10^{-30}$ Cm) and nitrile *IX* ($15.2 \cdot 10^{-30}$ Cm), found under identical conditions, and from our φ values (Table II, *B*) we can calculate the characteristic values of μ_c and μ_b ($10.7 \cdot 10^{-30}$ Cm and $21.6 \cdot 10^{-30}$ Cm, respectively) for ketone *IV*. The found dipole moment⁷ of ketone *IV* ($16.2 \cdot 10^{-30}$ Cm) corresponds to 42% of the boat at 75°C .

Circular Dichroism

Spectra of all the measured ketones *I*–*VIII* exhibit carbonyl $n \rightarrow \pi^*$ transition maxima at 292 nm (in dioxane). The corresponding $\Delta\epsilon$ values are given in Table III. Both the 2α -methyl-3-oxo derivatives *II* and *V* show weak negative Cotton effect ($\Delta\epsilon \sim -0.7$), similarly to 4,4-dimethyl-3-oxo-5 α -steroids ($\Delta\epsilon \sim -0.3$; see refs^{1,4,17}) known to exist predominantly in the chair conformation of the A ring¹⁻³. If we consider that an equatorial methyl group affects only little the magnitude of $\Delta\epsilon$ (~ 0.2 ; see ref.¹⁷), the value found for the 2α -derivatives *II* and *V* agrees well with the chair conformation. On the other hand, the 2β -methyl-3-oxo derivatives *III* and *VI* show a strong positive Cotton effect, compatible with a boat conformation. Analogous 3-oxo derivatives with a polar substituent (Br, Cl, OR) in position 2β and boat form of the A ring also have a strong positive Cotton effect¹⁸⁻²⁰.

In accord with the literature^{1,4}, unsubstituted ketones *I*, *IV*, *VII* and *VIII* show

a weak positive Cotton effect ($\sim +0.7$). Similarly to the dipole moments, the $\Delta\epsilon$ values for the unsubstituted ketones lie between the values found for the model ketones *II*, *III*, *V* and *VI*, being thus compatible with a chair-boat equilibrium. The methyl group at $C_{(2)}$ is equatorial both in the chair form of 2α -methyl derivatives and in the boat form of 2β -methyl derivatives and – according to molecular models – it is close to the carbonyl nodal plane: therefore its effect on $\Delta\epsilon$ can be neglected. Consequently, the characteristic $\Delta\epsilon$ values for the chair and boat form in the unsubstituted ketones can be approximated by the respective values for the 2α -methyl (*II* and *V*; mean value -0.65) and 2β -methyl (*III* and *VI*; mean $+3.75$) derivatives. Using these numbers, we estimated the population of the boat in the unsubstituted ketones *I*, *IV*, *VII* and *VIII* to be about 30% for all the compounds (Table III).

The sources of errors are similar to those in the case of dipole moments. If we assume that in both chair and boat model 2-methyl-3-oxo derivatives an equatorial methyl contributes to $\Delta\epsilon$ in dioxane by the value 0.2 (as derived by Kirk and Klyne¹⁷ for the chair form of six-membered ring ketones), the resulting errors in the population estimation are very low (several per cent). However, in triterpenoid 3-ketones, both conformers may be distorted and their geometry may considerably differ from the ideal one¹. The contribution of the methyl group in position 2 may thus be higher than 0.2 and different for both conformers. All this may lead to a systematic error which cannot be estimated because the geometry of the conformers (in solution) is not known. For this and other reasons, discussed already in the case of dipole moments, one cannot expect high accuracy from this method.

The band shape and the sense of Cotton effect in the CD spectra of 3-oxo derivatives of 4,4-dimethyl- 5α -steroids and triterpenoids have been analyzed by Tsuda and coworkers^{1,5}. These authors explain the so-called 4,4,8 β -trimethyl effect (*i.e.* change from a negative to a positive Cotton effect on transition from 4,4-dimethyl-3-oxosteroid derivatives to triterpenoids and similar derivatives having a 8 β -methyl group⁴) in terms of the chair and boat forms: the negative Cotton effect in 4,4-di-

TABLE III
CD spectra (in dioxane) and population of the boat form in ketones *I*–*VIII*

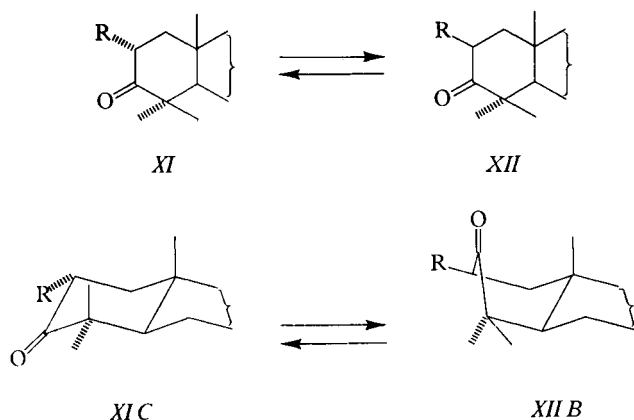
Parameter	<i>I</i> ^{a,b}	<i>II</i> ^c	<i>III</i> ^c	<i>IV</i> ^a	<i>V</i>	<i>VI</i>	<i>VII</i> ^{a,b}	<i>VIII</i> ^a
λ_{\max} (nm)	293	293	294	292	292	291	293	293
$\Delta\epsilon$	+0.76	-0.60	+3.65	+0.55	-0.71	+3.85	+0.63	+0.73
% boat	32	--	—	27	—	—	29	31

^a Another extremum at about 325 nm, $\Delta\epsilon$ -0.04 to -0.06 ; ^b similar values reported in ref.⁴; ^c see also ref.⁹.

methylsteroids is caused by the chair form whereas the positive effect in triterpenoids by the boat form. This interpretation agrees with our conclusion, although only qualitatively. The authors^{1,5} assume that 3-oxotriterpenoids exist predominantly in the boat form (twist T_1) and, on the basis of CD spectra, they admit only a small contribution of the chair form. According to our results, based not only on the CD spectra but also on other methods^{2,21} the boat population is less than 50%. An explanation of the 4,4,8 β -trimethyl effect by a mere deformation of the chair form of 3-oxotriterpenoids⁴ does not seem to be very probable.

Another indirect proof that in 3-oxotriterpenoids the boat and chair forms of the A ring are comparably populated follows from the previously described^{9,10,20,22} isomerization of 2 α - and 2 β -substituted ketones *XI* and *XII*, bearing various polar ($R = \text{Br, Cl, OCH}_3$) as well as nonpolar ($R = \text{CH}_3$) substituents at $C_{(2)}$. The results obtained with derivatives of allobetulone (*I*), 3-oxolupane-28-nitrile (*IV*) and allo-heterobetulone (*VIII*; 20 β ,28-epoxy-18 α ,19 β H-ursan-3-one) are summarized in Table IV.

Since in all 2 α -isomers *XI* the chair form *XIC* highly predominates whereas all 2 β -isomers exist predominantly in the boat form *XIIB** (see refs^{2,9,20,22} and references therein), the remaining conformer in the equilibrium (*i.e.* boat form in the 2 α -isomer and chair form in the 2 β -isomer) can be neglected and the isomerization equilibrium between the 2 α - and 2 β -isomers *XI* and *XII* is approximated by an equilibrium between the forms *XIC* and *XIIB*. The percentage of the 2 β -isomer *XII*, given in Table IV, describes the content of the form *XIIB* in the equilibrium $XIC \rightleftharpoons XIIB$ with sufficient accuracy. Given that up to 15% of the conformers are neglected (see the discussion of the dipole moments), the maximum error can be only $\pm 4\%$.



* For the sake of simplicity, formula *XIIB* shows one of the classical boat forms of the A ring; however, in the discussion below we consider the twist form T_1 or $T_1(B_3)$; see refs^{1,2}.

As seen from Table IV, the character of the substituent R on C₍₂₎ has only small influence on the equilibrium $XIC \rightleftharpoons XIIB$, although the substituents differ in the length and dipole of the C—R bond, van der Waals radii, non-bonding interactions, etc. Molecular models show that in both conformations XIC and $XIIB$ the bonds C—R and C=O are roughly coplanar with practically the same angle between them. Thus, both the dipole-dipole and non-bonding interactions of the substituent R with the carbonyl group are approximately the same. In the opposite case, larger differences between polar and non-polar substituents would occur. In both forms, the equatorial substituent R is oriented outwards, so that its interactions with the skeleton are negligible. The only difference which may arise from the different orientation of R with respect to the hydrogen atoms at C₍₁₎, depends on the actual geometry of the boat (twist) form. However, it seems that even these differences play no significant role and that the equilibrium $XIC \rightleftharpoons XIIB$ is governed by the difference between the chair and boat forms in 3-oxo derivatives rather than by the substituent R. We may therefore expect that the chair-boat equilibrium in the unsubstituted ketones ($XIC, XIIB, R = H$) will be close to the values in Table IV (~45% boat).

In conclusion, we may say that all our present as well as previous² results obtained from dipole moments, CD spectra, isomerization of 2-substituted ketones, vicinal interproton coupling constants and benzene- and lanthanide-induced shifts are in accord with a chair-boat equilibrium in the A ring of 3-oxotriterpenoids. The methods used for estimation of the conformer population are independent of each other and all give about $40 \pm 10\%$ of the boat form. Therefore, the assumed⁷ conformational homogeneity of the A ring (deformed chair) is not very probable. The absence of temperature dependence of ¹H NMR spectra⁷ does not exclude a chair-boat equilibrium: in the case of 3-oxotriterpenoids the temperature dependence may be insignificant because ΔH may be near to zero (see ref.² and references therein).

TABLE IV

Composition of equilibrium mixtures of isomeric 2-substituted 3-oxotriterpenoids

Substituent on C ₍₂₎	% 2 β -isomer ^a		
	<i>I</i>	<i>IV</i>	<i>VIII</i>
Br	42 \pm 3 (22)	—	40 \pm 3 (22)
Cl	43 \pm 5 (20)	—	—
OCH ₃	43 \pm 10 (20)	—	—
CH ₃	51 \pm 3 (9)	47 \pm 3 (10)	—

^a Acid-catalyzed isomerizations in chloroform at $22 \pm 2^\circ\text{C}$; references in parentheses.

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REFERENCES

1. Tsuda Y., Kiuchi F.: *Chem. Pharm. Bull.* **32**, 4806 (1984).
2. Klinot J., Buděšínský M., Klinotová E., Vystrčil A.: *This Journal* **51**, 593 (1986).
3. Burkert U., Allinger N. L.: *Tetrahedron* **34**, 807 (1978).
4. Witz R., Herrmann H., Lehn J.-M., Ourisson G.: *Bull. Soc. Chim. Fr.* **1963**, 1101.
5. Tsuda Y., Yamashita T., Sano T.: *Chem. Pharm. Bull.* **32**, 4820 (1984).
6. Lehn J.-M., Levisalles J., Ourisson G.: *Tetrahedron Lett.* **1961**, 682.
7. Lehn J.-M., Levisalles J., Ourisson G.: *Bull. Soc. Chim. Fr.* **1963**, 1096.
8. Bose A. K., Manhas M. S., Malinowski E. R.: *J. Amer. Chem. Soc.* **85**, 2795 (1963).
9. Klinot J., Světlý J., Kudláčková D., Buděšínský M., Vystrčil A.: *This Journal* **44**, 211 (1979).
10. Klinot J., Světlý J., Klinotová E., Vystrčil A.: *This Journal* **50**, 2918 (1985).
11. Halverstadt I. F., Kumler W. D.: *J. Amer. Chem. Soc.* **64**, 2988 (1942).
12. Vogel A. I.: *J. Chem. Soc.* **1948**, 1833.
13. Exner O.: *This Journal* **46**, 1002 (1981).
14. Sanchez J.: *Diss. Abstr. B* **28**, 116 (1967); according to McClellan A. L.: *Tables of Experimental Dipole Moments*, Vols 1 and 2. Freeman, San Francisco 1965 and Rahara Enterprises, El Cerrito 1974.
15. Allinger N. L., Carpenter J. G. D., DaRooge M. A.: *J. Org. Chem.* **30**, 1423 (1965).
16. Allinger N. L., Allinger J., DaRooge M. A.: *J. Amer. Chem. Soc.* **86**, 4061 (1964).
17. Kirk D. N., Klyne W.: *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1076.
18. Lehn J.-M., Ourisson G.: *Bull. Soc. Chim. Fr.* **1963**, 1113.
19. Lablache-Combiere A., Levisalles J., Pete J. P., Rudler H.: *Bull. Soc. Chim. Fr.* **1963**, 1689.
20. Klinot J., Riechtr V., Vystrčil A.: *This Journal* **40**, 1758 (1975).
21. Klinot J., Buděšínský M., Světlý J., Vystrčil A.: *This Journal*, in press.
22. Klinot J., Kliment M., Vystrčil A.: *This Journal* **39**, 3357 (1974).

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