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THE CONFORMATION OF ESTERS, ACIDS AND ALDEHYDES IN TERPENOIDS* +

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The C_4-axial carboxylic acid - ester and the acid itself in normal diterpenes and similar compounds have been found to shield the C_{10}-axial methyl group, when compared to compounds having a gem dimethyl group at C_4 or a C_4-equatorial acid or ester (1). For such shielding, the acid or ester has to stay in such a conformation that the plane passing through the C_4-axial carbon and the oxygen atoms attached to it has to be nearly parallel to the plane passing through C_2, C_{10} and the axial atoms on C_2 and C_{10}. Models show that the carbonyl oxygen slightly inclined towards the C_2-C_{10}-plane is actually better for such shielding. Two such conformations are possible for this effect viz. (a), when the carbonyl oxygen is turned towards C_6, and the other (b), when the carbonyl oxygen is turned away from C_6 (by rotating through 180^o). If (a) is correct, then the C_{10}-CH_3 is in front of the reference plane of the carbonyl and the methoxy methyl and the C_4-equatorial methyl group are behind it (2). Then if spectra of the methyl esters of the acids are taken in chloroform and benzene, the C_{10}-CH_3 should be deshielded in benzene, and the C_4-equatorial methyl and the methoxy methyl should be shielded. The examples given in Table 1, (I & II) and the several examples given in reference 1, show that this is indeed the case (3). Had the carboxylic acid ester been in conformation (b), then both the C_{10}- and C_4-methyl groups would have been shielded. In the case of the axial acids also, since C_{10}- is deshielded and C_4- is shielded, the same conformation holds good. However, in the case of the axial aldehydes, since both C_{10} and C_4 are shielded, conformation (b) must be assigned to them. The aldehyde proton is shielded by ~ 10 cps in both the equatorial and axial aldehydes in benzene, consistent with its position, behind the reference plane. These conformations appear quite reasonable, since in the case of the ester and the acid, the bulkier methoxyl group and hydroxyl group are turned away from the C_{10}-CH_3 and C_6-axial proton, whereas in the case of the aldehyde, the single proton is turned towards them.

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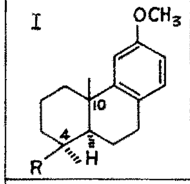
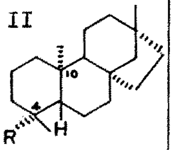
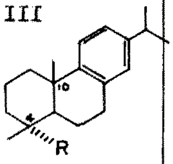
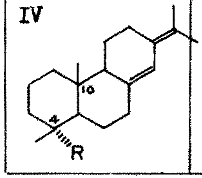
+Stereochemical studies by PMR spectroscopy XI.

TABLE 1

Compound	R = $C{\leqslant}^{O}_{OCH_3}$				R = $C{\leqslant}^{O}_{OH}$				R = CHO			
	Chemical shift in				Chemical shift in				Chemical shift in			
	$CDCl_3$		C_6H_6		$CDCl_3$		C_6H_6		$CDCl_3$		C_6H_6	
	C_{10}-CH_3	C_4-CH_3	C_{10}-CH_3	C_4-CH_3	C_{10}-CH_3	C_4-CH_3	C_{10}-CH_3	C_4-CH_3	C_{10}-CH_3	C_4-CH_3	C_{10}-CH_3	C_4-CH_3
I 	62.5	77	66.5	68.5	67	80	70	70	64	67	59	48
II 	45	70	50	60	51	74	58	67	47	59	41	46
III 	72.5	76.5	67.5	78.5	73	78	65	77	73	70	62	74
IV 	48	73	44	75	48	73	43	73	..	..	..	..

Since the methyl ester of a C_8-axial acid shields the C_{10}-CH_3 (IX, reference 1), the ester group in this case, has to be parallel to the plane passing through the C_{10}, C_{11}-carbon atoms and the axial groups on them, with the carbonyl group of the ester turned towards C_6. Again since a C_{10}-angular carboxylic acid ester (X, reference 1) shields the axial C_4-CH_3 in $CDCl_3$ and deshields it in benzene, the ester has to be nearly parallel to the plane passing through C_4, C_6 and the axial atoms on them, with the carbonyl pointing towards C_2 and slightly inclined to C_4. In complete agreement with this, the methoxy methyl of this C_{10}-ester, is shielded by the benzenoid ring C, and appears at 210 cps, whereas the methoxy methyl in podocarpic and dehydroabietic acid methyl esters (I & III) appear at $\sim$220 cps, in $CDCl_3$.

In the case of the C_4-equatorial esters, acids and aldehydes, models show that the most stable conformation would be that in which the carbonyl group eclipses the C_4-axial group, the methoxy methyl, hydroxyl or hydrogen atom concerned, pointing downwards (when the C_4-axial group is β). Studies in straight chain compounds have also shown that the most stable conformation of a carbonyl group bonded to a trigonal carbon atom, is that in which the carbonyl group eclipses a single bond (4). In the conformation mentioned above, the reference plane purpendicular to the carbon-oxygen bond, would just pass through the axial C_4-CH_3, and would leave the C_{10}-CH_3 behind it, thus shielding the C_{10}-CH_3 and having little effect on C_4-CH_3, in benzene. Table 1 shows that this is indeed the case (5). Any other conformation would not lead to the above results.

Recently, to explain, the pKa values of cyclohexane carboxylic acids, similar conformations have been suggested for equatorial carboxylic acids, and either of the two for the axial ones (6).

REFERENCES

1 See e.g. C.R. Narayanan and N.K. Venkatasubramanian, Tetrahedron Letters 3639 (1965) and references cited therein.

2 D.H. Williams and N.S. Bhacca, Tetrahedron 21, 2021 (1965); J.D. Connolly and R. MaCrindle, Chem. & Ind. 379 (1965).

3 The methoxy methyl of the esters of I and III, show a shielding effect of $\sim$ 20 cps in C_6H_6, compared to that in $CDCl_3$, but, substracting the shielding effect of $\sim$ 10 cps found for the corresponding C_4-CH_2-OMe of I, b.p. 185-190°/1.5 mm (bath temp.), $(\alpha)_D$ +49 and III, b.p.180-90°/ 1.5 mm (bath temp.), $(\alpha)_D$+ 59.7 the net shielding effect is $\sim$10 cps. The solvent shifts for the other groups in these methyl ethers are negligible, except the C_4-methylene holding the methoxyl, which also shows a shielding of $\sim$ 10 cps in benzene.

4 G.J. Karabatsos and N. Hsi, J. Am. Chem.Soc. 87, 2864 (1965).

5 I, podocarpic acid and derivatives, II, dihydromonogynol oxidation products, A.H.Kapadi and Sukh Dev, Tetrahedron Letters 1171, 2751(1964); III,dehydroabietic acid and derivatives; IV, neoabietic acid and derivatives.

6 J. Sicher, M. Tichy and F. Sipos, Tetrahedron Letters, 1393 (1966);
H. van Bekkum, P.E. Verkade and B.M. Wepster, ibid. 1401 (1966).