INFLUENCE OF THE SUBSTITUTING GROUPS OF SESQUITERPENE ALCOHOLS ON THE CHEMICAL SHIFTS OF C-METHYL GROUPS

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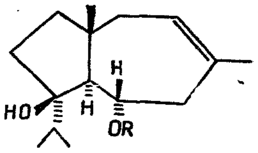
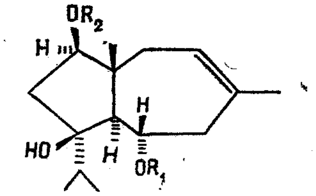
More than 20 esters of mono- and sesquiterpene alcohols of the camphane [1], carotane [2-5], humulane [6, 7], guaiane [8, 9], and germacrane [10, 11] series with aromatic and aliphatic acids have been isolated from plants of the genus *Ferula*, and their structures have been established. The determination of the positions of the acid residues in esters was carried out by comparing the CSs of the gem-acylic and gem-hydroxylic protons in the PMR spectra of the initial substances and the diols or triols obtained from them [1-11] and, in the case of diesters, of the products of partial hydrolysis [11].

Analysis of the PMR spectra of the esters has shown that on passing from alcohols to esters, in addition to a change in the CS of the signals of the gem-hydroxylic protons, the CSs of the signals of the C-methyl groups located vicinally to the ester group or spatially close to it also change (Table 1). We have turned our attention to the change in the CSs of the signals of the secondary methyl groups in the spectra of esters of ferutinol (I) and akitschenol (II) and of the tertiary methyl groups in derivatives of juniferol (III) and fexerol (IV). In the PMR spectra of (I) and its acetate (V), the difference between the CSs of the signals of the isopropyl group amounts to 4 Hz, and in the spectra of esters of ferutinol with aromatic acids (VI-XI) to 9-13 Hz.



I. R=H
V. R=CH_3CO
VI. R=$C_6H_3(OH)(OCH_3)CO—$
VII. R=$C_6H_4(OH)CO—$
VIII. R=$C_6H_4(OCH_3)CO—$
XI. R=$C_6H_3(OCH_3)(OH)CO—$
X. R=$C_6H_5CO—$
XI. R=$C_6H_3(OCH_3)_2CO—$



II. $R_1=R_2=H$
XII. $R_1=R_2=CH_3CO—$
XIII. $R_1=H$; $R_2=C_4H_7CO—$
XIV. $R_1=C_6H_4(OH)CO—$; $R_2=C_4H_7CO—$

The same pattern is observed in the spectra of mono- and diesters of akitschenol: Acetyl and angeloyl residues at C_2 and C_6 have little effect (3-4 Hz) on the difference of the CSs of the signals of the groups mentioned, while aryl residues at C_6 lead to a paramagnetic shift (15 Hz) of the signal of one of the methyls of the isopropyl group. The change in the CSs of the signals of the isopropyl radical in the spectra of esters of ferutinol and akitschenol is probably due to the anisotropic influence of the carbonyl in the benzene nucleus of the ester. What has been mentioned appears only in the case of esters with aromatic acids, which permits preference to be given to the influence of the benzene ring. The isopropyl group at C_4 and the hydroxyl at C_6 in ferutinol (jaeschkeandiol) have the same α orientation [12], which is in harmony with the influence of the substituent at C_6 on the isopropyl CS. A similar influence of the benzene nucleus in aromatic esters of ferutinol and akitschenol, and also the combined presence in one and the same plant of esters of both alcohols shows that in (II) the isopropyl group at C_4 and the hydroxyl at C_6 have the same configuration as in ferutinol. The similar values of the SSCCs of the C_6-H signal in the spectra of ferutinol and akitschenol confirm that in (I) and (II) the carotane nucleus is trans-linked and the

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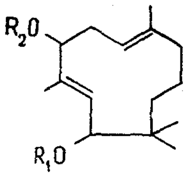
TABLE 1. Chemical Shifts (in ppm) and Δδ Values of the CSs of the Signals of the C-Methyl Groups of Esters*

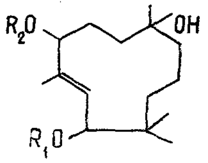
Substance	$C_1-CH\langle^{CH_3}_{CH_3}$	Δδ, Hz	Substance	C_1-2CH_3	Δδ, Hz
I. Ferutinol	0,86; 0,90	4	III. Juniferol	0,81; 0,85	4
II. Akitschenol	0,88; 0,90	2	IV. Fexerol	0,82; 0,92	10
V. Ferutinol acetate	0,87; 0,91	4	XV. Juniferin	0,88; 0,95	7
VI. Ferutin	0,79; 0,89	10	XVI. Juniferinin	0,78; 0,93	15
VII. Ferutinin	0,81; 0,89	8	XVII. Diacetate of (III)	0,76; 0,89	13
VIII. Ferutidin	0,79; 0,88	9	XVIII. Monoacetate of (III)	0,78; 0,91	13
IX. Teferin	0,81; 0,91	10	XIX. Acetate of (XV)	0,78; 0,90	12
X. Teferidin	0,80; 0,93	13	XX. Fexerin	0,77; 0,93	16
XI. Akiferin	0,78; 0,95	17	XXI. Fexerinin	0,88; 1,05	17
XII. Akitschenol acetate	0,90; 0,94	4	XXII. Fexeridin	0,88; 0,98	10
XIII. Akitschenol C_2-angelate	0,88; 0,91	3			
XIV. Akitschenin	0,77; 0,92	15			

*The PMR spectra were taken on a JNM-4H-100/100 MHz spectrometer in $CDCl_3$, 0 — HMDS [1-11].

C_6-OH group has the equatorial orientation. It follows from the SSCC values of the C_2-H (q, J_1 = 10.5, J_2 = 7.5 Hz) that the hydroxy group in (II) at C_2 has the pseudoequatorial orientation.

On the basis of the facts given, we propose the relative configuration (II) for akitschenol.





III. $R_1=R_2=H$
XV. $R_1=H$; $R_2=C_6H_3(OCH_3)(OH)CO-$
XVI. $R_1=CH_3CO$; $R_2=C_6H_4(OH)CO-$
XVII. $R_1=R_2=CH_3CO-$
XVIII. $R_1=CH_3CO$; $R_2=H$
XIX. $R_1=CH_3CO-$; $R_2=C_6H_3(OCH_3)\times$
$\times(O-COCH_3)CO-$
XX. $R_1=C_4H_7CO-$; $R_2=H$
XXI. $R_1=C_6H_3(OCH_3)(OH)CO-$; $R_2=H$

IV. $R_1=R_2=H$
XXII. $R_1=H$; $R_2=C_6H_3(OCH_3)(OH)CO-$

In the spectra of esters of juniferol (III) and fexerol (IV) a similar relationship is observed between the CSs of the tertiary methyl groups and the position of the acyl residues at C_2 or C_5. As can be seen from Table 1, in the spectra of juniferol (III) and juniferin (XV) the difference in the chemical shifts of the C_1-2CH_3 group is 4 and 7 Hz, respectively, and in fexerinin (XXI) it is 17 Hz. A comparison of the CSs of the C_1-2CH_3 groups in the spectra of esters of juniferol and of fexerol shows that the greatest value of the difference in the CSs is found when acid residues are present in the vicinal position to the gem-dimethyl group, where the influence of the carbonyl of the ester grouping is shown. In the case of C_5-monoesters there is only a slight difference in the C_1-2CH_3 CSs which is probably due to a displacement of the electron density to the carbonyl of the ester at C_5. The same influence of acyl residues in the vicinal position to a gem-dimethyl group has been observed in terpenoid coumarins of the iresane series, where an equatorial axial group at C_6' descreens a $C_5'-aCH_3$ group, and a $C_6'-aOAc$ group descreens a $C_5'-eCH_3$ group [13].

Thus, the facts given above permit the conclusion that the difference in the CSs of the signals of C-methyl groups in the PMR spectra of esters of sesquiterpene alcohols of the carotane and humulane series can be utilized for structural investigations.

SUMMARY

1. The comparative influence of substituting groups on the chemical shifts of the C-methyl groups of sesquiterpene alcohols of the carotane and humulane series in dependence on the nature and position of the substituent has been studied.

2. On the basis of the results obtained, a relative configuration of akitschenol has been put forward.

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TRITERPENES FROM THE LEAVES OF *Betula ermanii*

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Continuing a study of Far Eastern species of the genus *Betula* [1], from the leaves of *Betula ermanii** we have isolated two new triterpenes (I) and (II) (in order of increasing polarity).

The IR spectrum of triterpene (I) has the bands of hydroxyl absorption at 3570 and 3620 cm^{-1}, and also an absorption band at 1725 cm^{-1}, which is characteristic for an ester carbonyl. A fragment with m/e 143 (100%) in the mass spectrum of (I) showed the presence of a side chain in the form of a substituted tetrahydrofuran ring [2]. In the PMR spectrum of (I) there are the signals of the protons of eight tertiary methyl groups with δ (ppm): 0.78 (3H, s), 0.94 (6H, s), 0.98 (3H, s), 1.04 (3H, s), 1.12 (6H, s), and 1.21 (3H, s), and the signal of the protons of the methyl group of an acetate residue at 1.98 ppm (3H, s).

In the weak-field region a signal appears at 5.08 ppm (1H, multiplet), which could not be assigned solely with the aid of PMR spectroscopy to a definite proton. In the same region there are signals at 3.18 ppm (1H, triplet, $J \sim 8$ Hz), due to an axial proton, and at

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*The leaves were collected by V. I. Baranov, a post-graduate student in the chemotaxonomy laboratory, on August 12, 1975, in the Kamchatka oblast.

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