USE OF THE PARAMAGNETIC SHIFT AGENT Eu(DPM)$_3$ FOR STUDYING THE STRUCTURE AND STEREOCHEMISTRY OF CONFEROL AND CONFERONE

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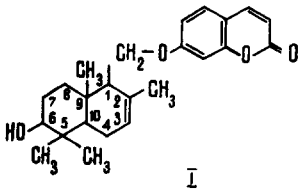
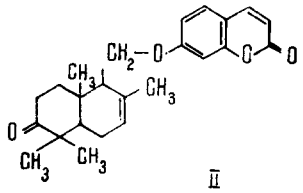
We have previously [1, 2] reported the isolation from Ferula conocaula of two new terpenoid coumarins – conferol and conferone – for which the probable formulas (I) and (II), respectively, have been proposed:



I



II

It was shown by means of NMR spectra that the OH group in (I) is axial and is located at C_6 or at C_8. The position of the hydroxyl in (I) and of the carbonyl in (II) at C_6 was suggested by analogy with other compounds of this group.

In the present paper, we give the results of a study of the structure and stereochemistry of conferol obtained by the use of europium tris(dipivaloylmethanate) Eu(DPM)$_3$* as shift agent in NMR spectra [3-5].

To obtain the values of ΔEu, representing the downfield shift of the signal on the addition of a mole of Eu(DPM)$_3$ to a mole of conferol, the spectra† were measured at various molar ratios of reagent to substance with the subsequent extrapolation of this ratio to 1.

Group *a*	δ, ppm, multiplicity, J, Hz ($CDCl_3$)	ΔEu
$C_5-CH_3^e$	0,89; s.	3,72
$C_5-CH_3^a$	0,85; s.	2,02
C_9-CH_3	0,85; s.	1,50
C_2-CH_3	1,63; s.	0,46
C_3-H	5,48; broadened signal $W_{\frac{1}{2}} = 9$ Hz	0,86
C_1-CH_2O	4,05 (center of an octet) J_{gem}=9,7 Hz; J_{1vic}=3,6 Hz J_{2vic}=5,7 Hz	0,77

* The Eu(DPM)$_3$ was kindly given to us by V. P. Zvolinskii and V. F. Zakharov (P. Lumumba People's Friendship University).

† On an Ha-100D instrument in $CDCl_3$, the signal of HMDS being taken as 0.

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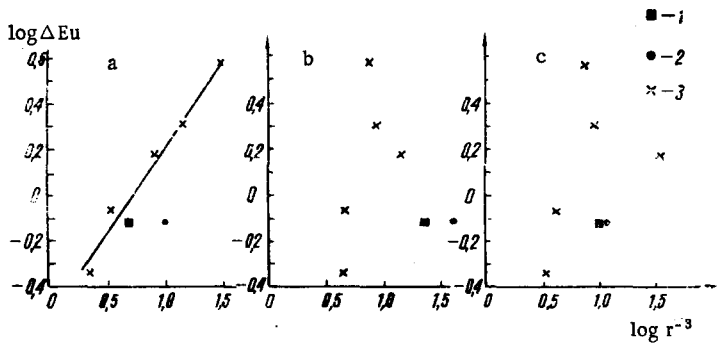


Fig. 1. Log ΔEu as a function of $\log r^{-3}$ for four configurations of the terpenoid residue of conferol. a) C_6–OH, trans linkage of the rings; b) C_8–OH, trans linkage of the rings; c) C_8–OH, cis linkage of the rings. 1) C_1–CH_2 equatorial; 2) C_1–CH_2 axial; 3) points corresponding to the other protons.

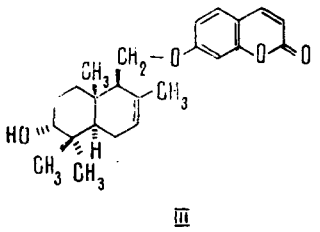
It is known [3-5] that to a first approximation the value of ΔEu is inversely proportional to the cube of the distance of the proton from the center of complex formation. In conferol, this center is the oxygen atom of the hydroxy group [6], and the paramagnetic shift of the signals must be substantially smaller as a result of coordination with other heteroatoms (in the first place, the carbonyl of the α-pyrone ring).

The distances from the hydroxyl oxygen atom to the protons, the signals of which appear fairly clearly in the spectrum and can therefore be used to determine the corresponding values of ΔEu, were measured for all the known variants of the structure and stereochemistry of conferol on Dreiding models.

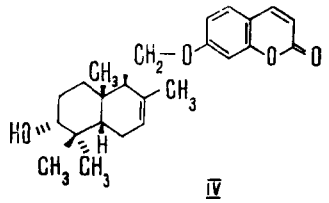
Of the sixteen possible isomers of conferol, to determine the relative configuration of the molecule it is necessary to consider eight variants. If the axial position of the hydroxy group is taken into account, the number of possible variants becomes four.

In Fig. 1b and c, the dependence of log ΔEu on $\log r^{-3}$ for all four possible configurations of the terpenoid residue of conferol, when the hydroxyl is located at C_8, is shown. It can be seen from this figure that in none of the cases considered is it possible to draw a straight line through the points. Conversely, for the variant of the structure with the hydroxyl at C_6 and the equatorial location of the methylene group at C_1, the points are clearly grouped around a straight line (Fig. 1a).

The question of the cis or trans linkage of the decalin nucleus remains open, since the differences in the distances from the oxygen atom to the groups mentioned exceed the error of measurement only insignificantly in the two cases. Thus, conferol has the structure (III) or (IV).



III



IV

In view of the fact that conferone is obtained by the oxidation of conferol [2], it may be assigned a structure corresponding to (III) or (IV) with the oxo group in position 6.

SUMMARY

On the basis of a study of the NMR spectra of conferol with additions of $Eu(DPM)_3$ the molecular structure proposed for it previously has been confirmed, and two variants of the relative configuration have been given. Conferone has the analogous structure with the oxo group in position 6.

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