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ON THE STRUCTURE OF PANAXATRIOL

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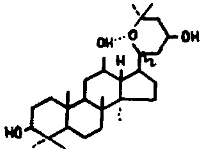
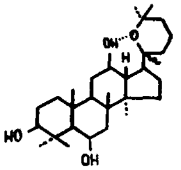
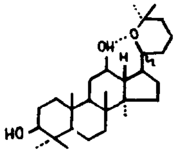
In the preceding papers (1,2) we reported the isolation of the main substance formed during the process of hydrolysis of panaxosides A,B,C, - panaxatriol. We proposed structure I for this substance. Almost simultaneously there appeared the paper of Shibata et al.(3). They proposed structure II for panaxatriol. The samples of panaxatriol isolated by both research groups proved out to be quite identical when directly compared*. Structures I and II differed from the structure of panaxadiol (III) established by Shibata et al.(4) in the presence of the third hydroxyl.



I



II



III

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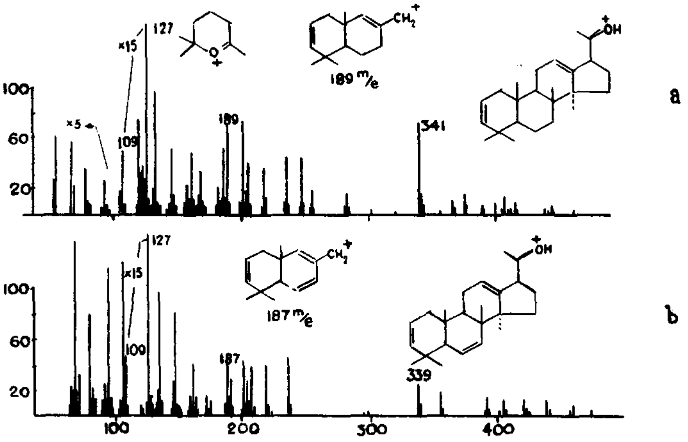
* Sh. Shibata, Private Communication, March 5, 1965.

The Japanese workers (3) used the analysis of NMR-spectra together with some additional data on mass spectrometry. The mass spectrum of panaxatriol showed peak at m/e 127 which corresponded to the fragment of trimethyltetrahydropyrane ring and this eliminated the presence of the hydroxyl in trimethyltetrahydropyrane ring.

Taking into consideration an adentity of the substances we have carried out detailed analysis of mass spectra of panaxadiol and panaxatriol (Fig. 1). Mass spectra of panaxadiol and panaxatriol showed m/e 127 as a base peak which corresponded to the fragment of trimethyltetrahydropyrane ring. This testified to the fact that there was no hydroxyl in trimethyltetrahydropyrane ring. Instead of peak m/e 341 (panaxadiol) there was m/e 339 peak in the spectrum of panaxatriol and the difference in two units of mass corresponded to additional multiple bonding (or to hydroxyl in original panaxatriol) in the skeleton part of panaxatriol. This is also indicated by the difference in two units of mass between peaks m/e 301 and m/e 299; m/e 185 and m/e 187; m/e 175 and m/e 173 in spectra of panaxadiol and panaxatriol, respectively.

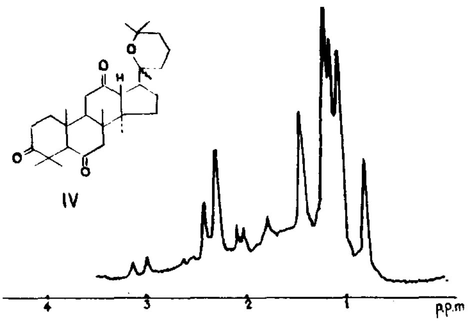
Bearing in mind the data on mass spectrometry we reinvestigated NMR spectra of panaxadion and panaxatrion and came to a conclusion that actually protons of only one CH_2 group got into the signal region at 2,3 p.p.m. in NMR spectrum of panaxatrion (Fig. 2). Providing that these protons must be equivalent and placed between the carbonyl and the quartenary carbon atom, positions 7 and 15 are possible for methylene group or positions 6 and 16 - for the carbonyl, respectively.

Fig. 1



Mass spectra of panaxadiol (a) and panaxatriol (b).

Fig. 2



NMR spectrum of panaxatrion (IY).

IR spectrum of panaxatrion testifies to the fact that all the carbonyl groups are in 6-membered ring (2) therefore for the third carbonyl of panaxatrion and for the hydroxyl of panaxatriol respectively, the only 6 -position is possible. In NMR spectrum of panaxatriol (2) proton at C_6 yields quartet at 4 p.p.m. with coupling constant J=7 cps. and J=11 cps., the half-band width of the signal is 27 cps. This, as it is known,(5) proves the axial position of the proton and equatorial one (6α) of the hydroxyl. Thus, the formula (II) represents panaxatriol.

NMR spectra were taken on JNM-60 spectrometer. $CDCL_3$ was used as a solvent. Chemical shifts were measured in p.p.m. from tetramethylsylane which served as an internal standard. Mass spectra were taken on MX-1303 spectrometer.

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