03.3-12 SIDE-CHAIN CONFORMATION IN 18-DEOXYALDOSTERONE, $C_{21}H_{28}O_4$. By J. F. Griffin, W. L. Duax, P. D. Strong, Medical Foundation of Buffalo, Inc.,73 High St., Buffalo, NY, J. W. Funder, Prince Henrys Hospital, Melbourne, Australia, S. Ulick, Veterans Administration Hospital, Bronx, NY.

18-Deoxyaldosterone hemihydrate crystallizes from methanol/water in space group $P2_12_12_1$ with two steroid molecules in the asymmetric unit; a = 19.878(3), b = 30.341(4), c=5.995(5)Å, Z=8. Integrated intensities for 2905 independent reflections were collected on a Syntex P3/F diffractometer using copper radiation. A structure solution from MULTAN-NQEST contained 48 atoms but did not refine below 40%. Application of a translation function in which the trial structure was translated 0.04 on y gave the final solution which refined to R = 7.2%. There are 4 hydrogen bonds in the structure which utilize the available donor groups, two hydroxyls and one water. The two independent steroid molecules have dramatically different side-chain and D-ring conformations. If we define the side-chain conformation by the torsion angle, τ, C16-C17-C20-O20, the normal conformation observed in 84/88 crystal structures is -20°, range = 0 to -40°. In the present study, τ = -28° in one molecule and -132° in the other. The latter conformation has been observed three times and always in conjunction with 16β-methyl or bromine substitution. In this secondary conformation the steric interaction between the C18 and C20 methyl or methylene groups, which appears to be the major determinant of the normal side-chain conformation, is relieved by an opening of the C13-C17-C20 bond angle from 112° to 120°, a remarkably large angle for a tetrahedral carbon not constrained in a ring. Research supported by NLM Grant No. LM-02353 and NIAMDD Grant No. AM-26546.

03.3-13 THE CRYSTAL STRUCTURE OF THE CATECHOL ESTROGEN 2-HYDROXYESTRONE

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Recent advances in neuroendocrine research suggests that the key to understanding and controlling ovulation lies in the investigation of neurotransmitters in the central nervous system. One class of these substances, catechol estrogens, is uniquely suited for a potential role in human reproduction physiology, combining the structure and function of both estrogens and catecholamines. We have undertaken a crystallographic analysis of such a compound, 2-hydroxyestrone (2-OHE_1), a major metabolite of estradiol. This compound ($C_{18}H_{22}O_3$) crystallizes in the orthorhombic space group $P2_12_12_1$ with a=9.564(1), b=8.042(1), c=19.344(2) Å and Z=4. The structure was solved with MULTAN and has refined to an R value of 0.043.

The B ring of the steroid nucleus adopts a $_7C^8$ half-chair; the C ring, a chair flattened at the C(11) end; and the D ring, a form intermediate between a C(14)α-envelope and a $_{14}C^{13}$ half-chair. The molecule suffers a pronounced twist along its length, evidenced by a large C(1)-C(10)-C(9)-C(8) torsion angle (169.0°). The A ring catechol is involved in a novel "chelate" hydrogen bond interaction with the C(17) keto group of a symmetry-related molecule. 2-Hydroxyestrone will be discussed in terms of the relationship between its structure and hydrogen bonding capacity and its affinity for estrogen and catecholamine receptor sites.

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03.3-14 THE CRYSTAL STRUCTURE OF 17-THIA-3-METHOXY-ESTRA-1,3,5(10) TRIENE-17-DIOXIDE. By V.M. Padmanabhan and S. Sinh, Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

The title compound, $C_{18}H_{24}O_3S$, 'estra-sulfone', a heterocyclic thia-steroid, has been totally synthesized (in Bio-Organic Division) to evaluate its biological activities. The compound crystallizes in the space group $P2_1/a$, a = 13.480, b = 10.563, c = 11.205 Å and β = 93.97° with Z = 4. Three-dimensional X-ray data (CuKα radiation) were collected on the Trombay-made computer-controlled four-circle diffractometer. The structure was solved using direct methods (MULTAN). The R factor with hydrogen atoms for 1850 reflections was 0.059.

Ring A shows complete aromaticity with a mean bond length of 1.39 Å. The bond lengths in rings B and C are close to the expected value of 1.54 Å and have distorted chair conformations. In ring D, C-S bond lengths are 1.83 and 1.81 Å indicating that the bondings involve 3d orbitals of sulfur. The pseudo-rotation parameters for the ring show 13 β envelope conformation. The B/C and C/D ring junctions are cis (which is unusual) and have 8α, 9α, 13β, 14β configuration. This appears to be the first X-ray determination of a steroid structure with sulfur in D ring.

03.3-15 THE CRYSTAL STRUCTURE OF DIETHYLAMMONIUM 2,5-DIHYDROXY-BENZEN-1,4-DISULPHONATE. By X. Solans, F. Plana and M. Font-Altaba. Dept. Crystallography and Mineralogy, University of Barcelona. Dept. X-ray and crystal structures Institute "Jaime Almera" (C.S.I.C.), Gran Via 585, Barcelona-7. Spain.

$C_6H_4O_2S_2O_6^{2-}$ $((C_2H_5)_2NH_2^+)_2$, monoclinic, $P2_1/a$, a = 11.533(3), b = 10.544(2), c = 8.888(2), β = 114.67(2)°, V = 982(9) $Å^3$, Z = 2, Dc = 0.78 Mg m^{-3}.

Intensity data were recorded on a Philips PW-1100 four circle diffractometer, using MoK radiation. 1138 reflections were measured in the range $2\theta \leq 25°$. 1122 of which were considered as observed applying the condition $I \geq 2.5\ \sigma(I)$.

The structure was solved with the MULTAN80 system of computer programs and refined by means of full matrix least-squares method with the SHELX76 program.

The hydrogen bonds determine the packing of the ions.