14β,15β-Dihydroxy-Gruppe von (VII) schließen läßt.

Die übrigen zwei isomeren Glykole, (VIII) und (IX), gehören damit zur 14α-Reihe, und sie ergeben bei der Oxydation tatsächlich das gleiche Ketol (XIII), Schmp. 241~245°, $[\alpha]^{10}_{D}$ $+236°$ ($CHCl_3$), UV : λ^{MeOH}_{max} 240.2 mμ (ε 16300), IR $\nu^{CHCl_3}_{max}$ cm^{-1} : 3420, 1749, 1708, 1667, 1619; die 17-Isomerisierungsreaktion von (XIII) mit methanolischer Kalilauge liefert immer das Ausgangsmaterial. Daraus lassen sich klar die Raumstrukturen der Glykol-Gruppen von (VIII) und (IX) erkennen : 14α,15α für (VIII) und 14α,15β für (IX).

Bei der Chromtrioxyd-Oxydation von (VI) und (VII) als auch (IX) in Eisessig ergab sich stets dasselbe Produkt, $C_{21}H_{28}O_5$, vom Schmp. 119~125° und 155° (Doppel-Schmp.); das IR-Spektrum läßt mit Wahrscheinlichkeit auf seine Struktur schließen, nämlich (XIV) oder (XV).

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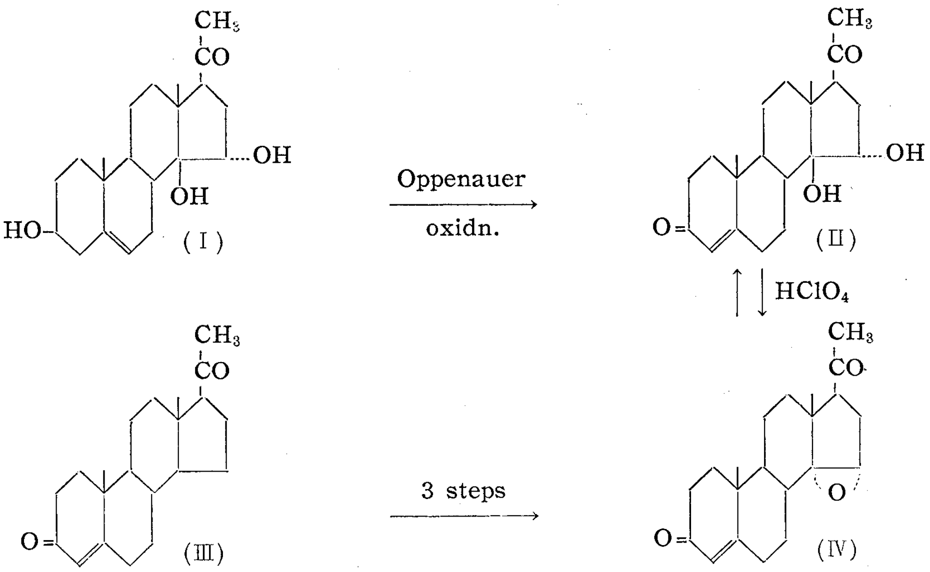
Structure of Purpnigenin

Purpnigenin[1] (I), m.p. 239~243°, $[\alpha]^{16}_{D}$ $+21.1°$ (MeOH), is the aglycone of a non-cardiotonic glycoside, purpnin, isolated from the leaves of *Digitalis purpurea* L. Oppenauer oxidation product, m.p. 203~205°, $[\alpha]^{17}_{D}$ $+130.6°$ (MeOH), of purpnigenin (I) is identical with 14,15-dihydroxyprogesterone (II), m.p. 203~205°, $[\alpha]^{25}_{D}$ $+126.1°$ (MeOH), produced by the hydrolytic cleavage of progesterone 14α,15α-epoxide (IV) with perchloric acid. Therefore, purpnigenin (I) has a pregnenolone skeleton and two hydroxyl groups at the positions 14 and 15 are *trans*-diaxial, according to the rule of epoxide ring opening.[2]



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[1] D. Satoh, H. Ishii, Y. Oyama : This Bulletin, 8, 657 (1960).
[2] R.E. Parker, N.S. Isaacs : Chem. Revs., **59**, 781 (1959).

Recently, Tsuda *et al.*[3] characterized all four 14,15-dihydroxyl isomers derived from progesterone (Ⅲ) and concluded that the structure of the isomer obtained by hydrolysis of the 14α,15α-epoxide of progesterone (Ⅳ), which was found to be identical through infrared spectra with the present specimen, should be 14β,15α-dihydroxyprogesterone (Ⅱ). Configuration of the hydroxyl group at 3 of purpnigenin (I) is most likely to be β-oriented in view of other natural Δ^5-3-hydroxy steroids.

On the basis of these considerations it would be most appropriate to assign the structure of 3β,14,15α-trihydroxy-14β-pregn-5-en-20-one (I) to purpnigenin which has 14β-hydroxyl group, i.e. C/D-ring *cis*-fused, similar to cardiac aglycones[4] and diginigenin-type steroids.[5]

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April 14, 1961.

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3) K. Tsuda : Personal communication.
4) L. F. Fieser, M. Fieser : "Steroids," 728 (1959). Reinhold Publishing Corp., New York.
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UDC 547.466.2.02

Assignment of the Absolute Configuration of Optically Active α-Amino Acid by Rotatory Dispersion Curves

Many problems on absolute configuration and stereochemistry have been solved by measurement of their anomalous rotatory dispersion curves.[1] Most of the optically active α-amino acids exhibit only plain dispersion curves over the presently accessible spectral ranges and it is impossible to utilize these plain curves for the determination of their absolute configuration. Recently, Djerassi, *et al.*[2] found that N-dithiocarbalkoxy-α-amino acids of L-series exhibit positive Cotton-effect curves.

Various optically active α-amino acids, especially these not found in nature, have been synthesized in this laboratory. For determining the absolute configuration of these amino acids, attempts have also been made to search for easily prepared α-amino acid derivatives, which show anomalous rotatory dispersion curves. Thus it was found that phthaloyl derivatives (I) of α-amino acids are most suitable for this purpose, because they can easily be prepared in a good yield by Nefkens' mild phthaloylation, and racemization does not occur in the course of this synthesis.[3] As shown in Fig. 1, phthaloyl derivatives of L- and D-α-amino acids exhibit anomalous rotatory dispersion curves. The resulting Cotton-effect curves can apparently be used for absolute configurational assignments of the α-asymmetric center, all members of L-series (L-methionine, L-alanine, L-aspartic acid, L-glutamic acid, and L-phenylalanine), which have so far been examined, show a similar

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1) C. Djerassi "Optical Rotatory Dispersion," (1960) McGraw-Hill Book Co., New York.
2) C. Djerassi, B. Sjöberg, A. Fredga : J. Am. Chem. Soc., **81**, 5002 (1959).
3) G. H. L. Nefkens, G. I. Tesser, R. J. F. Nivard : Rec. trav. chim., **79**, 688 (1960).