Ketones of intermediate steric hindrance give with lithium aluminum hydride approximately a 1:1 mixture of axial and equatorial alcohols. With methyl magnesium halide, the axial alcohol predominates distinctly. Thus the 'abnormal' mode of Grignard addition to 12-pregnanones and 17-a-*D*-homoandrostanones is the predicted one[24]. In the case of the hindered 4-, 6- and 11-ketones, both reactions afford the axial alcohol as the major product.

It is apparent that the results of lithium aluminum hydride reduction and Grignard addition with steroidal ketones are similar, and it seems that the same factors influence the stereochemistry of these two nucleophilic addition reactions.

Zusammenfassung. – Die Anlagerung von Methylmagnesiumhalogeniden an unkonjugierte sechsgliedrige Ringketone der Steroidreihe ergibt bei ungehinderten Ketonen ungefähr eine 1:1-Mischung von axialen und äquatorialen Alkoholen. Mit zunehmender sterischer Hinderung des Ketons bildet sich, ähnlich wie bei Reduktionen mit Lithiumaluminiumhydrid, mehr vom axialen Alkohol.

G. JUST and R. NAGARAJAN

Chemistry Department, McGill University, Montreal (Canada), June 4, 1962.

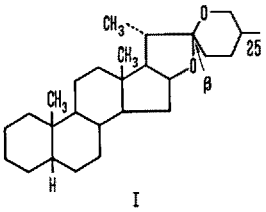
[42] G. S. FONKEN, J. A. HOGG, and A. V. MCINTOSH, J. org. Chem. *24*, 1600 (1959).

[43] J. A. ZDERIC, E. BATRES, D. C. LIMÓN, H. CARPIO, J. LISCI, G. MONROY, E. NECOECHEA, and H. J. RINGOLD, J. Amer. chem. Soc. *82*, 3404 (1960).

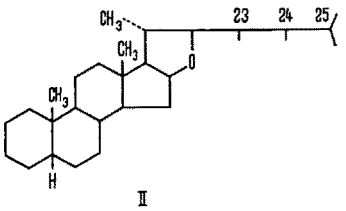
Nomenclature of Steroidal Sapogenins[1]

Nomenclature of steroidal sapogenins is covered under rules proposed at Stockholm (Sweden) in 1953, adopted as tentative at Zurich (Switzerland) in 1955[2] and published as definitive by the International Union of Pure and Applied Chemistry in 1960[3]. Unfortunately, sapogenin stereochemistry was not fully understood when the proposed rules were formulated. During the ensuing seven-year period the stereochemistry of the sapogenin skeleton was elucidated. The correct formulas were not, however, incorporated in the definitive nomenclature rules of 1960, which are based on structures published earlier in the tentative rules.

The present status of the Definitive Rules requires use of the formulas as shown, and the parent names 5α,22β-



I

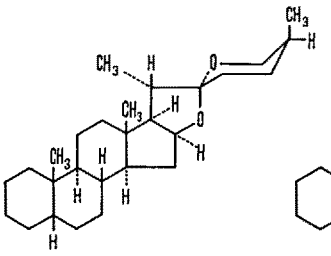


II

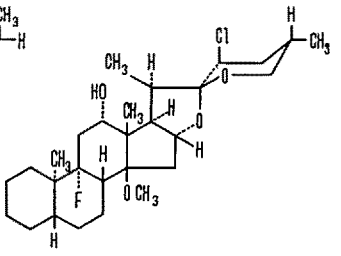
spirostan or 5β,22β-spirostan (I), and 5α- or 5β-furostan (II). In neither parent is there provision for designating known stereochemical variations possible at carbon 25; in both cases configurational representations at carbon 22 are equivocal. Furthermore, the structures of tigogenin and dihydrotigogenin published in the Rules as illustrative examples are incomplete and incorrect in light of present concepts[4]. Tentative Rules have already been published[5] which purport to remedy the situation. FIESER and FIESER have published opinions on this subject[6].

We wish to offer an alternate approach in the hope that our suggestions ultimately will receive formal adoption and in the meantime will extricate sapogenin nomenclature from the confusion of its recent past[7] and place it on a logical and general basis. Accomplishment of this immediate objective requires adoption of three ideas that already have won varying degrees of acceptance in nomenclature: (1) use of the parent name; (2) application of α- and β-configurations to an extended but nearly planar ring system as in present steroid practice; and (3) employment of the R- and S-designation of configuration at asymmetric centers not included in the planar ring system[8].

As parent names of hexacyclic steroidal sapogenins we recommend 5α,25R-, 5α,25S-, 5β,25R-, and 5β,25S-spirostan (III), in which the stereochemistry at each asymmetric center is implicitly and uniquely defined. The



III



IV

α- and β-terminology applies to all carbon atoms in rings A, B, C, D, and E, where an inversion of the skeleton at any center is expressed by numbering that center and designating the new configuration as α or β. The configuration so expressed is that of the free substituent at

[1] A summary of the personal views of the authors. Presented by the authors to an *ad hoc* Committee on Steroid Nomenclature (sponsored by the National Academy of Sciences and the National Research Council, and supported by a grant from the U.S. Air Force Office of Scientific Research) that met in Columbus, Ohio, October 13–15, (1961), under the chairmanship of R. C. ELDERFIELD.

[2] C. R. of the IUPAC Meeting, Zurich (1955).

[3] IUPAC Commission on the Nomenclature of Biological Chemistry, J. Amer. chem. Soc. *82*, 5575 (1960).

[4] M. E. WALL, Exper. *11*, 340 (1955). – M. E. WALL and H. A. WALENS, Chem. and Ind. *1957*, 818. – L. F. FIESER and M. FIESER, *Steroids* (Reinhold Publishing Corp., New York 1959), p. 824.

[5] IUPAC Information Bulletin No. 11 (Butterworth's Scientific Publications, London, October 1960), p. 56.

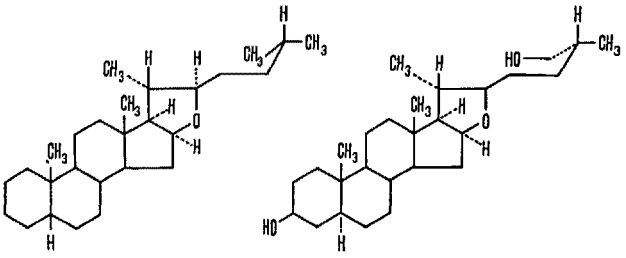
[6] L. F. FIESER and M. FIESER, Tetrahedron *8*, 360 (1960).

[7] L. F. FIESER and M. FIESER, *Steroids* (Reinhold Publishing Corp., New York 1959), p. 817.

[8] R. S. CAHN, C. K. INGOLD, and V. PRELOG, Exper. *12*, 81 (1956). This system has been recommended in the Tentative Rules for infrequent use in resolving ambiguous situations.

tertiary carbon atoms (CH_3 at carbons 10 and 13, H at carbons 5, 8, 9, 14, 16 and 17), and that of the skeletal carbon-to-carbon bond external to the ring system at secondary and quaternary carbon atoms (CH_3 at carbon 20, and C_{23} at carbon 22). New substituents are located only by carbon number if no skeletal inversions have occurred, but their configurations must be noted if their presence creates new asymmetric centers or inverts the parent skeleton at any center. Carbons 23, 24, 25 and 26 require use of the R- and S-convention. Each of these considerations is illustrated in naming the hypothetical example (IV), 9-fluoro-12α-hydroxy-14β-methoxy-23-chloro-5β, 10α, 16β, 20β, 22α-spirostan (23S, 25S).

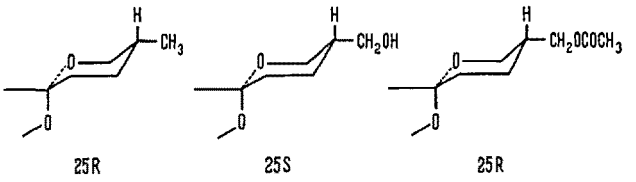
Derivatives of the sapogenins, the pseudosapogenins, dihydropseudosapogenins and congeners may be named from the parents, 5α- and 5β-furostan (V). One observes V to be nothing more than 16β, 22-epoxy-5β-cholestane (22R), but its frequent occurrence in sapogenin chemistry warrants making it a prototype, and its pentacyclic skeleton requires application of the foregoing conventions.



V VI

In practice one of the terminal carbon atoms usually bears an oxygen atom or other substituent, and configurational assignment at position 25 is therefore necessary. Dihydrotigogenin (VI) is formally 5α-furostan-3β, 26-diol (25R), and dihydropseudotigogenin 5α, 20β-furostan-3β, 26-diol (25R).

A precautionary word regarding the use of R and S is warranted where modification of substituents at or near position 25 may effect reversal of the configurational assignment, governed by the sequence rule[8], where indeed no inversion has occurred. The difficulty is illustrated by the following partial formulas:



25R 25S 25R

This apparent conflict is not a shortcoming of the system, for the correct stereochemistry will always ensue if the rules are followed. It does, however, present a barrier to the casual use of R- and S-assignments. For informal writing, discussion, and construction of models and formulas, we favour the use of the *D*- and *L*-convention with its convenient right and left hand mnemonic[9]. These symbols represent absolute configurations of the sapogenins and are compatible with the present proposal in that D and R represent the same configuration in the parent sapogenins.

Finally, it should be emphasized that this presentation of nomenclature is being made for the sole purpose of suggesting definitive rules. It is not intended to displace the trivial, semi-systematic and other names[10] in use. Instead it is an attempt to provide the primary standards for use in formal writing and indexing.

Zusammenfassung. Es werden Einzelheiten für den Gebrauch von Spirostan und Furostan, wenn nötig durch die Präfixe 5α, 5β, 25R und 25S modifiziert, für die Benennung der Steroid-Sapogenine bekanntgegeben. Diese Vorschläge sollen als formale Grundlage zur Nomenklatur gelten.

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Research Division, Marine Colloids, Inc., Rockland and Department of Chemistry, University of Maine, Orono (Maine, U.S.A.), May 9, 1962.

[8] G. P. MUELLER, Exper., *18*, 253 (1962).
[10] IUPAC Commission on the Nomenclature of Organic Chemistry, J. Amer. chem. Soc. *82*, 5545 (1960).

Some New Data on the Chromosomes of *Catarrhina*

Recent developments in cytology are providing considerable insight into the mechanisms of evolution as related to chromosome variation in mammals. In this respect, some recent work on Primate's chromosomes[1-3], seems very promising.

In the Table are reported the chromosomes numbers of the species of *Catarrhina* that I have studied recently, together with the data obtained by other workers for the same species[4].

The chromosome numbers of these groups of animals show a good deal of variation. All the species of the genus *Macaca, Papio* and *Theropithecus* have a diploid chromosome number of 42. Different species differ in some morphological characteristic in their chromosomes.

All the species I have investigated in the genus *Hylobates, Presbytis* and *Colobus* have 44 chromosomes, and they differ among each other for the morphology of some chromosomes.

The karyological situation in the genera *Cercocebus, Erythrocebus* and *Cercopithecus*, which are closely related from a systematic point of view, shows some peculiarities. All the species of the genus *Cercocebus* have 42 chromosomes. The genus *Erythrocebus* has a diploid number of

[1] M. A. BENDER and L. E. METTLER, Science *128*, 186 (1958).
[2] E. H. Y. CHU and M. A. BENDER, Science *133*, 1399 (1961).
[3] E. H. Y. CHU and N. H. GILES, Amer. Nat. *91*, 273 (1957).
[4] Sub-cutaneous tissue was obtained by biopsy and cultured one week *in vitro*. The culture method, hypotonic treatment, fixation and staining procedures used in the work have been described elsewhere (B. CHIARELLI, Caryologia *15*, 1 (1962)).