Riboflavin like many other dyes[54] can photosensitize the oxidization of a great variety of substrates in the presence of oxygen[55]. Such action can manifest itself as inactivation of microorganisms[55] hemolysis of red cells[55], inactivation of transforming principle[56], inactivation of tumor cells[57], and inactivation of a fungicide[58]. Of particular interest to botanists is the riboflavin-sensitized photoxidation of indole acetic acid[10]. It has been suggested that such destruction of this growth hormone is the origin of phototropism[10]. Another suggestion is that the substrate for photoxidation is the enzyme which produces indole acetic acid rather than the hormone itself[11]. Since the action spectrum of phototropism resembles that of riboflavin in the visible region but not in the ultraviolet region, it has been questioned whether riboflavin is the sensitizer for phototropism. However, light scattering by cellular material at shorter wavelengths could obscure the 375 mμ peak of riboflavin[12].

Résumé. Le spectre d'absorption, les caractéristiques luminescentes et photochimiques de la riboflavine sont présentés. L'interprétation des données expérimentales d'autres auteurs sur la décomposition photochimique de l'eau sensibilisée par la riboflavine est critiquée. Il faut distinguer deux cas: dans les réactions photochimiques qui ont lieu en l'absence de donneurs d'électrons ajoutés, la portion ribosique de la riboflavine se comporte en donneuse d'électrons et elle est détruite. Par contre, en présence de donneurs d'électrons ajoutés, la riboflavine agit comme véritable photosensibilisateur et n'est pas consumée dans l'ensemble de la réaction photochimique.

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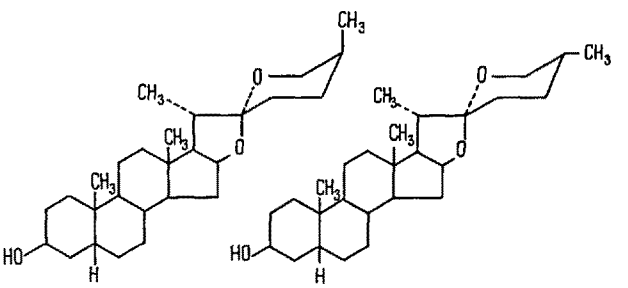
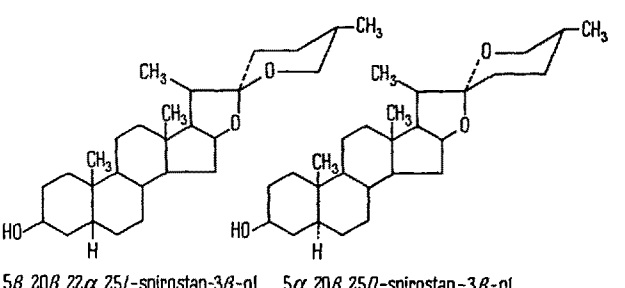
A Mnemonic for Configurations of Steroidal Sapogenins

The spiroketal side chain of steroidal sapogenins presents nomenclature and formula writing problems which remain difficult even though structural and conformational aspects are now reasonably secure. The latter have been summarized by FIESER and FIESER[1], whose clarity of presentation conceals the confusing variety of names and multiplicity of prefixes in the original literature. Resolution of the chemical problems has removed most of the naming conflicts but has left unsolved the selection of a concise systematic nomenclature for these compounds.

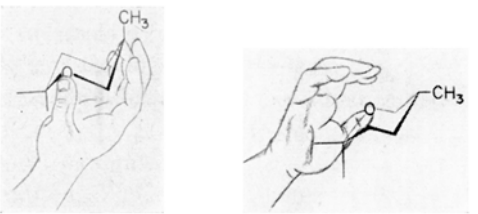
If we adopt the spirostan nomenclature set forth in IUPAC Definitive Rule 3.8[2], keeping in mind what we now know about structure, we may use the *D* and *L* convention for carbon 25[3].



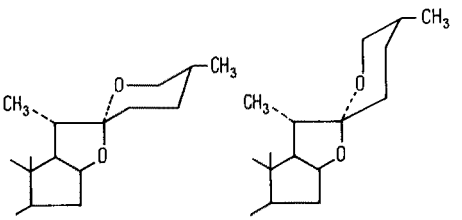


[1] L. F. FIESER and M. FIESER, *Steroids* (Reinhold Publishing Corp., New York 1959), p. 817.
[2] *Definitive Rules for the Nomenclature of Amino Acids, Steroids, Vitamins, and Carotenoids*, J. Amer. Chem. Soc. *82*, 5575 (1960).
[3] This suggestion was first introduced in an unpublished manuscript by Dr. B. RIEGEL and the author, which came to the attention of Dr. M. E. WALL. He graciously recognized and adopted our convention and first published the use of *D* and *L* in this connection (see Exper. *11*, 340 (1955)).

By this method the handling of the methyl group at carbon 25 becomes simple and informative. The use of 25*D* and 25*L* expresses absolute configuration at carbon 25 in the open or closed ring, it fosters straight-forward nomenclature, and it lends itself to the useful right- and left-hand mnemonic. The latter is illustrated[4] below for a 25*D* carbon atom, using the right hand in each case, to



show operation of the method in dealing with both possible configurations at carbon 22. It requires imaginary



orientation of the right hand so the wrist is correspondent with carbon 22 and the thumb with the ring-F oxygen atom. The methyl then lies in the direction indicated by the natural curve of the fingers. The left hand is used similarly for 25*L* sapogenins. Conformational changes incurred through conversion from one chair form to another, as illustrated, or even to a boat form, do not alter configuration at carbon 25 and the method remains valid.

By remembering that the isosapogenins belong to the 25*D* family and the normal or neosapogenins to the 25*L* family, one is able handily to categorize any written stereochemical formula. Conversely, this mnemonic offers a quick, convenient device to assist in writing, verification, discussion, and naming of spirostan formulas.

Zusammenfassung. Die Beweggründe für den Gebrauch der *D*- und *L*-Konvention in der Nomenklatur der Steroid-Sapogenine sowie ihre Anwendung auf die Konfigurationsanalyse und Formelaufstellung werden diskutiert.

G. P. MUELLER

G. D. Searle and Co., Skokie (Illinois, U.S.A.), March 12, 1962.

[4] Thanks are due Dr. L.J.CHINN for his preparation of the sketches.

The Hydroxyskatoles

Substances which are considered to be sulphatoxyskatoles or their degradation products appear to be excreted in the urine in certain pathological conditions (for references see SPRINCE[1] and RODNIGHT[2]). However, until recently, none of the corresponding hydroxy compounds had been described in the literature.

In 1956 TEUBER and STAIGER obtained a substance which they described as 5-hydroxyskatole by the action of potassium nitrosodisulphonate on 2,3-dihydroskatole but neither any proof of structure nor analytical data were given[3]. Three years later HORNING et al. reported the preparation of 6-hydroxyskatole by the hydrogenation of 6-benzyloxyskatole (obtained by an application of the Fischer Indole synthesis). However, no experimental details were given[4]. In 1961 ACHESON and HANDS obtained 5-hydroxyskatole by the hydrogenation of 5-benzyloxygramine in the presence of Adams Platinum catalyst[5]. These authors later reported that the hydrogenation of 6-benzyloxygramine in the presence of the same catalyst gave what appears to have been a mixture of 6-hydroxyskatole and 6-benzyloxyskatole along with unchanged starting material[6].

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The hydroxyskatoles

Hydroxyskatole position of OH group	M. p. (°C)	M. p. reported in literature	Crystalline form	Analysis found C	H	N	calculated C	H	N
4–[a]	123	—	Colourless small prisms from benzene/light petroleum[b]	74.00	6.07	9.34	73.45	6.16	9.52
5–	114	108–109[3], 116[5]	Colourless prisms from benzene light petroleum[b] or chloroform/carbon tetrachloride	73.72	6.22	9.52	73.45	6.16	9.52
6–[a,c]	162	149–151[4]	Colourless fine plates from benzene/light petroleum[b]	73.22	6.24	9.63	73.45	6.16	9.52
7–[a]	82.5	—	Colourless fine needles from light petroleum[b]	73.75	6.43	9.27	73.45	6.16	9.52

[a] Analytical samples were purified on a silica-gel column with adsorption from benzene and elution with 2% ethyl acetate in benzene.
[b] B.D.H. AnalaR grade (B.p. 80–100°).
[c] The methyl ether was prepared by the action of dimethyl sulphate in boiling benzene on the anhydrous sodium derivative of 6-hydroxyskatole, and purified by sublimation *in vacuo* and recrystallisation from light petroleum.