tetrachloride essentially as has recently been described by Whitmore.[2] In many runs we found it practical to dissolve the silicon tetrachloride in either pure benzene or a mixture of dry ether and benzene (recovered from previous runs) rather than in pure ether. Yields were ordinarily 20–45%. Isopropylmagnesium bromide, however, gave 5–6% yield of the trichloride,[3] together with an equal weight of the dichloride (11% yield, based on the Grignard reagent).

For the preparation of diisobutylsilicon dichloride equimolar quantities of the Grignard reagent and isobutylsilicon trichloride (in benzene) were placed in reaction. The yield was about 20%.

(2) Whitmore, *et al.*, THIS JOURNAL, **68**, 475 (1946).

(3) Booth and Spessard, *ibid.*, **68**, 2660 (1946).

Silicon tetrachloride was inert toward ethynylsodium, HC≡CNa, or ethynebis-(magnesium chloride), ClMgC≡CMgCl.

NEW COMPOUNDS, $RSiCl_3$ AND R_2SiCl_2

Substance	B. p. °C.	B. p. Mm.	d^{20}_4	Anal., Cl Calcd.	Anal., Cl Found	
p-$CH_3OC_6H_4SiCl_3$	128–130	13	1.46	44.04	43.62	44.32
p-$C_2H_5OC_6H_4SiCl_3$	137–138	13	1.36	41.62	41.42	41.18
$(i\text{-}C_4H_7)_2SiCl_2$	67–69	11	1.06	38.31	39.20	38.90
$(i\text{-}C_4H_9)_2SiCl_2$	93	16	1.00	33.26	33.26	33.17

NORTHWESTERN UNIVERSITY
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CHARLES D. HURD
W. A. YARNALL

RECEIVED SEPTEMBER 13, 1948

COMMUNICATIONS TO THE EDITOR

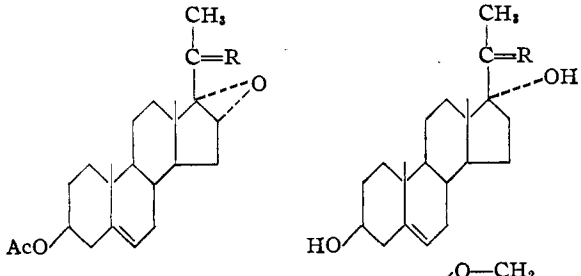
17α-HYDROXYSTEROIDS

Sir:

The recent communication by Plattner, Heusser and Feurer[1] impels us to record certain work on the reduction of steroid oxides which has been under way in these Laboratories for some time.

We have likewise prepared Reichstein's substances J and O by the reduction of 16,17-oxido-allopregnane-3β-ol-20-one acetate with lithium aluminum hydride. Furthermore, we have investigated the lithium aluminum hydride reduction of 16,17-oxido-5-pregnene-3β-ol-20-one acetate. The nature of the resulting 3,17,20-triol mixture was confirmed by oxidation with periodic acid to dehydroisoandrosterone (m. p. 148–149°; acetate, m. p. 166–168°).

We wish, particularly at this time, to report a novel procedure for the preparation of 17α-hydroxy steroids bearing a ketone group at position 20. The focal point in the facile preparation of these derivatives has been the protection of the 20-keto group through the formation of cyclic ketals. The 16,17-oxido-20-ketals undergo smooth reduction with lithium aluminum hydride and the resulting products are readily cleaved to the desired 17α-ol-20-ones.



(1) Plattner, Heusser and Feurer, *Helv. Chim. Acta*, **31**, 2210 (1948).

16,17-Oxido-5-pregnene-3β-ol-20-one Acetate (I).—Plates from methanol, m. p. 154–155°; $[\alpha]^{26}D$ −9.0° (chloroform). *Anal.* Calcd. for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C, 74.43; H, 8.72. It was prepared by the action of perbenzoic acid on derivatives of 5,16-pregnadiene-3β-ol-20-one.

Ketal of 16,17-Oxido-5-pregnene-3β-ol-20-one Acetate (II).—From the oxido-pregnene (I) and ethylene glycol by refluxing a benzene solution with p-toluenesulfonic acid monohydrate as catalyst as thick, needle-like prisms from benzene-methanol, m. p. 195–197°; $[\alpha]^{27}D$ −37.8° (chloroform). *Anal.* Calcd. for $C_{25}H_{36}O_5$: C, 72.07; H, 8.71. Found: C, 71.92; H, 8.67.

Ketal of 17α-Hydroxypregnenolone (III).—From the reduction of the ketal (II) with lithium aluminum hydride in benzene–ether solution as plate-like prisms from acetone, m. p. 185–187°; $[\alpha]^{26}D$ −44.8° (chloroform). *Anal.* Calcd. for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64. Found: C, 73.63; H, 9.70.

17α-Hydroxypregnenolone (5-Pregnene-3β,17α-diol-20-one) (IV).—From the ketal (III) by cleavage with sulfuric acid in aqueous methanol as fine prisms from methanol, m. p. 265°[2]; $[\alpha]^{28}D$ −34.4° (2 parts ethanol–1 part dioxane). *Anal.* Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.42; H, 9.84. Acetylation of the 17α-hydroxypregnenolone with acetic anhydride-pyridine gave the acetate, needles from benzene–petroleum ether (b. p. 35–60°), m. p. 232–234°.[2]

By the Oppenauer oxidation of 16,17-oxidopregnenolone (16,17-oxido-5-prenene-3β-ol-20-one) we have incidentally prepared 16,17-oxidoprogesterone (16,17-oxido-4-pregnene-3,20-dione) as fine prisms from aqueous methanol, m. p. 205–207°; $[\alpha]^{27}D$ +160.8° (chloroform). *Anal.* Calcd. for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59. Found: C, 76.50; H, 8.68.

The investigations are being continued.

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EDWIN W. MEYER
ISABELLE RYDEN

RECEIVED JANUARY 31, 1949

(2) *Cf.* Fuchs and Reichstein, *Helv. Chim. Acta*, **24**, 804 (1941) Hegner and Reichstein, *ibid.*, **24**, 828 (1941).

THE RESOLUTION OF SPARTEINE

Sir:

In consideration of the recently reported syntheses of sparteine[1,2] we wish to record herein the resolution of *dl*-sparteine, the total synthesis of which was first announced from this Laboratory.[3] Synthetic *dl*-sparteine was resolved by means of β-camphorsulfonic acid, and both *d*- and *l*-sparteine were isolated and identified.

Equimolar portions of racemic sparteine and *d*-β-camphorsulfonic acid in ethanol gave ***l*-sparteine *d*-β-camphorsulfonate.** After two recrystallizations from acetone the specific rotation remained constant, $[\alpha]^{29}D$ 24.8 ± 0.5° (*C*, 1.932 in chloroform), and consistent with that of an authentic sample of the *d*-β-camphorsulfonate of natural *l*-sparteine, $[\alpha]^{29}D$ 24.4 ± 0.5° (*C*, 2.298 in chloroform). Both natural and synthetic salts melted at 240–241°, as did a mixture of the two. ***l*-Sparteine dipicrate,** yellow needles, m. p. 207–208°, was prepared directly from the *d*-β-camphorsulfonate salt in ethanol by the addition of ethanolic picric acid (*Anal.* Calcd. for $C_{27}H_{32}N_8O_{14}$: C, 46.82; H, 4.66; N, 16.18. Found: C, 47.13; H, 4.54; N, 15.94). The melting point was depressed when the compound was mixed with *dl*-sparteine dipicrate, m. p. 208°, undepressed when mixed with natural *l*-sparteine dipicrate, m. p. 208°.[4]

Following the separation of the *l*-sparteine *d*-β-camphorsulfonate, *d*-sparteine-enriched base was freed from the mother liquor and was converted, by treatment with *l*-β-camphorsulfonic acid,[5] to ***d*-sparteine *l*-β-camphorsulfonate.** After three recrystallizations from acetone, this salt melted at 239–241° and exhibited a specific rotation, $[\alpha]^{22}D$ −24.0 ± 0.5° (*C*, 2.040 in chloroform), approximately equal and opposite to that of its antipode. ***d*-Sparteine dipicrate,** yellow needles, m. p. 208–209°, was prepared directly from the *l*-β-camphorsulfonate salt and showed no depression in melting point when mixed with the dipicrate of natural *d*-sparteine,[6] m. p. 208°.[7] ***d*-Sparteine monoperchlorate,** colorless needles, m. p. 174°, was prepared by dissolving *d*-sparteine *l*-β-camphorsulfonate in a small amount of water, acidifying to *p*H 1–2 with 65% perchloric acid, and then basifying with ammonium hydroxide. The perchlorate separated on cooling and was recrystallized from ethanol–ether. A mixture with the monoperchlorate of natural *d*-sparteine,[6] m. p. 173°,[7] was also 173°.

The infrared absorption spectra of natural *l*-, resolved *l*-, natural *d*-, and resolved *d*-sparteine dipicrates were determined[8] and were found to be identical for these samples in the crystalline state and very slightly different from that of crystalline *dl*-sparteine dipicrate.[3]

(1) Clemo, Raper and Short, *Nature*, **162**, 296 (1948).

(2) Sorm and Keil, *Coll. Czechoslov. Chem. Commun.*, **13**, 544 (1948).

(3) Leonard and Beyler, THIS JOURNAL, **70**, 2298 (1948).

(4) Moureu and Valeur, *Bull. soc. chim.*, [3] **29**, 1135 (1903).

(5) Obtained by resolution of *dl*-β-camphorsulfonic acid according to the method of Burgess and Gibson, *J. Soc. Chem. Ind.*, **44**, 496T (1925).

(6) We wish to acknowledge the kindness of Dr. Léo Marion, National Research Council, Ottawa, Canada, in supplying us with authentic samples of *d*-sparteine dipicrate and *d*-sparteine perchlorate.

(7) Marion and Ouellet, THIS JOURNAL, **70**, 691 (1948); Marion and Turcotte, *ibid.*, **70**, 3253 (1948); Marion and Cockburn, *ibid.*, **70**, 3472 (1948).

(8) The authors are indebted to Mrs. James L. Johnson for determination of the infrared absorption spectra.

THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS NELSON J. LEONARD
URBANA, ILLINOIS ROGER E. BEYLER

RECEIVED JANUARY 14, 1949

CRYSTALLINE XYLAN AND MANNAN

Sir:

I wish to report the isolation of a crystalline xylan from barley straw and birchwood. The weaker linkages of the xylan-rich fraction of the hemicelluloses of these materials, purified by the method of Salkowski, were hydrolyzed under mild conditions (0.2% oxalic acid at 100°); the reducing value of the hydrolysate was virtually constant after five hours. The insoluble portion from the hydrolysis, on autoclaving at 120°, was soluble in water to the extent of about 0.2%; on cooling to 60–70°, hexagonal platelets with rounded corners separated. The xylan was purified by heating a water paste for five hours at 120°, readily filterable spherocrystals being obtained. Barley xylan is purified more readily than birch xylan. Aging of the amorphous xylan or contact with dilute alkali renders it insoluble in 3 *N* sodium hydroxide. Wet heat at 120° and *p*H 5 restores its solubility. Attempts to prepare a slash pine xylan failed. The crystals are doubly refractive and give typical crystalline X-ray diffraction patterns. Crystalline D-xylose was prepared in good yield and its identity confirmed. A diphenylhydrazine test for arabinose in the mother liquor was negative. This, coupled with the high pentosan analysis, indicates relatively pure xylan. Breddy–Jones and Wise–Appling xylose determinations on 3% nitric acid hydrolysates confirmed this finding. Osmotic pressure measurements on methylated barley xylan indicate a degree of polymerization of 39. A newly developed aldose end-group method gave the

	Material from selective hydrolysis		Repeatedly recrystallized xylan	
	Barley	Birch	Barley	Birch
Pentosans as xylan (cor. for uronic acids), %	97.4	92.4	99.5	97.9
Uronic anhydride (cor. for CO_2 from xylose), %	2.4	6.4	0.38	2.39
Ash, %	0.85	..	0.34	0.39

same value. Birch xylan, compared viscometrically with barley xylan, had a degree of polymerization of 35. Optical rotational measurements indicate a 1,4′,β-linkage. This is based on the rotational shift method of Reeves and comparisons with Haworth's esparto xylan.

Mannan "A" of ivory nut readily forms supersaturated solutions of 1% concentration. Such a solution crystallizes if heated to 60–70° for several days. The crystals initially are rods and gradually become dumb-bell shaped as growth continues. Slight double refraction is evident. A mannan-rich fraction from slash pine gave similar crystals. Repeated recrystallization did not alter the facility or habit of crystallization. The crystals assayed only 50% mannan and had a light tan color.

This work will be published in full at a later date.

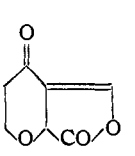
THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN ALBERT P. YUNDT

RECEIVED JANUARY 15, 1949

THE STRUCTURE OF PATULIN

Sir:

We are reporting elsewhere in detail the considerations which led us to reject the accepted structure[1] (I, *and/or* tautomers) for the well-known mold metabolite and antibiotic, patulin, in favor of a new expression (II, R = OH). Here we rerecord the synthesis of (II, R = H), which we designate as *desoxypatulin*, since its relevant physical properties resemble those of patulin so closely as to provide very strong support for our structural views.



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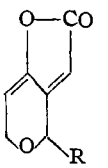
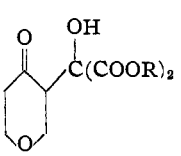
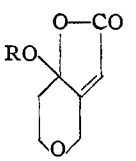


II

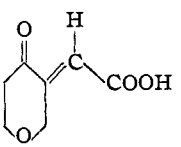
Condensation of tetrahydro-γ-pyrone with ethyl mesoxalate gave the ketol (III, R = Et), m. p. 58.5–60° (Calcd. for $C_{12}H_{18}O_7$: C, 52.55; H, 6.57. Found: C, 52.73; H, 6.67). When the corresponding acid (III, R = H) was heated with acetic anhydride and acetic acid, among the products obtained were: (i) the *cis*-acid (IV, R = H), m. p. 122–123° (Calcd. for $C_7H_8O_4$: C, 53.85; H, 5.13. Found: C, 53.77; H, 5.18), (ii) the lactol acetate (IV, R = Ac), m. p. 121.5–123° (Calcd. for $C_9H_{10}O_5$: C, 54.55; H, 5.05. Found: C, 54.64; H, 5.02), (iii) the *trans*-acid (V), m. p. 153° (Calcd. for $C_7H_8O_4$: C, 53.85; H, 5.13. Found: C, 53.89;



III



IV



V

H, 5.25). Treatment of (IV, R = Ac) with warm acetic anhydride–acetic acid–sulfuric acid[2] gave desoxypatulin (II, R = H), m. p. 46–48° (Calcd. for $C_7H_6O_3$: C, 60.80; H, 4.35. Found: C, 60.62; H, 4.37), whose ultraviolet spectrum possessed a single maximum at 273 mμ (log ε, 4.17) (patulin: $\lambda_{max.}$, 276 mμ (log ε, 4.22)), and whose infrared spectrum in the double bond region reproduced in detail the very characteristic spectrum of patulin in the same region (Fig. 1).

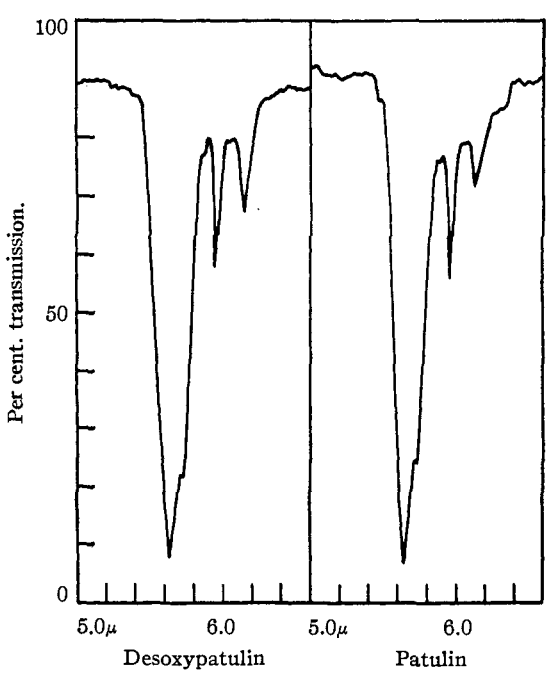
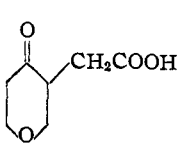
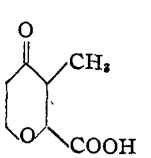


Fig. 1.—Spectra in CH_2Cl_2.

Further support for the structure (II, R = OH) was forthcoming when the oily acid (VI), obtained by the hydrogenation either of the *cis*-acid (IV, R = H) or the *trans*-acid (V), was shown to be identical, through comparison of the methyl ester 2,4-dinitrophenylhydrazones, m. p. 149–150°, with the acid $C_7H_{10}O_4$ originally obtained by Ber-



VI



VII

(1) For references *cf. Quart. Reviews Chem. Soc.*, **2**, 53 (1948).

(2) *Cf.* Shaw, THIS JOURNAL, **68**, 2510 (1946).

gel, *et al.*,[3] from patulin, and assigned by them the structure (VII).[4]

(3) Bergel, Morrison, Moss and Rinderknecht, *J. Chem. Soc.*, 415 (1944).

(4) A reduction of our *trans*-acid and the first comparison of (VI) with Bergel's acid was carried out by Professor Pl. A. Plattner and Dr. Engel (Zürich). We thank Professor Plattner warmly for his cooperation, and for samples of derivatives of Bergel's acid which enabled us to carry out the similar correlation with the *cis*-acid (IV, R = H).

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RECEIVED JANUARY 17, 1949

NEW BOOK

Carotinoide. By PAUL KARRER AND ERNST JUCKER, Chemical Institute of the University of Zurich. (Lehrbücher und Monographien aus dem Gebiete der Exakten Wissenschaften, 17. Chemische Reihe, Band III.) Verlag Birkhäuser, Basel, Switzerland, 1948. 388 pp. 17 × 24.5 cm. Price, 39.-Swiss francs (paper binding); 43.-Swiss francs (linen binding).

With the rapid expansion of chemical research in the past twenty-five years, the organization and correlation of diverse observations in complex fields has become a great problem to all specialists, research workers, teachers and students. Although *Chemical Abstracts* and the numerous review journals provide leads to many isolated facts, there is as yet no satisfactory substitute for the comprehensive monograph written by an authority in the field. For this reason, there are widespread benefits when so productive research workers as Professor Karrer and his collaborator, Dr. Jucker, summarize the studies of the carotenoids, a highly specialized field in which they have made many significant contributions over a long period.

If a technical book is to be more than a handbook, the authors must select their material carefully, omitting the extraneous observations and including and emphasizing the pertinent facts that lead to progress in the field. The choice of material will of necessity reflect the aims, the interest and the experience of the writers. The readers, on the other hand, will examine the book from their particular points of view seeking new information often with a view toward further application in their own fields.

This new monograph on the carotenoids is divided into two parts; a general section of 100 pages and a special section of 231 pages. The general part contains rather brief descriptions of the state or condition of the carotenoids in plants and animals (4 pp.); the origin and physiological significance of the carotenoids in plants and animals (10 pp.); the isolation of the carotenoids (9 pp.); the chemical constitution of the carotenoids, represented by 31 formulas (8 pp.); *cis-trans* isomerization of the carotenoids (5 pp.); methods for determination of the chemical structure (10 pp.); relationship between constitution and color of the carotenoids (7 pp.); and partial syntheses of carotenoids (5 pp.). The last 35 pages of this general section are devoted to tables showing the occurrence of carotenoids in various species of plants and animals classified according to families. For these tables alone, 434 publications are cited. Here is a mass of information not readily available elsewhere.

The second part of this monograph describes the individual carotenoid pigments; particularly, their occurrence, with tables illustrating sources; methods for their preparation; their chemical constitution; their properties such as absorption maxima, solubility, optical activity, adsorbability, etc.; *cis-trans* isomers; and various derivatives of the pigments. Some 28 pigments of known structure and 37 pigments of unknown structure as well as numerous derivatives of these substances are described. Finally, there are 12 colored pictures of carotenoid crystals and 28 figures of spectral absorption curves determined in various solvents. Two indexes provide references to the plants and animals in which the pigments occur and to the usual subject matter.

All this diverse material has been brought together according to a carefully arranged outline, so that the included facts are readily found by readers with different points of view. As a result, this book provides a service to everyone interested in the carotenoid pigments, although at the price quoted ($13.50) it is rather expensive. Unfortunately, there are some omissions of important data; hence, this monograph cannot be relied upon as an impartial source of information.

All chemists, especially those in the food and fodder industries where determinations of the carotenoid pigments have contributed so much to the improvement of our food supply, will be amazed to find few if any references to the careful spectral absorption work carried out in the United States during the past fifteen years. Most of the American results, which have been obtained with different instruments calibrated in different ways and which are in remarkably good agreement, differ significantly from many of those presented in the monograph. As one example, Figure 28 showing lycopene with smaller absorption coefficients than carotenes is contrary to all this uncited experience and to the theories concerning the spectral absorption capacity of unsaturated compounds.

In view of Professor Karrer's contributions, chemists interested in the chromatographic adsorption method will not be surprised that so much emphasis has been placed upon the use of zinc carbonate as an adsorbent. They will be astonished, however, to find that so little attention has been devoted to other adsorbents which have been widely used and which occasionally have made possible separations and identifications not included in this monograph, specifically the separation of neoxanthin and violaxanthin and the confirmation of the identity of violaxanthin from leaves with violaxanthin from pansies. Variation of the adsorption sequence with variation of the solvent and adsorbent is not reported. For the one adsorption sequence of the carotenoids that is summarized in the form of a table, there is no record of the solvent and the adsorbent.

The universal occurrence of carotenoid pigments in the photosynthetic apparatus of green plants and the possible role of these pigments in the utilization of solar energy have stimulated a great deal of biological, physiological and chemical investigation in the past decade, but none of these publications are cited in the present monograph. This work on chloroplast pigments has led to the discovery of many new carotenoids that are not included in this book. Examples are: neoxanthin from leaves, dinoxanthin from dinoflagellates, diadinoxantin from diatoms and dinoflagellates, etc. The fact that fucoxanthin is the principal xanthophyll of diatoms is omitted as is also the universal occurrence of zeaxanthin in green leaves. No mention