

Reinecken, and ourselves. In previous diagrams the horizontal was drawn extending to 50% iron because the liquidus is extremely flat in this region and it was assumed to be quite flat. Knowing from our work the actual composition of the iron-rich layer, it is apparent that the horizontal extends to only 40% iron and that from 40 to 50% iron there is an ascent in temperature. The curve as drawn by us does no great violence to the experimental points of other workers. We have drawn the limits of the two liquid region as if the mutual solubility decreased with rising temperature, since this is what our figures indicate. Since, however, the sides of the gap are certainly very straight and our accuracy not much better than one per cent., it is easily possible that the sides slope in the other direction, that is, that the (real or hypothetical) critical solution temperature is approached by raising, not lowering, the temperature.

Acknowledgment.—Two of us (J. H. W. and G. B. S.) are indebted to the Consolidated Mining and Smelting Company of Trail, B. C., for Fellowships which enabled them to pursue this work, and for funds for the purchase of apparatus and chemicals.

Summary

1. The eutectic temperature and composition of the system iron-tin have been determined.
2. The equilibrium curve for tin-iron solid phase in contact with tin-iron liquid phase, the liquidus curve, has been determined from the melting point of tin, 232°, up to 1134°, the temperature of the miscibility gap.
3. The existence of a miscibility gap has been proved and its limits determined from 1134 to 1300°.

WINNIPEG, MAN.

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[CONTRIBUTION FROM THE CHEMICAL DIVISION OF THE PROCTER & GAMBLE CO.]

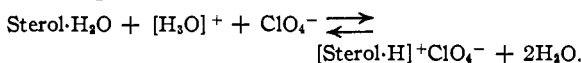
Colorless Crystalline Perchloric and Hexafluorophosphoric Acid Salts of Sterols. The Color Formation between Sterols and Perchloric Acid

BY WILLY LANGE, ROBERT G. FOLZENLOGEN AND DON G. KOLP

Introduction.—The general object of this paper is to show that common sterols form colorless crystalline salts when properly treated with stoichiometric quantities of perchloric or hexafluorophosphoric acids. In the presence of excess acid, the colorless salts are transformed to already well recognized halochromic compounds.

Formation of Colorless Sterolium Salts.—It has been found that colorless, well formed crystals of Sterol·HClO₄ are precipitated when sterols containing the 3(β)-hydroxy-Δ⁵-ene groups are dissolved in chloroform and then treated with stoichiometric quantities of perchloric acid containing more than 55% HClO₄. The sterols capable of yielding colorless salts include cholesterol, stigmasterol, beta-sitosterol and ergosterol. Since the sterolium salts hydrolyze instantaneously on contact with excess water, it is possible to recover quantitatively the unchanged sterol by allowing hydrolysis to proceed in the presence of a water-insoluble solvent for the sterol.

The precipitation of the perchlorate may be carried out with anhydrous sterol as well as with the compound containing water of crystallization. Salt precipitation and hydrolysis may be written as an equilibrium reaction



In the absence of excess acid the crystals, which are hexagon-shaped microscopic plates, remain colorless for a day or so when suspended in the

chloroform solution or even longer when stored in dry form in a desiccator. They appear to be stable against shock and friction, but burn fiercely when heated on a spatula. In the reaction between sterol and perchloric acid, chloroform may be replaced with other oxygen- and nitrogen-free solvents, such as carbon tetrachloride, bromoform, ethylene chloride, trichloropropane, 1,4-dichlorobutane, Skellysolve B, benzene, toluene, and monochlorobenzene.

Hexafluorophosphoric acid (60–70% HPF₆) is the only other mineral acid found which reacts in the same manner as perchloric acid. Its use is advantageous in certain respects because its salts are non-inflammable.

Alteration of one of the two essential groups in common sterols results in failure to observe the formation of crystallized salts, while color formation takes place, *i. e.*, a halochromic ion is formed when a conjugated double bond system could be formed under the dehydrating influence of the strong acid. The introduction of a second (conjugated) double bond into ring B makes the sterol molecule very sensitive toward an excess of acid but does not change its ability to form a colorless crystalline precipitate with perchloric acid. The precipitability is lost, however, when the iso-octyl chain in 17-position is replaced with a ketonic oxygen atom.

Information on crystallized salts or addition compounds of sterols with strong mineral acids from which the sterols may be recovered un-

changed by treatment with water, appears to be limited.^{1,2} Hydrohalic acid addition products precipitate when gaseous hydrogen chloride or bromide is passed into non-alcoholic solutions of sterols.³

Color Formation.—When the sterols are precipitated with an excess over the stoichiometric quantity of perchloric or hexafluorophosphoric acid, they are slowly digested by the free mineral acid and halochromic compounds are formed, a pronounced purple color appearing in the solution. Water hydrolyzes these compounds instantaneously and the color disappears. Esterification of the hydroxy group, *e. g.*, acetylation, facilitates the color formation with perchloric acid.⁴ The halochromic ion is not stable and apparently polymerizes, resulting in the formation of hydrocarbons, $(C_{27}H_{44})_x$, probably of dimeric and trimeric nature, and the appearance of a brownish color in the acid chloroform solution. Color formation and polymerization are less pronounced with hexafluorophosphoric acid, probably a weaker acid than perchloric. The use of perchloric acid, replacing sulfuric acid in sterol color tests, has recently been suggested by Schaltegger.⁵

On the basis of published information^{6,7,8,9} and the new experimental data, it appears that the following sequence of reactions may take place when a sterol, in an inert solvent, is brought into contact with perchloric acid or another strong mineral acid

- (1) Sterol + acid \rightarrow colorless sterolium salt (ordinarily remaining dissolved)
- (2) Sterolium salt + excess of acid \rightarrow colorless cholestadiene
- (3) Cholestadiene + acid \rightarrow strongly purple-colored halochromic salt
- (4) Unstable purple halochromic salt \rightarrow polymerization to $(C_{27}H_{44})_x$ (brownish halochromic salt with mineral acid)

Color formation between steroids in chloroform solution and concd. perchloric acid (and similarly with other strong acids) appears to take place whenever the steroid has a conjugated double bond system in rings A and B or whenever it forms such a system under the influence of an acid. Thus, $\Delta^{3,5}$ -cholestadiene instantaneously forms a dark red halochromic compound, while sterols with a single double bond in 5-position form a sim-

ilar compound comparatively slowly. The wave lengths of the absorption maxima and minima of some of these colored complexes in chloroform solution are tabulated in Table I.¹⁰ The presence of a second, conjugated double bond in ring B of the unreacted sterol (ergosterol) gives rise to an additional pronounced maximum (625 $m\mu$) in the visible region. Replacement of the iso-octyl

TABLE I
ABSORPTION SPECTRA MAXIMA AND MINIMA OF STEROID-PERCHLORIC ACID REACTION PRODUCTS IN CHLOROFORM SOLUTION

	Absorption maxima ($m\mu$)	Minima ($m\mu$)
$\Delta^{3,5}$ -Cholestadiene	398 496	446
Cholesterol	388 500 about 550	453
Phytosterols (Eastman)	386 498 about 550	451
Stigmasterol	389 499 about 550	440
beta-Sitosterol	390 498 about 550	435
Ergosterol	388 488	626 437 552
Ergosterol acetate	388 495	625 437 535
Dehydro-iso-androsterone	425 494 552	440 538

chain in 17-position with a carbonyl oxygen atom (dehydro-iso-adrosterone) resulted in a shift of the 390 $m\mu$ maximum to the right and reduction of its intensity, while a very weak maximum (shelf), usually observed with common sterols at about 550 $m\mu$, became more pronounced, with the maximum in the center remaining unchanged.

It is assumed that the first step in the color formation with cholesterol is the formation of a cholestadiene, although efforts to isolate this monomeric hydrocarbon have not been successful. The assumption is supported by the fact that $\Delta^{3,5}$ - and $\Delta^{2,4}$ -cholestadiene, under the influence of perchloric acid, form polymerization products very similar to or identical with the hydrocarbon obtained from cholesterol. The polymerized hydrocarbons have the same analytical composition and their absorption spectra in neohexane show almost the same maxima positions (Fig. 1). Intensity differences for corresponding maxima of the recrystallized compounds appear to be due to different ratios of dimer and trimer in the compounds. The recrystallized hydrocarbons, when treated with perchloric acid in chloroform solution, show, in the visible part of the spectrum, a pronounced adsorption maximum at 395 $m\mu$ ($\alpha = 13.50$), with indications of a shelf on each side.

The absorption spectra of the colored compounds formed in the reaction between sterol and perchloric acid change considerably with time.¹¹ The absorption intensities of the maximum at about 490 $m\mu$ and the minimum at about 450 $m\mu$

(10) Solutions of 10 mg. of the steroid in 50 cc. of chloroform were shaken for five minutes (dehydro-iso-androsterone, ergosterol and its acetate thirty seconds only) with 1 cc. of 70% perchloric acid and read after thirty minutes.

(11) For color variations in the Liebermann-Burchard test see W. M. Sperry and F. C. Brand, *J. Biol. Chem.*, **180**, 315 (1943); M. E. Wall and E. G. Kelley, *Anal. Chemistry*, **19**, 677 (1947).

- (1) J. Mauthner and W. Suida, *Monatsh.*, **24**, 648 (1903).
- (2) F. H. Gayer and C. E. Fawkes (to Continental Research Corp.), U. S. Patent 2,248,346 (1941).
- (3) L. Yoder (to Iowa State College Res. Foundation), U. S. Patent 2,322,906 (1943); V. R. Mattox, B. F. McKenzie and E. C. Kendall, *THIS JOURNAL*, **70**, 2662 (1948).
- (4) J. A. Gardner and M. Williams, *Biochem. J.*, **15**, 371 (1921); F. E. Kelsey, *J. Biol. Chem.*, **127**, 15 (1939).
- (5) H. Schaltegger, *Helv. Chim. Acta*, **29**, 285 (1946).
- (6) O. Rosenheim, *Biochem. J.*, **23**, 47 (1929); L. F. Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1936, p. 117; M. C. Nath, M. K. Chakravorty, and S. R. Chowdhury, *Nature*, **157**, 103 (1946); H. Schaltegger, *ref. 5*.
- (7) J. Mauthner and W. Suida, *Monatsh.*, **17**, 29 (1896).
- (8) G. S. Whitby, *Biochem. J.*, **17**, 5 (1923).
- (9) F. Wokes, *ibid.*, **22**, 830 (1928).

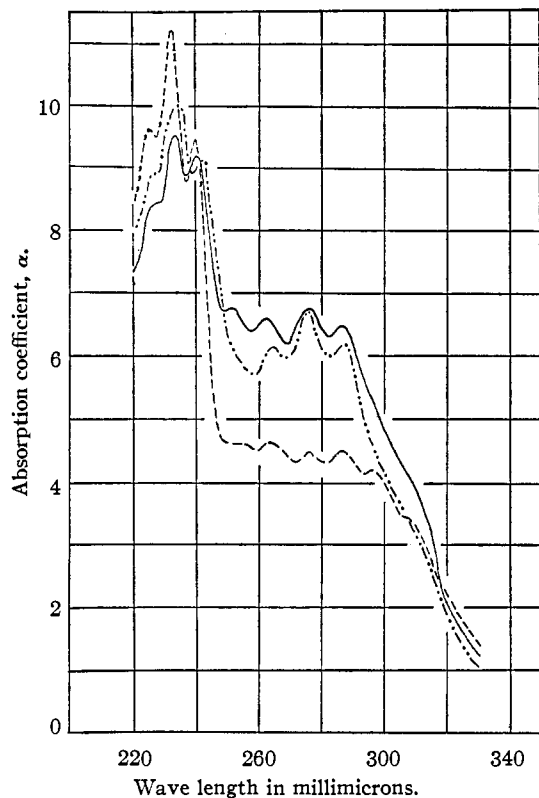


Fig. 1.—Absorption spectra of polymeric hydrocarbons, $(C_{27}H_{44})_x$, in neohexane: ---, from cholesterol; —, from $\Delta^{5,6}$ -cholestadiene; - · - ·, from $\Delta^{2,4}$ -cholestadiene. $\alpha = \log(I_0/I_x)/cd$, where I_0 = transmission of solvent cell, I_x = transmission of solution cell, c = concn. in g. per liter, and d = cell thickness in cm.

always increase while the maximum at about 390 $m\mu$ rises rapidly in the early stages and then drops to a certain level which it holds without much further change. The position of the maximum at 394–395 $m\mu$ is identical with that of the polymeric hydrocarbon (395 $m\mu$).

Steroid-containing natural oils and fats, dissolved in chloroform and treated with perchloric acid of a concentration higher than about 55% $HClO_4$, develop a pink color with the characteristic absorption spectra shown in Fig. 2. Oils containing components which discolor with strong mineral acids show the typical color and spectrum when reacting with acid after partial hydrogenation.

Experimental

Sterolium Perchlorates

Materials.—Chloroform used in the investigation was washed with water, dried and distilled. A trace of alcohol in the solvent vastly decreases the precipitability of sterolium salts, and a trace of acetone may completely prevent precipitation. A commercial aqueous solution of perchloric acid containing 70% $HClO_4$ was used in the various tests. Upon dilution of the perchloric acid, the lower limit for precipitation of cholesterolium perchlorate was observed at 55.6% $HClO_4$, or at an approximate ratio of 1 mole $HClO_4$: $4\frac{1}{8}$ moles H_2O .

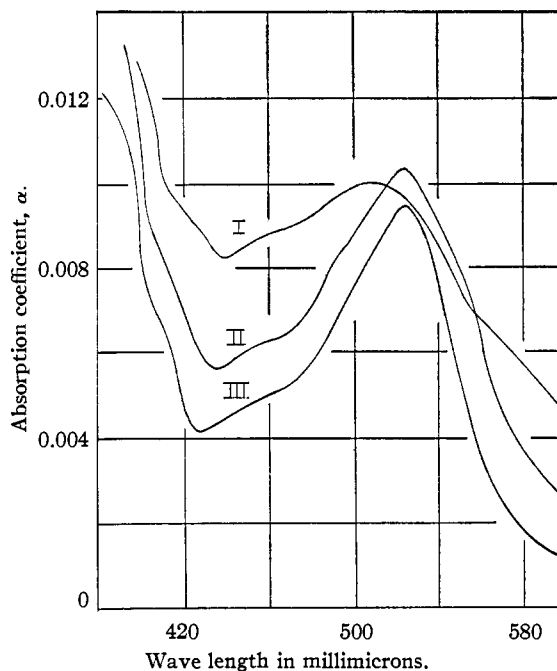


Fig. 2.—Absorption spectra of fats dissolved in chloroform and treated with perchloric acid: I, partially hydrogenated linseed oil (I. V. 80); II, cocoa butter; III, partially hydrogenated soybean oil (I. V. 75).

Cholesterolium Perchlorate.—Ten cc. of a solution containing 1 g. of cholesterol (m. p. 149° and $[\alpha]_D^{25} -37.5$ in chloroform) in chloroform were shaken vigorously for a few seconds, in a glass-stoppered flask, with 0.372 g. of a 70% perchloric acid, which is a ratio of 1 mole sterol to 1 mole $HClO_4$. A thick mass of white crystals formed immediately, the solution remaining colorless. The mixture was stored for one minute at room temperature and filtered through a sintered glass crucible, using vigorous suction. Care was taken not to suck undried air through the crystal cake for more than twenty seconds. The crystal cake was freed from adhering liquid by pressing on a dry porous plate and then dried in a desiccator over potash pellets and thin slices of solid paraffin. The crystals were analyzed for perchloric acid by titration of the acid. The identity of the acid was verified by quantitative precipitation in the form of nitron perchlorate.

Anal. Calcd. for $C_{27}H_{46}O \cdot HClO_4$: $HClO_4$, 20.64. Found: $HClO_4$, 20.59.

A portion of the dried crystals was decomposed by shaking with water and chloroform. The sterol was recovered quantitatively from the solvent; melting point (149°) and optical rotation ($[\alpha]_D^{25} -37.5$) remained unchanged.

The results of microscopic and X-ray examination of cholesterol monohydrate and cholesterolium perchlorate, prepared from the monohydrate, are summarized

	Cholesterol monohydrate	Cholesterolium perchlorate
Principal	68.4 strong	64.6 strong
X-ray spacings, Å.	8.49 weak 5.77 medium 3.81 weak	6.47 weak 5.85 medium 3.91 weak
Crystal system	Monoclinic ¹³	Orthorhombic or monoclinic

(12) J. D. Bernal, D. Crowfoot and I. Fankuchen, *Trans. Roy. Soc. London*, **A289**, 135, (1940).

	Cholesterol monohydrate	Cholesterolum perchlorate
Crystal habit	Rhomb-shaped plates (see Fig. 3)	Hexagon shaped plates (see Fig. 3)
Interference figure	Biaxial	Biaxial
Extinction	Oblique	Parallel
Elongation	Negative	Negative

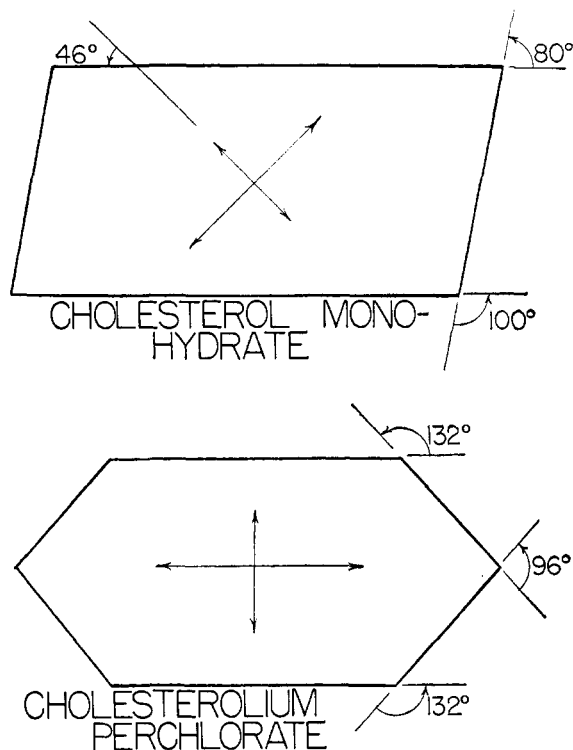


Fig. 3.—Crystal habit of cholesterol monohydrate and cholesterolum perchlorate.

The conditions necessary for precipitation of sterols with perchloric acid and the composition of the precipitates obtained under various conditions were determined. Ten cc. portions of solutions of cholesterol in chloroform were shaken for a few seconds with a known quantity of a 70% perchloric acid and then handled as described before, with the difference that the perchlorates were dried in the sintered glass crucible. The crystal yields decreased when more dilute chloroform solutions were used and larger quantities of perchloric acid were required for quantitative precipitation, resulting in increased decomposition and color formation. A quantitative yield of pure perchlorate crystals was obtained when 10 cc. of a 10% cholesterol solution was treated with 0.544 g. of 70% perchloric acid (molar ratio of HClO_4 :sterol = 1.46). The addition of about 0.38 g. of the aqueous acid (molar ratio of 2.05) was necessary to achieve the same result with a 5% cholesterol solution. When the concentration of the solution was reduced to 2.5% cholesterol, a yield of 73.9% pure perchlorate was obtained upon addition of 0.147 g. of 70% perchloric acid (molar ratio of 1.58); to achieve quantitative precipitation, it was necessary to use about 0.30 g. of the aqueous acid (molar ratio of 3.24), however, the product was cherry red and the sterol was in the process of decomposition.

Stigmasterolum, beta-Sitosterolum, Ergosterolum, and 7-Dehydrocholesterolum Perchlorates.—When stig-

masterol, beta-sitosterol and ergosterol¹³ were treated under similar conditions as described for cholesterol, they crystallized from chloroform solutions as white perchlorates. For the preparation of ergosterolum perchlorate, 1 g. of ergosterol was dissolved in 35 cc. of chloroform and mixed with 0.39 g. of a 70% perchloric acid (in a molar ratio of 1.077 mole HClO_4 :1 mole ergosterol). Instantaneously, a white crystal sludge formed, and the filtration was carried out after a few seconds. The crystals were kept in the desiccator overnight. A yield of 1.1139 g. of an almost white salt (88.9% of the theoretical) was obtained. For 7-dehydrocholesterol¹⁴ the procedure was the same as with ergosterol. Also, the same sensitivity toward an excess of acid was observed.

TABLE II
ANALYSES OF STEROLIUM PERCHLORATES

		HClO_4 , %	
		Calcd.	Found
Stigmasterolum perchlorate	$\text{C}_{28}\text{H}_{48}\text{O}\cdot\text{HClO}_4$	19.59	19.72
beta-Sitosterolum perchlorate	$\text{C}_{29}\text{H}_{50}\text{O}\cdot\text{HClO}_4$	19.51	19.58
Ergosterolum perchlorate	$\text{C}_{28}\text{H}_{44}\text{O}\cdot\text{HClO}_4$	20.22	20.76
7-Dehydrocholesterolum perchlorate	$\text{C}_{27}\text{H}_{44}\text{O}\cdot\text{HClO}_4$	20.72	21.14

Sterolium Hexafluorophosphates

Investigation showed that sterols, dissolved in chloroform, formed colorless salts with concd. sulfuric acid or anhydrous difluorophosphoric acid and these salts remained in solution. Concd. tetrafluoroboric acid did not form a precipitate. Anhydrous fluorosulfonic acid reacted vigorously with sterols and decomposed them, while the reaction with anhydrous perchloric acid was even more vigorous and destructive.

Hexafluorophosphoric acid is in its reactions quite similar to perchloric acid as far as formation of insoluble salts is concerned.¹⁵ An aqueous solution containing 65.2% HPF_6 ¹⁶ precipitated colorless crystals from chloroform solutions of cholesterol, commercial phytosterol mixtures, stigmasterol, beta-sitosterol, ergosterol, and 7-dehydrocholesterol. The dry salts were stable, in a desiccator, and did not burn when heated. In addition to the observed stability, decreased color formation, as compared with perchloric acid, was observed when the fluoro acid was used in excess, and this was particularly noticeable with ergosterol and 7-dehydrocholesterol. Precipitation was almost as quantitative as with perchloric acid.¹⁷

Cholesterolum Hexafluorophosphate.—*Anal.* Calcd. for $\text{C}_{27}\text{H}_{44}\text{O}\cdot\text{HPF}_6$: HPF_6 , 27.43. Found: HPF_6 , 26.98 (titration and precipitation in the form of nitron hexafluorophosphate).

Steroids which do not Form Crystallized Perchlorates.—The following steroids were tested, in chloroform solution, with a 70% perchloric acid and did not form crystallized salts: Cholesteryl acetate, cholesterol dibromide, 3(β)-hydroxycholestane (dihydrocholesterol), 3(α) hydroxycholestane (epi-dihydrocholesterol), 3(α)-hydroxycopropane (epi-coprosterol), Δ^4 -cholesten-3-one, dehydro-isandrosterone¹⁸ (Δ^5 -androsten-3(β)-ol-17-one), Δ^2 -chol-

(13) Courtesy of the Research Laboratories of the Upjohn Company, Kalamazoo, Michigan.

(14) Courtesy of the E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

(15) W. Lange and E. Müller, *Ber.*, **63**, 1058 (1930).

(16) Courtesy of the Ozark-Mahoning Company, Tulsa, Okla.

(17) In working with this acid, care must be taken to prevent the formation of a crystallized hydrate of the acid, which takes place at acid concentrations between 50–55% HPF_6 . Thus, the HPF_6 concentration, after salt precipitation, should be below about 45%.

(18) Courtesy of Hoffmann-LaRoche, Roche-Organon, Inc., Nutley, N. J.

estadiene, $\Delta^{3,5}$ -cholestadiene, β -7-hydroxycholesterol, and trans-cholestane-3,5,8-triol.

Formation of Polymeric Hydrocarbons

Cholesterol.—A solution of 10 g. of cholesterol in 100 cc. of chloroform was shaken with 10 g. of a 70% perchloric acid. After the initially formed crystals had been digested and the clear liquid was dark reddish-brown, the solution was washed neutral with water, dried and the solvent evaporated. The tough, light brown residue was free of cholesterol and was dissolved in 175 cc. of hot ethyl acetate. Upon cooling, 4.4 g. of a resinous, light orange precipitate was obtained, obviously not homogeneous and also containing ash, m. p. 144–150°.

Anal. Calcd. for $(C_{27}H_{44})_2$: C, 87.96; H, 12.04; mol. wt., 737. Found: C, 87.34; H, 11.75; mol. wt., 718; ash.

The hydrocarbon was brominated in ether solution.

Anal. Calcd. for $(C_{27}H_{44}Br_2)_2$: Br, 30.26; mol. wt., 1056. Found: Br, 29.2; mol. wt. (Barger-Rast), 1074.

In another preparation, the reaction mixture was kept for one hour after the liquid had become clear and was then washed neutral with water. The precipitate obtained from the ethyl acetate solution was recrystallized twice from a mixture of toluene and ethyl acetate. The slightly yellow material seemed to darken at 128° and melted completely at about 200–205°.¹⁹

Anal. Calcd. for $(C_{27}H_{44})_3$: C, 87.96; H, 12.04; mol. wt., 1105. Found: C, 87.77; H, 11.89; mol. wt. (Rast-Tiedcke), 1032.

$\Delta^{3,5}$ -Cholestadiene.—Five grams of the hydrocarbon in 250 cc. of chloroform was shaken with 5 g. of a 70% perchloric acid for one minute. The solution was washed neutral with water and processed further as has just been described. The slightly yellow recrystallized material softened at 152° and was completely melted at 203°.¹⁹

Anal. Calcd. for $(C_{27}H_{44})_2$: C, 87.96; H, 12.04. Found: C, 87.57; H, 12.00; mol. wt. (Barger-Rast), 1140.

$\Delta^{2,4}$ -Cholestadiene.—The reaction product, prepared similar to that of the 3,5-diene, was slightly yellow, softened at 132° and was completely melted at about 200°.¹⁹

(19) See Fig. 1 for absorption spectrum.

Anal. Calcd. for $(C_{27}H_{44})_2$: C, 87.96; H, 12.04. Found: C, 87.72; H, 11.95; mol. wt. (Barger-Rast), 926.

Fractional crystallizations of the various preparations of the polymeric hydrocarbon gave products with very good analytical data for C and H. While molecular weights differed between values for a dimeric and trimeric compound, no fractions higher than a trimer have been observed. The specific rotation of the fractions in chloroform was positive.

Acknowledgment.—We wish to express our thanks to Miss Ruth Daniels for help with the spectrophotometric measurements.

Summary

1. Common sterols containing the 3(β)-hydroxy- Δ^5 -ene grouping are precipitated instantaneously from sufficiently concentrated chloroform solutions in the form of well-crystallized, colorless salts, with the composition Sterol·HClO₄ or Sterol·HPF₆, by the addition of sufficiently concentrated perchloric or hexafluorophosphoric acids.

2. The sterolium salts hydrolyze instantaneously upon contact with an excess of water, with quantitative recovery of the unchanged sterols.

3. An excess of acid over the stoichiometric quantity results in slow digestion of the crystals and formation of strongly purple colored halochromic compounds, with final degradation of the color, probably in the following steps: (a) colorless sterolium salt, dissolved in dilute solution, (b) colorless cholestadiene, (c) unstable halochromic cholestadiene salt, (d) stable, discolored halochromic salt of a polymeric hydrocarbon $(C_{27}H_{44})_x$, with the trimer being the highest polymer observed.

CINCINNATI 17, OHIO

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[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY¹]

Cuprammonium-Glycoside Complexes. IV. The Conformation of the Galactopyranoside Ring in Solution

BY RICHARD E. REEVES

In a preceding communication of this series² it was shown that the behavior in cuprammonium solution of twelve complex-forming D-glucopyranoside derivatives can be interpreted in terms of a single ring conformation, namely, the Sachse strainless ring chair form in which the sixth carbon atom and the ring oxygen atom project on the same side of the plane formed by carbon atoms 1, 2, 4 and 5. This ring conformation has been designated C1, and its mirror image, 1C. Examination of nineteen substances belonging or related to the galactose series now reveals that the D-galac-

topyranoside ring can also be regarded as ordinarily possessing the C1 conformation.

By a conductometric method it was established that the D-glucopyranosides form cuprammonium complexes only with the hydroxyl pairs on the second and third or third and fourth carbon atoms. This same situation is believed to apply to the galactose series. Examination of suitably substituted methyl and phenyl D-galactopyranosides has revealed the formation of levorotatory complexes at both of these sites, but no indication of reaction involving any other pair of hydroxyl groups.

Since reaction is limited to adjacent hydroxyl groups, the projected angle between carbon-oxygen valences for each complex-forming pair of hy-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Reeves, *THIS JOURNAL*, 71, 215 (1949).