

hours. The starting material was quantitatively recovered.

One-half gram of XXVIII was refluxed in 10 cc. of dry toluene for four hours. The solution was cooled and evaporated under reduced pressure. The residue was recrystallized from petroleum ether and colorless prisms were obtained; m. p. 122–123°. This corresponded to the m. p. of 1,2,6-trimethylbenzimidazole*, indicating ring closure had occurred.

All attempts to hydrolyze 3-benzalamino-4-acetaminotoluene (XXX) and 4-benzalamino-3-acetaminotoluene (XXXI) with alcoholic potassium hydroxide, or to oxidize them directly with nitrobenzene failed to give a crystalline product. The tolimidazoles were successfully obtained by carrying out the oxidation and hydrolysis in the same reaction mixture. Three grams (0.012 mole) of XXX was dissolved in 6 cc. of freshly distilled nitrobenzene. To this solution was added a solution of 0.76 g. (0.014 mole) of potassium hydroxide in 40 cc. of hot dry ethyl alcohol, and the reaction mixture heated on a steam-bath for four and one-half hours. The solution was cooled overnight and filtered. The filtrate was evaporated under reduced pressure and the residue thoroughly washed with petroleum ether. This product was the potassium salt of the imidazole, which may be obtained in quantitative yields. Subsequent washing with water converted the potassium salt into the imidazole. Recrystallization from benzene gave colorless needles of the 2-phenyl-5(6)-methylbenzimidazole (II); m. p. 249–250°; yield, 2 g. (80%).

Three grams of XXXI was hydrolyzed and oxidized in

the same manner as in the above experiment; yield, 1.8 g. (78%); m. p. 249–250°. Mixed m. p. with product obtained in the above experiment was 249–250°. Therefore, the same imidazole was obtained in both experiments.

Summary

1. The monoacyl derivatives have been shown to be the probable intermediates in the formation of the tolimidazoles from 3,4-diaminotoluene and organic acids.

2. Roeder and Day's mechanism for the splitting out of water in the formation of benzimidazoles has been extended to the tolimidazoles.

3. It has been shown that the tautomerism of the imidazoles probably cannot be explained by any one theory alone and it is possible that it involves both prototropy and electromerism depending upon the conditions.

4. Changing the radical in position 2 from a methyl to a phenyl group was shown to have no apparent immobilizing effect upon the orientation of the imidazole ring relative to the aromatic nucleus.

5. An improved method for the preparation of 4-nitro-3-amino-toluene is reported.

PHILADELPHIA, PA.

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Pro- γ -carotene

BY L. ZECHMEISTER AND W. A. SCHROEDER

A remarkable class of naturally occurring polyene pigments is composed of those C₄₀-carotenoids which contain several *cis*-double bonds in their chromophores. Such a configuration manifests itself in a lower melting point, higher solubility and especially by a spectrum in which the bands have been shifted to much shorter wave lengths than those present in the spectrum of the corresponding all-*trans*-carotenoid. These new pigments crystallize well and are then fairly heat resistant in this form. Their solutions, however, undergo isomerization, slowly when heated and very rapidly when treated with iodine or other suitable catalysts¹ *e. g.*, hydrochloric acid. Melt-

ing of crystals also causes isomerization. A complicated mixture of stereoisomers is thus formed in which large amounts of the corresponding ordinary carotenoid occur. The latter forms the top zone in a chromatogram of the mixture while the unchanged fraction of the starting material forms the lowest zone (or one near the lowest).

It has been suggested² that the prefix "pro" be attached to the current name of the all-*trans* carotenoid in order to designate the compounds belonging to the class under consideration. Such a nomenclature does not point to any essential difference in structure from the so-called "neo"-carotenoids which have been detected as artificial products. The absorption maxima of the latter are only moderately lower than those of the start-

(1) L. Zechmeister and P. Tuzson, *Biochem. J.*, **32**, 1305 (1938); *Ber.*, **72**, 1340 (1939); L. Zechmeister, L. Chohnoky and A. Polgár, *ibid.*, **73**, 1678 and 2039 (1939); G. Ph. Carter and A. E. Gillam, *Biochem. J.*, **33**, 1325 (1939); H. H. Strain, "Leaf Xanthophylls," Carnegie Institute of Washington Publ. No. 490, 1938, and THIS JOURNAL, **63**, 3448 (1941). For bixin and crocetin see P. Karrer, A. Helfenstein, R. Widmer and Th. B. van Itallie, *Helv. Chim.*

Acta, **12**, 741 (1929), and R. Kuhn and A. Winterstein, *Ber.*, **66**, 209 (1933), and **67**, 344 (1934).

(2) L. Zechmeister, A. L. LeRosen, F. W. Went and L. Pauling, *Proc. Nat. Acad. Sci.*, **27**, 468 (1941).

ing carotenoid, the spectrum of which differs greatly from that of the pro-carotenoid.

A final nomenclature would designate the spatial arrangement of each double bond, *e. g.*; "3,5-*cis*- γ -carotene." It can, however, only be introduced after a determination of the configuration. Tentative names and prefixes, used in the literature at the present time, will then have to be discarded ("labile, stable, neo, pro," etc.). The simple prefixes *cis* and *trans* should be reserved for those cases in which the indicated configuration is valid for all conjugated double bonds or for all those which in principle can assume that configuration.

It has not yet been possible to obtain pro-carotenoids from ordinary carotenoids, which, when kept at room temperature, heated, or catalyzed, yield considerable amounts of their neo-forms.

A representative of the pro-series, polyycopene, $C_{40}H_{56}$, was first observed in Tangerine tomato (*Lycopersicum esculentum*) extracts² and later crystallized by LeRosen and one of the authors.³ In the present paper a description is given of the isolation and properties of pro- γ -carotene, $C_{40}H_{56}$. The following absorption maxima (in petroleum ether) characterize the compounds in question.

Lycopene	504.5, 473.5, 445.5 $m\mu$
Neo-lycopene A	500.5, 470, 441
Prolycopene	470.5, 445
γ -Carotene	495 463 $m\mu$
Neo- γ -carotene A	489.5, 458.5
Pro- γ -carotene	464 (435)

Pro- γ -carotene occurs in the ripe fruit of the palm trees, *Butia capitata* and *B. eriospatha* Becc., as well as in the berries of *Pyracantha angustifolia* Schneid.⁴ In the plants studied a complicated polyene mixture is present which includes γ -carotene, lycopene, β -carotene and sometimes polyycopenes. The pro- γ -carotene content of the material used for the isolation is 40 to 50 times less than the polyycopene content of the Tangerine tomato. Approximately 0.3 mg. of pure crystals can be isolated per kilo of *B. capitata* fruit.

The isomerization of pro- γ -carotene caused by melting the crystals, by heating in solution and by iodine or hydrochloric acid catalysis is described below. Each minor layer (except some, formed by hydrochloric acid catalysis) of the chromatogram of such an isomerization mixture gives a similar mixture of stereoisomers when cut out, eluted and

catalyzed. Of the 64 theoretically possible stereoisomers^{2,5} of γ -carotene, 10 have been observed in this investigation. Of a total of eleven conjugated double bonds six may assume the *cis*-configuration. In pro- γ -carotene, however, one or possibly two such double bonds remain in the *trans*-configuration. This is confirmed by the formation of small amounts of a stereoisomer, the absorption maxima of which are of 4-6 $m\mu$ shorter wave length than those of pro- γ -carotene. It seems, therefore, that the conjugated double bond system of the latter contains 6 or 7 *trans*- and 5 or 4 *cis*-double bonds.

Some other pigments of *B. capitata* are listed in Table I. In this table two " γ -carotene" zones appear, having approximately the same spectrum. In unpublished experiments with other plants a similar separation has been observed as well as a yet unexplained variation in the melting points of samples of different origin. Should the existence of two γ -carotenes⁶ be substantiated in experiments now in progress, it remains to be shown to which series pro- γ -carotene belongs.

Acknowledgment.—We are greatly indebted to Dr. W. Hertrich, Curator of the Huntington Botanical Garden, who kindly placed the facilities of the Garden at our disposal. Furthermore, we wish to thank Dr. G. Oppenheimer and Mr. G. Swinehart for microanalytical assistance and Mr. M. Gschwind for practical help.

Experimental

Chromatographic experiments were carried out on calcium hydroxide (Shell Brand lime, chemical hydrate; 98% through 325 mesh). The petroleum ether used, "Skellysolve," had a boiling range of 60-70°. Spectra are given for this solvent unless otherwise indicated. They were determined with an Evaluating Grating Spectroscope (Zeiss, light filter BG-7).

Isolation and Properties of Pro- γ -carotene.—Twenty kilos of the ripe, bright yellow fruit of *Butia capitata* (2-3 cm. in diameter; collected in Southern California in November) were mashed in a mortar, freed from the seeds, and kept in methanol overnight. Contact with the solvent longer than one to two days should be avoided; if the material cannot be worked up promptly, the whole fruit may be preserved for some time by placing in large jars containing a 2-3 cm. layer of methanol.

The material was pressed out in a fruit press, the liquid discarded and the wet fibrous cake was passed twice through an electric grinder. To four portions, each corresponding to 5 kilos of fresh fruit, were added one liter of methanol and one liter of petroleum ether. These solvents form a two-phase system. The mixture of material

(2) LeRosen and Zechmeister, *THIS JOURNAL*, **64**, 1075 (1942).

(4) L. Zechmeister and W. A. Schroeder, *Sci.*, **94**, 609 (1941).

(5) L. Pauling, *Fortsch. Chem. org. Naturstoffe*, **8**, 203 (1939).

(6) Two positions are possible for the isolated double bond.

and solvents was shaken mechanically for fifteen minutes and permitted to stand some time. The upper layer was intensely orange; the lower only slightly colored. This extraction was repeated twice, the volume ratio of methanol and petroleum ether added being now 1:10. A final treatment with pure petroleum ether is advantageous. The solid residue was pressed out and ground between extractions. The total volume for 20 kilos of fresh fruit was 37.5 liters of petroleum ether and 6.5 liters of methanol. A large volume of water was added slowly, the upper phase washed three times, dried quickly with sodium sulfate, and concentrated *in vacuo* at 40° to about 4 liters. The liquid was diluted with 0.5 volume of peroxide-free ether, kept for one day over a layer of 30% methanolic potassium hydroxide and then washed alkali free. During the washing semi-solid material appears at the interface and is discarded. After drying, the pigment solution was concentrated *in vacuo* to 100 ml. and the evaporation repeated after 200 ml. of petroleum ether had been added. The dark red, viscous liquid was diluted with petroleum ether to one liter.

After filtration to remove colorless material, the solution was chromatographed in a conical percolator (32 × 15 × 8 cm.), in order to obtain a rough separation of the pigments. In the course of developing with 5 liters of petroleum ether numerous pigment layers appeared. The upper section consisted of minor zones and a main red lycopene zone accompanied by some of its neo-forms. The middle section had a red zone of γ -carotene at the top and a brilliant orange zone of pro- γ -carotene at the bottom. Finally, the lower section contained β -carotene which constitutes about one-half of the polyene pigment content of the fruit. Each of the sections was cut out, eluted with ethyl alcohol, transferred into petroleum ether and repeatedly chromatographed in cylindrical adsorption tubes

until separation of the individual pigments was obtained. The spectra of the latter were determined before and after the addition of iodine (Table I).

The pro- γ -carotene solution was chromatographed a third time on a smaller column (25 × 4 cm.), developed with petroleum ether and then with the same solvent containing 2% acetone. The orange zone (75 mm. wide) was eluted with ether and after evaporation the dry residue was dissolved in the minimum amount (0.5 ml.) of petroleum ether in a centrifuge tube. On cautious addition of a few milliliters of methanol, with stirring, red crystals appeared immediately mixed with some colorless particles of microscopic size.

The sample was centrifuged and washed with methanol in the centrifuge tube in which it was recrystallized from benzene on addition of methanol. The crystals were treated three times with methanol at 40° and recrystallized from benzene and methanol. These latter operations were repeated. The yield was 5.9 mg. or approximately 0.3 mg. per kilo of fresh fruit. The total amount of crystals at our disposal was 14 mg. In the combined mother liquors only small quantities of pro- γ -carotene are present while a new compound (Table I) having a one-banded spectrum (432.5 m μ) is accumulated.

TABLE I
CAROTENOID PIGMENTS PRESENT IN THE RIPE FRUIT OF
Butia capitata^a

Compound ^b	Spectrum (m μ) in petroleum ether ^c					
	—Before addition— of iodine			—After addition— of iodine		
Rubixanthin	496.5	464.5	(437.5)	494	461.5	
<i>Lycopene</i>	504.5	474	(445.5)	502	472	442
<i>Neo-lycopene</i> ^d	500.5	469	(440)	502	471	
<i>Neo-lycopene</i> ^d	500	469	(441)	502	471	(442)
A prolycopene		477	448	502.5	471	(443)
Unknown		472	444		469	442
{ γ -Carotene	497	465.5	(437)	495.5	463.5	
{ γ -Carotene	495	463		495.5	461.5	
A prolycopene		471.5	443.5	499.5	469.5	441.5
A prolycopene		466.5	439	500.5	469.5	442.5
A prolycopene	490.5	464	(437.5)	501	469	(440)
Neo- γ -carotene ^d	490	459.5	430	497	465.5	(436)
Pro- γ -carotene		464	(435)	493.5	461	
Unknown			432.5			432.5
A β -carotene iso- mer	482	451.5		484.5	454	
β -Carotene	485.5	454		484.5	453.5	

^a The compounds are listed in the order of decreasing adsorption affinity on calcium hydroxide. ^b Compounds italicized have been definitely identified, in most cases by mixed chromatogram. Other compounds have been tentatively identified by spectrum and column position. ^c Parentheses denote indistinct bands which are difficult to read. ^d The complete homogeneity of this pigment zone is questionable.

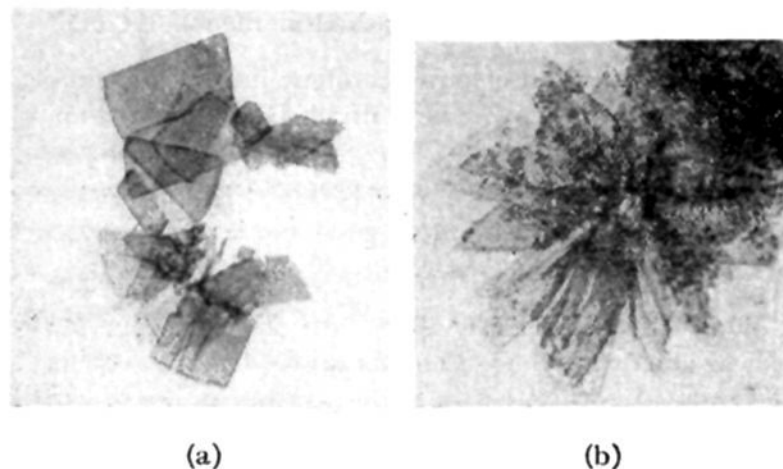


Fig. 1.—Pro- γ -carotene, crystallized from benzene and methanol (430 ×): (a) slow crystallization; (b) rapid crystallization.

Macroscopically, pro- γ -carotene forms brick-red, glittering plates. Under the microscope individual crystals are dull brownish-yellow with intensely orange crossings. Some curved crystal edges are typical (Fig. 1). The melting point (118–119° cor., after previous shrinkage, in a Berl block, sealed tube filled with carbon dioxide) is lower than that of γ -carotene but a little higher than that of prolycopene (111°). For analytical purposes the samples should be dried in high vacuum at 25° for 45 minutes.

Anal. Calcd. for C₄₀H₅₆: C, 89.48; H, 10.52. Found: C, 88.99; H, 10.65 (for ash free substance). *Mol. wt.* 0.098 mg. in 1.619 mg. of exaltone ($k = 21.3$): $\Delta = 2.5^\circ$. Calcd. for C₄₀H₅₆: 537. Found: 515. As proved by chromatography of a petroleum ether solution of the melt, the main portion of the pigment remained unaltered during this determination, which was carried out rapidly.

Pro- γ -carotene is easily soluble in cold benzene, in petroleum ether and in other common organic solvents with the exception of alcohols. The color of dilute solutions in petroleum ether or carbon disulfide is almost identical

with that of β -carotene. When partitioned between petroleum ether and methanol containing enough water to form two phases, it is epiphasic. The spectra in various solvents are listed in Table II.

TABLE II

SPECTRA OF PRO- γ -CAROTENE IN VARIOUS SOLVENTS

Solvent	Before addition of iodine		After addition of iodine		
	(m μ) ^a		(m μ) ^a		
Carbon disulfide	493.5	460.5	528	490.5	(433.5)
Acetone	(493.5)	463	493	462	(434)
Pyridine	481	450.5	481.5	452.5	
Benzene	477	447.5	507.5	474.5	(444)
Carbon tetrachloride	475.5	445.5	506	473	443
Chloroform	473	(444)	505	470.5	(441.5)
Dioxane	470	442	500	469.5	(441.5)
Ethanol	(465)	(437)	(491.5)	466	(436.5)
Ethyl acetate	464	(436)	492.5	463.5	(436)
Petroleum ether	464	(435)	493.5	461	(433.5)
Ether	462	(435)	494	461	(433)
Methanol	462	(434)	(490)	460	

^a Parentheses indicate that the band is very indistinct. In some solvents pro- γ -carotene shows a faint shadow at higher wave lengths. These solvents with the approximate position of the shadow are: carbon disulfide, 527; chloroform, 502; dioxane, 499; petroleum ether, 492; ethyl acetate, 493; ether, 491; and methanol, 491 m μ .

The concentration of pro- γ -carotene in solution can be determined by means of the Pulfrich Gradation Photometer using light filter S 47 (k = extinction coefficient; c = mg. pigment per 100 ml. of petroleum ether solution)

k	0.3	0.5	0.7	0.9
c	.20	.33	.47	.61

Pro- γ -carotene is easily adsorbed from petroleum ether on calcium hydroxide. On this adsorbent the sequence from top to bottom is: lycopene, cryptoxanthin, γ -carotene, polycopene, pro- γ -carotene, a β -carotene isomer and β -carotene. (It is difficult to obtain a good separation of polycopene and neo- γ -carotenes on calcium hydroxide.) The color of the adsorbate of β -carotene is almost identical with that of pro- γ -carotene. On washing the column with petroleum ether the migration is slow; it becomes much faster if 3% acetone or 5-10% benzene is added to the solvent. On calcium carbonate no fixation occurs but on aluminum oxide (Baker's anal., ignited powder), pro- γ -carotene is adsorbed from petroleum ether. Ether, alcohol or alcohol-petroleum ether mixtures are suitable eluents.

Isomerization Phenomena.—(a) 1.4 mg. of pro- γ -carotene crystals in 100 ml. of petroleum ether was treated with a solution of 35 μ g. of iodine in 0.3 ml. of the same solvent. After one and one-half minutes standing at room temperature, the solution was poured on a column (20 \times 3 cm.) and was completely adsorbed five minutes later. On developing with petroleum ether containing 2% acetone, a chromatogram was obtained in which the layers were separated by colorless interzones (Table III).

(b) The petroleum ether solution of about 1 mg. of pro- γ -carotene was refluxed for thirty minutes, and developed on a column with the solvent mentioned containing 1% acetone. Most of the starting material remained unchanged while some γ -carotene appeared at the top; two

TABLE III

STEREISOIMERS OF PRO- γ -CAROTENE OBTAINED BY IODINE ISOMERIZATION^a

Color of adsorbate	Spectrum (m μ) in petroleum ether		After addition of iodine
	Before addition of iodine	After addition of iodine	
Red (γ -carotene)	495	463	(435) 492.5 460
Orange	489.5	458.5	492 460.5
Orange	489	458	492.5 460.5
Pink	488.5	457.5	492.5 460.5
Orange	488.5	457	492.5 460.5
Orange	489	457	492 460
Orange (pro- γ -carotene)	463	(434)	492.5 460.5

^a In the order of decreasing adsorption affinity on calcium hydroxide.

minor zones were observed below pro- γ -carotene, the one immediately below having the spectrum 458.5, (432.5) m μ ; on addition of iodine the spectrum changed to 493, 461 m μ . The lowest zone was present only in traces.

(c) A small quantity of pro- γ -carotene was melted and kept between 130 and 135° for twenty minutes, in a sealed tube filled with carbon dioxide, and then plunged into ice water. The chromatogram of the petroleum ether solution, after developing with the solvent containing 3% acetone, consisted of seven zones: γ -carotene, three neo-isomers (about 488, 457 m μ), pro- γ -carotene and finally two pigments below, having absorption maxima at 489.5, 458 and 457.5 m μ , respectively. The weak adsorbability of the zone immediately below pro- γ -carotene is remarkable; on the basis of its spectrum one would rather expect a position much above pro- γ -carotene. After addition of iodine the spectrum of each stereoisomer was converted within a few seconds into that of the same equilibrium mixture (492.5, 460 m μ).

(d) One mg. of pro- γ -carotene in 10 ml. of petroleum ether was mechanically shaken with 5 ml. of concd. hydrochloric acid for one hour. After the solution had been washed acid-free and dried, the chromatogram was developed with petroleum ether containing 2% acetone. Seven zones were formed: an unknown brownish zone fixed at the top, then γ -carotene, and three of its neo-forms (spectra as in Expt. c); no unchanged pro- γ -carotene was present. The two lowest yellow zones migrated much more rapidly than the other zones and showed spectra 477.5, 447.5 and 480, 450 m μ , respectively, which approximate that of α -carotene. On the addition of iodine the wave length of the maxima of the two lowest layers decreased a few millimicrons while each of the four γ -isomers gave the expected equilibrium spectrum (492.5 and 460 m μ).

In the course of the above isomerizations some crystallized γ -carotene was isolated (494, 462, 434 m μ). It did not separate in a mixed chromatogram from samples obtained from two different plants while it separated easily from rubixanthin.

Summary

1. From the ripe fruit of *Butia capitata* Becc. (Palmae) a new carotenoid, pro- γ -carotene, C₄₀H₅₈,

has been isolated in quantities of 0.3 mg. per kilo and its properties described.

2. Pro- γ -carotene is a naturally occurring stereoisomer of γ -carotene to which its relationship is analogous to that of polycopene to lycopen. It is suggested that 6 or 7 double bonds of the pro- γ -carotene chromophore have *trans*- and 5 or 4 *cis*-configuration.

3. The following operations convert pro- γ -carotene into a mixture of stereoisomers which includes γ -carotene: melting of crystals, reflux-

ing of solutions or treatment of a cold solution with iodine or concd. hydrochloric acid. If the latter is used as a catalyst, the chromatogram also includes minor pigments which do not belong to the stereochemical series discussed.

4. On addition of iodine to a solution of any stereoisomer of the γ -carotene series the spectrum shifts instantaneously to that of an equilibrium mixture, the components of which separate on the Tswett column.

PASADENA, CALIFORNIA

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[CONTRIBUTION FROM THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH, DIVISION OF ORGANIC CHEMISTRY]

7-Benzoxysterols and their Use in the Preparation of 7-Dehydrosterols

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In an attempt to secure free 7(α)-hydroxycholesterol by treatment of 7(α)-benzoxysterol benzoate with a methanolic solution of sodium methylate at room temperature we found that the diester yielded almost quantitatively the 7-monoester, 7(α)-benzoxysterol. The resistance of the ester linkage in position 7 was also evident when the hydrolysis was conducted by boiling for three hours with 2% methanolic potassium hydroxide solution. The recovered material contained, according to the spectrographic assay, 35% of a monobenzoate which was undoubtedly the 7-monoester, since cholesteryl benzoate is completely saponified under these conditions, as well as by treatment with sodium methylate in the cold.

7(α)-Benzoxysterol, in contradistinction to the free diol, is not precipitable by digitonin in 90% ethanol. Though it is known that the presence of a benzoxy group in position 4, adjacent to a free 3-hydroxyl group, prevents the digitonin reaction,¹ the hindering effect of such a group in the more remote position 7 is noteworthy.

The position of the benzoxy group in the monoester follows from its conversion to (free) 7-dehydrocholesterol either by pyrolysis² or treatment with boiling dimethylaniline.^{3,4} By contrast, the 3-monobenzoate of the diol^{5,6} on pyrolysis forms a cholestatriene.⁵ The dehydrosterol in

the crude reaction mixture can be separated from unreacted material and by-products by means of digitonide, an advantage which is not obtained when the dibenzoate is used as the starting material.

The analogous conversion of 7(α)-benzoxystigmasteryl benzoate to 7-dehydrostigmasteryl benzoate *via* the 7-monoester showed that the method can be employed generally for the preparation of 7-dehydrosterols.

Experimental

7(α)-Benzoxysterol.—To 10 g. of 7(α)-benzoxysterol benzoate dissolved in benzene (200 cc.) a solution of sodium methylate (Mathieson) (6.66 g.) in absolute methanol (333 cc.) was added, and the mixture was allowed to stand at room temperature for three days. It then was poured on cracked ice and extracted repeatedly with cold water. Evaporation of the benzene yielded an oil which was redissolved in hexane and adsorbed on a column of aluminum oxide. Elution was effected with benzene containing increasing amounts (0.5 to 5%) of methanol. Most of the eluted material (6.74 g.) was essentially homogeneous, as shown by the specific rotations. The final fractions (673 mg. together) with rotations of +100 or lower were of gelatinous consistency and probably contained some 7(α)-hydroxycholesterol. Subsequent work on the corresponding stigmasteryl derivative showed that with a shorter hydrolysis time, twelve to twenty-four hours, the amount of diol formed was negligible, so that the chromatographic purification could be dispensed with. It sufficed to recrystallize the crude material from benzene-pentane mixtures, or from hexane, from which it formed fine filamentous needles; m. p. 110–115°. The melting point varied somewhat with the rate of heating, $[\alpha]_D^{25}$ +111°; 1.2% in chloroform.

Anal. Calcd. for $C_{28}H_{50}O_3$: C, 80.58; H, 9.95. Found: C, 80.41, 80.50; H, 9.85, 9.93.

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(5) Eckhardt, *Ber.*, **71**, 461 (1938).

(6) Rosenberg, U. S. Patent 2,215,725 (1940).