TABLE I

3,4-DIHYDROXYPHENACYL CHLORIDE QUATERNARY SALTS

Bases	M.P.	Color	Yield, %	Reaction Time, min.	Reaction Temp.	Formula	Chlorine, % Calcd.	Chlorine, % Found
Benzothiazole	248	White	18	120	100	$C_{15}H_{13}O_3SNCl$	10.99	11.30
Hexamethylenetetramine	195	White	53	180	[a]	$C_{14}H_{19}O_3N_4Cl$	10.86	10.65
Isoquinoline	269	Yellow	15	45	100	$C_{17}H_{14}O_3NCl$	11.25	11.42
N-Methylmorpholine	228	White	15	30	100	$C_{13}H_{14}O_4NCl$	12.51	12.54
Pyridine	277	Brown	38	5	30–60	$C_{13}H_{12}O_3NCl$	13.40	13.43
3-Bromopyridine	255	Tan	9	10	160	$C_{13}H_{11}O_3NClBr$	10.30	10.29
Nicotinic acid	255	White	8	20	160	$C_{13}H_{12}O_5NCl$	11.48	11.61
2-Chloropyridine	302	Yellow	10	5	160	$C_{13}H_{11}O_3NCl_2$	[b,c]	
3-Chloropyridine	255	Brown	26	15	160	$C_{13}H_{11}O_3NCl_2$	11.55	11.50
3-Cyanopyridine	237	White	32	15	160	$C_{14}H_{11}O_3N_2Cl$	[c,d]	
Quinoline	265	Red-brown	18	60	100	$C_{17}H_{14}O_3NCl$	11.25	11.62

[a] In 200 ml. boiling acetone. [b] Calcd.: C, 52.01; H, 3.62. Found: C, 52.10; H, 3.68. [c] Average of two carbon and hydrogen analyses by Weiler and Strauss, 164 Banbury Road, Oxford, England. [d] Calcd.: C, 57.81; H, 3.78. Found: C, 57.73; H, 3.9 1

phenacyl)-3-bromoquinolinium chloride[3] might produce an extension of the life span of mice carrying Leukemia L1210, led us to synthesize the series of similar compounds listed in Table I. Except as indicated in the footnotes, the salts were prepared by heating 0.054 mole of 3,4-dihydroxyphenacyl chloride with 0.060 mole of the appropriate base in the absence of solvent, then recrystallizing from methanol, using activated carbon to remove colored impurities. None of them was effective against Adenocarcinoma 755 or Sarcoma S180, nor against Leukemia L1210.

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(2) Screening data were obtained through the service of the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health.

(3) C. T. Bahner, W. K. Easley, G. E. Biggerstaff, E. Brown, M. Close, M. M. Isenberg, H. D. Lyons, L. Norton, E. Stephen, B. Stump, B. G. W. Blanc, and M. Watkins, *J. Am. Chem. Soc.*, **75**, 1472 (1953).

Santonin and Related Compounds. XXIII.[1] The Aromatization of 3-Keto-9-carbethoxy-$\Delta^{1,4}$-hexahydronaphthalene

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A survey of the literature[1,2] shows that the aromatization of a number of naphthalenic dienones proceeds in a variety of ways involving the migration of the angular methyl[2b] and/or the ring-methylene groups[2a] (and the hydroxyl or acetoxyl group).[2c] It seemed of interest to explore the course of the rearrangement of the bicyclic dienone with the electron-withdrawing group at the ring-fusion. An attractive paper has appeared describing the major shift of the carbethoxyl group at the given position in the cyclohexadienone system.[3] Plieninger and Suehiro[3] have shown that 4-carbethoxy-3,4-dimethylcyclohexa-$\Delta^{2,5}$-dien-1-one (I) rearranged with dilute sulfuric acid, predominantly to 1-carbethoxy-2,3,5-xylenol (II), which structure, though not firmly established, is beyond reasonable doubt. In addition, the parent xylenol was isolated in a small quantity. It is somewhat unexpected that the migration of the carbethoxyl group proceeded in such a way more readily than that of the angular methyl group, which has been more commonly encountered in the similar reactions.[2b]

Initially 3-keto-9-carbethoxy-$\Delta^{1,4}$-hexahydronaphthalene (III) was selected for the starting material, which was prepared in a 30% yield from the corresponding monoenone (IV)[4] by the selenium dioxide oxidation in the usual manner.[5] The dienone-ester III was characterized as the crystalline semicarbazone and 2,4-dinitrophenylhydrazone. This ketone exhibited the ultraviolet spectrum, $\lambda_{max}^{C_2H_5OH}$ 244.5 mμ, being in good agreement with the maximum (244 mμ) earlier described for the $\Delta^{1,4}$-3-dienone structure.[6] It is notable that, in contrast to the steroid chemistry,[6] the transformation of the monoenone IV into the corresponding cross-conjugated dienone III produces a remarkable batho-

(1) Part XXII, M. Hirakura, M. Yanagita, and S. Inayama, *J. Org. Chem.*, **26**, 3061 (1961).

(2) (a) R. B. Woodward and T. Singh, *J. Am. Chem. Soc.*, **72**, 494 (1950). (b) A. S. Dreiding, W. J. Pummer, and A. J. Tomasewski, *J. Am. Chem. Soc.*, **75**, 3159 (1953). (c) S. Goodwin and B. Witkop, *J. Am. Chem. Soc.*, **79**, 179 (1957).

(3) H. Plieninger and T. Suehiro, *Chem. Ber.*, **89**, 2789 (1956).

(4) (a) E. C. duFeu, F. J. McQuillin, and R. Robinson, *J. Chem. Soc.*, 53 (1937). (b) A. S. Hussey, H. O. Liao, and R. H. Baker, *J. Am. Chem. Soc.*, **75**, 4727 (1953). (c) W. G. Dauben, R. C. Tweit, and R. L. MacLean, *J. Am. Chem. Soc.*, **77**, 48 (1955).

(5) For example see: M. Yanagita, S. Inayama, M. Hirakura, and F. Seki, *J. Org. Chem.*, **23**, 690 (1958).

(6) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, 1959, p. 20.

chromic shift (+7.5 mμ) in the ultraviolet region.[7] In the infrared spectrum, III has a peak at 1669 cm.$^{-1}$, fitting the preceding dienone system.[8] These spectral data, together with the elemental analyses of its derivatives, verified structure III. As is frequently observed in the selenium dioxide oxidation of the Δ^4-3-octalones,[9] the present dienone formation from IV was found to be accompanied also by a trace of a monoselenium compound $C_{13}H_{14}O_3Se$, whose light absorption is analogous to that of the selenium dienone[9] (see Experimental).

The aromatization of the dienone-ester III was brought about by customary methods, earlier employed for the same dienone derivatives.[2] First, when III was warmed with 50% sulfuric acid at 65–70° for thirty minutes, a 36% of the dienone was recovered in a forerun. The residual mixture was divided into the bicarbonate- and alkali-soluble fractions. On acidification, the latter gave predominantly a 32% yield of 4-carbethoxy-*ar*-2-tetralol (V. R = C_2H_5), while the former portion afforded only trace amounts of the free acid (V. R = H) of the ester. These products were identified by direct comparison (light absorption spectra and mixture melting point) with authentic samples, prepared as described in the Experimental.[10] In order to improve the yields of the products, the reaction period was extended to nine hours, and the resulting mixture was immediately subjected to chromatography on silica gel. Thus, the yield of the isolated ester was raised to 52%, while the free acid was secured in a slightly better yield (2.3%) than in the original reaction. In addition, the mother liquors of these materials reacted with *p*-nitrobenzoyl chloride in pyridine to give a trace of the benzoate, derived from *ar*-2-tetralol.[11] Under these conditions, no recovery of III could be made.

Second, the dienone-ester III was allowed to react with acetic anhydride–sulfuric acid at room temperature under the conventional conditions.[2a] The usual processing of the reaction furnished an acetate mixture, which was directly hydrolyzed with dilute methanolic potassium hydroxide at room temperature. As described above, the hydrolyzate was separated with aqueous bicarbonate solution; the soluble portion gave a 17% yield of the free acid (V. R = H), while the insoluble fraction gave a reasonable yield (27%) of *ar*-2-tetralol.[11] In this anhydrous reaction, however, III could not be recovered unchanged. In view of its recovery from the aqueous acid reaction, III appears to be more strongly resistant to such acidic conditions than the monocyclic analog I,[3] which has been reported to readily migrate to the phenolic ester II under the similar conditions. This difference in the migration rates may be attributed to the greater rigidity of the angular carbethoxy group in the bicyclic system III than in the monocyclic one I.

Earlier we proposed[5] that the aromatizations of the simple dienones occur more readily with warm dilute sulfuric acid than with anhydrous acid; however, in the present work the migration of III seemed to take place with the latter acid almost as smoothly as with the former acid. Both reactions furnished comparable total yields of the *ar*-2-tetralol derivatives in the same system. However, no evidence for the ring-methylene migration in III, *viz.*, the formation of the alternative hydroxy acids, could be found. The possibility of the secondary formation of *ar*-2-tetralol itself from V (R = H or C_2H_5) during rearrangement must be considered, but this was ruled out by finding that these compounds remained unaffected on acid treatment under more forcing conditions. It may be assumed that the direct formation of this phenol from III may involve first hydrolysis of the ester group, followed by decarboxylative-aromatization of the dienone-ring (as indicated in VI).[12]

On repetition of Prelog's method for the immediate conversion of the triester (VII. R = C_2H_5) into the monoacid (V. R = H), attempts were made to degrade stepwise the starting triester under milder conditions. Unexpectedly, the triester was quite inert to refluxing with concentrated hydrochloric acid alone. When heated however with this acid and glacial acetic acid (10:7), the triester was partially hydrolyzed to an acidic solid, whose analytical figures agreed with the dicarboxylic acid with one ester group left untouched. Even under these conditions, fair amounts (about 30%) of the ester were recovered unchanged. The orientation of the untouched group has not as yet been resolved. On the other hand, refluxing the triester in dilute methanolic potassium hydroxide led to a practically quantitative yield of the free tricarboxylic acid (VII. R = H). The latter acid was readily didecarboxylated to the monoacid (V. R = H) by the same procedure as previously reported for the direct formation of this acid from the triester.[10] Earlier proof of structure V (R = H) was chiefly based on the comparisons of the ultraviolet spectra with those of a variety of the analogous hydroxy acids.[10] This assignment was complemented by the infrared spectra of the monoacid and its ethyl ester, which exhibited strong bands at 867 cm.$^{-1}$, and 878 and

(7) A private communication from Dr. T. Suehiro, Department of Chemistry, Gakushuin University, Tokyo, Japan, has recently informed us that, also in the monocyclic series I, a similar transformation of the mono- into the dienone contributed a bathochromic shift estimated as almost the same (+9 mμ) as found in the present case.

(8) Ref. 6, p. 170.

(9) T. Miki, *J. Pharm. Soc. Japan*, **75**, 403 (1955); K. Florey and A. R. Restivo, *J. Org. Chem.*, **22**, 406 (1957), and others cited therein.

(10) V. Prelog, D. Metzler, and D. Jeger, *Helv. Chim. Acta*, **30**, 675 (1947).

(11) G. Schroeter, *Ann.*, **426**, 120 (1922).

(12) A similar mechanism has been disclosed for the aromatization of the other dienone-ester; A. S. Dreiding and A. J. Tomasewski, *J. Org. Chem.*, **19**, 241 (1954).

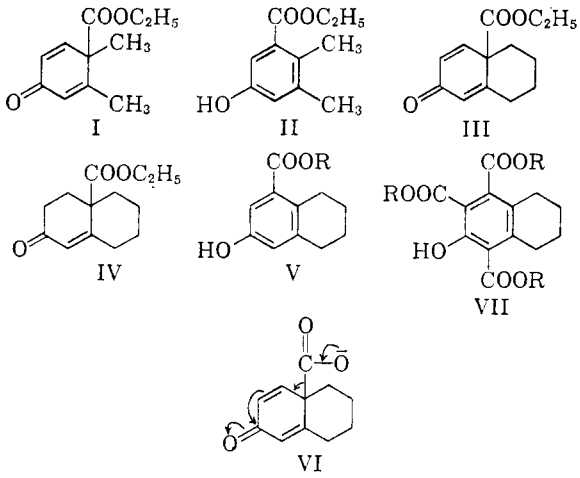
858 cm.$^{-1}$, respectively, both attributable to isolated hydrogens on a benzene ring.[2b] From the foregoing results, it is clear that, in the dienone-phenol rearrangement, the migration aptitude of the carbethoxy grouping is greater than that of the ring-methylene group at the same carbon atom, irrespective of the media used.

EXPERIMENTAL[13]

All temperatures are uncorrected. Infrared absorption spectra were measured with a Perkin-Elmer Model 21 double-beam spectrophotometer.

9-Carbethoxy-Δ^4-3-octalone (IV) was prepared by condensation of 2-carbethoxycyclohexanone with 4-diethylamino-2-butanone as reported previously.[5b] A 70% yield of IV was realized; $n^{25}D$ 1.5042; b.p. 140–143° at 2.5 mm.; $\lambda_{max}^{C_2H_5OH}$ 237 mμ (log ε 4.02). Reported; b.p. 139–141° at 2.5 mm.;[5b] and 154–156° at 3.8 mm.,[5c] and $n^{25}D$ 1.5043.[5b,c]

It formed a 2,4-dinitrophenylhydrazone as deep red prisms, m.p. 117–119 (from ethyl acetate–ethanol); $\lambda_{max}^{CHCl_3}$ 257 mμ (ε 18,490), 287.5 mμ (ε 5732) (inf.), 386 mμ (ε 31,520).



Anal. Calcd. for $C_{19}H_{22}O_6N_4$: C, 56.71; H, 5.51; N, 13.92. Found: C, 56.75; H, 5.34; N, 14.07.

This unsaturated oil was purified through a semicarbazone, white needles, m.p. 203–205° (from ethanol).

Anal. Calcd. for $C_{14}H_{21}O_2N_3$: C, 60.19; H, 7.58; N, 15.04. Found: C, 60.31; H, 7.79; N, 15.03.

Acidic hydrolysis of the semicarbazone regenerated the dienone as a colorless oil, b.p. 143–145° at 4 mm.; $n^{20}D$ 1.5042; $\lambda_{max}^{C_2H_5OH}$ 237 mμ (ε 14,282); $\nu_{max(cm.^{-1})}^{CCl_4}$ 1724 (CO of ester), 1686 (CO of Δ^4-3-monoenone), 1629 (C = C of Δ^4-3-monoenone).[8]

3-Keto-9-carbethoxy-$\Delta^{1,4}$-hexahydronaphthalene (III). Principally by the general procedure reported for the dehydrogenation of the Δ^4-3-octalones,[4] the above monoenone (IV, 3.0 g.) was heated to reflux with selenium dioxide (1.5 g.) in a mixture of *t*-butyl alcohol (200 cc.) and glacial acetic acid (2 cc.) for 30 hr. After the freshly sublimed dioxide (1.0 g.) was added, reflux was continued for 20 hr. A red-brown oily product was repeatedly fractionated to a pale yellow liquid (III, 0.90 g., 30%), b.p. 145–147° at 4 mm.; $\lambda_{max}^{C_2H_5OH}$ 244.5 mμ (ε 8645), typical of the $\Delta^{1,4}$-3-dienone;[6] $\nu_{max(cm.^{-1})}^{CCl_4}$ 1733 (CO of ester), 1669 (CO of $\Delta^{1,4}$-3-dienone), 1639 and 1613 (C = C of $\Delta^{1,4}$-3-dienone).[8]

The residue from the distillation was extracted with a warm mixture of ether and acetone. The combined extracts were passed through an alumina column to remove most of the selenium, and evaporated to leave minute amounts of a crystalline solid, a selenium compound, which was only slightly soluble in ether. Recrystallization from pyridine by addition of ethyl acetate afforded fine prisms, m.p. 218–220°; $\lambda_{max}^{C_2H_5OH}$ 247 mμ (ε 9646), 303 (ε 1172); $\nu_{max(cm.^{-1})}^{Nujol}$ 1731 (5.78 μ) (CO of ester), 1650 (6.06 μ) (CO of $\Delta^{1,4}$-3-dienone), 1633 (6.13 μ) and 1600 (6.25 μ) (C=C of $\Delta^{1,4}$-3-dienone).[14]

Anal. Calcd. for $C_{13}H_{14}O_3Se$: C, 52.50; H, 4.75. Found: C, 52.35; H, 5.06.

Rearrangement of the dienone-ester (III). A. *With aqueous acid.* This reaction was carried out by a slight modification of the procedure reported previously.[2b] A light brown solution of 0.50 g. of III in 5 cc. of 50% sulfuric acid was warmed at 65–70° on a water bath for 30 min. The red-brown reaction, which deposited a semisolid, was poured into ice water, and an oil which separated was taken up in ether. The ethereal solution was washed successively with the saturated bicarbonate and with 2% sodium hydroxide solution. Drying and evaporation of the ether left a pale yellow oil (0.352 g.), which was fractionated to 0.18 g. (36%) of III, b.p. 138–140° at 2 mm.; $\lambda_{max}^{C_2H_5OH}$ 245 mμ (ε 9400).

Acidification of the bicarbonate wash gave trace amounts of 4-carboxy-*ar*-2-tetralol (V. R = H), m.p. 201–202° (from ether–petroleum ether), undepressed with an authentic sample, made as described below; $\lambda_{max}^{C_2H_5OH}$ (213) mμ (ε 11,378), 305 mμ (ε 2618). It gave no coloration with ferric chloride.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.27. Found: C, 69.03; H, 6.56.

The alkaline wash was acidified and left in an ice box to deposit 0.16 g. (32%) of the crude carbethoxytetralol (V. R = C_2H_5), m.p. 122–125°. Recrystallization from dilute methanol formed colorless needles, m.p. 124–126°, undepressed on admixture with an authentic sample described below; $\lambda_{max}^{C_2H_5OH}$ 213 mμ (ε 14,980), 307 mμ (ε 3815). It gave no coloration with ferric chloride.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.38; H, 7.31.

Alkaline hydrolysis of the above ester gave rise to a quantitative yield of the free acid (V. R = H), m.p. and mixed m.p. 201–203°.

In another run, the reaction period was extended to 9 hr., and the crude products were directly subjected to chromatography on silica gel. The first elutions with petroleum ether and ether–petroleum ether furnished a total 0.265 g. (53%) of the carbethoxytetralol (V. R = C_2H_5), m.p. and mixed m.p. 124–125°. The following elutions with ether afforded 0.01 g. (2.3%) of the carboxytetralol (V. R = H), m.p. and mixed m.p. 199–200°.

The mother liquors of the recrystallization of the ethyl ester were evaporated to leave a brown oil (0.08 g.), which reacted with *p*-nitrobenzoyl chloride (0.1 g.) in pyridine (2 cc.). The benzoate (18%) was recrystallized from methanol to form colorless needles, m.p. 110–112°, undepressed with the same derivative of *ar*-2-tetralol, described below.

B. *With anhydrous acid.* Under the general conditions as reported earlier,[2a] 0.50 g. of III was dissolved in 10 cc. of acetic anhydride containing 5 drops of concd. sulfuric acid and left at room temperature for 48 hr. After being worked up as usual, the resulting acetate mixture, a colorless liquid (0.34 g.), b.p. 128–130° at 2 mm., was immediately hydrolyzed with 5% methanolic potassium hydroxide at ordinary temperature for 2 days. Most of the solvent was removed under reduced pressure and the residue was acidified and extracted with ether. The ethereal extracts were washed with

(13) Microanalyses were carried out by Mrs. Ch. Inayama and ultraviolet measurement by Miss M. Suzuki, both of this school.

(14) Florey and Restivo[9] have stated that the absorption peaks of the analogous selenium dienones are at 244–245, 257–258, and 305–306 mμ (ultraviolet) and at 6.08–6.12, 6.16–6.20, and 6.26–6.28 μ (infrared).

aqueous bicarbonate solution, dried, and evaporated. The residual light brown oil (0.14 g.) crystallized from petroleum ether to give 0.09 g. (27%) of *ar*-2-tetralol, m.p. and mixed m.p. 59°.[11]

Acidification of the bicarbonate wash gave 0.075 g. (17%) of the carboxytetralol (V. R = H), m.p. and mixed m.p. 200–202°.

1,3,4-Tricarbethoxy-ar-2-tetralol (VII. R = C_2H_5). As reported previously,[10] this was made by the condensation of ethyl cyclohexane-1-one-2-glyoxalate and diethylacetone dicarboxylate in the presence of anhydrous sodium ethoxide. The product (crude 75%), a pale yellow oil, gave a violet coloration with ferric chloride, and was used for the following step without further purification.

Hydrolysis and decarboxylation of the triester (VI. R = C_2H_5). A. *With concd. hydrochloric acid alone.* The triester (0.5 g.) was heated to reflux in 5 cc. of concd., hydrochloric acid for 2 hr., and the starting ester (0.45 g.) was recovered unchanged.

B. *With concd. hydrochloric acid plus acetic acid.* A solution of 0.45 g. of the triester in 10 cc. of concd. hydrochloric acid and 7 cc. of glacial acetic acid was heated to reflux on an oil bath (160–170°) for 4 hr. The mixture was concentrated under reduced pressure, and the residual oil was mixed with water, and extracted with ether. The ethereal extracts were washed with aqueous bicarbonate; acidification of the bicarbonate wash furnished 0.16 g. (36%) of the tetralol-monoester diacid as a crystalline solid, m.p. 151–153° dec. Recrystallization from ethyl acetate–hexane formed colorless prisms m.p. 171–173° dec.; $\lambda_{max}^{C_2H_5OH}$ 220 mμ (ε 23,878), 275 mμ (ε 3858), 350 mμ (ε 5629). It showed a violet coloration with ferric chloride.

Anal. Calcd. for $C_{15}H_{16}O_7$: C, 58.44; H, 5.23. Found: C, 58.43; H, 5.34.

The ethereal layer, removed from the bicarbonate wash, gave 0.14 g. (32%) of the starting ester.

C. *With alkali.* A solution of 6.9 g. of the triester in 80 cc. of 10% methanolic potassium hydroxide was heated to reflux for 3 hr. Worked up as usual, the bicarbonate-soluble fractions gave a brown mass, which crystallized from ethyl acetate: VII (R = H), 4.86 g., 92%. Further recrystallization from ethyl acetate–hexane formed colorless prisms, m.p. 228–230° dec.; $\lambda_{max}^{C_2H_5OH}$ 215 mμ (ε 25,257), 324.5 mμ (ε 4835), 353 mμ (ε 3102). It gave a violet coloration with ferric chloride.

Anal. Calcd. for $C_{13}H_{12}O_7$: C, 55.72; H, 4.33. Found: C, 55.79; H, 4.44.

D. *Selective didecarboxylation of the above triacid* (VII. R = H). This was carried out by an application of the previous method[10] used for the direct conversion of the triester into the monoacid. A solution of 1.0 g. of the above triacid in 70 cc. of concd. hydrochloric acid and 30 cc. of glacial acetic acid was violently refluxed at 180–190° (bath temperature) for 25 hr. The reaction solution was allowed to stand overnight at room temperature, giving 0.60 g. (88%) of the desired monoacid (V. R = H), m.p. 197–200°. The mother liquors afforded an additional 0.06 g. (total 0.66 g., 97%). Recrystallization from ethyl acetate–hexane formed colorless prisms, m.p. 201–203° [15]; $\lambda_{max}^{C_2H_5OH}$ 215 mμ (ε 11,535), 306 mμ (ε 2611); the infrared spectrum exhibited a strong band at 867 cm.$^{-1}$, due to isolated hydrogens on a benzene ring.[2b] An analytical sample was dried at 120° and 3 mm.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.68; H, 6.44.

An ethyl ester (V. R = C_2H_5), was made quantitatively with ethanol–sulfuric acid as colorless needles, m.p. 124–126° (from dilute methanol); $\lambda_{max}^{C_2H_5OH}$ 213 mμ (ε 18,060), 306 mμ (ε 3014); the infrared spectrum exhibited two strong bands at 878 and 858 cm.$^{-1}$, due to isolated hydrogens on a benzene ring.[2b] An analytical sample was dried at 80° and 3 mm.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.91; H, 7.20.

ar-2-Tetralol. This was prepared by catalytic hydrogenation of 2-naphthol as reported previously[11]; m.p. 59° (from petroleum ether). A *p-nitrobenzoate* was made with benzoyl chloride; m.p. 110–112° (from methanol).

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(15) Prelog *et al.*[10] have reported briefly that, on heating with hydrochloric acid in a sealed tube at 180°, the triester (VII. R = C_2H_5) gave an unspecified yield of the monoacid (V. R = H), m.p. 203°.

Stereospecific Oxidation of a Methylthio Steroid to the Sulfoxide by *Calonectria decora*

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Strains of the culture *Calonectria decora* have been reported to modify steroids by processes involving 1,2-dehydrogenation[1] and hydroxylation at C-12 and C-15.[2] We have now found that fermentation of 17β-acetoxy-7α-methylthioandrost-4-en-3-one (I) with *Calonectria decora* (CBS) resulted in hydrolysis of the acetate and oxidation of the methylthio group to yield 17β-hydroxy-7α-methylsulfinylandrost-4-en-3-one (II).

The structure of II was tentatively assigned on the basis of its elemental analysis, infrared spectrum, and conversion to 17β-hydroxyandrosta-4,6-dien-3-one (III). However, comparison of the acetate IV derived from acetylation of II with a synthetic sample of V[3] prepared by the monoperphthalic acid oxidation of I showed differences in melting point, rotation, and papergram mobility.

Confirmation of the structure assigned to II was provided by oxidation of IV with monoperphthalic acid to yield 17β-acetoxy-7α-methylsulfonylandrost-4-en-3-one (VI), which was identical with a sample obtained by peracid oxidation of I.

(1) E. Vischer, Ch. Meystre, and A. Wettstein, *Helv. Chim. Acta*, **38**, 835 (1955).

(2) A. Schubert, G. Langbein, and R. Siebert, *Chem. Ber.*, **90**, 2576 (1957). Schubert and Siebert, *ibid.*, **91**, 1856 (1958), describe the product from progesterone as 12β,15α-dihydroxy-progesterone. A product obtained from the fermentation of 11β-hydroxyprogesterone with *C. decora* was characterized as the 11β,15α-dihydroxylated derivative by Schubert, Siebert, and Koppe, *Angew. Chem.*, **70**, 742 (1958).

(3) R. E. Schaub and M. J. Weiss, *J. Org. Chem.*, submitted for publication.