tion was complete (usually *ca.* 75 hr.) and then an additional 5 hr. The *p*H was adjusted to between 4 and 5. Most of the alcohol was removed by distillation, the residual solution filtered while hot, and the filtrate allowed to cool. The light tan, crude, crystalline hesperetin was collected by filtration and air-dried; yield, 1.78 g. (72%), m.p. 225–227° with softening at 218°. The crude product was recrystallized by solution in hot isopropyl alcohol (10–11 ml.), cooling, and permitting the mixture to stand 12 hr. in a refrigerator. The recrystallized hesperetin (1.15 g.) melted at 228–229.5° (lit.,[6,17] m.p. 226°). The purest hesperetin obtained in this study melted at 228.5–229.2°. By sublimation, a product, m.p. 232.8°, has been previously reported.[18]

Dimorphous forms of hesperetin triacetate. A 7.00-g. quantity of hesperetin, m.p. 226–228°, was dissolved in a mixture of 45 ml. of acetic anhydride in 45 ml. of pyridine and permitted to stand at room temperature for 24 hr. The mixture was poured into 800 ml. of crushed ice-water, and the precipitated product collected and dissolved in 100 ml. of boiling 95% ethanol. Cooling the ethanol solution at 0° for 12 hr. gave 8.00 g. (80%) of the crude triacetate. Recrystallization from 75 ml. of 95% ethanol gave 7.50 g., m.p. 141.5–143.5°, and two additional crystallizations gave 6.68 g. of hesperetin triacetate, m.p. 143.5–144.5°. In another example of this purification, the melting point after the fourth crystallization was 143.5–144.2°. After a fifth crystallization hesperetin triacetate, m.p. 126.5–127°, was obtained.

Anal. Calcd. for $C_{22}H_{20}O_9$: C, 61.67; H, 4.71; CH_3CO, 30.14. Found: (For dimorph, m.p. 126.5–127°): C, 61.89; H, 4.78. (For dimorph, m.p. 143.5–144.5°): C, 61.94; H, 4.98; CH_3CO, 29.6. The residue from the acetyl determination was isolated, recrystallized from ethanol and shown to be hesperetin by melting point and mixed melting point determination.

Hesperetin triacetate, m.p. 143.4–144.2°, was dissolved in hot 95% ethanol, and the resulting solution filtered into a flask containing seed crystals of the dimorph, m.p. 126.5–127°. Upon cooling, the total separated hesperetin triacetate was collected, air-dried, and found to melt 126.5–127°. When the dimorph, m.p. 126.5–127°, was melted on a Kofler hot stage[19] and held at 130–135° for several minutes, crystals grew in the melt and remelted between 145 and 147°. Samples of both dimorphs were weighed, dried in a drying pistol *in vacuo* for 1 hr., and reweighed. No change in weight was observed.

In Nujol mull, the infrared spectrum of the dimorph, m.p. 143.5–144.5°, showed strong or medium absorption bands at 1760, 1685, 1618, 1581, 1520, 1444, 1330, 1279, 1269, 1212, 1190, 1136, 1130, 1076, 1060, 1028, 903, and 809 cm^{-1}. The Nujol spectrum of the dimorph, m.p. 126.5–127°, showed strong or medium absorption bands at 1755, 1670, 1616, 1570, 1515, 1438, 1331, 1282, 1262, 1249, 1210 (broad), 1180, 1129, 1074, 1060, 1025, 899, and 817 cm^{-1}. In carbon tetrachloride solution, the dimorphs gave identical infrared spectra, showing absorption bands at 1775, 1691, 1618, 1437, 1369, 1327, 1188 (broad), 1127, 1073, 1023, and 898 cm^{-1}. The ultraviolet absorption spectrum of the high-melting dimorph in absolute ethanol showed maxima at 220 mμ (ϵ 38.7 × 10^3), 259 mμ (ϵ 11.2 × 10^3), and 314 mμ (ϵ 3.89 × 10^3), and minima at 241 mμ (ϵ 6.22 × 10^3) and 288 mμ (ϵ 1.81 × 10^3).

3-Bromohesperetin triacetate. This substance was prepared as previously described.[11,12] In a potassium bromide pellet, the infrared spectrum of 3-bromohesperetin triacetate showed strong or medium absorption bands at 1771, 1692, 1620, 1580, 1517, 1432, 1372, 1273, 1202, 1180, 1127, 1071, 1022, 903, and 810 cm^{-1}.

Diosmetin triacetate from 3-bromohesperetin triacetate and pyridine. A 0.5-g. sample of 3-bromohesperetin triacetate was dissolved in 20 ml. of cold pyridine and stored for 1 week at −5°. The mixture was then placed in a desiccator containing concd. sulfuric acid. The desiccator was evacuated and stored at −5°. When all of the pyridine had been absorbed by the sulfuric acid, the reaction vessel was removed and the residue triturated with cold methanol. After standing at *ca.* 5° overnight, 0.29 g. (70%) of diosmetin triacetate was collected by filtration and recrystallized from methanol; m.p. 195–197° (lit. m.p.[20] 195–196°). The solid state spectrum (potassium bromide pellet) was identical with that of diosmetin triacetate obtained as previously described.[12]

Anal. Calcd. for $C_{22}H_{18}O_9$: C, 61.97; H, 4.26. Found: C, 62.55, 62.28; H, 4.30, 4.27.

AVERY LABORATORY
THE UNIVERSITY OF NEBRASKA
LINCOLN, NEB.

(16) Melting points are uncorrected and were observed in capillary tubes. The infrared measurements were carried out with a Perkin-Elmer Model 21 double-beam recording spectrophotometer. A Cary recording spectrophotometer was employed for ultraviolet spectral measurements.

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Steroidal Esters of 3-Indoleacetic Acid[1-3]

JOHN F. HOFERT AND HAROLD M. SELL

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As alterations of the lyophilic properties of the alcohol portion might enhance the activity for parthenocarpic fruit induction in the tomato,[4,5] steryl esters of 3-indoleacetic acid have been prepared and tested for biological activity.

Attempts to synthesize the esters using 3-indoleacetyl chloride[6,7] and free sterol in pyridine[8] resulted in the formation of a highly insoluble orange-red material. The preparation of the esters was accomplished by using the free sterol, silver carbonate, and approximately twice the theoretical amount of acyl chloride in benzene or petroleum ether. The products were purified by recrystallization to constant melting point followed by removal of the final traces of free sterol with digitonin.[9]

(1) Journal Article No. 2594 of the Michigan Agricultural Experiment Station.

(2) This research was supported by a grant from the National Science Foundation.

(3) From the masters thesis of J. Hofert, Michigan State University.

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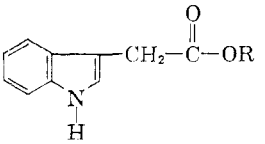
TABLE I

PROPERTIES OF STERYL 3-INDOLEACETATES



R	Formula	M.P.[a]	$[\alpha]_D^{23}$ in $CHCl_3$	Yield,[b] %	Carbon		Hydrogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Cholesteryl	$C_{37}H_{53}NO_2$	194.5–195	−36	80	81.7	82.0	9.8	9.8	2.6	2.7
Ergosteryl	$C_{38}H_{51}NO_2$	179–180	−76	23	82.4	82.3	9.3	9.2	2.5	2.7
7-Dehydrocholesteryl	$C_{37}H_{51}NO_2$	169–170	−55	11	82.0	82.0	9.5	9.3	2.6	2.5
Cholestanyl	$C_{37}H_{55}NO_2$	172–173	+13	64	81.4	81.4	10.2	10.2	2.6	2.5
β-Sitosteryl	$C_{39}H_{57}NO_2$	153–154	−32	7	81.9	81.7	10.0	9.9	2.4	2.5

[a] Corrected. [b] Based on crude material.

Physical properties of the steryl 3-indoleacetates prepared are reported in Table I. Cholesteryl, cholestanyl, and sitosteryl esters displayed indole absorption (280 to 300 mμ), whereas the ergosteryl and 7-dehydrocholesteryl esters also exhibited absorption for their conjugated diene system.

EXPERIMENTAL

Recrystallization of 3-indoleacetic acid. Ten grams of commercial 3-indoleacetic acid was dissolved in 350 ml. of peroxide-free ethyl ether. The small amount of solid remaining was removed by filtration. Two hundred milliliters of dry petroleum ether[10] (b.p. 40–45°) was then slowly added to the filtrate. The solution was stored in the refrigerator overnight at −10° and yielded 8.1 g. of white crystals, m.p. 169–170°. This material was used for the synthesis of 3-indoleacetyl chloride.

A. Preparation in benzene. Cholesteryl 3-indoleacetate. Equal weights (3.0 g.) of cholesterol (0.008 mole, recrystallized from 95% ethanol and dried *in vacuo* at 100°), silver carbonate (0.01 mole) and freshly prepared 3-indoleacetyl chloride[7] (0.016 mole) were shaken in 10 ml. of anhydrous thiophene–free benzene for 18 hr. at 30°. The silver chloride and carbonate were then removed by suction filtration and washed with 10 ml. of benzene. The filtrate was concentrated to dryness under reduced pressure and the residue treated with hot methanol. The white to gray crystals which failed to dissolve were collected by filtering the hot solution. Upon cooling the filtrate to room temperature an amorphous powder precipitated (total yield of crude product based on cholesterol was 80%). One gram of the combined material was treated with 0.8 g. of digitonin.[9] The final product was recrystallized from chloroform-95% ethanol and weighed 0.67 g.

Ergosteryl 3-indoleacetate. The procedure previously described for the preparation of cholesteryl 3-indoleacetate was followed through removal of the silver residues. Concentration of the filtrate *in vacuo* was aided by bubbling nitrogen through the solution. Two solid fractions were obtained, one from filtration and the other from evaporation of the benzene. Complete removal of the solvent yielded a brown tar which could not be purified. The two fractions were recrystallized separately by dissolving in enough chloroform to effect solution and adding an equal volume of 95% ethanol. The two white crystalline fractions were combined and treated with digitonin.[9] Final recrystallization of the product involved dissolving in ethyl ether, evaporation of the solvent at room temperature until crystals began to form, and then adding to this solution an equal volume of petroleum ether (b.p. 40–45°).

7-Dehydrocholesteryl 3-indoleacetate. Using 7-dehydrocholesterol, 3-indoleacetyl chloride and silver carbonate, the mixture was heated at 30° for 18 hr. and filtered. After most of the benzene had been removed by concentration in an atmosphere of nitrogen under reduced pressure, a brown oil formed. Enough chloroform was added to the oil to produce a homogeneous solution which was then volatilized and cooled by passing a stream of nitrogen over the surface. The cooling and concentration caused a brown oil to form from which the cold chloroform was decanted. Addition of 95% ethanol to the supernatant liquid precipitated white crystals which after two-fold recrystallization from chloroform-95% ethanol resulted in the analytical product.

B. Preparation in petroleum ether. Cholestanyl 3-indoleacetate. Equal weights (3.94 g.) of cholestanol (0.01 mole), freshly prepared 3-indoleacetyl chloride (0.02 mole) and silver carbonate (0.1 mole) were refluxed gently in a round bottom flask heated by a water bath at 40–45° in 110 ml. of dry petroleum ether (b.p. 40–45°). A motor stirrer kept the silver carbonate in suspension during the heating period while hydrogen chloride passed through the condenser. After 2 hr. of heating 10 ml. of dry benzene was added and the temperature was maintained until hydrogen chloride evolution ceased. Thirty milliliters more benzene was added and the water bath temperature increased to 55–60° for an additional 30 min. After filtering the silver salts from the warm solution, fractions of material were obtained by additions of petroleum ether. Recrystallizations from absolute ethanol gave the crude products (64% based on cholestanol). Treatment with digitonin and final recrystallization from chloroform-95% ethanol gave the purified product.

β-Sitosteryl 3-indoleacetate. Proportions of sterol, 3-indoleacetyl chloride, silver carbonate, and solvent were used as in the previous preparation. After 3 hr. of heating, hydrogen chloride production ceased, 40 ml. of dry benzene was added and the bath temperature raised to 45–50° for an additional 2 hr. Concentrating the filtrate, removing the silver precipitates, and adding petroleum ether (b.p. 40–45°) gave material which was treated with Norite A, recrystallized three times from 95% ethanol and then purified further by digitonin treatment. A final recrystallization from 95% ethanol gave fluffy flakes of the ester.

Biological properties. Biological activity of the steroidal esters was determined by employing the tomato ovary test[11] and using 3-indoleacetic acid as a control. For all

(10) Washed with sulfuric acid, water, dried over calcium chloride, and distilled over sodium.

(11) S. H. Wittwer, *Univ. of Missouri Bull.*, 371 (1943).

practical purposes, the steryl esters were inactive in this test.

DEPARTMENT OF AGRICULTURAL CHEMISTRY
MICHIGAN STATE UNIVERSITY
EAST LANSING, MICH.

The Effect of Solvent on the Ultraviolet Absorption Spectra of Phosphine Oxides and Sulfides

V. BALIAH AND P. SUBBARAYAN

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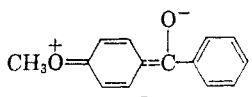
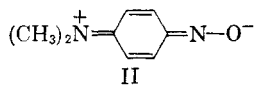
From a study of the effect of solvent on the ultraviolet absorption spectra of sulfones, it was suggested[1] that the sulfur-oxygen bond in sulfones is semipolar and not doubly covalent. It was interesting to study in a similar way the nature of the phosphorus-oxygen and phosphorus-sulfur bonds in phosphine oxides and phosphine sulfides, respectively.

From the data recorded in Table I it is seen that the solvent effect on the absorption spectra of phosphine oxides and phosphine sulfides is analogous to that observed for sulfones.[1] With change of solvent from cyclohexane to ethanol there is practically no change in λ_{max} for phosphine oxides and sulfides, while for ketones, there is a considerable bathochromic shift. This shift is even more pronounced for *p*-nitrosodimethylaniline. In the case of ketones and *p*-nitrosodimethylaniline, polar structures (I and II) make a more significant contribution to the excited state than to the ground state; the excited state is thus more stabilized in a polar solvent and a red shift of the λ_{max} is seen to occur with change of solvent from cyclohexane

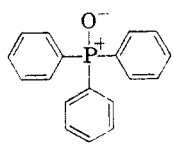


I

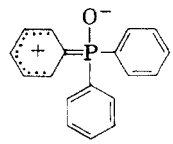


II

to ethanol. If the phosphorus-oxygen and phosphorus-sulfur bonds in phosphine oxides and sulfides are semipolar, both the ground and excited states are zwitterionic (as illustrated by III and IV) and they will be stabilized almost to the same extent in a polar solvent. Hence there will be no significant change in λ_{max} with change of solvent. Such a semipolar concept of the phosphorus-oxygen linkage in phosphine oxides is in conformity with the experimental evidence supplied by the parachors,[2] dipole moments,[3] and bond refractions.[4]



III



IV

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TABLE I

SOLVENT EFFECT ON THE ABSORPTION SPECTRA OF TRIARYLPHOSPHINE OXIDES, TRIARYLPHOSPHINE SULFIDES, AND DIARYL KETONES[a]

	C_6H_{12}		C_2H_5OH	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
$(C_6H_5)_3PO$	224	23,000	224	26,100
$(p\text{-}CH_3\cdot C_6H_4)_3PO$	231	32,800	232	35,500
$(p\text{-}CH_3O\cdot C_6H_4)_3PO$	244	43,700	246	46,000
$(p\text{-}CH_3\cdot C_6H_4)_3PS$	227	30,800	227	30,300
$(p\text{-}CH_3O\cdot C_6H_4)_3PS$	240	35,300	242	35,300
$(C_6H_5)_2CO$	249	18,900	253	17,500
$(p\text{-}CH_3\cdot C_6H_4)_2CO$	258	22,100	265	20,600
$(p\text{-}CH_3O\cdot C_6H_4)_2CO$	279	22,300	295	21,900
$p\text{-}(CH_3)_2N\cdot C_6H_4\text{'}NO$	393	23,800	428	28,600

[a] The high intensity bands only are given. Wave lengths are in mμ.

EXPERIMENTAL

Tri-p-anisylphosphine oxide. A saturated solution of potassium permanganate was added in excess to tri-*p*-anisylphosphine[5] (3.5 g.) dissolved in glacial acetic acid. After 2 to 3 hr., sodium bisulfite was added to decolorization and the acid was neutralized carefully with ammonium hydroxide. The oil (3 g.) that was obtained solidified on cooling and scratching with a few drops of ether. Recrystallization from petroleum ether (b.p. 60–70°) gave shining needles, melting at 142–143°.

Anal. Calcd. for $C_{21}H_{21}O_4P$: C, 68.45; H, 5.74. Found: C, 68.03; H, 5.64.

Tri-p-anisylphosphine sulfide. A mixture of tri-*p*-anisylphosphine[5] (3.5 g.) and sulfur (0.4 g.) in carbon disulfide (25 ml.) was refluxed for 2 hr. Distillation of the carbon disulfide left an oily product (3.2 g.) which solidified on cooling. It crystallized from ethanol as colorless needles and melted at 109–110°.

Anal. Calcd. for $C_{21}H_{21}O_3PS$: C, 65.63; H, 5.51. Found: C, 65.12; H, 5.36.

Tri-p-tolylphosphine oxide. To *p*-tolylmagnesium bromide prepared from magnesium (5.2 g.) and *p*-bromotoluene (36.7 g.) dissolved in sodium-dried ether (100 ml.) was added phosphoryl chloride (7.6 g.) in dry ether (50 ml.) during the course of 0.5 hr. with vigorous shaking and cooling in a freezing mixture. The resulting complex was decomposed with a saturated solution of ammonium chloride and the ether layer was separated. The aqueous layer was extracted twice with ether and the combined ether extracts were washed with sodium hydroxide solution to remove any di-*p*-tolylphosphinic acid formed. The ethereal extract was dried with anhydrous sodium sulfate and the ether was removed by distillation. The oily product (12 g.) that was left

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