studying certain model compounds related to citrinin prompted the preparation of 6-hydroxyisochroman (IV) since this compound upon oxidation might be expected to give the unique *p*-methylene quinoid structure (V) characteristic of citrinin.

Although the preparation of isochroman has been previously described[6,7] no substituted compounds of known orientation have been reported. After several unsuccessful attempts to prepare the desired 6-hydroxyisochroman by modifications of the methods reported in the literature, a satisfactory procedure was developed using a different approach. *m*-Hydroxy-β-phenylethyl alcohol, prepared from the corresponding methoxy compound[8] was converted by the Gattermann reaction into 4-hydroxy-3-(β-hydroxyethyl)-benzaldehyde. Upon reduction of the latter to the carbinol, water spontaneously split out to form 6-hydroxyisochroman.

This method has been extended to the preparation of other substituted 6-hydroxyisochromans and the properties of these compounds and their relationship to citrinin are presently under investigation.

Experimental

All melting points are uncorrected.

m-Hydroxy-β-phenylethyl Alcohol.—In a three-liter round-bottomed flask fitted with a reflux condenser was placed 65.2 g. (0.43 mole) of *m*-methoxy-β-phenylethyl alcohol,[8] 940 ml. of glacial acetic acid and 100 ml. of 48% hydrobromic acid. After vigorously refluxing for six hours, the excess acid was distilled off at atmospheric pressure, the residue diluted with 200 ml. of water and the solution neutralized by the cautious addition of solid sodium carbonate. Three hundred ml. of a saturated sodium carbonate solution was then added and the mixture boiled for 30 minutes. The cooled alkaline solution was extracted with ether and the ether in turn extracted with 2 *N* sodium hydroxide. From the alkaline solution the phenol was recovered by strong acidification with concd. hydrochloric acid followed by ether extraction. After drying and removal of the ether the product was vacuum distilled giving 30.2 g. (54%) of a yellow, highly viscous oil boiling at 168–173° (4 mm.).

Anal. Calcd. for $C_8H_{10}O_2$: C, 72.00; H, 6.60. Found: C, 72.01; H, 6.65.

A 3,5-dinitrobenzoate was obtained in the usual manner as light yellow needles, m.p. 146.5–147°.

Anal. Calcd. for $C_{15}H_{12}O_7N_2$: N, 8.43. Found: N, 8.51.

2-(β-Hydroxyethyl)-4-hydroxybenzaldehyde.—In a 250-ml. wide-mouthed bottle fitted with a stirrer, reflux condenser and gas inlet tube was placed 6.0 g. (0.044 mole) of *m*-hydroxy-β-phenylethyl alcohol, 7.8 g. (0.066 mole) of anhydrous zinc cyanide, a pinch of sodium chloride and 50 ml. of anhydrous ether. The reaction mixture was cooled in an ice-bath and 8.8 g. (0.066 mole) of anhydrous aluminum chloride dissolved in 50 ml. of cold anhydrous ether added. Anhydrous hydrogen chloride was passed through the reaction mixture with ice-bath cooling until the ether was saturated with hydrogen chloride (about 2 hr.). The reaction mixture was then allowed to come to room temperature and hydrogen chloride added for another five hours. At the end of this time a viscous, pink oil had settled out. The ether was decanted, the imide hydrochloride washed with a small volume of anhydrous ether and then hydrolyzed by boiling in water. After extracting with ether, drying and distilling 3.3 g. (45.8%) of the aldehyde was obtained as a faintly pink oil boiling at 153–162° (6 mm.).

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.00; H, 6.03. Found: C, 64.87; H, 6.25.

The semicarbazone, prepared in the usual manner, was obtained as light tan crystals, m.p. 244–245° dec.

Anal. Calcd. for $C_{10}H_{14}O_3N_3$: N, 18.75. Found: N, 19.21.

6-Hydroxyisochroman.—In a 200-ml. three-necked flask fitted with a mercury-seal stirrer, reflux condenser and dropping funnel was placed 0.65 g. (0.018 mole) of lithium aluminum hydride in 25 ml. of dry ether. A solution of 3.0 g. (0.018 mole) of 2-(β-hydroxyethyl)-4-hydroxybenzaldehyde in 40 ml. of anhydrous ether was added dropwise at such a rate that a gentle reflux was maintained. After standing for one hour with stirring the mixture was hydrolyzed with dilute hydrochloric acid and the ether layer separated and dried. On removal of the ether 1.8 g. (66%) of a colorless oil was obtained boiling at 153–162° (7 mm.).

Anal. Calcd. for $C_9H_{10}O_2$: C, 69.56; H, 7.25. Found: C, 69.21; H, 7.13.

A 3,5-dinitrobenzoate was readily obtained as yellow needles melting at 152.5–154°.

Anal. Calcd. for $C_{16}H_{12}O_7N_2$: N, 8.14. Found: N, 8.16.

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(6) von Braun and Zobel, *Ber.*, **56**, 2149 (1923).

(7) Buschmann and Michel, German Patents 614,461 (May 23, 1935); 617,646 (Aug. 8, 1935); *C. A.*, **30**, 492 (1936).

(8) Natelson and Gottfried, THIS JOURNAL, **61**, 1001 (1939).

2-Methyl-2-monoalkylaminopropyl and Dialkylaminoethyl Aryloxyacetates[1]

BY J. STANTON PIERCE, WILLIAM K. EASLEY AND H. H. HANNABAS, JR.

Most of the plant growth-regulating substances reported are acids and their salts, esters or amides.[2,3] In the study of over one thousand compounds as plant growth-regulating substances, Thompson, Swanson and Norman[4] included two alkylaminoalkyl aryloxyacetates, β-diethylaminoethyl 2,4-dichlorophenoxyacetate and β-diethylaminoethyl 2,4,5-trichlorophenoxyacetate, although no physical constants or analyses are given.

Since so many of the simple salts and esters of aryloxyacetates have been found to be active hormones for plant growth, it seemed well to prepare for study a few alkylaminoalkyl aryloxyacetate hydrochlorides, which are esters and at the same time are salts, usually soluble in water.

In the work reported below, esters were formed with phenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid and β-naphthoxyacetic acid and dimethylaminoethanol, diethylaminoethanol and various 2-methyl-2-monoalkylaminopropanols. The latter compounds, secondary amino alcohols, were chosen for this study, since in this Laboratory hydrochlorides of many 2-methyl-2-monoalkylaminopropyl esters of alkoxybenzoic acids,[5] arylacetic and alkarylacetic acids[6] and alkoxyhydrocinnamic acids[7] have been found to crystallize more readily than corresponding esters of 2-monoalkylaminoethanols and 2-monoalkylaminobutanols. The hydrochlorides of some of the esters in this study were obtained as crystalline solids and some as oils. The crystalline products

(1) Acknowledgment is made to Dr. E. Emmet Reid, Research Adviser to the Chemistry Department of the University of Richmond, for his advice in this work.

(2) F. A. Gilbert, *Chem. Revs.*, **39**, 199 (1946).

(3) M. S. Newman, W. Fones and M. Renoll, THIS JOURNAL, **69**, 718 (1947).

(4) H. E. Thompson, C. P. Swanson and A. G. Norman, *The Botanical Gazette*, **107**, 476 (1946).

(5) J. S. Pierce, J. M. Salsbury, W. W. Haden and L. H. Willis, THIS JOURNAL, **64**, 2884 (1942).

(6) J. S. Pierce, W. W. Haden and R. D. Gano, *ibid.*, **67**, 408 (1945).

(7) J. S. Pierce, R. D. Gano and J. M. Lukeman, *ibid.*, **70**, 255 (1948).

TABLE I

DIALKYLAMINOETHYL ARYLOXYACETATE HYDROCHLORIDES

$ROCH_2COOCH_2CH_2NR'_2 \cdot HCl$

R	R'	Yield, % Crude	Yield, % Purified	M.p., °C. (uncor.)	Formula	Chlorine, % Calcd.[a]	Chlorine, % Found[b]
$2,4\text{-}Cl_2C_6H_3$	CH_3	66	43[c]	169–170	$C_{12}H_{16}O_3NCl_3$	10.78	10.59
$2,4\text{-}Cl_2C_6H_3$	C_2H_5	81	26[c]	140–141	$C_{14}H_{20}O_3NCl_3$	9.94	9.68
$2,4,5\text{-}Cl_3C_6H_2$	CH_3	64	53[d]	175–176.5	$C_{12}H_{15}O_3NCl_4$	9.76	9.76
$2,4,5\text{-}Cl_3C_6H_2$	C_2H_5	73	43[d,e]	157–159	$C_{14}H_{19}O_3NCl_4$	9.07	8.92

[a] Ionizable chlorine. [b] Analysis by R. L. Kersey, Jr. [c] Recrystallized from acetone. [d] Recrystallized from acetone and ether. [e] Prepared as the free base by M. S. Newman, William Fones and Mary Renoll.[8]

TABLE II

2-METHYL-2-ALKYLAMINOPROPYL ARYLOXYACETATE HYDROCHLORIDES

$ROCH_2COOCH_2C(CH_3)_2NHR' \cdot HCl$

R	R'	Yield, % Purified	M.p., °C. (uncor.)	Formula	Chlorine, % Calcd.	Chlorine, % Found[c]
C_6H_5	$n\text{-}C_3H_7$	27	130–131	$C_{15}H_{24}O_3NCl$	11.75	11.52
C_6H_5	$n\text{-}C_4H_9$	30	130.5–131.5	$C_{16}H_{26}O_3NCl$	11.23	10.81
C_6H_5	$n\text{-}C_5H_{11}$	26	146–147	$C_{17}H_{28}O_3NCl$	10.75	10.55
$\beta\text{-}C_{10}H_7$	$n\text{-}C_4H_9$	22	160–162	$C_{20}H_{28}O_3NCl$	9.69	9.49
$\beta\text{-}C_{10}H_7$	$n\text{-}C_5H_{11}$	19	155–157	$C_{21}H_{30}O_3NCl$	9.33	9.17
$2,4\text{-}Cl_2C_6H_3$	$n\text{-}C_5H_{11}$		129–130	$C_{17}H_{26}O_3NCl_3$	8.90[b]	8.94
$2,4,5\text{-}Cl_3C_6H_2$	$n\text{-}C_5H_{11}$[c]	25	153–154	$C_{17}H_{25}O_3NCl_4$	8.18[b]	8.17
$2,4,5\text{-}Cl_3C_6H_2$	$n\text{-}C_6H_{13}$[c]		148–149	$C_{18}H_{27}O_3NCl_4$	7.93[b]	7.49

[a] Analyses by R. L. Kersey, Jr., and W. E. Reid, Jr. [b] Ionizable chlorine. [c] Acknowledgment is made to Gildo Suffredini for his assistance in the preparation of this compound.

and some of the oils will be tested[8] as plant growth-regulating substances.

The acids used in this work were purchased from Eastman Kodak Co. or were made from the corresponding potassium phenolate and potassium chloroacetate.[9,10] Potassium β-naphthoxyacetate and potassium 2,4,5-trichlorophenoxyacetate were recrystallized from water and the free acids from glacial acetic acid.

Phenoxyacetyl chloride was purchased from Eastman Kodak Co. The other acid chlorides were prepared by the reaction of the acid with excess thionyl chloride.[11] In the preparation of β-naphthoxyacetyl chloride and 2,4-dichlorophenoxyacetyl chloride, three molar quantities of thionyl chloride were used and in the preparation of 2,4,5-trichlorophenoxyacetyl chloride, six molar quantities were used. In each case the reaction mixture was refluxed gently until it became liquid. This usually required 1 to 1.5 hours. In all cases the thionyl chloride was distilled off on a water-bath, at atmospheric pressure and under a vacuum and after the addition of toluene, under a vacuum. The acid chlorides thus prepared were used without further purification.

β-Dimethylaminoethyl 2,4-Dichlorophenoxyacetate Hydrochloride.—A mixture of 0.1 mole each of 2,4-dichlorophenoxyacetyl chloride and β-dimethylaminoethanol, in 30 ml. of chloroform, was refluxed gently for 5 hours. The reaction mixture was poured slowly into 800 ml. of hot 0.25 *N* sodium hydroxide solution and the chloroform was evaporated off. An oil separated. This oil was dissolved in isopropyl ether and the solution was saturated with dry hydrogen chloride. The crystalline precipitate of crude dimethylaminoethyl 2,4-dichlorophenoxyacetate hydrochloride was filtered with suction; yield 21.8 g. On recrystallization from anhydrous acetone the yield was 14.2 g., 43%, m.p. 169–170°.

2-Methyl-2-*n*-amylaminopropyl 2,4,5-Trichlorophenoxyacetate Hydrochloride. $2,4,5\text{-}Cl_3C_6H_2OCH_2COOCH_2C(CH_3)_2NHC_5H_{11} \cdot HCl$.—To 0.1 mole of 2-methyl-2-*n*-amylamino-1-propanol hydrochloride, in 25 ml. of chloroform, was added slowly a solution of 0.1 mole of 2,4,5-trichlorophenoxyacetyl chloride, in 25 ml. of chloroform. The reaction mixture was refluxed gently for 5 hours and was poured into 500 ml. of boiling water. The chloroform was evaporated off and excess alkali was added. The aqueous solution was decanted from the oily lower layer. The oily product was dissolved in 100 ml. of ether. The ethereal solution was filtered and stirred with 50 ml. of *N* hydrochloric acid. A heavy white crystalline precipitate of 2-methyl-2-*n*-amylaminopropyl 2,4,5-trichlorophenoxyacetate hydrochloride was formed. The product was filtered with suction, washed with ether and air-dried; yield 10.7 g. (24%), m.p. 152–154°. On recrystallization from absolute ethanol and isopropyl ether the m.p. was 153–154°.

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(8) Tests will be carried out by Dr. R. F. Smart, of the Department of Biology, University of Richmond.

(9) F. Spitzer, *Ber.*, **34**, 3192 (1901).

(10) R. Pokorny, THIS JOURNAL, **63**, 1768 (1941).

(11) V. H. Freed, *ibid.*, **68**, 2112 (1946).

Cyclopropanes. VIII.[1] Cyclopropanecarboxaldehyde

BY LEE IRVIN SMITH AND EDGAR R. ROGIER

In connection with the work described in a previous paper[2] considerable amounts of cyclopropanecarboxaldehyde were required. Catalytic conversion of tetrahydrofurfuryl alcohol to dihydrofuran, and thermal rearrangement of the latter to cyclopropanecarboxaldehyde, as described by Wilson,[3] proved impractical in our hands for preparation of large amounts of the aldehyde. Application of the Oppenauer oxidation to cyclopropylcarbinol, with

(1) Paper VII, L. I. Smith and E. R. Rogier, THIS JOURNAL, **73**, 3840 (1951).

(2) Cyclopropanes. V, L. I. Smith and E. R. Rogier, *ibid.*, **73**, 3831 (1951).

(3) C. L. Wilson, (a) *J. Chem. Soc.*, 53, 58 (1945); (b) THIS JOURNAL, **69**, 3002 (1947).