some difficulty, the vapors showing a distinct reluctance to pass into the fractionating column. Heats of vaporization were calculated by the integrated form of the Clausius–Clapeyron equation

$$L = \frac{R(T_1T_2)}{T_2 - T_1} \ln \frac{P_2}{P_1}$$

Infrara Data

The infrared spectra were observed in the Infrared Laboratory of the School of Chemistry under the direction of Dr. Bryce L. Crawford, Jr., using a Perkin–Elmer model 12C single-beam spectrometer. Spectra were recorded both for the pure liquid and for the dilute solution in carbon disulfide. Rocksalt and KBr prisms were used in the appropriate regions and a cell thickness of 0.025 mm. was used in all cases. The observed frequencies of the seven compounds are given in Table IV. The spectrum of tetramethoxygermane as a pure liquid using a KBr prism is given in Fig. 1; that of the pure liquid using a NaCl prism in curve (a) Fig. 2 and that of the 10% carbon disulfide solution with a NaCl prism in curve (b) Fig. 2.

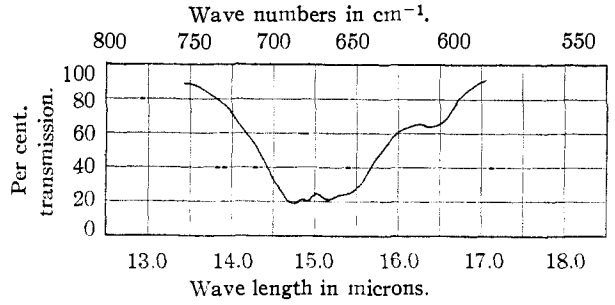


Fig. 1.—Infrared spectrum of tetramethoxygermane using a KBr prism.

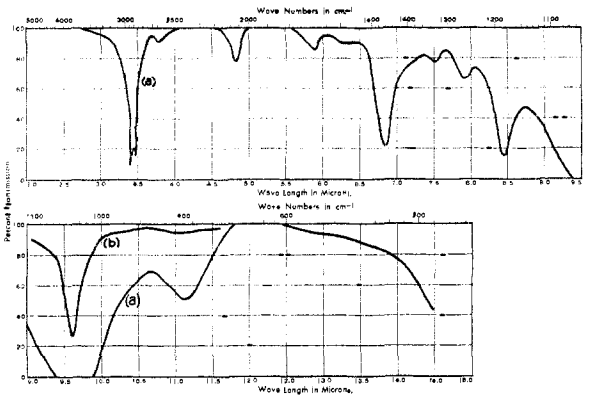


Fig. 2.—Curve (a), infrared spectrum of tetramethoxygermane using a NaCl prism; Curve (b), infrared spectrum of a 10% solution of tetramethoxygermane using a NaCl prism.

The strong absorption near 1040 cm.$^{-1}$ and the strong band near 680 cm.$^{-1}$ were observed with all these compounds and presumably arises from vibrations characteristic of the central GeO_4^{-4} configuration.

Extreme precautions had to be taken to avoid too much hydrolysis of the compounds while filling the cells. Occurrence of hydrolysis is readily detected through observation of the 3400 cm.$^{-1}$ OH band in the hydrolysis products.

MINNEAPOLIS 14, MINNESOTA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, THE UNIVERSITY OF PENNSYLVANIA, AND THE LABORATORY OF CHEMICAL PHARMACOLOGY, NATIONAL CANCER INSTITUTE, NATIONAL INSTITUTES OF HEALTH]

The Synthesis of Deaminocolchinic Acid Anhydride[1,2]

BY JOHN KOO[3]

RECEIVED JULY 15, 1952

2,3,4-Trimethoxybenzosuber-5-ene-5,6-dicarboxylic anhydride (V), deaminocolchinic acid anhydride, has been synthesized. 2,3,4-Trimethoxybenzosuber-5-one (VI), an interesting intermediate for preparation of compounds related to colchicine, and some of the intermediates needed in the preparation of V and VI have been obtained by improved methods.

The complete syntheses of some methoxybenzosuberenedicarboxylic anhydrides[4,5] with properties corresponding to that of Windaus' N-benzoylcolchinic anhydride[6] have indicated the desirability of making a further study of 2,3,4-trimethoxybenzosuber-5-ene-5,6-dicarboxylic anhydride (V). This anhydride was then obtained by an essentially similar route and proved to be identical with the deaminocolchinic acid anhydride,[2,7] an important degradation product from natural colchicine.

It appears desirable to outline in some detail the experimental procedures employed in our synthesis of V, especially in view of the fact that the preparation by our method of some of the needed intermediates could not be reproduced readily by other workers[8] in the field. In addition, several compounds, such as 2,3,4-trimethoxybenzosuber-5-one[8,9] (VI), an interesting intermediate for the preparation of compounds related to colchicine, have been prepared by greatly improved procedures in the course of this work.

(1) The work carried out in this paper was supported in part by a Grant-in-aid from the American Cancer Society recommended by the Committee on Growth of the National Research Council.

(2) Reported in part in a Communication to the Editor (E. C. Horning, M. G. Horning, J. Koo, M. S. Fish, J. A. Parker, G. N. Walker, R. M. Horowitz and G. E. Ullyot, THIS JOURNAL, **72**, 4840 (1950)).

(3) American Cancer Society Postdoctoral Fellow, 1948–1950. National Cancer Institute Special Research Fellow, 1950–1952.

(4) E. C. Horning and J. Koo, THIS JOURNAL, **73**, 5830 (1951).

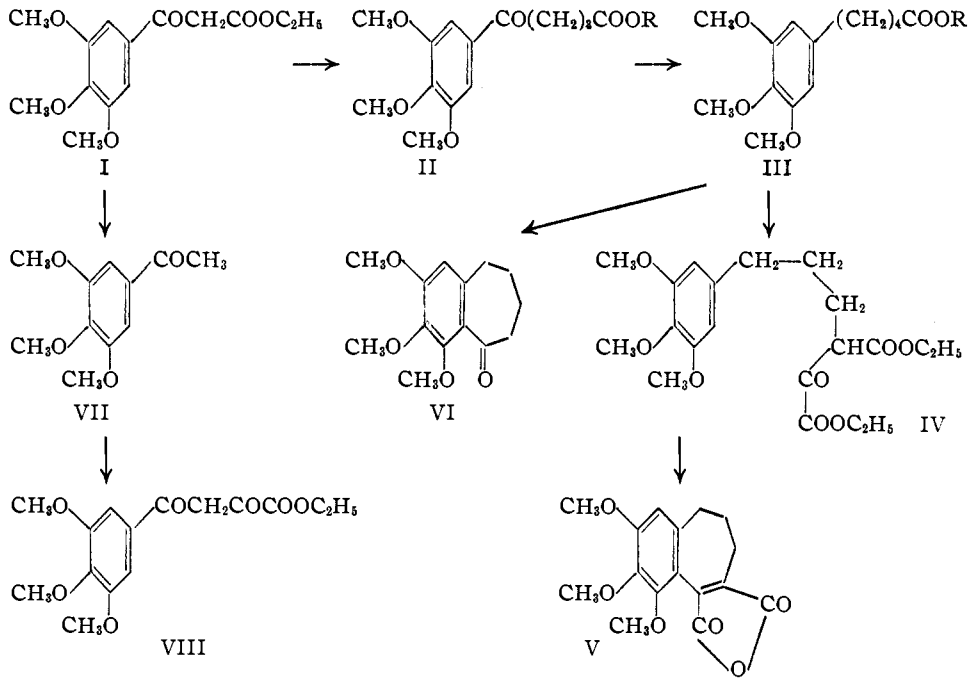
(5) J. Koo and E. C. Horning, Abstracts of the Boston Meeting of the Am. Chem. Soc., April, 1951, p. 38M.

(6) A. Windaus, *Ann.*, **439**, 59 (1924).

(7) J. W. Cook, T. Y. Johnston and J. D. Loudon, *J. Chem. Soc.*, 537 (1950).

(8) A. G. Anderson, Jr., and H. F. Greef, THIS JOURNAL, **74**, 2923 (1952).

(9) R. D. Haworth, D. P. Moore and P. L. Pauson, *J. Chem. Soc.*, 1045 (1948); D. Caunt, W. D. Crow, R. D. Haworth and C. A. Vodoz, *ibid.*, 1631 (1950).



Perkin and Weizmann[10] originally prepared ethyl 3,4,5-trimethoxybenzoylacetate (I) by ketonic cleavage with an ammonia–ammonium chloride solution of ethyl 3,4,5-trimethoxybenzoylacetoacetate, obtained in turn by condensation of 3,4,5-trimethoxybenzoyl chloride with sodioethyl acetoacetate. No yields were reported. Anderson and Greef[8] stated that they could obtain only very low yields of I in the cleavage of the substituted acetoacetic ester. They published an alternate two-step synthesis involving condensation of 3,4,5-trimethoxybenzoic acid with methyllithium and condensation of the resulting trimethoxyacetophenone with diethyl carbonate. This gave I in a 32% over-all yield. We have obtained the product in a 75% over-all yield starting from 3,4,5-trimethoxybenzoic acid by modification of the procedure of Perkin and Weizmann. Close adherence to the conditions listed in the experimental section was, however, necessary in order to obtain reproducible results.

γ-(3,4,5-Trimethoxybenzoyl)-butyric acid (II, R = H) had been prepared[9] by condensation of I with ethyl β-iodopropionate, followed by hydrolytic cleavage with hot dilute sulfuric acid. We followed essentially the same procedure, except that the more readily available methyl β-bromopropionate was employed. In addition to the acid (II, R = H), a neutral by-product was isolated and later identified as the corresponding ethyl ester (II, R = C_2H_5), which may well be the same material as the neutral impurity mentioned by Haworth, *et al.*[9] Combined yields of acid and ester were 86 to 90%. Hydrogenation with palladium–carbon in acetic acid converted II (R = H) to δ-(3,4,5-trimethoxyphenyl)-valeric acid (III, R = H) in 90% yield. This reaction had previously[9] been accomplished by a Wolff–Kishner reduction. Treatment of the acid III (R = H) with ethanol–sulfuric acid produced its ethyl ester (III, R = C_2H_5), which was also obtained by direct hydrogenation of II (R = C_2H_5). Condensation of III (R = C_2H_5) with ethyl oxalate gave ethyl α-ethoxalyl-δ-(3,4,5-trimethoxyphenyl)-valerate (IV), which was cyclized with sulfuric–phosphoric acids[4] to 2,3,4-trimethoxybenzosuber-5-ene-5,6-dicarboxylic anhydride (V).

Haworth, *et al.*,[9] obtained 2,3,4-trimethoxybenzosuber-5-one (VI) by treatment of III (R = H) with phosphorus pentoxide or phosphorus pentachloride–stannic chloride in 64 and 84% yield, respectively. This cyclization has now been accomplished in 94% yield by the use of polyphosphoric acid in a simple and convenient process.[11]

3,4,5-Trimethoxyacetophenone (VII) has previously been prepared by several different methods.[8,12–14] Hydrolysis and decarboxylation of ethyl 3,4,5-trimethoxybenzoylacetate (I) with dilute sulfuric acid furnished VII in 94% yield. The reverse reaction, carbethoxylation of VII to I, was reported by Anderson and Greef.[8] Condensation of VII with ethyl oxalate yielded the previously unknown ethyl 3,4,5-trimethoxybenzoylpyruvate (VIII).

Experimental[15,16]

3,4,5-Trimethoxybenzoyl Chloride.—3,4,5-Trimethoxybenzoic acid was prepared by an improvement in the usual procedure[17] more suited to large-scale preparation, carrying out the methylation of gallic acid in a nitrogen atmosphere

(10) W. H. Perkin, Jr., and C. Weizmann, *J. Chem. Soc.*, **89**, 1649 (1906).

(11) H. R. Snyder and F. X. Werber, THIS JOURNAL, **72**, 2962, 2965 (1950).

(12) V. J. Harding, *J. Chem. Soc.*, **105**, 2796 (1914).

(13) E. Haggett and S. Archer, THIS JOURNAL, **71**, 2255 (1949).

(14) E. C. Horning, J. Koo and G. N. Walker, *ibid.*, **73**, 5826 (1951).

(15) All melting points are corrected.

(16) For complete infrared spectra for Compounds V and VI, order Document 3720 from American Documentation Institute, % Library of Congress, N.W., Washington 25, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(17) F. Mauthner, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 537.

and by adding the dimethyl sulfate dropwise with stirring at a temperature lower than 5°. This permitted a colorless crude product, m.p. 163–166° (reported[17] 167°), to be obtained in 90–95% yield. It was used in the next step without further purification.

Treatment of this acid with a two-mole excess of purified thionyl chloride,[18] using thiophene-free benzene, removing excess solvent and thionyl chloride *in vacuo* and recrystallizing the product from benzene–petroleum ether, gave a 95% yield of colorless needles, m.p. 76–78° (reported[10] 77–78°).

Ethyl 3,4,5-Trimethoxybenzoylacetoacetate.—The following modification of Perkin and Weizmann's procedure[10] gave the best yields. A sodium ethoxide solution was prepared by dissolving 31.5 g. of sodium in 500 ml. of absolute ethanol and adding 150 ml. of absolute ether. To two-thirds of the warm solution was added 121.5 g. of ethyl acetoacetate, and vigorous stirring started. After 10 minutes, one-half of a solution of 104 g. of 3,4,5-trimethoxybenzoyl chloride in 680 ml. of absolute ether was added dropwise during 30 minutes. The remainder of the sodium ethoxide solution was added 20 minutes later, followed after another 10 minutes by the rest of the acid chloride solution, which again was added over 30 minutes. Stirring was continued for 5 hours, interrupted during the night, then continued for another 3 hours. The thick paste was collected with suction, washed with ether, dissolved in 1500 ml. of water and the solution acidified below 5°. An oil separated, which solidified to yield 130 g. (90%) of colorless material, m.p. 80–83°. Recrystallization from dilute ethanol provided plates melting at 83–85° (reported[10] 85°).

The mono-2,4-dinitrophenylhydrazone, prepared by the usual procedure, formed bright yellow cottony needles from ethanol–ethyl acetate, m.p. 160°.

Anal. Calcd. for $C_{22}H_{24}O_{10}N_4$: C, 52.38; H, 4.80. Found: C, 52.58; H, 5.03.

Ethyl 3,4,5-Trimethoxybenzoylacetate (I).—In the following modification of Perkin and Weizmann's procedure[10] essentially complete cleavage of the starting material was obtained. A mixture of 60 g. of finely ground ethyl 3,4,5-trimethoxybenzoylacetoacetate and 100 g. of ammonium chloride was placed in a large erlenmeyer flask, and a homogeneous suspension produced by the gradual addition of 500 ml. of warm water (35°) with shaking. Another 2000 ml. of water warmed to 35° was added all at once, followed by 500 ml. of 15% aqueous ammonia. The flask was then shaken vigorously and its contents kept at 30°. Most of the starting material dissolved rapidly, but a portion became occluded by the crystalline reaction product which soon began to separate. Shaking was therefore interrupted every two minutes and the solid crushed with a flattened glass rod. After 10 to 15 minutes, the mixture was chilled rapidly by adding ice and kept in the ice-box for 2 hours. The colorless product (46 g., 88%) was collected and recrystallized from dilute ethanol to yield 44 g. of leaflets, m.p. 93–94° (reported[10] 95°).

The 2,4-dinitrophenylhydrazone crystallized in fine orange needles from ethanol–ethyl acetate, m.p. 174°.

Anal. Calcd. for $C_{20}H_{22}O_9N_4$: C, 51.95; H, 4.80. Found: C, 52.08; H, 4.80.

γ-(3,4,5-Trimethoxybenzoyl)-butyric Acid (II, R = H).—To a solution of 3.5 g. of sodium in 250 ml. of absolute ethanol was added, at 40°, 28.2 g. of ethyl 3,4,5-trimethoxybenzoylacetate. The mixture was stirred for 10 minutes, then maintained below 0° during the dropwise addition with continued stirring of 2.17 g. of methyl β-bromopropionate. An interval of an hour was allowed to elapse between the addition of the first 0.17-g. portion of the bromo ester and of the remainder. The suspension was stirred for an additional 3 to 4 hours at 5–10°, allowed to stand at 10° overnight, diluted with ice-water and acidified with dilute hydrochloric acid. Extraction with ether followed by washing, drying and evaporating yielded 40 g. of a pale yellow oil, which was too unstable for purification.

The crude ester was refluxed with 250 ml. of 20% sulfuric acid for 45 hours. The mixture was chilled and the partly gummy crude acid treated with 200 ml. of 5% sodium hydroxide. Neutral material was removed by filtration and the filtrate acidified to yield 23 g. (81%) of almost colorless crystalline material. Recrystallization from water gave colorless plates, m.p. 118–120° (reported[9] 120–121°).

The 2,4-dinitrophenylhydrazone formed bright red crystals from ethyl acetate, m.p. 200–201°.

Anal. Calcd. for $C_{20}H_{22}O_9N_4$: C, 51.95; H, 4.80. Found: C, 52.12; H, 5.09.

Ethyl γ-(3,4,5-Trimethoxybenzoyl)-butyrate (II, R = C_2H_5).—The neutral material (1.5 g., 5%), obtained by filtration of the alkaline solution of the crude acid II (R = H), crystallized from dilute ethanol in small colorless prisms, m.p. 66–68° (reported[9] 68°).

The 2,4-dinitrophenylhydrazone formed red cottony needles from ethanol–ethyl acetate, m.p. 150–151°.

Anal. Calcd. for $C_{22}H_{26}O_9N_4$: C, 53.87; H, 5.44. Found: C, 53.45; H, 5.48.

In a similar experiment, the yield of keto acid II (R = H) was 71% and that of the ester II (R = C_2H_5), 19%.

δ-(3,4,5-Trimethoxyphenyl)-valeric Acid (III, R = H).—A solution of 30 g. of the keto acid II (R = H) in 160 ml. of acetic acid was hydrogenated at 60° and 20–40 lb. pressure with 12 g. of 5% palladium–carbon catalyst during 4 hours. The catalyst was removed and the filtrate concentrated to 100 ml., then stirred and diluted with 300 ml. of ice-water. The crystalline solid was collected after 2 hours. The yield of colorless material, m.p. 66–68° (reported[9] 70°) was 25 g. (90%).

Ethyl δ-(3,4,5-Trimethoxyphenyl)-valerate (III, R = C_2H_5).—Esterification of the acid III (R = H) with absolute ethanol and concd. sulfuric acid gave an 83% yield of colorless oil, b.p. 151° (0.3 mm.), 157–158 (0.75 mm.), 162° (1 mm.).

The compound was also obtained in 93% yield by the hydrogenation of the ester II (R = C_2H_5), using a procedure analogous to the one employed in the case of the acid.

Anal. Calcd. for $C_{16}H_{24}O_5$: C, 64.59; H, 8.11. Found: C, 64.83; H, 8.26.

2,3,4-Trimethoxybenzosuber-5-ene-5,6-dicarboxylic Anhydride (V).—Ethyl α-ethoxalyl-δ-(3,4,5-trimethoxyphenyl)-valerate (IV) was prepared as follows: To alcohol-free potassium ethoxide (from 1.6 g. of potassium) in 30 ml. of dry ether was added 8 g. of ethyl oxalate in 30 ml. of dry ether. After 1 or 2 minutes, 11 g. of III (R = C_2H_5) in 30 ml. of dry ether was added. The mixture was refluxed gently for 5 hours and then kept at room temperature for 24 hours. Ice-water (60 ml.) was added, and the aqueous layer separated, acidified and extracted with ether. The ether solution was washed with dilute sodium bicarbonate, then with water, and dried. Evaporation of the ether gave 10 g. (68%) of a pale yellowish oil, which was used immediately for the cyclization.

A mixture of 10 ml. of concd. sulfuric acid and 10 ml. of 85% phosphoric acid was added to 2.5 g. of the keto ester IV at 0° with stirring. The solution was kept at room temperature for 1 hour, warmed to 30°, diluted with a mixture of 15 ml. of concd. sulfuric acid and 5 ml. of 85% phosphoric acid, then gradually heated to 60°. After cooling, it was poured into 400 ml. of ice-water. The yellow crystalline solid was dissolved in ether; the solution washed with dilute sodium bicarbonate and water, then dried over magnesium sulfate. Evaporation yielded 1.52 g. (80%) of material, m.p. 110–113°. Purification was effected by passing a benzene solution through a silica gel column, evaporating the eluate, and crystallizing the residue from ether. The pure product formed tiny yellow needles, m.p. 119–120°.

Anal. Calcd. for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 62.89; H, 5.32.

The compound formed a colorless solution when slightly warmed with 5% aqueous sodium hydroxide. Upon acidification it turned yellow after a short time and finally deposited the yellow crystalline anhydride.

The infrared absorption spectrum exhibited two sharp peaks at 5.43 and 5.66 μ, characteristic of the cyclic anhydride grouping.

2,3,4-Trimethoxybenzosuber-5-one (VI).—A mixture of 3 g. of δ-(3,4,5-trimethoxyphenyl)-valeric acid (III, R = H) and 20 g. of polyphosphoric acid[11] was heated on the steam-bath at 75–80° with frequent stirring for 50 minutes. The reddish reaction product was cooled and poured with stirring into 60 ml. of ice-water. The suspension was extracted with ether five times and the extract washed with water, sodium bicarbonate solution and again water. Drying and

(18) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 381.

evaporation yielded 2.64 g. (94%) of a colorless crystalline solid, m.p. 97–100°. Recrystallization from ethanol–water gave shiny rhombs, m.p. 99.5–101.5° (reported[9] 102°).

The infrared absorption spectrum showed the ketone band at 5.96 μ.

3,4,5-Trimethoxyacetophenone (VII).—A suspension of 10 g. of ethyl 3,4,5-trimethoxybenzoylacetate (I) in 100 ml. of 14% sulfuric acid was refluxed for 6 hours, then cooled to yield 7.01 g. (94%) of solid, m.p. 75–77°. Recrystallization from 30% ethanol furnished colorless needles, m.p. 79–80° (reported 73–74°,[8] 77–79°[13]).

Ethyl 3,4,5-Trimethoxybenzoylpyruvate (VIII).—A solution of 5.2 g. of ethyl oxalate in 40 ml. of dry ether was added with stirring to alcohol-free potassium ethoxide (from 0.93 g. of potassium), followed after 10 minutes by a suspension of the ketone VII in 40 ml. of dry ether. A yellow solid separated rapidly. The mixture was refluxed for 1 hour, allowed to stand at room temperature overnight and diluted with cold water. Acidification of the aqueous phase yielded 6.1 g. (81%) of yellow crystals, m.p. 94–96°, which after recrystallization from ethanol–water formed bright yellow needles, m.p. 96–97°.

Anal. Calcd. for $C_{15}H_{18}O_7$: C, 58.06; H, 5.80. Found: C, 58.27; H, 5.64.

The mono-2,4-dinitrophenylhydrazone crystallized in bright yellow needles from ethanol, m.p. 203–205°.

Anal. Calcd. for $C_{21}H_{21}O_{10}N_4$: C, 51.53; H, 4.33. Found: C, 51.65; H, 4.46.

Acknowledgment.—The author wishes to express his appreciation to Dr. E. C. Horning for his sponsorship and helpful discussion during the course of this work at the University of Pennsylvania. He is also indebted to Mrs. Sarah M. Woods of the University of Pennsylvania and to Dr. W. C. Alford and his associates of the National Institutes of Health for the microanalyses.

BETHESDA 14, MARYLAND

[CONTRIBUTION FROM THE HARRISON LABORATORY OF CHEMISTRY, THE UNIVERSITY OF PENNSYLVANIA, AND THE LABORATORY OF CHEMICAL PHARMACOLOGY, NATIONAL CANCER INSTITUTE, NATIONAL INSTITUTES OF HEALTH]

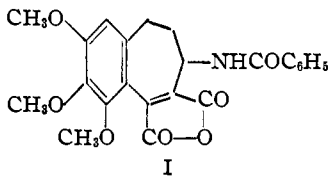
Analogs of Windaus' Anhydride. Synthesis of 2,3-Dimethoxy-9-benzoylaminobenzosuber-5-ene-5,6-dicarboxylic Anhydride[1,2]

BY JOHN KOO[3]

RECEIVED SEPTEMBER 25, 1952

2,3-Dimethoxy-9-benzoylaminobenzosuber-5-ene-5,6-dicarboxylic anhydride (XI), an analog of Windaus' anhydride, and a few related compounds, have been synthesized.

The structure of Windaus' N-benzoylcolchinic anhydride[4] has been established as 2,3,4-trimethoxy-7-benzoylaminobenzosuber-5-ene-5,6-dicarboxylic anhydride (I) by the syntheses of deaminocolchinic anhydride (2,3,4-trimethoxybenzosuber-5-ene-5,6-dicarboxylic anhydride)[5,6] and of *dl*-colchinol methyl ether.[7]



I

In view of the tumor-damaging activity of colchicine[8] and of some of its derivatives,[9] in which I proved to be inactive when tested against Sarcoma 37 in mice, it was thought desirable to develop general methods for the preparation of analogous compounds, in which some of the substituents would be located in different positions. The purpose of this paper is to report on the syntheses of 2,3-dimethoxy-9-benzoylaminobenzosuber-5-ene-5,6-dicarboxylic anhydride (XI) and of the closely related ethyl 2,3-dimethoxy-9-benzoylaminobenzosuber - 5 - ene - 6 - carboxylate (XIII). The anhydride XI differs from Windaus' anhydride I by the position of the benzoylamino group and by the absence of one of the methoxyl groups. The methods for the synthesis of aminobenzosuberenes outlined in this paper might be applicable to the preparation of compounds analogous to colchicine itself.

The present investigation forms an extension of previous work[5,6,10] on the synthesis of benzosuberene derivatives. The required starting material, γ-(3,4-dimethoxybenzoyl)-butyric acid (II) was prepared in improved yield (60 instead of 31%) by carrying out the Friedel–Crafts reaction[10] at −10 to −15°. Treatment of its ethyl ester[10] (III) with hydroxylamine hydrochloride in pyridine furnished the oxime (IV) in 91% yield. Catalytic hydrogenation of this oximino ester did not yield the corresponding amino ester, but gave the lactam V in almost quantitative yield. Alkaline hydrolysis of V and benzoylation of the resulting amino acid VI, which was not isolated, produced the benzoylamino acid VIII. It was found subsequently that this acid could be prepared more readily by catalytic hydrogenation and benzoylation of the oximino acid VII, which in turn was obtained in 88% yield from II with hydroxylamine hydrochloride in pyridine.

Esterification of the benzoylamino acid VIII

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(2) Presented in part before the Organic Division of the American Chemical Society at Boston, Mass., on April 4, 1951.

(3) American Cancer Society Postdoctoral Fellow, 1948–1950. Special Research Fellow of the National Cancer Institute, National Institutes of Health.

(4) A. Windaus, *Ann.*, **439**, 59 (1924).

(5) E. C. Horning, M. G. Horning, J. Koo, M. S. Fish, J. A. Parker, G. N. Walker, R. M. Horowitz and G. E. Ullyot, THIS JOURNAL, **72**, 4840 (1950).

(6) J. Koo, *ibid.*, **75**, 720 (1953).

(7) H. Rapoport, A. R. Williams and M. E. Cisney, *ibid.*, **73**, 1414 (1951).

(8) H. Lettré and H. Fernholz, *J. Physiol. Chem.*, **278**, 175 (1943); B. Goldberg, L. G. Ortega, A. Goldin, G. E. Ullyot and E. B. Schoenbach, *Cancer*, **3**, 124 (1950).

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(10) E. C. Horning and J. Koo, THIS JOURNAL, **73**, 5830 (1951).