and of their respective acetates. The production of 5-hydroxy-7-methoxy-2,6-dimethylchromone from 5,7-dihydroxy-2-methylchromone in this manner is in accordance with the well established behavior of phloroglucinol and its derivatives[6] and indicates the accuracy of the formulation (V) for the methylation product of genistein (IV) obtained under similar conditions.[7] Confirmation of the structure (V) will be provided in a forthcoming publication.

Experimental

5-Hydroxy-7-methoxy-2,6-dimethylchromone.—A solution of 5,7-dihydroxy-2-methylchromone (0.5 g.) in methanol (10 ml.) and methyl iodide (10 ml.) containing sodium (0.2 g.) was refluxed during 12 hours, when most of the solvent was removed under reduced pressure. Addition of water (50 ml.) and excess 2 *N* hydrochloric acid to the residue furnished a crystalline precipitate which after purification from methanol gave rise to eugenitin (0.4 g.) in colorless needles, m.p. 162–163°, undepressed on admixture with an authentic specimen and exhibiting an intense blue ferric reaction in alcohol.

Anal. Calcd. for $C_{11}H_9O_3(OMe)$: C, 65.44; H, 5.49; OMe, 14.09. Found: C, 65.35; H, 5.74; OMe, 13.24.

The acetate, prepared by the sodium acetate–acetic anhydride method had m.p. 171° alone or in admixture with an authentic specimen.

Acknowledgment.—The author thanks Smith, Kline & French Laboratories for the hospitality of their laboratories, where most of this work was performed, Mrs. Rita Preis for the analysis, Mr. Samuel Rump for the ultraviolet absorption curves which were determined in methanol solution using a Cary recording quartz spectrophotometer, Model 11 M, and Professor H. Schmid for specimens of natural eugenitin and the acetate.

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The Preparation of Nicotinaldehyde

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RECEIVED JULY 7, 1952

Although the preparation of nicotinaldehyde has been carried out by several methods,[1–5] the yields and the isolation procedures leave much to be desired. We have found that the conversion of acyl hydrazides to aldehydes by means of potassium ferricyanide[6] in ammoniacal solution can be applied to nicotinyl hydrazide. Nicotinaldehyde can be obtained in yields of 60–65% in form of its phenylhydrazone, but regeneration of the aldehyde is difficult. An improvement upon this procedure has been discovered in the reaction of nicotinyl hydrazide with sodium metaperiodate in ammoniacal solution whereby yields of 60–70% of crude nicotinaldehyde can be realized. Methylamine can replace ammonia in this synthesis.

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Experimental

To a stirred and chilled solution of 11 g. of sodium metaperiodate in 150 cc. of water, 100 cc. of ammonium hydroxide was added slowly until the precipitate first formed went into solution. Usually a crystal mass separated on continued cooling.

A solution of 6.5 g. of crude nicotinyl hydrazide in 75 cc. of about 8% ammonium hydroxide was added to the stirred ice-cold periodate solution as rapidly as the gas evolution permitted. Stirring and cooling were continued for five minutes, the mixture was allowed to stand for 15 more minutes, and then precipitated with a solution of 12 g. of barium acetate in 50 cc. of water. The precipitate was filtered, the filtrate was nearly neutralized with acetic acid and saturated with sodium chloride. The aldehyde was extracted into chloroform, and was fractionated. It boiled at 97–99° (26 mm.).[4] Its phenylhydrazone melted at 157° (uncor.).[4] The aldehyde could also be purified through the bisulfite addition product.

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Physical Adsorption from Mixtures of Gases.[1] III. Ethane and Carbon Dioxide on Chromic Oxide Gel at −78°

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RECEIVED JUNE 5, 1952

Hill[2] has suggested that perhaps the most important postulate of the Brunauer–Emmett–Teller[3] theory of multimolecular adsorption is that adsorbed molecules after the first layer have the evaporation–condensation properties of the liquid state. He further suggested that studies of adsorption from mixtures of gases would provide a test of this postulate, and he made the necessary extension of BET theory. At that time, there were no suitable data for comparison with the theory.

Since then Arnold[4] has reported studies of adsorption from mixtures of oxygen and nitrogen on anatase, and we[5] have reported similar studies from mixtures of oxygen–nitrogen and oxygen–argon on chromic oxide gel. Arnold's system showed considerable discrepancies between theory and experiment, even at low pressures, whereas our systems agreed at least semi-quantitatively with theory up to relative pressures of about 0.4, the maximum we used.

The mixtures used by both Arnold and us obeyed Raoult's law reasonably well. To test the theory under somewhat more drastic conditions, we have made similar studies with mixtures of carbon dioxide and ethane, which deviate so far from ideality that in most proportions they are not miscible in the condensed phase.

For the theoretical calculations, vapor pressure data for the mixtures were required. Because such data were not available for carbon dioxide and ethane, we determined them approximately.

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(1) This research was supported jointly by the Office of Naval Research and the Institute-sponsored Research Fund of Southern Research Institute. The paper was presented at the Adsorption Symposium, Fall Meeting, American Chemical Society, Atlantic City, N. J., September 20, 1949.

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Experimental Details

Apparatus.—For the adsorption measurements, the apparatus described previously was used with two modifications: the thermostat and the analyzer. The thermostat was a one-liter dewar flask packed with crushed Dry Ice. In the bottom of the dewar flask was a one-watt heater, used according to the suggestions of Scott.[6]

For analysis of the gases, the model B-T Gow-Mac thermal-conductivity cell was used. The voltage applied to the bridge was held constant within ±0.03%, the cell was enclosed in a housing thermostated within ±0.1°, and the unbalance voltage was measured potentiometrically.

The effect of differences in pressure between the unknown and reference cells was briefly investigated. It was found that a differential of 0.1 atmosphere when the reference gas was in both cells produced about as much effect as the presence in the unknown of 3% of the other gas. Therefore, a leveling bulb and manometer were used to adjust the pressure in the reference cell to within 1 mm. of the pressure in the unknown cell. Either gas could be used as reference, and, to minimize errors, the gas with the greater partial pressure in the unknown was always used as reference. Individual readings could be made with good reproducibility and sensitivity.

Materials.—Research-grade ethane was obtained from Phillips Petroleum Company. It was warranted to be 99.9% pure, and its vapor pressure differed by not more than 0.1% from the data of the "International Critical Tables." The method of generating carbon dioxide was basically that described by Skipper, *et al.*[7]

The adsorbent was approximately 3.7 g. of the same chromic oxide gel used previously.[5]

Procedure.—The procedure was essentially one of those used before.[5] A measured quantity of one gas was added to the system and allowed to equilibrate, and then a measured quantity of the second gas was added. Before equilibration with the mixture, the thermostat was removed and the sample was allowed to warm up to room temperature. Thus most of the adsorbed gas was desorbed and, when the thermostat was replaced, adsorption occurred directly from the mixtures. This facilitated the approach to equilibrium. In some cases, the sample was heated to about 100° between adsorptions to make the desorption more complete. The quantity of the first gas added to the system was held constant throughout a run, while increments of the second gas were added successively.

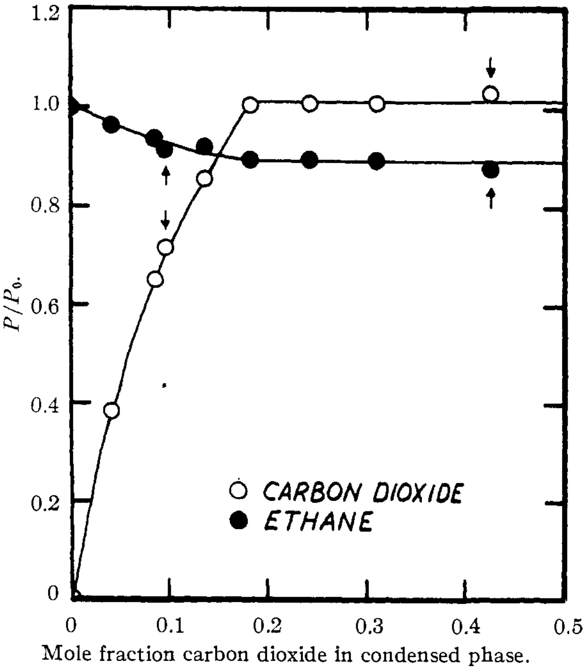

Fig. 1.—Vapor pressures of mixtures of carbon dioxide and ethane. The arrows indicate independent spot checks.

Results

The vapor pressures of mixtures of ethane and carbon dioxide at −78° are shown in Fig. 1. (P_0 in all three figures means the vapor pressure of the appropriate pure component.) The graph shows only the data for the approach from the side with

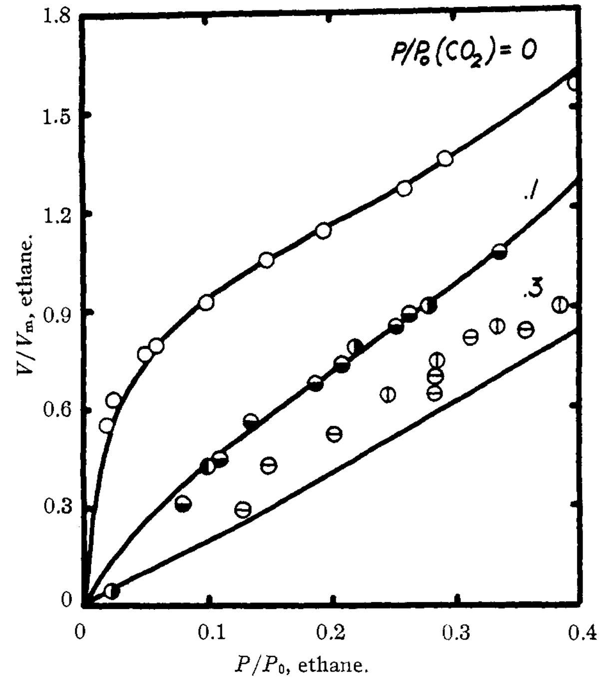

Fig. 2.—Ethane adsorbed as function of ethane pressure carbon dioxide pressure being constant.

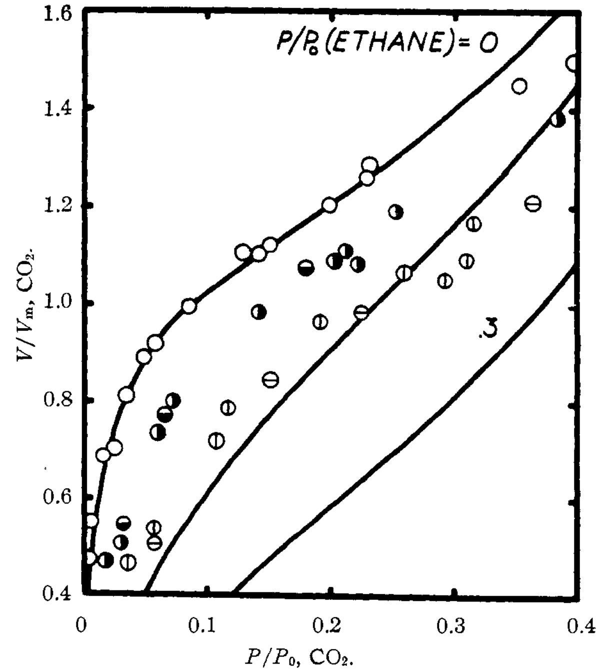

Fig. 3.—Carbon dioxide adsorbed as function of carbon dioxide pressure, ethane pressure being constant.

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ethane in excess, to the mixture with two condensed phases. The other approach is not included because the ethane is so slightly soluble in the carbon dioxide that the quantity of dissolved ethane could not be measured in our apparatus with reasonable accuracy. However, the measurements indicated that the condensed mixture in the carbon dioxide-rich part of the diagram developed two phases before the mole fraction of ethane in the condensed phase reached 0.03.

In the region with two condensed phases the measured partial relative pressure of carbon dioxide slightly exceeds 1.0, an obvious thermodynamic impossibility. The discrepancy is, however, within the expected error of the measurements.

The comparison between the theoretical and experimental adsorptions is shown in Figs. 2 and 3. Both graphs show isotherms of the volume of one gas adsorbed as function of its partial pressure, with the partial pressure of the other gas constant. It is obvious that the experimental procedure previously described does not measure directly isotherms in which one partial pressure is held constant. However, from each directly measured isotherm in which the quantity of one component was held constant, there could be extracted points for several isotherms of the type shown. Thus no two points of any single isotherm from mixtures were obtained in the same experimental run.

In Figs. 2 and 3 the curves are the predictions calculated from the theory, and the circles are the measured points. The completely open circles are points measured with only one gas present. The half-blackened circles are points of the isotherm in which the relative pressure held constant is 0.1; the circles with only a dividing line are points of the isotherm in which the constant relative pressure is 0.3. The direction of the dividing line in any circle indicates which gas was added first (and held constant) during the run from which the point was obtained. A horizontal dividing line means that ethane was added first; a vertical line, that carbon dioxide was first.

The values of the BET constants used in the theoretical calculations are as follows:

	C	V_m, ml. at S.T.P.
Ethane	48.6	82.4
Carbon dioxide	106.0	94.4

Hill's equation (14), which assumes unrestricted adsorption, was used for the calculations.

For carbon dioxide, the saturation pressure used was that of the solid.

Discussion

The disagreement between theory and experiment is considerable. Because this investigation was originally proposed as a means of verifying the BET assumption that adsorbed layers after the first have the evaporation–condensation properties of the bulk liquid, a few of the calculations were repeated with the assumption that the liquid mixture obeys Raoult's law. This assumption improves the situation for carbon dioxide, but aggravates it more for ethane than it improves it for carbon dioxide. However, there is not much difference in the over-all accuracy of prediction whether Raoult's law or the observed vapor pressure data are used. Thus the experimental results cannot be said to verify the BET assumption in question.

At the same time, it is not at all clear that the results disprove the assumption. The discrepancies first appear, and very strongly, at low pressures where it is unlikely that the properties of the second and higher adsorbed layers have very much effect. The discrepancies in these regions suggest some other limitation of the theory, probably the assumption that there are no horizontal interactions in the first layer.

Part of the disagreement may be due to the fact that the saturation pressure used for carbon dioxide was that of the solid. If the assumption that layers of adsorbate after the first have the vapor-pressure properties of the bulk material is correct, then certainly the saturation pressure of the solid is appropriate for these layers, since that is the stable phase in bulk under these conditions. Even if the vapor pressure of the liquid is more appropriate for the first layer, the choice we have made yields a value for C which must partially compensate for the error in P_0.

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D-Fructose Hemihydrate

BY FRANK E. YOUNG, FRANCIS T. JONES AND DALE R. BLACK

RECEIVED MARCH 25, 1952

D-Fructose frequently crystallizes from concentrated solutions as spherulitic aggregates of fine needles. Although these spherulites were reported to be D-fructose hemihydrate by Honig and Jesser in 1888[1] their conclusion, based on meager evidence, has not since been verified. Wolfrom and Thompson[2] recently suggested that this phase is an unstable dimorph of anhydrous D-fructose rather than the hemihydrate, as a result of their work on the corresponding phase of L-fructose. The existence of D-fructose hemihydrate is established by the work reported here, in which its preparation is also described.

Experimental

Preparation.—Seed crystals of fructose hemihydrate usually can be obtained at 0° from a solution containing over 75% fructose seeded with powdered anhydrous fructose. Vigorous stirring of this solution must be avoided because it would result in a transformation to fructose dihydrate instead of the hemihydrate.[3] The hemihydrate also frequently crystallizes spontaneously at about 25° from solutions containing about 83% fructose. Although it is metastable under these conditions, the hemihydrate sometimes may be kept for months before anhydrous fructose appears. In either case, it crystallizes as densely packed spherulitic

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