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.

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The Preparation of Nicotinaldehyde

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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.

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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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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