fraction II. Hydrolysis and subsequent sugar analysis by paper chromatography now showed rhamnose to be the only sugar present. The processing of the back part of the zone will be discussed in the next section. The yellow solid obtained from the combined eluates from the first (forward) part of the zone was recrystallized three times, then dried at 100° for 1 hr. It had a m.p. 183–184°, as did authentic quercitrin. No lowering of the melting point occurred on admixture of the two, and the isolated quercitrin showed no separation from authentic quercitrin by paper chromatography. One of the components (the forward portion) of fraction III from the column has, therefore, been identified as quercitrin; yield approximately 12 mg.

Properties of a Quercetin Glucoside.—The back part of the zone from the paper strips mentioned above was eluted, placed back again on fresh paper strips as before, and the strips chromatographed in 5% acetic acid. After 14 hours the new zone was about 5 cm. wide. The forward 2 cm. was cut off and discarded. The back 3 cm. was eluted and the ethyl alcohol evaporated and the solid hydrolyzed by refluxing for 2 hr. with 2% sulfuric acid. A sugar analysis made as described above showed glucose to be present as the predominant sugar with only a trace of rhamnose left from the quercitrin. The solid formed in the hydrolysis was identified as quercetin in the same manner as described for fraction I. Lack of sufficient material prevented further meaningful characterization of this compound. It may be identical with the quercetin glucoside reported, but not positively identified, from apricots.[3] It does show separation from both isoquercitrin and quercimeritrin on paper chromatograms processed in 15% acetic acid. Final yield of slightly impure product was about 5 mg.

Identification of Isoquercitrin.—The solid from flavonoid fraction IV was dissolved in 10 ml. of ethyl alcohol and put on strips by the procedure already described. The strips were processed in 15% acetic acid, air-dried for 3 hr., and the zone at R_f 0.45 was cut out and eluted with ethyl alcohol in an air-tight chamber. A total of 40 strips was processed, and after evaporation of the alcohol the solid was recrystallized eight times from hot water by cooling. The solid was dried at 110° for 1 hr. yielding a m.p. of 225–227°. It was identified as isoquercitrin by the methods previously described for this compound in *Vaccinium myrtillus*[4]; yield approximately 20 mg.

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The Preparation of Nicotinyl Chloride

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Procedures for the preparation of nicotinyl chloride now in use seem to be modifications of the method of Meyer and Graf.[1] Salts of nicotinic acid are treated in various solvents and under varying conditions with thionyl chloride, and the product is vacuum distilled from pyridine or quinoline. The processes are tedious and often unsatisfactory.

We have now developed a more convenient method of preparation based upon the work of Adams and Ulich.[2] Potassium nicotinate suspended in benzene is treated with oxalyl chloride. The by-products, potassium chloride, carbon dioxide and carbon monoxide, are insoluble in benzene or are gases. No hydrogen chloride is formed and hence no hydrochloride. The nicotinyl chloride may be used immediately in the reaction flask in benzene solution, or siphoned off under anhydrous conditions, or distilled under vacuum after removal of the solvent.

Experimental

Sixteen and one-tenth grams of potassium nicotinate, which had been ground to pass a 100-mesh sieve and dried in an oven at 135°, and 75 ml. of anhydrous benzene was placed in a three-necked flask which was equipped with a stirrer and reflux condenser closed with a drying tube. The flask and contents were chilled in an ice-bath, and then 12.5 g. of oxalyl chloride in 25 ml. of anhydrous benzene was added at such a rate that the temperature remained low. Stirring was continued and 15 to 20 minutes after all the oxalyl chloride had been added, the unmelted ice in the bath was removed. The bath was allowed to come to room temperature, and heating was begun at a rate such that the bath began to simmer in about 30 minutes. After an additional 30 minutes heating at this temperature, the flask was allowed to cool. The cooled solution was siphoned off under anhydrous conditions and fractionated. The oily residue distilled at 75–90° (10–12 mm.). The yield was 85% or better.

Anal. Calcd. for C_6H_4ClNO: Cl, 24.70. Found: Cl, 24.82. On exposure to the air the oily chloride soon solidified to nicotinic acid hydrochloride.

Anal. Calcd. for $C_6H_6ClNO_2$: Cl, 22.01. Found: Cl, 22.09. A sample of the oily acyl chloride treated with absolute ethanol formed ethyl nicotinate, b.p. 222–224°.

The preparation was successful using 0.5 molar proportions. Sodium nicotinate did not give as good results as the potassium salt.

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The Neutron Irradiation of Crystalline Vitamin B_{12}

BY D. T. WOODBURY AND CHARLES ROSENBLUM

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Vitamin B_{12} is a hexacovalent coördination complex of cobalt with the empirical formula[1,2] $C_{61-64}H_{86-92}N_{14}O_{14}PCo$. It is labeled[3,4] with radioactive cobalt by adding cobalt 60 to the fermentation medium in which it is produced. Direct activation of cobalt in crystalline vitamin B_{12} by neutron irradiation in a pile was thought to be improbable because of the relatively high temperatures of such a nuclear reactor, and because the high γ-ray recoil energy[5] involved in the formation of a cobalt 60 atom is far in excess of normal bond energies and should result in ejection of the radioactive cobalt atom. Radioactivation by exchange with the free Co^{60} atom is also unlikely because of the exchange stability[6] of the central cobalt atom.

In view of a report[7] that such direct activation was possible, two 21-mg. samples of crystalline vitamin were irradiated in evacuated, sealed quartz ampules in the Brookhaven National Laboratories pile for $\simeq$ 48 hours and 138

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