linear gradient of HOAc from 0 to 0.4 M. The separation was monitored by TLC on cellulose plates using the following solvent systems: (A) *n*-BuOH–HOAc–H_2O (12:3:5) and (B) PhOH–H_2O (3:1). **1**, which emerged from the column immediately after aspartic acid, had R_f 0.28 in solvent A and 0.43 in solvent B. The appropriate fractions were pooled and evapd *in vacuo*. The residue was recrystallized from MeOH–H_2O giving 120 mg of **1**, mp 223–225°, $[\alpha]_D^{20}$ − 46.0° (*c* 1 in H_2O) and −29.7° (*c* 1 in 5N HCl).

DiMe ester hydrochloride. (MeOH–HCl): δ (D_2O) 4.7 (1H, *t*, J = 8 Hz, H2), 3.9 and 3.8 (3H each, *s*, 2- and 4-CO_2Me), 3.7 (1H, *m*, H5), 3.45 (1H, *m*, H4) and 2.65 (2H, *m*, H3). This diMe ester (50 mg) was heated with Se (250 mg) at 250° for 30 min. After cooling, the mixture was extracted with EtOAc and the extract taken to dryness. The residue was purified by PLC giving 2,4-dicarbomethoxypyrrole, identified by comparison with an authentic sample.

Amino acid distribution. Samples of fresh algae were macerated and extracted with 70% EtOH and amino acid fractions separated using Dowex-50W columns. The individual components were resolved by 2-D TLC in solvents A and B and on paper electrophoresis (pH 4.5).

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TYRAMINE FROM *THEOBROMA CACAO*

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Key Word Index—*Theobroma cacao*; Sterculiaceae; migraine headaches; tyramine.

Tyramine [1] (4-hydroxyphenethylamine) and phenethylamine [2] have been implicated as agents in foods (especially cheese and cocoa-based food stuffs) which trigger the onslaught of severe migraine headaches ('dietary migraines') in certain individuals. Recent reports have noted that tyramine is absent from cocoa based products and have thus implicated phenethylamine as the principal culprit in these cases [2–4]. This note reports the isolation and identification of tyramine from *Theobroma cacao* beans (seeds) and cocoa based products. To our knowledge, this is the first time tyramine has been identified as a naturally occurring constituent of cacao.

Plants. Unroasted seeds of *Theobroma cacao* (unfermented or, fermented) were supplied by Dr. Victor C. Quensel of the Cocoa Research Unit, University of the West Indies, Trinidad. 'Raw' and 'roasted' fermented cacao beams were also supplied by Hershey Foods Corporation, Hershey, PA 17033. Powdered confectionary cocoa (Hershey) was purchased locally.

Previous work. The alkaloids dopamine and salsolinol have been detected in powdered confectionary cocoa. [5] Tyramine is a logical precursor of these compounds.

Present work. TLC [6–8] and HPLC [8] (high performance liquid chromatography with electrochemical detection) and combinations thereof were utilized to identify and quantitate levels of tyramine in various cacao and cocoa samples. EtOAc–acetone extractions of the basified (pH = 10.3) acidic extract (0.1 M $HClO_4$) of pulverized cacao samples were subjected to analysis (see Experimental). The method of standard addition was used to quantitate the tyramine. The tyramine concentrations found in *Theobroma cacao* were as follows (μg/g): unfermented-unroasted, 3.9 ± 0.1; fermented-unroasted, 11.5 ± 0.1; Hershey's 'raw', 3.4 ± 0.1; Hershey's 'roasted' 3.6 ± 0.1; Hershey's powdered, 8.3 ± 0.4. This is the first report of the isolation and identification of tyramine from cacao sources.

EXPERIMENTAL

Pulverised cacao or cocoa samples (1 g), either freshly ground or defatted with petrol; were prepared for analysis by reciprocal shaking (for 15 min) with 10 ml of 0.1 M $HClO_4$. 2 ml aliquots of the supernatants were basified with conc NH_4OH (to pH = 10.3) and satd with NaCl. The solns were extracted with 3 × 4 ml vols of EtOAc–Me_2CO (2:1). The dried (2 g Na_2SO_4)

organic phases were conc. under N_2. The solid was redissolved in either 200 μl of EtOAc or 2 ml of the HPLC mobile phase. The TLC conditions have been defined elsewhere [6–8].

A Bioanalytical Systems Model LC-30 liquid chromatograph (West Lafayette, Indiana) was used with a 'slurry packed' 15 cm microparticulate C_{18} (Waters Associates) column. The mobile phase consisted of a mixture of 400 ml of 0.1 M ammonium acetate, 20 ml of spectrograde MeOH, and 8 ml of 0.1 M octyl sodium sulfate. The potential of the amperometric detector was controlled at +950 mV vs S.C.E.

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SUGAR ACCUMULATION IN CHEMICALLY DEBUDDED POTATO TUBERS DURING COLD STORAGE

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Key Word Index—*Solanum tuberosum*; Solanaceae; potato; starch–sugar conversion at low temperature; chemical debudding; tuber aging.

Abstract—Potato tuber buds may be excised by immersion of the tubers in a mixture of EtOH–Me_2CO (1:1) for 4 hr. This enabled the study of the effect of tuber aging (at 17°) on the starch-to-sugar conversion during storage at 4°, in the absence of complications due to sprouting. Sugar accumulation during a two-week period of storage at 4° decreased with increasing time of prior storage at 17°.

INTRODUCTION

For a variety of reasons it is considered best to store potatoes at 4° [1]. Storage of potato tubers at such low temperatures, however, is associated with starch degradation and concomitant sugar accumulation. This phenomenon is not only interesting from a biochemical and physiological standpoint [2–4], but it also has important implications in the commercial processing of potatoes [5].

In the course of our study of the control of starch–sugar conversion in the local 'Up-to-Date' potato variety, it was difficult to maintain a continuous supply of tubers because of the appearance of sprouting during storage at 17°. Attempts to overcome this by spraying the growing plants with maleic hydrazide, treating the stored tubers with CIPC, or excising the sprouts by hand, were unsuccessful because of undesirable side effects. This paper describes a new chemical debudding technique and its use in a study of the effect of tuber aging on starch–sugar conversion at low temperature.

RESULTS AND DISCUSSION

Attempts to debud potato tubers with 95% EtOH, which has been used successfully to debud cucumber plants [6], delayed tuber sprouting for a short period only. Absolute EtOH delayed sprouting for two months, apparently due to its effect as a dehydrating agent.

In an attempt to improve the effectiveness of EtOH, the effect of other compounds (urea, Me_2CO) known to aid penetration into plant tissues [7] was tested. Mixtures of EtOH and urea caused brown patches and sunken areas on the tuber surface, but mixtures of EtOH and Me_2CO did not produce such side effects and were very effective in debudding the tubers (Table 1). Better results were obtained with mixtures of EtOH–Me_2CO; immersion in this mixture debudded the tubers completely. Such chemically debudded tubers were kept at 17° and 90% rel. humidity for up to 9 months without noticeable changes in appearance.

Analysis showed that for *ca* 110 days storage at 17° the level of sugar was comparable in intact and in chemically