A NOTE ON THE MELTING POINT OF α-SOLANINE

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ABSTRACT

A discussion of the problems involved in the determination of the melting point of α-solanine is combined with an estimation of the reliability of this physical property for establishing the purity of a preparation.

INTRODUCTION

The importance of the glycoalkaloids in potatoes has received new emphasis in the recent literature (12). A review of the information on α-solanine has shown that almost every reference to its isolation used the melting point as one measure of purity. The values reported cover a wide range, from as low as 228 C to as high as 286 C, as shown in Table 1.

Kuhn and Löw (3) reported a value of 265 C and stated that they were not able to obtain the value of 285 C reported by Soltys and Wallenfels (9). Some years later, however, they reported the melting point to be 286 C (4). Rooke, et al. (7) stated that a preparation showed shrinking at 235 C and melted sharply at 280 C. Allen and Kuć (1) reported 228-229 C. Paquin and Lepage (5) reported that crystals began to brown at 238-240 C, lose shape and become glassy at 248-249 C, and form a gelatinous mass at 260-262 C. They also reported an odor of burning sugar. No serious attempt at an explanation for this wide melting point range or for the possible differences in purity, which might be represented, was found in these papers.

Workers at this laboratory recently prepared a sample of α-solanine to be available as a primary standard for all analytical research on the potato glycoalkaloids in the United States and Canada. This product was isolated from flowers from a mixture of several varieties. The flowers were collected without stems and dried, within 24 hours, by heating in mechanical convection ovens at 80 C, usually overnight. The isolation procedure included extraction by grinding in 3% acetic acid in a Waring Blendor.[2] After standing for 24 hours at room temperature, the suspension was filtered and the crude glycoalkaloids were precipitated by adding concentrated NH_4OH to pH 9.5 - 10. After digestion in a steambath and cooling overnight in a cold room, the suspension was filtered and the precipitate was washed with 1% NH_4OH. This precipitate was dried overnight at room temperature followed by drying at 80 C *in vacuo* for at least 4 hours. The brittle precipitate was redissolved in 3% acetic acid, the glycoalkaloids reprecipitated with NH_4OH and treated in the same manner as above. The dried precipitate was dissolved in 80% ethanol by refluxing, filtered hot and allowed to crystallize. These crystals were recrystallized three times as follows: The crystals were redissolved by heating in 95% ethanol, the hot plate was turned off and the solution let

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TABLE 1.—*Literature melting points for α-solanine.*

Authors	Melting point, C
Allen and Kuć (1)	228-229
Paquin and Lepage (5)	248-249
Schreiber (8)	260-270[1]
Kuhn and Löw (3)	265
Prelog and Jeger (6)	276-278
Kuhn and Löw (4)	286
Sołtys and Wallenfels (9)	285
Zitnak (11)	284-286
Wolf and Duggar (10)	285-287
Dabbs and Hilton (2)	283+
Rooke, Bushill, Lampitt and Jackson (7)	280

[1] Decomposition points for 12 solanine preparations varied between 245 and 280 C but eight were in the 260-270 range.

cool slowly to room temperature on the hot plate using a round bottomed flask, containing cold water, as a condenser. The crystallization was completed in the refrigerator overnight. The crystals were filtered, rinsed with ice-cold 95% ethanol and dried at 80 C *in vacuo* to constant weight. The yield of this material averaged 0.7% on a dry weight basis. The yield of crude ammonia precipitate averaged 3.2%. This final material was shown, using thin-layer chromatography (TLC), to contain less than 1% of chaconine when iodine was used as the detecting agent and antimony trichloride detection indicated even less. The specific rotation, $[\alpha]^{20}_{D}$ was —57 (C 0.91, pyridine). Kuhn and Löw (4) reported —59, Allen and Kuć (1) reported —60.6, and Schreiber (8) reported values of —54.8 to —61.3 for a series of α-solanine isolations.

The melting point was routinely determined by use of a Kofler micro hot stage, by differential scanning calorimetry (DSC) and by the ordinary capillary melting point technique. As the purity increased through repeated recrystallizations the melting point increased as shown in Table 2. The maximum melting point which could be obtained by these techniques was 262.5 to 263.5 C (see Table 2). Since this sample had been shown to be essentially pure by TLC and optical rotation, it was thought that the higher melting point (283-286 C) may have been obtained because of the presence of different crystalline forms or by means of special techniques. The crystalline form was later shown to have no effect.

Zitnak (13) had reported the value of 284 C and was kind enough to give us the method he used (11). This method involves the use of thin-glass capillary melting point tubes and an electrically-heated oil bath in which the rate of rise in temperature can be controlled over a broad range. With the bath temperature rising rapidly, the sample was inserted into the bath at 240 C and the heating continued, at the fast rate, to 270 C. At this point, the rate of rise was slowed to 1°-2° per min. A moderate browning occurred between 275-278 C, the sample began to expand at about 283 C, and in the range of 283-286 C it sintered and frothed. This could possibly be the method employed by those reporting melting points in the range of 280-286 C.

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[2] Mention of specific manufacturers or products does not imply endorsement by the United States Department of Agriculture over others not mentioned.

TABLE 2.—*Melting point of α-solanine during purification.*[1]

Method	Crystallization number 1	2	3	4
1. Kofler micro hot stage	223	242	261	262.5-263.5
2. Capillary tube (placed in bath at room temperature)	222-223	240-242	261	262-263
3. Capillary tube (placed in bath at 240 C)[2]	—	—	—	283-286
4. Differential thermal analysis (standardized against tin)	—	241[3] 278-280[4]	259-261[3] 280+[4]	262[3] 283-286[4]

[1] Recrystallization from 95% ethanol.

[2] According to Zitnak (11).

[3] First deviation from tangent.

[4] With decomposition and frothing.

Frothing is usually an indication of decomposition rather than melting, especially when working with carbohydrate-containing materials. Therefore, the resulting melt was examined by the TLC technique on silica gel. The chromatogram showed a considerable amount of solanidine as well as varying amounts of intermediate R_f materials. Samples melted on the hot stage, or in melting point tubes at a rate slow enough to see the melting, did not show this decomposition if the heating was discontinued immediately after melting at 262 C. DSC curves show a definite inflection at 262 C and complete decomposition with frothing at 285 C.

From these experiments it seems likely that 262-263 C is the melting point and that decomposition takes place at 284-286 C. However, they really prove only that the melting point is not a very reliable measure of the purity of an α-solanine preparation. Final proof must involve other techniques such as TLC and specific rotation. The melting point may be used as a guide for determining the progress of purification but only to a point of small change after recrystallization and by following very definite procedures. If a melting point is reported, the method employed should be given.

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