

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

## THE NON-VOLATILE ACIDS OF THE DRIED APRICOT

By E. K. NELSON

RECEIVED JUNE 26, 1924

PUBLISHED NOVEMBER 5, 1924

Kunz and Adam<sup>1</sup> find that citric acid is the predominating acid of apricots, but state that malic acid is also present. Bigelow and Dunbar<sup>2</sup> state that the acid of the apricot has not been positively identified. The evidence, however, seems to be that tartaric, or perhaps *d*-malic acid is present in this fruit, for the reason that a positive increase in polarization was obtained on treating it with uranium acetate.

The Bureau of Chemistry undertook an investigation to determine, by the ester distillation method, what acids are present in dried apricots.

Eleven and four-tenths kilograms of dried apricots was boiled with water and the mixture was thoroughly pressed in a cider press. The juice was evaporated to a sirupy consistency in a vacuum pan and the sirup was diluted with two volumes of alcohol in order to precipitate the pectin. After the pectin had been removed by filtration, the solution was evaporated and treated twice with absolute alcohol which was distilled each time from a salt-bath in order to remove the last traces of water.

The acids were then esterified by refluxing with absolute alcohol containing 2.5% of hydrochloric acid, the operation being repeated after distillation of the alcohol. The alcohol was removed by distillation and the esters were dissolved in ether and filtered from a large quantity of insoluble material. The ethereal solution was then shaken with a solution of sodium hydroxide, to remove unesterified acids, washed and dried with anhydrous sodium sulfate. The ether was removed by evaporation, and the esters were submitted to fractional distillation at 10 mm., the distillates being refractionated at the same pressure.

TABLE I  
FRACTIONATION OF APRICOT ACID ESTERS AT 10 MM.

No.	1	2	3	4	5	6	7	8	
°C.	87-100	100-110	110-125	125-135	135-140	145-155	155-165	165-173	Residue
G.	0.97	1.1	5.8	162.0	22.0	8.3	4.6	77.0	24.5

To 0.7 g. of each fraction, dissolved in 3.5 cc. of absolute alcohol, was added 0.5 cc. of hydrazine hydrate. The solution was mixed well and allowed to stand overnight.

Fraction 1 gave a little crystalline hydrazide which on recrystallizing from alcohol melted at 237-238°. A crystallographic examination failed

<sup>1</sup> Kunz and Adam, *Z. oesterr. Apoth. Ver.*, **44**, 187 (1906). *Z. Nahr. Genussm.*, **12**, 670 (1906).

<sup>2</sup> Bigelow and Dunbar, *J. Ind. Eng. Chem.*, **9**, 767 (1917).

to confirm the presence of oxalic dihydrazide, so that it is doubtful whether oxalic acid is present. No. 2 gave a hydrazide melting at 165–170°. A mixture with *l*-malic dihydrazide melted at 171–174°, showing the product to be impure *l*-malic dihydrazide. No. 3 also gave impure *l*-malic dihydrazide. No. 4 gave a hydrazide which melted at 178–179°. A mixture with *l*-malic dihydrazide melted at the same temperature. The product is, therefore, *l*-malic dihydrazide. No. 5 gave a hydrazide melting at 172–174°, which is *l*-malic dihydrazide. The filtrate gave a small quantity of a benzylidene compound on treatment with benzaldehyde. No. 6 gave a hydrazide melting at 164–168° which is impure *l*-malic dihydrazide. The filtrate yielded a small quantity of a benzylidene compound without sharp melting point. No. 7 also gave *l*-malic dihydrazide and a benzylidene compound melting, not sharply, at about 160°. No. 8 gave a hydrazide which crystallized in clusters of prisms melting at 145°. Citric trihydrazide was prepared in the same way and a mixture of the two melted at 145°. The product is therefore citric trihydrazide.

The benzylidene compound prepared from this melted, not sharply, at 183–185°, the benzylidene compound of citric trihydrazide at 193–196°, and a mixture of the two at 185–187°.

### Summary and Conclusion

The non-volatile acids of the dried apricot consist of a mixture of *l*-malic acid and citric acid, in the proportion of about 25 to 10, with traces of an unidentified acid which may be oxalic acid.

WASHINGTON, D. C.

---

[CONTRIBUTION FROM THE PATHOLOGICAL DIVISION, BUREAU OF ANIMAL INDUSTRY,  
UNITED STATES DEPARTMENT OF AGRICULTURE]

## A NEW LUPINE ALKALOID, SPATHULATINE, ISOLATED FROM LUPINUS SPATHULATUS (RYDB.)

BY JAMES FITTON COUCH

RECEIVED JUNE 28, 1924

PUBLISHED NOVEMBER 5, 1924

Our present knowledge of the lupine alkaloids is incomplete. Five European species of the genus *Lupinus* have been thoroughly examined; one American species has been examined in Germany, and five more have been investigated by American chemists. The available data that pertain to these alkaloids may be summarized as shown in Table I.

References to two other alkaloids, lupinidine and lupanidine, will be found in the literature. The former was the name that the sparteine from *L. luteus* bore for more than twenty years before it was recognized as identical with the base from *Spartium scoparium*. The name lupanidine was applied to an undetermined alkaloidal residue from *L. polyphyllus*, that has since been recognized as hydroxylupanine.