Chemical examination of the roots of Phaseolus multiflorus / by Frederick B. Power and Arthur H. Salway.

9.

CHEMICAL EXAMINATION

OF THE ROOTS OF

PHASEOLUS MULTIFLORUS

BY

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AND

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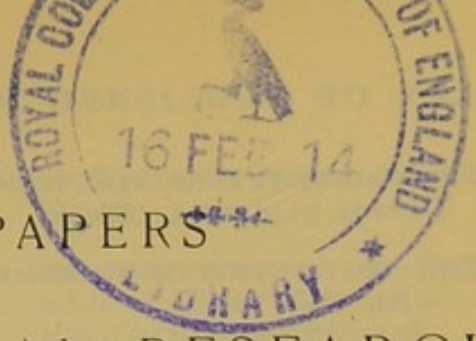

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CHEMICAL EXAMINATION

OF THE ROOTS OF

PHASEOLUS MULTIFLORUS.*

BY

FREDERICK B. POWER AND ARTHUR H. SALWAY.

In the small, but very comprehensive and useful work, entitled:—'The Treasury of Botany,' edited by Lindley and Moore, a description is given of the "Scarlet Runner Bean" (*Phaseolus multiflorus*, Lam.), and in connection therewith (Edit. 1899, Part II, p. 874) there occurs the following statement:—"It is worthy of notice that the roots are narcotic and poisonous."

It has been impossible for the present authors to ascertain when or by whom the observation was made respecting the toxic properties of these roots, as no other reference to the subject could be found in the available literature. The roots of the cultivated and mature plants are slender or fibrous,[1] presenting no suggestion of their being edible, and they could hardly be regarded as an attractive or digestible food for cattle.

Inasmuch as the scarlet runner bean is much esteemed and so largely used as a culinary vegetable, it seemed of interest to ascertain whether the properties attributed to the roots could be confirmed by their chemical examination and physiological tests.

EXPERIMENTAL.

The material used for this investigation was obtained from plants cultivated at Dartford, Kent, and was collected in the early autumn. It consisted of the roots, with a small portion of the aerial stem attached, and represented the variety of the plant bearing scarlet flowers, which is designated by some botanists as *Phaseolus multiflorus*, Lam., var. *β-coccineus* (compare Luerssen, 'Med. Pharm. Botanik,' Bd. II., p. 880). The fresh material, on drying, lost about three-fourths of its weight.

A portion (10 grammes) of the ground, air-dried roots was

* Communication from the Wellcome Chemical Research Laboratories, London, E.C., to the Pharmaceutical Society of Great Britain, April 8, 1913, and reprinted from *The Pharmaceutical Journal and Pharmacist*, April 19, 1913.

[1] In the above-mentioned 'Treasury of Botany,' Pt. II., p. 873, it is noted that "*Phaseolus multiflorus* (*coccineus*), the Scarlet Runner, a native of Mexico, has a *thick, tuberous rootstock*, and annual, twining stems, showy scarlet or white flowers, numerous on the peduncles, and rough pods." In the same work (p. 874) it is also recorded that "the Scarlet Runner Bean, *P. multiflorus*, is usually considered to be a half-hardy annual, and is treated as such, although in reality it is a tender perennial, having *tuberous roots* which may be taken up and preserved during winter for planting in spring. It is a native of South America, and is stated to have been introduced in 1633."

first tested for the presence of an alkaloid, but with a negative result.

Separation of an Enzyme.

A quantity (160 grammes) of the ground material was macerated with water at the ordinary temperature for about forty-eight hours, and the mixture then filtered under pressure. To the clear, filtered liquid twice its volume of alcohol was added when an abundant, flocculent precipitate was produced. This was collected, washed with a little alcohol, and dried in a vacuum desiccator over sulphuric acid, after which it could be reduced to a brown powder. It then amounted to 3·2 grammes, or 2 per cent. of the weight of the root. The substance gave the biuret reaction, and readily hydrolysed amygdalin, thus proving its enzymic activity. Inasmuch as no trace of hydrogen cyanide could be detected during the above-described maceration of the root with water, it may be concluded that no cyanogenetic glucoside was present.

Extraction of the Root with Alcohol, and Distillation of the Extract with Steam.

For the purpose of a general examination of the constituents of the root, 2 kilogrammes of the ground, air-dried material were completely extracted in a large Soxhlet apparatus with hot alcohol. After the removal of the alcohol a dark coloured, viscid extract was obtained, which amounted to 280 grammes. The greater portion (265 grammes) of this extract was mixed with water, and distilled in a current of steam. On extracting the distillate with ether, and removing the solvent, about 0·2 gramme of a brown, limpid essential oil was obtained, which, unlike many of the products obtained in a similar manner, gave no reaction for furfuraldehyde.

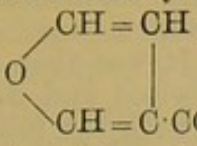
After the above-described operation there remained in the distillation flask a reddish-brown, aqueous liquid (A), together with a quantity of resinous material (B). The latter was separated by filtration, and well washed with water, the washings being added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

Isolation of Furan-β-monocarboxylic Acid, $C_5H_4O_3$.

The aqueous liquid was repeatedly extracted with ether, the ethereal extracts united, washed with a little water, dried, and the solvent removed, when about 1 gramme of a brown, oily product was obtained. This was redissolved in ether, the ethereal solution shaken with aqueous ammonium carbonate, and the alkaline liquid then acidified and extracted with ether. This ethereal liquid was dried and evaporated, when a residue was obtained which slowly crystallised. The crystals were drained on a porous tile, and then dissolved in a little hot water, when, on cooling, glistening colourless leaflets were deposited, which melted at 120°, and gave no colouration with ferric chloride. A small portion of this acidic substance was esterified by heating with methyl alcohol and concentrated sulphuric acid, when an odour resembling that of methyl benzoate was produced. The crystalline substance did not consist, however, of benzoic acid, since when mixed with the latter

a considerable depression of the melting point ensued. On the other hand, it agreed closely in its characters with the furan-



β-carboxylic acid, which was recently isolated for the first time by Rogerson[2] from the bark of *Euonymus atropurpureus*, Jacquin, this acid having been found to melt at 121-122°, and to yield a methyl ester possessing an odour very similar to that of methyl benzoate. When a little of the above-described substance was mixed with furan-β-carboxylic acid, no depression of the melting-point was observed. No doubt respecting the identity of the two substances could, therefore, be entertained.

The ethereal liquid, which had been shaken with aqueous ammonium carbonate, as above described, was next extracted successively with aqueous sodium carbonate and sodium hydroxide, but nothing definite was isolated from these extracts nor from the ethereal liquid remaining after this treatment.

The aqueous liquid which had been extracted with ether, was subsequently extracted several times with amyl alcohol, the latter extracts being then united, washed with a little water, and evaporated to dryness under diminished pressure. A small quantity (about 5 grammes) of a dark-coloured, viscid residue was thus obtained, which was glucosidic in character, but nothing definite could be isolated from it.

The aqueous liquid which had been extracted with both ether and amyl alcohol, as above described, had a dark-brown colour, and it was, therefore, treated with a slight excess of basic lead acetate. An abundant light-brown precipitate was thus produced, which was collected, suspended in water, decomposed by hydrogen sulphide, and the mixture filtered. The filtered liquid gave on evaporation an amorphous product, which was of an indefinite character, and appeared to contain no tannin. The filtrate from the basic lead acetate precipitate was deprived of lead by means of hydrogen sulphide, and concentrated under diminished pressure to the consistency of a syrup. This evidently contained a considerable proportion of sugar, since it readily reduced Fehling's solution, and from a small portion of the liquid *d*-phenylglucosazone (m.p. 212°) was prepared. On heating a little of the liquid with an alkali hydroxide it developed ammonia.

Isolation of Allantoin, $C_4H_6O_3N_4$.

The syrupy, aqueous liquid, which had been purified by means of basic lead acetate, as above described, was found to yield a precipitate with mercuric nitrate in the presence of dilute nitric acid. The entire remaining portion of the aqueous liquid was, therefore, treated with this reagent, the precipitate collected, well washed with hot water, then suspended in water, and decomposed by hydrogen sulphide. The filtrate, after removing the excess of hydrogen sulphide, was

[2] *Journ. Chem. Soc.*, 1912, **101**, 1044.

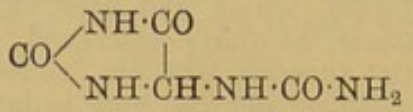
exactly neutralised with ammonia, and concentrated to a small volume. On keeping the liquid for some time a colourless, crystalline solid separated, which was collected and recrystallised from hot water. It was then obtained in colourless, rhombic prisms, which melted and decomposed at 227°. This compound was analysed, with the following results :—

0·1247 gave 0·1385 CO_2 and 0·0436 H_2O. C = 30·3; H = 3·9.

0·0322 gave 9·8 C.c. N_2 at 20° and 765 Mm. N = 35·4.

$C_4H_6O_3N_4$ requires C = 30·4; H = 3·8; N = 35·4 per cent.

The above-described substance possessed acidic but not basic properties, being readily soluble in aqueous sodium carbonate, but not more soluble in dilute hydrochloric acid than in water. It agreed completely in its composition and characters with allantoin.



which was isolated not long since by Titherley[3] from comfrey root (*Symphytum officinale*, Linné), and is stated to have been obtained, among other sources, from French beans.[4] Its identity with allantoin was furthermore confirmed by the reaction first observed by Schiff[5], which consists in mixing a crystal of the substance with an aqueous solution of furfuraldehyde, to which a few drops of concentrated hydrochloric acid have previously been added, when a violet colouration is slowly produced.

Examination of the Resin (B).

The resin, which had been separated from the aqueous liquid in the manner previously described, was intimately mixed with purified sawdust, the mixture dried, and then extracted successively, in a Soxhlet apparatus, with light petroleum, ether, chloroform, ethyl acetate, and alcohol. The several extracts were then separately examined.

Petroleum Extract of the Resin.

This extract was a soft, dark-green solid, and amounted to 19 grammes. It was heated for several hours in alcoholic solution with 16 grammes of potassium hydroxide, after which the greater portion of the alcohol was removed, water added, and the alkaline liquid repeatedly extracted with ether.

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The above-mentioned ethereal extract was washed, dried, and the solvent removed, when 0·5 gramme of a yellowish solid remained. By the fractional crystallisation of the latter from a mixture of alcohol and ethyl acetate, two substances were isolated, which melted at 73-74° and 130° respectively. The former compound possessed the properties of a hydrocarbon, and its melting-point indicated it to be pentatriacontane, $C_{35}H_{72}$, although the amount was too small for analysis.

The compound melting at 130° was crystallised from a

[3] *Pharmaceutical Journal*, 1912, **88**, 92.
[4] H. Ackroyd, *Biochem. Journ.*, 1911, **5**, 405.
[5] *Ber. d. deutsch. chem. Ges.*, 1877, **10**, 773.

mixture of ethyl acetate and alcohol, when it separated in colourless plates, and was analysed.

0·0648 gave 0·1992 CO_2 and 0·0712 H_2O. C = 83·8; H = 12·2.

$C_{27}H_{46}O$ requires C = 83·9; H = 11·9 per cent.

The substance is thus seen to agree in composition with a phytosterol, and it gave the colour reaction of that class of compounds.

The aqueous alkaline solution of potassium salts resulting from the hydrolysis of the petroleum extract of the resin, after having been shaken with ether to remove the unsaponifiable material, as above described, was acidified with dilute sulphuric acid, when a precipitate of fatty acids was produced. On extracting the mixture with ether it was observed that a small portion of the precipitate was very sparingly soluble in that liquid. This material was, therefore, collected and crystallised from dilute pyridine, when it separated in felted masses of colourless plates, melting at 275°. When dissolved in acetic anhydride and chloroform, and a few drops of concentrated sulphuric acid added, a transient pink colouration, rapidly changing to blue, and then to green, was produced. The substance thus possessed the characters of a phytosterolin[6] (phytosterol glucoside), but the amount available was not sufficient for analysis or for ascertaining its homogeneity. It yielded an acetyl derivative melting at 162°.

Examination of the Fatty Acids.

The ethereal solution of fatty acids, obtained as described above, yielded 5 grammes of a semi-solid product, which was distilled under diminished pressure, when 4 grammes passed over at 250-265°/60 Mm., leaving a non-volatile, dark-coloured residue. The distilled acids were then separated into solid and liquid portions by the usual method of conversion into their lead salts, and treatment of the latter with ether.

The Solid Acids.—These amounted to about 1 gramme. After one crystallisation from alcohol they melted at 55°, and gave the following result on analysis :—

0·1167 gave 0·3274 CO_2 and 0·1312 H_2O. C = 76·5; H = 12·5.

$C_{18}H_{36}O_2$ requires C = 76·1; H = 12·7 per cent.

$C_{20}H_{40}O_2$ requires C = 76·9; H = 12·8 per cent.

The melting-point and analysis of the above product clearly indicated it to be a mixture of fatty acids, but their separation could not be effected with the small amount of material available.

The Liquid Acids.—These acids amounted to about 2 grammes. When distilled under diminished pressure they passed over at 220-240°/18 Mm. as a yellow oil. An analysis and a determination of the iodine value gave the following results :—

0·1099 gave 0·3070 CO_2 and 0·1120 H_2O. C = 76·2; H = 11·3.

0·1734 absorbed 0·2583 Iodine. Iodine value = 149.

$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. I.V. = 90·1.

$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent, I.V. = 181·4.

[6] *Journ. Chem. Soc.*, 1913, **103**, 399.

It appears probable from the above results that the liquid acids consisted chiefly of a mixture of oleic and linolic acids. with a small proportion of a fatty acid of lower carbon content.

Ether, Chloroform, and Ethyl Acetate Extracts of the Resin.

These extracts were dark-coloured, amorphous solids, amounting to 2·3, 3·5, and 1·8 grammes respectively. Nothing of a definite nature was isolated from them, but the ethyl acetate extract was found to be glucosidic in character.

Alcohol Extract of the Resin.

This extract was a dark-brown solid, amounting to 8·5 grammes. It was digested with hot alcohol, when the greater portion, consisting of indefinite, amorphous material, was dissolved, leaving a small amount of a sparingly soluble substance.

Isolation of a New Crystalline Glucoside, Phaseosaponin, $C_{50}H_{84}O_{20}$.

The above-mentioned small amount of sparingly soluble substance was collected, and found to consist for the most part of a crystalline, organic sodium compound. It was, therefore, dissolved in a hot mixture of alcohol and dilute acetic acid, when, on cooling, colourless, glistening leaflets separated, which were free from inorganic material. This crystalline substance, which melted and decomposed at 238°, was analysed.

0·1210, when heated at 125°, lost 0·0128 H_2O. $H_2O = 10·6$

0·1082 of anhydrous substance gave 0·2356 CO_2 and 0·0820 H_2O.

$C = 59·4$; $H = 8·4$

$C_{50}H_{84}O_{20} \cdot 7H_2O$ requires $H_2O = 11·2$ per cent.

$C_{50}H_{84}O_{20}$ requires $C = 59·8$; $H = 8·4$ per cent.

The above-described substance possessed all the characters of a saponin. Thus it was found to be glucosidic, and it yielded an abundant persistent froth, when a few drops of its alcoholic solution were vigorously shaken with water. Furthermore, when dissolved in acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, a purplish-red colour was produced. With consideration of the known molecular weights of some of the saponins, it is deemed probable that the substance possesses the formula ascribed to it rather than the simpler expression $C_{25}H_{42}O_{10}$, which would conform equally well with the hydrolytic products obtained. The amount of material, however, did not permit of determining its molecular weight. As it is apparently a new compound, it is proposed to designate it *phaseosaponin*, with reference to its source.

In order to ascertain the nature of the hydrolytic products yielded by the saponin, all the remaining substance available (0·2 gramme) was heated for several hours in a reflux apparatus with 5 per cent. hydrochloric acid, sufficient alcohol having been added to effect its complete solution. The alcohol was then removed in a current of steam, when a

colourless, gelatinous product separated. This was collected, washed with hot water, and dried at 125°. It then melted and decomposed at about 200°. Although this hydrolytic product could not be crystallised, having been obtained from a pure glucoside it was presumed to be homogeneous, and was therefore analysed.

0·0763 gave 0·2088 CO_2 and 0·0722 H_2O. C = 74·6; H = 10·5.
$C_{26}H_{44}O_4$ requires C = 74·3; H = 10·5 per cent.

In accordance with the usual terminology of hydrolytic products of the saponins, this substance may be designated *phaseosapogenin.*

After the removal of the above hydrolytic product from the acid, aqueous liquid, the latter was carefully neutralised with sodium carbonate and evaporated to dryness under diminished pressure. The residue was then digested with alcohol, the mixture filtered, and the filtrate evaporated, when a small quantity of a syrupy liquid remained. This product yielded a very small amount of an osazone, which separated in yellow leaflets, melting at 180°. It thus appeared probable that the sugar formed by the hydrolysis of the glucoside was rhamnose. In accordance with this conclusion and the composition of the above-mentioned product, the hydrolysis of the glucoside may be represented by the following equation :—

$$C_{50}H_{84}O_{20} + 4H_2O = C_{26}H_{44}O_4 + 4C_6H_{12}O_5.$$

In connection with the above-described glucoside, it is of interest to note that A. W. van der Haar[7] obtained from the leaves of *Polyscias nodosa*, Forst. (Nat. Ord. Araliaceæ), an amorphous saponin, the analysis and molecular weight determination of which were stated to lead to the formula $C_{25}H_{42}O_{10}$. In a subsequent investigation of the *Polyscias* saponin by the same author[8] a crystalline sapogenin was obtained as a hydrolytic product, to which, in accordance with a molecular weight determination, the formula $C_{26}H_{44}O_4$ was assigned. If, however, this substance were derived from the above-mentioned *Polyscias* glucoside, the formula of the latter would necessarily require to be doubled, and to be represented as $C_{50}H_{84}O_{20}$. Notwithstanding the apparent agreement in composition of the glucosides from the roots of *Phaseolus multiflorus* and the leaves of *Polyscias nodosa* respectively, it is evident that neither these substances nor their hydrolytic products are identical.

Physiological Tests.

The following products from the roots of the scarlet runner bean were kindly tested for us with respect to their activity by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, to whom our best thanks may here be expressed. In all the experiments the material was administered to a dog by the mouth.

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[7] *Arch. Pharm.*, 1909, 247, 215.
[8] *Arch. Pharm.*, 1912, 250, 424.

I. The protein material, which possessed the properties of an enzyme, was given in an amount of 1 gramme, representing 50 grammes of the root, but without any observable effect.

II. An alcoholic extract, representing about 60 grammes of the root, was administered, but no trace of activity of any kind was perceptible.

III. A quantity of the roots of the white-flowered variety of *Phaseolus multiflorus* being available, these were also physiologically tested. An alcoholic extract of this material, representing about 70 grammes of the dried root, was given as in the preceding experiments, but with a perfectly negative result.

Summary and Conclusions.

The material used for this investigation consisted of the air-dried roots, together with a small portion of the attached aerial stem, of *Phaseolus multiflorus*, Lam., or "Scarlet Runner Bean," and was collected in the autumn from plants grown in Kent. Although the amount of this material available was but about 2 kilogrammes, the following constituents were isolated or identified:—(i.) An enzyme, which readily hydrolysed amygdalin; (ii.) a small amount of an essential oil; (iii.) furan-β-carboxylic acid, $C_5H_4O_3$ (m.p. 120°); (iv.) allantoin, $C_4H_6O_3N_4$; (v.) a phytosterol, $C_{27}H_{46}O$ (m.p. 130°), and apparently a little pentatriacontane, $C_{35}H_{72}$; (vi.) a small amount of substance having the characters of a phytosterol glucoside (*Journ. Chem. Soc.*, 1913, **103**, 399); (vii.) a new crystalline glucoside, *phaseosaponin*, $C_{50}H_{84}O_{20}$ (m.p. 238°), which on hydrolysis was resolved into a substance, *phaseosapogenin*, $C_{26}H_{44}O_4$, and a sugar which appeared to be rhamnose; (viii.) a mixture of solid and liquid fatty acids, the latter being unsaturated. The roots also contained, besides some resin and amorphous glucosidic material, a quantity of sugar, which yielded *d*-phenylglucosazone (m.p. 212°). No alkaloid was present, nor could any trace of a compound capable of yielding hydrogen cyanide be detected.

Physiological tests, in conjunction with the chemical examination, have afforded no evidence that the roots of the scarlet runner bean possess the toxic properties ascribed to them. It is known that the seed of *Phaseolus lunatus*—the so-called Lima bean—as obtained from plants growing wild, contain the cyanogenetic glucoside phaseolunatin (*Proc. Roy. Soc.*, 1903, **72**, 285), which is not present in the seed of the cultivated plant, and a similar condition has been observed by Professor H. E. Armstrong and his collaborators to exist in the case of the stems and leaves of the white clover, *Trifolium repens*, Linné (*Nature*, 1913, **90**, 636; compare also Mirande, *Compt. rend.*, 1912, **155**, 651). Whether the scarlet runner bean in a wild state or cultivated in a tropical climate may produce roots which exhibit poisonous properties the authors are at present unable to determine.

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