

**Chemical examination of scammony root and of scammony / by Frederick B. Power and Harold Rogerson.**

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**Publication/Creation**

London : Wellcome Chemical Research Laboratories, 1912.

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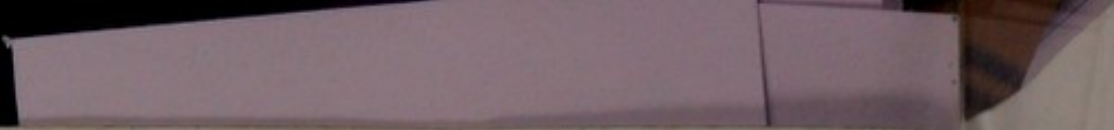
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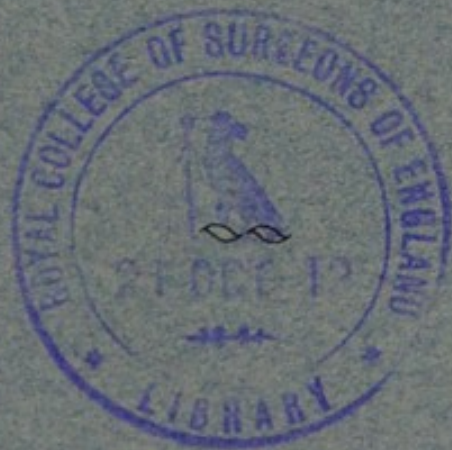
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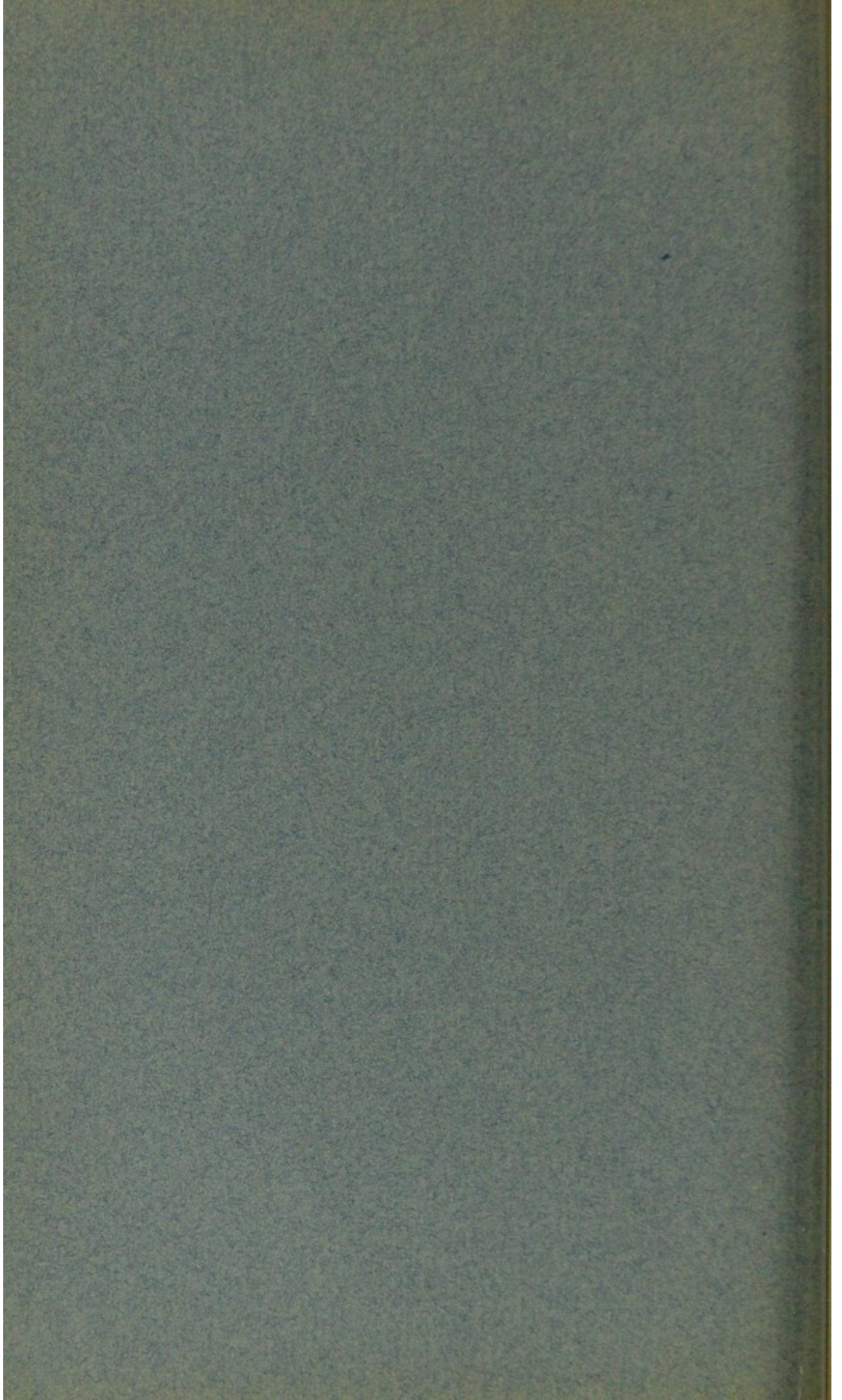
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CHEMICAL EXAMINATION  
OF  
SCAMMONY ROOT  
AND OF  
SCAMMONY

BY  
FREDERICK B. POWER, PH.D.  
AND  
HAROLD ROGERSON, M.Sc.  
(From the Transactions of the Chemical Society, Vol. 101, 1912)



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XLIX.—*Chemical Examination of Scammony Root and of Scammony.*

By FREDERICK BELDING POWER and HAROLD ROGERSON.

THE gum-resin obtained by incision from the living root of *Convolvulus Scammonia*, Linné (Nat. Ord. *Convolvulaceae*), and commonly designated as scammony or "virgin scammony," has been known and used medicinally for many centuries (compare "Pharmacographia," 2nd edit., p. 439). The value of this product depends on its resinous constituent, which, however, is now most frequently prepared by extracting the dried scammony root with alcohol, and precipitating the resin with water. The resin of scammony, as obtained from either of these sources, is still recognised by several of the national Pharmacopœias, although at the present time it appears to have been displaced to a large extent by the resin from the root of *Ipomoea orizabensis*, Ledanois—commonly known as "Mexican Scammony Root," the two products being generally regarded as chemically identical (compare this vol., p. 1). The term "scammonin," as applied to the resin of scammony, is therefore considered to be synonymous with the "jalapin" of Mayer (*Annalen*, 1855, **95**, 129), which designates the ether-soluble resin of the above-mentioned species of *Ipomoea*.

Considerable attention has hitherto been devoted to the sugars contained in scammony root, and especially to those produced by the hydrolysis of scammony resin and "jalapin" (compare Votoček, *Zeitsch. Zuckerind. Böhm.*, 1903, **27**, 257; 1905, **30**, 20, 117; *Ber.*, 1904, **37**, 3859, 4615; Requier, *J. Pharm. Chim.*, 1904, [vi], **20**, 148, 213; 1905, [vi], **22**, 435, 492, 540). Apart from these products, however, the previously recorded investigations pertaining to scammony root or its resin have been either of a somewhat fragmentary nature or based on the erroneous assumption that the resin is a homogeneous substance.

One of the earliest investigations of scammony resin was by Johnston (*Phil. Trans.*, 1840, Part II., p. 341), who assigned to the product obtained from the gum-resin known as scammony the formula  $C_{40}H_{33}O_{20}$ , or, according to present notation,  $C_{20}H_{33}O_{10}$ . Keller (*Annalen*, 1857, **104**, 63; 1859, **109**, 209) gave to "scammonin" the formula  $C_{38}H_{64}O_{16}$ , whereas Spirgatis (*Annalen*, 1860, **116**, 289, and *Arch. Pharm.*, 1894, **232**, 241, 482) believed it to possess the formula  $C_{34}H_{56}O_{16}$ , which is the same as that assigned by Mayer to "jalapin" (*loc. cit.*, and this vol., p. 2). Kromer (*J. Chem. Soc.*, 1893, **64**, i, 423) considered scammony resin to be

represented by the formula  $C_{88}H_{156}O_{42}$ . These discrepancies of statement respecting the ultimate composition of scammony resin may, however, readily be understood if it be considered that, like other similar products from convolvulaceous plants, it does not represent an individual substance, but is a somewhat complex mixture.

Inasmuch as the present authors have recently made a complete investigation of the resin of *Ipomoea orizabensis* (this vol, p. 1), with which, as already noted, the resin of scammony has been presumed to be identical, it was deemed desirable to subject the latter to a comparative examination. For this purpose the resin was prepared directly from the root, and also from the product known as virgin scammony.

### EXPERIMENTAL.

#### I.—*Examination of Scammony Root.*

The material employed consisted of a good quality of Levant scammony root (from *Convolvulus Scammonia*, Linné).

As a preliminary experiment, 50 grams of the ground material were successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at  $100^{\circ}$ , were obtained:

Petroleum (b.p. $40-60^{\circ}$ )	extracted	0.32 gram	= 0.64 per cent.
Ether	"	4.00 "	= 8.00 " "
Chloroform	"	0.38 "	= 0.76 " "
Alcohol	"	4.50 "	= 9.00 " "
Total.....		9.20 grams	= 18.40 per cent.

*Determination of the Total Resin.*—Fifty grams of the ground material were completely extracted in a Soxhlet apparatus with hot alcohol. To the liquid thus obtained 25 c.c. of water were added, the alcohol then evaporated, and the separated resin thoroughly washed with hot water, after which it was dried in a water-oven until of constant weight. The mean of two nearly concordant determinations was an amount equivalent to 9.65 per cent. of resin in the root. The proportion of this crude resin which was soluble in ether, as determined by its complete extraction in a Soxhlet apparatus, was equivalent to 97 per cent. of its weight.

#### *Extraction of the Root with Alcohol.*

For the purpose of a complete examination of the constituents of the root, a quantity (50.35 kilograms) of the ground material was extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, 13.89 kilograms of a soft, dark-coloured extract were obtained.

*Isolation of Sucrose.*

Inasmuch as sucrose has previously been isolated from scammony root by Requier (*J. Pharm. Chim.*, 1905, [vi], **22**, 435, 492), it was deemed desirable to ascertain its presence in the root under examination. For this purpose a quantity (500 grams) of the above-mentioned alcoholic extract was mixed with water to separate the resin, the dark-coloured aqueous liquid filtered, and treated with an excess of milk of lime. The mixture was then filtered, the alkaline filtrate saturated with carbon dioxide, again filtered, and the clear liquid evaporated under diminished pressure to the consistency of a syrup. By treating the latter with successive portions of alcohol a product was finally obtained, which was completely soluble in alcohol of about 85 per cent. strength. The solution of this product, when decolorised by a little animal charcoal and inoculated with a trace of sucrose, gradually deposited a quantity (1.4 grams) of a crystalline substance. After recrystallisation from dilute alcohol, the substance was obtained in small, colourless prisms, melting at 184—185° (compare this vol., p. 4), and was identified as sucrose. (Found, C=41.9; H=6.5. Calc., C=42.1; H=6.4 per cent.)

*Distillation of the Extract with Steam: Separation of an Essential Oil.*

A quantity (2.3 kilograms) of the alcoholic extract was mixed with water, and distilled in a current of steam. The distillate, which contained some oily drops, was extracted with ether, the ethereal liquid being dried and the solvent removed, when a small amount (0.35 gram) of an essential oil was obtained. This had a reddish-yellow colour, a persistent odour, and gave the colour reaction for furfuraldehyde.

After the above-described operation, there remained in the distillation flask a dark-coloured aqueous liquid (A) and a quantity of a soft resin (B). The resin was repeatedly washed with hot water until the latter remained colourless, and the washings added to the main portion of aqueous liquid.

*Examination of the Aqueous Liquid (A).**Isolation of Scopoletin,  $(\text{CH}_3\cdot\text{O})(\text{OH})\text{C}_6\text{H}_2\cdot\overline{\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}}$ .*

The aqueous liquid was concentrated under diminished pressure, and extracted with ether, which, however, removed only a small quantity of resinous material and a trace of fluorescent substance.



It was then extracted many times with chloroform, and the chloroformic liquids shaken with aqueous sodium carbonate, which removed practically all of the dissolved substance. On acidifying the alkaline liquid, a quantity (0.25 gram) of a crystalline substance was precipitated. This was dissolved in chloroform, the solvent evaporated, and the residue recrystallised from absolute alcohol, when the substance separated in pale yellow needles melting at 203—204°. With alkalis it gave a brilliant blue fluorescence, and was identified as scopoletin. (Found, C=62.5; H=4.4. Calc., C=62.5; H=4.2 per cent.) Its identity was further confirmed by the preparation of the acetyl derivative melting at 176—177°.

*Isolation of 3:4-Dihydroxycinnamic Acid,*  
 $C_6H_3(OH)_2 \cdot CH:CH \cdot CO_2H.$

The original aqueous liquid, which had been extracted with ether and chloroform as above described, was next shaken with successive portions of amyl alcohol. The amyl-alcoholic liquids were then united, washed with a little water, and distilled under diminished pressure, when a quantity of a dark-coloured, syrupy product was obtained. This was heated for a few minutes with a 10 per cent. solution of potassium hydroxide, the alkaline liquid being then acidified and extracted with ether. The ethereal liquid was subsequently shaken with aqueous ammonium carbonate, and the alkaline liquid acidified, when a quantity (15 grams) of a crystalline substance was precipitated. When recrystallised from very dilute alcohol, it separated in pale yellow, prismatic needles, which melted and decomposed at 223—225°, and its aqueous solution gave a dark green colour with ferric chloride. An analysis of the substance proved it to be 3:4-dihydroxycinnamic acid\* (Found, C=59.7; H=4.6. Calc., C=60.0; H=4.4 per cent.), and its identity was further confirmed by the preparation of the dimethyl ether melting at 180—181°.

After extracting the aqueous liquid with the above-mentioned solvents, it was heated in a current of steam for the removal of the last traces of amyl alcohol, and to the warm liquid a slight excess of a solution of basic lead acetate was added, when a copious

\* It may be noted in this connexion that in our previous investigation of Jalap (*J. Amer. Chem. Soc.*, 1910, **32**, 80) it was not observed that 3:4-dihydroxycinnamic acid is a constituent of the drug. Through the kindness of Messrs. W. Ransom & Son, of Hitchin, who have supplied us with material for further examination, we have now been able to ascertain that the respective acid is also contained in Jalap tubers, although apparently in much smaller amount than in the roots of Scammony and *Ipomoea orizabensis*.

yellow precipitate was produced. This was collected, washed, then suspended in water, and decomposed by hydrogen sulphide. After filtering the mixture, concentrating the filtrate under diminished pressure, and treating the residue with a solution of potassium hydroxide, a further small amount of 3:4-dihydroxycinnamic acid was obtained.

The filtrate from the precipitate produced by basic lead acetate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to the consistency of a syrup. This readily reduced Fehling's solution, and yielded *d*-phenylglucosazone, melting at 205—206°. In order definitely to establish the presence of dextrose, a portion of the syrup was heated with acetic anhydride, when penta-acetyldextrose, melting at 130—131°, was obtained. Another portion of the syrup was heated with dilute sulphuric acid, and after this treatment a small amount of scopoletin was isolated, thus indicating the presence of a glucoside of the latter substance.

#### *Examination of the Resin (B).*

The crude resin which had been separated from the aqueous liquid (A), as previously described, formed a dark brown mass, which when dry could be reduced to a light brown powder, and when treated with a little animal charcoal was obtained nearly colourless. After drying in a vacuum over sulphuric acid, it melted at 125—130°.

*Optical Rotation of the Crude Resin.*—For this determination a portion of the resin which had been obtained by the previously described assay of the root was first employed, its solution being deprived of colour by heating with a little animal charcoal (compare this vol., p. 8). A solution in absolute alcohol, of which 5 c.c. contained 0.3062 gram of resin, gave  $\alpha_D -1^\circ 13'$  in a 1-dcm. tube, whence  $[\alpha]_D -19.87^\circ$ .

Another determination, with the use of a little of the above-described resin (B), gave the following result:

A solution in absolute alcohol, of which 5 c.c. contained 0.4660 gram of resin, gave  $\alpha_D -1^\circ 53'$  in a 1-dcm. tube, whence  $[\alpha]_D -20.20^\circ$ .

*Preliminary Extraction of the Crude Resin with Different Solvents.*—In order to ascertain the general characters of the crude resin, a small portion (10 grams) of it was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents. The amounts of extract, dried at 100°, were as follows:

Petroleum (b. p. 40—60°) extracted	4.5	per cent.
Ether	92.5	" "
Chloroform	0.4	" "
Alcohol	1.8	" "
Loss	0.8	" "
	100.0 per cent.	

For the purpose of a complete examination, the total amount of resin (866 grams) obtained by the above-described operation was employed. It was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a large Soxhlet apparatus with petroleum (b. p. 40—60°), ether, chloroform, ethyl acetate, and alcohol.

#### I. *Petroleum Extract of the Resin.*

This extract, after the removal of the solvent, was a dark brown, soft solid, amounting to 40 grams. It was dissolved in ether, and the ethereal solution extracted successively with aqueous ammonium carbonate and sodium carbonate, but only a trace of fatty material was removed by the latter solvent. The ether was then evaporated, and the residue heated for some time in a reflux apparatus with an alcoholic solution of potassium hydroxide, after which the mixture was diluted with water, and the alcohol removed in a current of steam. The alkaline liquid was then thoroughly extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when a quantity (4.5 grams) of a dark-coloured, crystalline product was obtained.

#### *Isolation of a Phytosterol, C<sub>27</sub>H<sub>46</sub>O.*

The above-mentioned crystalline product was recrystallised from a mixture of ethyl acetate and dilute alcohol, when it separated in pearly leaflets melting at 135—136°, which gave the colour reaction of the phytosterols:

0.7296, on heating at 110°, lost 0.0316 H<sub>2</sub>O. H<sub>2</sub>O = 4.3.

0.1114\* gave 0.3418 CO<sub>2</sub> and 0.1238 H<sub>2</sub>O. C = 83.7; H = 12.3.

C<sub>27</sub>H<sub>46</sub>O, H<sub>2</sub>O requires H<sub>2</sub>O = 4.5 per cent.

C<sub>27</sub>H<sub>46</sub>O requires C = 83.9; H = 11.9 per cent.

A determination of the specific rotatory power gave the following result:

0.5146,\* made up to 20 c.c. with chloroform, gave  $\alpha_D - 1^{\circ}33'$  in a 2-dcm. tube, whence  $[\alpha]_D - 30.1^{\circ}$

The above-described substance was thus shown to be a phytosterol, and its identity was further confirmed by the preparation of an acetyl derivative, which separated from ethyl acetate in flat needles melting at 122—123°.

\* Anhydrous substance.

The alkaline liquid, from which the phytosterol had been removed by extraction with ether, was acidified, and again extracted with ether. This ethereal liquid was first shaken with a solution of ammonium carbonate, which, however, removed nothing. It was then shaken with aqueous sodium carbonate, which removed a quantity of fatty acids, and on finally evaporating the ether only a trace of amorphous material remained.

#### *Identification of the Fatty Acids.*

The sodium carbonate liquid obtained as above described was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed. An oily product was thus obtained, which consisted of a mixture of acids. These were separated into liquid and solid portions by means of their lead salts.

*The Liquid Acids.*—When distilled under diminished pressure, these acids passed over between  $220^{\circ}$  and  $240^{\circ}/15$  mm. as a pale yellow oil, and amounted to 9 grams. An analysis and a determination of the iodine value gave the following results:

0.1684 gave 0.4746  $\text{CO}_2$  and 0.1750  $\text{H}_2\text{O}$ . C=76.9; H=11.5.

0.3322 absorbed 0.6355 iodine. Iodine value=191.3.

$\text{C}_{18}\text{H}_{34}\text{O}_2$  requires C=76.6; H=12.1 per cent. Iodine value=90.1.

$\text{C}_{18}\text{H}_{32}\text{O}_2$  „ C=77.1; H=11.4 „ „ Iodine value=181.4.

$\text{C}_{18}\text{H}_{30}\text{O}_2$  „ C=77.7; H=10.8 „ „ Iodine value=274.0.

The above results would thus indicate that the liquid acids consisted of a mixture of oleic, linolic, and linolenic acids.

*The Solid Acids.*—These acids, when recrystallised from ethyl acetate, melted at  $55$ — $57^{\circ}$ , and amounted to 5 grams:

0.1476 gave 0.4102  $\text{CO}_2$  and 0.1690  $\text{H}_2\text{O}$ . C=75.8; H=12.7.

0.1758 neutralised 0.0359 KOH. Neutralisation value=204.

$\text{C}_{16}\text{H}_{32}\text{O}_2$  requires C=75.0; H=12.5 per cent. Neutralisation value=219.1.

$\text{C}_{18}\text{H}_{36}\text{O}_2$  requires C=76.1; H=12.7 per cent. Neutralisation value=197.5.

It would thus appear that the solid acids consisted of a mixture of palmitic and stearic acids, the latter predominating.

#### *II. Ethereal Extract of the Resin.*

This extract, after the removal of the solvent, was a dark brown mass, which could easily be reduced to a light brown powder, and was stable in the air. It amounted to 800 grams. After treatment with a little animal charcoal it was obtained nearly colourless, and its optical rotatory power was then determined, with the following result: A solution in absolute alcohol, of which 5 c.c.

contained 0.3536 gram of the resin, gave  $\alpha_D -1^{\circ}21'$  in a 1-dcm. tube, whence  $[\alpha]_D -19.1^{\circ}$ .

*Hydrolysis of the Ethereal Extract with Barium Hydroxide.*

A quantity (500 grams) of the dry ethereal extract of the resin was dissolved in alcohol, and, after the addition of a little water, a cold saturated solution of barium hydroxide was gradually added until the liquid showed an alkaline reaction. It was then kept at a temperature of 35—45°, and the alkalinity maintained by the further occasional addition of small portions of solution of barium hydroxide. This treatment was continued until the liquid gave no turbidity when mixed with water, after which the alcohol was removed by distillation in a current of steam, and a dark brown precipitate which had formed was collected.

*Isolation of Ipuranol,  $C_{23}H_{38}O_2(OH)_2$ .*

The above-mentioned dark brown precipitate amounted to 30 grams, and consisted for the most part of a barium compound. It was treated with acetic acid, when a small portion remained undissolved, and this, after being dried, was crystallised from a mixture of pyridine and ethyl acetate. The substance then separated in colourless, microscopic needles, melting at 285—290°, and was identified as ipuranol. (Found, C=72.2; H=10.6. Calc., C=72.6; H=10.5 per cent.) When heated with acetic anhydride the substance yielded diacetylipuranol, which, after crystallisation from ethyl acetate, melted at 162°.

The liquid from which the above-mentioned dark brown precipitate had separated was treated with carbon dioxide for the removal of the excess of barium, and, after filtration, dilute sulphuric acid was added until a precipitate just ceased to be produced, any excess of the mineral acid being carefully avoided. The liquid was again filtered, and then distilled in a current of steam until volatile acids ceased to pass over.

*Isolation of d- $\alpha$ -Methylbutyric and Tiglic Acids.*

The above-mentioned distillate, which amounted to about 6 litres, was neutralised with sodium carbonate, and concentrated to a small volume, then acidified, and extracted with ether. The ethereal liquid was dried, and the solvent removed, when a quantity (50 grams) of a colourless liquid was obtained, which was distilled under the ordinary pressure. The main portion passed over between 160° and 200°, whilst the last fraction (1.5 grams), which

was unsaturated, became solid on cooling. In order to remove the small amount of unsaturated acid contained in the principal portion, the latter was treated with potassium permanganate in alkaline solution at  $0^{\circ}$ . On subsequently recovering the unchanged acid it was found to distil at  $172\text{--}175^{\circ}$ , and to possess the odour of a valeric acid. (Found, C=58.4; H=9.8. Calc., C=58.8; H=9.8 per cent.)

The density of the acid was 0.9356 at  $24^{\circ}$ , and a determination of its specific rotatory power gave, in a 50 mm. tube at  $24^{\circ}$ ,  $\alpha_D + 8^{\circ}33'$ , whence  $[\alpha]_D + 18.2^{\circ}$ .

It was evident from these results that the above-described liquid consisted of *d*- $\alpha$ -methylbutyric acid.

The solid contained in the last fraction of the volatile acids was recrystallised from water, when it separated in flat needles melting at  $64\text{--}65^{\circ}$ , and was identified as tiglic acid. (Found, C=59.9; H=8.3. Calc., C=60.0; H=8.0 per cent.)

The aqueous liquid, from which the above-described acids had been extracted with ether, was distilled in a current of steam, when the distillate was found to contain very small amounts of formic and valeric acids.

*Non-volatile Products of the Alkaline Hydrolysis.*—After the removal of the *d*- $\alpha$ -methylbutyric and tiglic acids by distillation with steam, as above described, there remained in the distillation flask a dark yellow liquid, which was concentrated under diminished pressure to the consistency of a viscid syrup. This product amounted to 335 grams. When further dried, it could be reduced to a light brown powder, which, however, became glutinous on exposure to the air. It was freely soluble in water, and did not reduce Fehling's solution until after boiling with a dilute mineral acid.

The entire amount of the above-mentioned syrupy product was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol.

#### *Ether and Chloroform Extracts of the Hydrolysed Resin (II).*

These extracts were dark-coloured, viscid masses, amounting to 62 and 25 grams respectively. They were only sparingly soluble in water, and after heating with a 5 per cent. solution of sulphuric acid in aqueous alcohol yielded but small quantities of methyl jalapinate (m. p.  $47\text{--}49^{\circ}$ ) and jalapinic acid (m. p.  $67\text{--}68^{\circ}$ ), together with traces of formic and valeric acids. The liquids obtained by this treatment reduced Fehling's solution, but no osazone could be prepared from them.

*Ethyl Acetate Extract of the Hydrolysed Resin (II).*

This extract was a viscid mass, and amounted to 18 grams. When thoroughly dried it could be reduced to a light brown powder, which soon became glutinous on exposure to the air, but was only sparingly soluble in water. When heated with a 5 per cent. solution of sulphuric acid in aqueous alcohol, a little methyl jalapinate was obtained, together with small amounts of jalapinic, formic, and valeric acids. After the removal of the sulphuric acid from the remaining aqueous liquid, it reduced Fehling's solution and yielded *d*-phenylglucosazone (m. p. 205—206°), together with a small amount of an osazone melting at 180—182°. The latter was identical with an osazone of the same melting point prepared from the below-mentioned alcohol extract of the hydrolysed resin after treatment with dilute sulphuric acid, and was evidently rhamnosazone.

*Alcohol Extract of the Hydrolysed Resin (II).*

This represented the chief portion of the hydrolysed ethereal extract of the resin, and amounted to 230 grams. It was a light-coloured, amorphous mass, which could easily be powdered, and was stable in the air. It was readily soluble in water and in alcohol, and did not reduce Fehling's solution until after heating with a mineral acid. The aqueous solution was optically active, and a determination of the specific rotatory power gave the following result:

An aqueous solution, of which 5 c.c. contained 0.4798 gram of the extract, dried at 110°, gave  $\alpha_D -5^{\circ}30'$  in a 2-dcm. tube, whence  $[\alpha]_D -28.6^{\circ}$ .

A quantity (150 grams) of the above-described product was dissolved in water, and such an amount of sulphuric acid added that the solution (1500 grams) contained 5 per cent. of its weight of acid. After heating the liquid for about three hours in a reflux apparatus, it was distilled in a current of steam until volatile products ceased to pass over. The distillate was then extracted with ether, the ethereal liquid being dried, and the solvent removed. A small quantity of liquid acid, distilling between 172° and 175°, was thus obtained, which was identified by means of its silver salt as a valeric acid. (Found, Ag=51.4. Calc., Ag=51.7 per cent.) The aqueous liquid from which the valeric acid had been removed was found to contain a small amount of formic acid.

After the removal of the volatile acids as above described, the distillation flask contained a dark yellow liquid with a cake of solid material floating on the surface. The whole was extracted

with ether, which dissolved the solid substance, and the ethereal liquid was then shaken with aqueous sodium carbonate. On finally evaporating the ether, a small amount of a neutral substance was obtained, which separated from ethyl acetate in leaflets melting at 47—49°, and was evidently methyl jalapinate.

*Isolation of Jalapinic Acid, C<sub>15</sub>H<sub>30</sub>(OH)·CO<sub>2</sub>H.*

*(Hydroxyhexadecylic Acid.)*

The sodium carbonate extract of the above-mentioned ethereal liquid, which was almost solid, was treated with dilute sulphuric acid, and the liberated organic acid dissolved in ether. On removing the solvent, a quantity (30 grams) of an oily product was obtained, which solidified to a crystalline mass. This was recrystallised from dilute acetic acid, when a substance separated in small needles melting at 67—68°, which was identified as jalapinic acid, C<sub>16</sub>H<sub>32</sub>O<sub>3</sub>.\* (Found, C=70·3; H=11·8. Calc., C=70·6; H=11·7 per cent.)

A portion of the acid was converted into its methyl ester, which, when recrystallised from ethyl acetate, separated in leaflets melting at 47—49°. (Found, C=71·0; H=11·9. Calc., C=71·3; H=11·9 per cent.)

The optical rotatory power of the ester was determined, with the following result:

3·7256, made up to 20 c.c. with chloroform, gave  $\alpha_D + 0^\circ 21'$  in a 2-dcm. tube, whence  $[\alpha]_D + 0\cdot94^\circ$ .

The yellow, aqueous liquid, which had been extracted with ether as above described, was treated with barium hydroxide for the removal of the sulphuric acid, and, after filtration, concentrated under diminished pressure. A portion of the resulting syrup was treated with phenylhydrazine acetate, and the product examined according to the method described by A. G. Perkin (Trans., 1910, 97, 1777), when two osazones were obtained. The chief portion of the product melted at 205—206°, and was evidently *d*-phenylglucosazone, whilst a small amount of a compound was separated which melted at 180—182°, and agreed in its characters with rhamnosazone. Another portion of the syrup was heated with acetic anhydride, when from the resulting product there was obtained a small quantity of penta-acetyldextrose, which separated from dilute alcohol in needles melting at 129—130°. No crystalline acetyl derivative of a methylpentose could be isolated, such as has

\* The so-called "scammonic acid" of previous investigators, to which the formula C<sub>16</sub>H<sub>30</sub>O<sub>3</sub> was assigned, is identical with jalapinic acid.



been described by the authors in connexion with products obtained from the ethereal extract of the resin of *Ipomoea orizabensis* (this vol., p. 17), thus affording evidence that the latter differs appreciably in character from the corresponding resin of scammony root.

As the hydrolysed ethereal extract of the original resin evidently consisted in part of derivatives of both methyl jalapinate and jalapinic acid, it was deemed of interest to ascertain the relative proportions in which they were present. For this purpose a small quantity (5 grams) of the above-described alcoholic extract of the hydrolysed resin was acetylated by means of acetic anhydride in the presence of a trace of pyridine, the product dissolved in ether, and the ethereal liquid shaken with aqueous potassium hydroxide. By this means 2.5 grams of acidic material were removed, and on subsequently evaporating the ether 4.7 grams of a neutral product were obtained. Both these products on heating with dilute sulphuric acid yielded jalapinic acid and a mixture of sugars, the neutral acetyl derivative also yielding a small amount (0.1 gram) of methyl jalapinate.

### III., IV., and V. *Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.*

These extracts were dark-coloured, amorphous products, amounting to 2.6, 2.8, and 3.4 grams respectively. They were examined, but nothing definite could be isolated from them.

### II.—*Examination of Scammony.*

For the purpose of comparing the previously described resin from scammony root with that obtained from the gum-resin known as scammony, a quantity of the latter was procured directly from Smyrna. The material possessed the general characters ascribed to an authentic product, although on incineration it yielded 3.52 per cent. of ash, which is slightly in excess of the pharmacopœial limits (compare, however, Guiques, *Bull. sci. pharmacol.*, 1909, 16, 448, and Goris and Fluteaux, *ibid.*, 1910, 17, 15). No starch or sugar was present.

A determination of the total resin was made by extracting 50 grams of the powdered material with alcohol in a Soxhlet apparatus, and mixing the concentrated alcoholic liquid with water, the precipitated resin being then thoroughly washed, and dried in a water-oven until of constant weight. The amount of resin obtained was 41.55 grams, being thus equivalent to 83.1 per cent. of the weight of scammony employed. It was completely soluble in ether. Neither the portion of the scammony which was insoluble

in alcohol, nor the aqueous liquid obtained by the precipitation of the resin appeared to contain any substance of interest.

The optical rotatory power of the resin was determined with a small portion which had been decolorised by treatment with animal charcoal.

A solution in absolute alcohol, of which 5 c.c. contained 0.5042 gram of the resin, gave  $\alpha_D -2^{\circ}8'$  in a 1-dcm. tube, whence  $[\alpha]_D -21.15^{\circ}$ .

Thirty grams of the resin were dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum (b. p. 40—60°) and ether. The petroleum removed only 0.1 gram of soft, amorphous material, whereas the remainder of the resin, which was extracted by the ether, could easily be reduced to a powder, and after treatment with animal charcoal was obtained nearly colourless.

A solution in absolute alcohol, of which 5 c.c. contained 0.4384 gram of the purified ethereal extract of the resin, gave  $\alpha_D -1^{\circ}56'$  in a 1-dcm. tube, whence  $[\alpha]_D -22.03^{\circ}$ .

For the further examination of the ethereal extract of the resin a small quantity (25 grams) was hydrolysed with a solution of barium hydroxide in the manner described in connexion with the corresponding extract of the resin from scammony root. The volatile acids (3.2 grams) obtained by this treatment consisted of a mixture of tiglic acid (m. p. 64°) and a valeric acid (b. p. 172—175°), the former being present in predominating amount.

After the removal of the above-mentioned volatile acids by distillation in a current of steam, there remained a dark yellow, strongly acid liquid, which was concentrated under diminished pressure to the consistency of a syrup. The latter was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with ether, chloroform, ethyl acetate, and alcohol. The first three solvents removed 1.9, 0.85, and 0.3 gram respectively of amorphous, syrupy products, which were glucosidic in character, but the amounts did not permit of their further examination. The alcohol, on the other hand, removed 10.2 grams of an amorphous product, which, when dried, could be reduced to a powder, and was stable in the air. It was optically active.

An aqueous solution, of which 5 c.c. contained 0.2624 gram of the above product, gave  $\alpha_D -3^{\circ}6'$  in a 2-dcm. tube, whence  $[\alpha]_D -29.5^{\circ}$ .

In order to ascertain the nature of the above-mentioned alcohol extract of the hydrolysed resin, a quantity (8 grams) was acetylated

by means of acetic anhydride. The resulting product was poured into water, the precipitated compound dissolved in ether, and the ethereal liquid extracted with a solution of potassium hydroxide. On subsequently drying the ethereal liquid and evaporating the solvent, there remained about 7 grams of a light-coloured, amorphous mass. The alkaline liquid, when acidified and extracted with ether, yielded 2 grams of an amorphous, acidic product, thus showing that the hydrolysed resin was, for the most part, neutral in character. The above-mentioned neutral portion (7 grams) of the acetylated product, when heated with dilute sulphuric acid, gave small amounts of jalapinic acid (m. p. 67—68°) and methyl jalapinate (m. p. 47°), together with a sugar from which a little *d*-phenylglucosazone (m. p. 205—206°) was prepared.

### Conclusions.

From the results of the preceding investigation it will be seen that the resins obtained from scammony root and from the gum-resin known as scammony, although similar in their general characters, are not perfectly identical. On the other hand, a comparison of the resin from scammony root with that obtained from the root of *Ipomoea orizabensis* (this vol., p. 1) shows that these two products differ very considerably in their composition. Both of these resins are exceedingly complex in character, but consist to a large extent of the glucosides and methylpentosides of jalapinic acid,  $C_{15}H_{30}(OH)CO_2H$ , and its methyl ester. Whilst, however, the methylpentose obtained by the hydrolysis of the resin from scammony root appears to be identical with rhamnose, that from the resin of *Ipomoea orizabensis* (*loc. cit.*, p. 17) yields a crystalline tetra-acetyl derivative, which had not heretofore been described. The resin from the last-mentioned source contained, among other substances, small amounts of hentriacontane,  $C_{31}H_{64}$ , and cetyl alcohol,  $C_{16}H_{34}O$ , which were not present in the resin from scammony root, and, furthermore, very marked differences were observed in extracting both the crude resins and the products of their alkaline hydrolysis with various solvents. It is not to be expected, however, that products of this nature would be uniform in composition, and the differences which have now been observed to exist between them may not be constant, or such as appreciably to influence their therapeutic value.

In view of the complexity of the above-mentioned resins, it is evident that they cannot be represented by chemical formulæ, a fact which we had previously indicated in connexion with the investigation of jalap resin (*J. Amer. Chem. Soc.*, 1910, **32**, 112).

The names by which the resins now under consideration have heretofore been designated, such as "jalapin" or "scammonin," with the assumption that they were individual substances, should, therefore, also be discarded.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,  
LONDON, E.C.

The first part of the book is devoted to a general introduction to the subject of the history of the world, and to a description of the various methods which have been employed by historians in the collection and arrangement of their materials.

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