barium $BaCO_3.1.5H_2CO_3$. The work should also have been attributed to Keiser and Leavitt, and Keiser and McMaster. JAS. LEWIS HOWE.

[CONTRIBUTION FROM THE WELLCOME CHEMICAL RESEARCH LABORATORIES, LONDON.]

CHEMICAL EXAMINATION OF JALAP.[1]

BY FREDERICK B. POWER AND HAROLD ROGERSON.

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Under the title of *Jalapa* (Jalap) the various national Pharmacopoeias recognize the dried tuberous root of *Exogonium purga*, Bentham (*Ipomoea purga*, Hayne). The only constituent of the tuber possessing chemical interest is the resin, which is largely used medicinally. This resin (*Resina Jalapae* of the Pharmacopoeias), like many similar products obtained from plants belonging to the family of Convolvulaceae, is of a glucosidic nature. It has been the subject of numerous chemical investigations during the past century, and the literature relating thereto is therefore considerable in extent. A review of the more important of these publications has been given by Hoehnel[2] in connection with an investigation entitled "Ueber das Convolvulin, das Glycosid der Tubera Jalapae (*Ipomoea purga*, Hayne)." A quite complete account of this subject and of other closely related so-called glucoside resins, together with citations of the literature, have also been recorded by van Rijn ("Die Glykoside," Berlin, 1900), and by Tschirch ("Die Harze," Bd. II, Leipzig, 1906).

It would not be expedient in this place to consider in detail the various statements of earlier investigators respecting the composition of jalap resin or the products obtained therefrom, especially as many of these statements are not only conflicting, but are evidently based upon incorrect observations and deductions. In order, however, to indicate the unsatisfactory state of present knowledge respecting the chemical characters of this resin, a brief exposition of the subject may be given.

The chief portion of jalap resin, which is insoluble in ether and commonly designated as "convolvulin,"[3] although a completely amorphous product, has at various times been assigned the following empirical formulas: $C_{31}H_{50}O_{16}$ (Mayer); $C_{21}H_{35}O_{10}$ (Kayser); $C_{24}H_{40}O_{12}$ (Laurent);

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[1] Communicated, in abstract, to the International Congress of Applied Chemistry, London, June 1, 1909. Presented at the meeting of the New York Section of the American Chemical Society, October 30, 1909.

[2] *Arch. Pharm.*, **234**, 647 (1896).

[3] In English pharmacy the portion of jalap resin which is insoluble in ether is still frequently designated by the original and more appropriate name of "jalapin." The latter term, however, is now more commonly employed to denote the resin of scammony and of Mexican Male jalap (*Ipomoea orizabensis*, Ledanois), both of which are completely soluble in ether.

$C_{32}H_{62}O_{16}$ (Taverne); $C_{61}H_{108}O_{27}$ (Kromer); $C_{54}H_{96}O_{27}$ (Hoehnel). It has been stated by the last-mentioned investigator,[1] whose results alone need be somewhat further considered, that "convolvulin," when treated with bases, yields the following products: methylethylacetic acid; "purgic acid;" and "convolvulic acid." Purgic acid, which has been regarded as dibasic, and possessing the formula $C_{25}H_{46}O_{12}$, has been described as forming a yellowish, extremely hygroscopic, varnish-like mass, readily soluble in ether. Convolvulic acid, which is insoluble in ether, and was regarded as monobasic, was obtained as a white, amorphous powder, to which the formula $C_{45}H_{80}O_{28}$ was assigned. Both of these products were found to be glucosidic; the purgic acid, when heated with dilute mineral acids, having yielded a sugar, a product regarded as decylenic acid, $C_{10}H_{18}O_2$, and hydroxylauric acid, $C_{12}H_{24}O_3$, while convolvulic acid, by the same treatment, yielded a sugar and convolvulinolic acid, $C_{15}H_{30}O_3$. In the latter instance it was assumed that the hydrolysis might be represented by the following equation:

$$C_{45}H_{80}O_{28} + 5H_2O = 5C_6H_{12}O_6 + C_{15}H_{30}O_3.$$

A consideration of the results obtained in the present investigation will doubtless render it evident that many of the conclusions which have previously been recorded respecting the composition of jalap resin and various amorphous products obtained therefrom are erroneous. In the first place, it would be quite fallacious to assign to the so-called "convolvulin" any empirical formula whatsoever, inasmuch as we have shown that by successive extraction with various solvents, such as chloroform, ethyl acetate, and alcohol, it may be further resolved into several products, all of which, moreover, are amorphous and of indefinite composition. Similar conditions exist with regard to the character of the amorphous products obtained by the alkaline hydrolysis of the resin, such as the so-called "purgic" and "convolvulic" acids, to which empirical formulas have likewise been assigned. Both of the last-mentioned products are complex mixtures, some of the constituents of which are not even glucosidic. We have shown, for example, that the alcohol extract of the resin, when hydrolyzed by baryta, yields a product which, like the original resin, is capable of being further resolved when successively extracted with ether, chloroform, ethyl acetate, and alcohol. The last-mentioned alcohol extract, when heated with dilute sulphuric acid, affords, moreover, not only sugar and convolvulinolic acid, $C_{15}H_{30}O_3$, as indicated by Hoehnel in the case of a less completely purified product, but also ipurolic acid, $C_{14}H_{28}O_4$, and several volatile acids, while a portion of it apparently remains unchanged. It is thus obvious that the "convolvulic acid" of Hoehnel can not be regarded as an individual

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[1] *Loc. cit.*

substance, nor can its degradation be represented in the manner suggested by him.

Notwithstanding the numerous investigations of jalap resin, it will be apparent from the observations above noted that the statements concerning its composition and character are not only widely divergent, but that in many respects they are based upon quite erroneous assumptions. It has therefore been deemed desirable to subject this resin to a more complete examination, and the results of the present research are summarized at the end of this paper.

Experimental.

The material employed in this investigation consisted of an original bale of Jalap tubers of good quality, as indicated by the percentage yield of resin when assayed by the methods described below.

As a preliminary experiment, 50 grams of the finely ground material, representing an average sample of 75 kilograms of the drug, were successively extracted in a Soxhlet apparatus with various solvents, whereby the following amounts of extract, dried at 100°, were obtained.

		Gram.		Per cent.
Petroleum (b. p. 40–60°)	extracted	0.19	=	0.38
Ether	"	0.34	=	0.68
Chloroform	"	0.27	=	0.54
Alcohol	"	5.90	=	11.80
Water	"	11.15	=	22.30
	Total,	17.85	=	35.70

Determination of Total Resin.—I. The first method employed in this determination was essentially that of the British Pharmacopoeia. Fifty grams of the finely ground material were thoroughly extracted in a Soxhlet apparatus with hot alcohol (94 per cent.). To the liquid thus obtained 25 cc. of water were added, and the alcohol removed by distillation, after which the residue was brought into a dish and heated on a water bath in order to remove the last traces of alcohol. The separated resin was then thoroughly washed with hot distilled water, and finally dried in a water oven until of constant weight. Two concurrent determinations yielded 4.7 grams of resin, corresponding to 9.4 per cent. of total resin in the drug. The proportion of this crude resin which was soluble in ether, as determined by its complete extraction in a Soxhlet apparatus, corresponded to 11.6 per cent. of its weight.

II. The second method employed for the determination of the resin was that of the United States Pharmacopoeia (eighth revision), which, however, as in the preceding method, was modified by conducting the extraction of the drug in a Soxhlet apparatus. The amounts of resin, representing the ether extract and the portion insoluble in ether, were

1.0 and 9.5 per cent. respectively, the total resin being thus 10.5 per cent. of the weight of the drug.

It will be observed that the results obtained by the two above-mentioned methods of assay differ appreciably, as might be expected, but the relative merits of these methods need not be here discussed.

Extraction of the Jalap with Hot Alcohol and Distillation of the Extract with Steam.—For the purpose of a complete examination of the drug, 75 kilograms of the ground material were completely extracted with hot alcohol. After the removal of the greater portion of the alcohol, 23.8 kilograms of a soft extract were obtained. A quantity of this extract was brought into a large flask, some water added, and the mixture distilled with steam until volatile products ceased to pass over. A distillate was thus obtained, which contained some oily drops floating on the surface. After this operation there remained in the distilling vessel a dark colored, aqueous liquid (*A*) and a quantity of soft resin (*B*). The resin was repeatedly washed with warm water until the latter remained colorless, and the washings added to the aqueous liquid.

Examination of the Steam Distillate. Separation of an Essential Oil.

The distillate obtained as above described was extracted with ether, the ethereal liquid being dried with anhydrous sodium sulphate and the solvent removed. A very small amount (2.4 grams) of an essential oil was thus obtained, which, when distilled under diminished pressure, passed over between 80 and 160°/60 mm. This oil, when freshly distilled, had a pale yellow color, but became very dark on standing. It possessed a disagreeable and persistent smoky odor. A dilute alcoholic solution of the oil gave with ferric chloride a deep brownish red color. Its density was 0.8868 at 20°/20°, and it was optically inactive.

Examination of the Aqueous Liquids (A).

The aqueous liquid remaining in the distillation flask, after the above-described treatment with steam, was separated from the resin, and, together with the washings from the latter, evaporated to a small volume. As the dark colored sirup thus obtained deposited nothing on standing, it was diluted with water, and a solution of basic lead acetate added until no further precipitate was produced.

Basic Lead Acetate Precipitate.—This was collected, thoroughly washed with water, and then suspended in water and decomposed by hydrogen sulphide. After filtration, the liquid was concentrated, and shaken with several successive portions of ether. The combined ethereal liquids were repeatedly extracted with a solution of sodium carbonate, and subsequently with a 10 per cent. solution of sodium hydroxide. The first sodium carbonate extracts were dark in color and showed a blue fluorescence. They were acidified and extracted with ether, but the ethereal liquid, on evaporation, yielded only a small amount of an uncrystallizable sirup, which, however, developed with ammonia a blue fluorescence, and gave with ferric chloride a dark green coloration. This fluorescence was evidently due to the presence of a little β-methylaesculetin, a substance which was subsequently isolated in small amount from the chloroform extract of the resin. The extract obtained by means of sodium hydroxide had a dark red color. It was acidified and extracted with ether, but yielded nothing definite.

Filtrate from the Basic Lead Acetate Precipitate.—This was treated with hydrogen sulphide for the removal of the lead, the mixture filtered, and the filtrate concentrated under diminished pressure. It was then repeatedly shaken with ether, and the combined ethereal liquids extracted with several successive portions of aqueous sodium carbonate. The first sodium carbonate extracts had a red color and showed a blue fluorescence. When acidified, and again extracted with ether, a small amount of a sirup was obtained, which deposited a trace of a crystalline substance, but not sufficient to permit of its identification. The sirupy product developed with ammonia a blue fluorescence, and gave with ferric chloride a violet coloration. The ethereal liquid, after extraction with sodium carbonate, was shaken with a 10 per cent. solution of sodium hydroxide, when a dark red, aqueous liquid was obtained. This, however, when acidified and again extracted with ether, yielded nothing definite. The ethereal liquid, which had been completely extracted with the above-mentioned alkalis, was finally dried with calcium chloride and the solvent removed, but only a small amount of a dark red sirup was obtained.

The aqueous liquid which had been extracted with ether, as above described, contained a quantity of sugar, since it readily reduced Fehling's solution and yielded *d*-phenylglucosazone, which, after recrystallization from dilute pyridine, melted at 217–218°. For the further examination of the aqueous liquid it was concentrated to the consistency of a sirup, which, after dilution with alcohol, was mixed with purified sawdust, and the thoroughly dried mixture then successively extracted in a Soxhlet apparatus with chloroform, ethyl acetate, and alcohol. The first two solvents removed but a relatively small amount of material, the larger proportion being subsequently extracted by the alcohol. These extracts were all of a sirupy nature, and, although exhaustively examined, nothing crystalline could be separated from them. They were observed to contain, besides sugar, traces of the fluorescent principle previously referred to, which was evidently β-methylaesculetin.

Examination of the Resin (B).

This product, which had been obtained from the alcoholic extract of the drug as previously described, corresponds to the *Resin of Jalap* of the various national Pharmacopoeias.

Optical Rotation of the Crude Resin.

It has been indicated by P. Guigues[1] that the specific optical rotatory power of certain convolvulaceous resins is a factor which may be utilized for discriminating between them, and for the detection of substitutes and adulterants. This factor was therefore determined for the resin employed in the present investigation with the following result. A quantity of the crude resin was dissolved in 50 cc. of alcohol, and the solution boiled with successive, small portions of animal charcoal until it became practically colorless. The rotation of this liquid in a 1 dcm. tube was α_D —2° 0′, and the amount of substance contained in 10 cc. of the liquid, after drying at 105–110°, was 0.5400, hence $[\alpha]_D$ —37.0°. This result is in fairly close agreement with the figures recorded by Guigues and by Cowie[2] for a decolorized jalap resin, which are $[\alpha]_D$ —36.0 and —37.3° respectively.

Preliminary Extraction of the Crude Resin with Different Solvents.

In order to ascertain the general character of the crude resin, a weighed amount (about 5 grams) was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with various solvents. The percentages of extract, dried at 110°, were as follows:

I. Petroleum (b. p. 40–60°)	extracted	1.9
II. Ether	"	9.7
III. Chloroform	"	24.1
IV. Ethyl acetate	"	22.0
V. Alcohol	"	38.8
	Loss,	3.5
		100.0

For the purpose of a complete examination of the constituents of the resin, a large quantity of the crude material was employed. This was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted first with ethyl acetate, and subsequently with alcohol. The alcohol extract was then again extracted with ethyl acetate in a similar manner, after which the undissolved material was removed by means of alcohol, this portion being designated as the "alcohol extract of the resin." The entire amount of material removed by ethyl acetate was then mixed with a large quantity of purified sawdust, and the mixture thoroughly dried, after which it was submitted to prolonged successive extractions with petroleum (b. p. 40–60°), ether, chloroform,

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[1] *J. pharm. chim.* [6], **22,** 241, and *Chem. Zentr.*, **1907,** I, p. 309; *Bull. soc. chim.* [4], **3,** 872 (1908). Compare also Power and Rogerson, *Am. J. Pharm.*, **80,** 251 (1908), and Cowie, *Pharm. J.*, **82,** 89 (1909).

[2] *Loc. cit.*

and ethyl acetate. The extracts obtained by these various solvents, together with the above-mentioned alcohol extract, were then separately investigated.

I. *Petroleum Extract of the Resin.*

This extract, after the removal of the solvent, was a very dark colored soft solid. The amount employed for the investigation of its acidic constituents was about 60 grams, but for the examination of the non-saponifiable constituents an additional 60 grams was used.

The extract was dissolved in a large volume of ether, and the ethereal liquid extracted with two successive portions of aqueous sodium carbonate. These alkaline liquids, which possessed a deep red color, were separately acidified, again extracted with ether, and the solvent removed. The product from the first extraction (*a*) amounted to about 12 grams, and that from the second extraction (*b*) to 3 grams. When distilled under diminished pressure, they both passed over for the most part between 220 and 240°/25 mm., and solidified on cooling to a white, crystalline mass. They were then recrystallized from ethyl acetate, and finally from glacial acetic acid, when the product (*a*) melted at 58–60° and the product (*b*) at 60–62°. These products consisted of saturated acids, and they were analyzed with the following results:

(*a*) 0.1804 gave 0.4974 CO_2 and 0.2008 H_2O. C = 75.2; H = 12.4
(*b*) 0.1454 gave 0.4024 CO_2 and 0.1620 H_2O. C = 75.5; H = 12.4
$C_{16}H_{32}O_2$ requires C = 75.0; H = 12.5 per cent.
$C_{18}H_{36}O_2$ requires C = 76.1; H = 12.7 per cent.

It would thus appear that the above-mentioned products consisted chiefly of a mixture of palmitic and stearic acids, the former predominating.

The ethereal liquid which had been extracted with sodium carbonate, as above described, was subsequently shaken with a 10 per cent. solution of sodium hydroxide. This alkaline liquid had a deep red color. It was acidified and extracted with ether, when, after removing the solvent, a small amount of a sirupy product was obtained. The latter deposited a little of a substance in the form of rosettes of needles, which melted at 205–206°, but the amount was too small for further examination.

The ethereal liquid, after extraction with sodium carbonate and hydroxide, was washed with water, dried, and the solvent removed. The residual product, which amounted to 35 grams, was hydrolyzed by heating in a reflux apparatus for several hours with an alcoholic solution of potassium hydroxide. The alcohol was then removed, water added, and the mixture shaken with ether. As an inseparable emulsion was thus formed, the mixture was made slightly acid, then completely extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. This alkaline liquid was acidified, and distilled with steam, when a distillate was obtained which contained a few oily drops floating on the surface. The distillate was extracted with ether, the ethereal liquid being dried and the solvent removed, when a small amount of an oily acid was obtained. This was converted into a silver salt, and the latter analyzed.

0.1280 of salt gave on ignition 0.0560 Ag. Ag = 43.7.
$C_8H_{15}O_2Ag$ requires Ag = 43.0 per cent.

Although the figures thus obtained are in fairly close agreement with those required for the silver salt of an octoic acid, it is possible that the oily acid was a mixture.

The distillate, after extraction with ether, was found to contain small amounts of formic and butyric acids.

After the removal of the volatile acids by distillation, as above described, the contents of the distillation flask were extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A small amount (about 2 grams) of an oily product was thus obtained, which became partially solid. By converting this product into a lead salt, and treating the latter with ether, an approximate separation of the acids was effected. The portion of lead salt which was soluble in ether yielded, after treatment with sulphuric acid, 0.6 gram of a dark orange-colored oil. This was unsaturated, and a determination of its iodine value gave the following result:

0.5328 absorbed 0.7601 iodine. Iodine value = 142.6.
$C_{18}H_{34}O_2$, with one ethylenic linking, requires I = 90.0 per cent.
$C_{18}H_{32}O_2$, with two ethylenic linkings, requires I = 181.4 per cent.

The oily acid therefore appears to have consisted largely of linolic acid.

The portion of lead salt which was insoluble in ether yielded 1.2 grams of solid acid, which distilled at 220–230°/15 mm., and, after recrystallization from glacial acetic acid and ethyl acetate, melted at 62°. This evidently consisted of palmitic acid.

Unsaponifiable Constituents of the Petroleum Extract.

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

As noted above, the portion of the petroleum extract which was insoluble in a solution of sodium carbonate and sodium hydroxide was hydrolyzed, the product acidified, extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. After this treatment the ethereal liquid was washed, dried, and the solvent removed, when an oily product was obtained which solidified on cooling. This was dissolved in alcohol, and the solution concentrated, when, after standing for some time, a quantity of a substance was deposited in the form of large, colorless plates. After recrystallization from a mixture of ethyl acetate and dilute alcohol, it separated in flattened needles, which melted at 134–135°.

0.1148 of the air-dried substance, when heated at 110°, lost 0.0054 H_2O.
$H_2O = 4.7$.
0.1094 of anhydrous substance gave 0.3360 CO_2 and 0.1180 H_2O.
$C = 83.8$; $H = 12.0$.
$C_{27}H_{46}O, H_2O$ requires $H_2O = 4.5$ per cent.
$C_{27}H_{46}O$ requires $C = 83.9$; $H = 11.9$ per cent.

The substance thus agrees in composition with a phytosterol, and it gave the color reactions yielded by this class of substances.

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

0.1349 of anhydrous substance, dissolved in 25 cc. of chloroform, gave in a 2 dcm. tube a_D —0°21′, whence $[\alpha]_D$ —32.4°.

A small amount of the phytosterol was converted into its acetate, which separated from its solution in acetic anhydride in leaflets, melting at 119–120°.

The mother liquor from the phytosterol was evaporated, and the residue distilled under 15 mm. pressure, when the following fractions were eventually obtained: (I) Below 180°; (II) 180–190°; (III) 190–200°; (IV) 200–225°; (V) 225–250°; (VI) 250–300°; (VII) 300–320°/15 mm. The first four of these fractions contained a crystalline solid. This was collected and recrystallized several times, first from light petroleum and then from ethyl acetate. It was thus obtained in small leaflets, melting at 50–51°, and was analyzed.

0.1114 gave 0.3230 CO_2 and 0.1434 H_2O. $C = 79.1$; $H = 14.3$.
$C_{16}H_{34}O$ requires $C = 79.3$; $H = 14.1$ per cent.

This substance was thus identified as cetyl alcohol.

The above-mentioned fractions (V) and (VI) were of an oily nature, and yielded nothing definite, whereas fraction (VII), on standing for a long time, deposited a small amount of a crystalline substance. This was separated, and recrystallized from ethyl acetate, when it formed glistening leaflets, melting at 56–57°. It yielded color reactions similar to those given by the phytosterols. After further crystallization from ethyl acetate, and finally from absolute alcohol, its melting point and properties remained unchanged. The substance was then analyzed.

0.0986 gave 0.2906 CO_2 and 0.1230 H_2O. $C = 80.4$; $H = 13.9$.
$C_{18}H_{36}O$ requires $C = 80.6$; $H = 13.4$ per cent.

The composition of this substance is thus seen to agree with the formula $C_{18}H_{36}O$, and, as it differs in its properties from any substance of this formula which has hitherto been described, it would appear to be a new compound. The amount of substance, however, was too small to admit of this conclusion being confirmed.

The liquid portion of fraction (VII), from which the above-described solid had been separated, was stirred with slightly diluted alcohol, when it deposited a further quantity of phytosterol, identical with that previously obtained.

II. *Ether Extract of the Resin.*

This extract, after the removal of the solvent, was a very dark colored, soft solid. The amount employed for its investigation was about 200 grams.

Isolation of a New, Dihydric Alcohol, Ipurganol, $C_{21}H_{32}O_2(OH)_2$.

During the process of extracting the resin with ether it was observed that a small amount of a solid substance was deposited from the ethereal liquid. This was collected, and purified by extracting it in a small Soxhlet apparatus with absolute alcohol, when it was obtained perfectly white. It was subsequently crystallized from dilute pyridine, when it separated in clusters of very small needles, melting at 222–225°. The amount of this substance obtained from 200 grams of the ether extract was about 4.5 grams. On analysis it gave the following result:

0.1047 gave 0.2752 CO_2 and 0.0946 H_2O. C = 71.7; H = 10.0.
$C_{21}H_{34}O_4$ requires C = 72.0; H = 9.7 per cent.

This substance would thus appear to possess the formula $C_{21}H_{34}O_4$, and, so far as known to us, no substance of this formula has hitherto been described. It is therefore to be regarded as a new compound, and, with reference to the source from which it has been obtained and its alcoholic nature, it is proposed to designate it *ipurganol.*

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

0.1760 of substance, dissolved in 25 cc. of pyridine, gave in a 2 dcm. tube. α_D—0.6333°, whence $[\alpha]_D$ —44.9°.

A portion of ipurganol was heated with acetic anhydride for about 2 hours, when, on cooling, a crystalline product was obtained. This was recrystallized from ethyl acetate, from which it separated in fine, colorless needles, melting at 166–167°.

0.0898 gave 0.2268 CO_2 and 0.0714 H_2O. C = 68.9; H = 8.8.

$C_{21}H_{32}O_4(CH_3.CO)_2$ requires C = 69.1; H = 8.7 per cent.

This substance is thus seen to be *diacetylipurganol*, and affords evidence of the presence in ipurganol of two hydroxyl groups.

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

0.3132 of substance, dissolved in 25 cc. of pyridine, gave in a 2 dcm. tube α_D —0.902°, whence $[\alpha]_D$ —36.0°.

An attempt to prepare a methyl derivative of ipurganol was not successful.

Ipurganol yields color reactions which are similar to those given by the phytosterols. Thus, if the substance be dissolved in chloroform with a little acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, a purplish pink coloration is first produced, which changes to blue, then to bright green, and finally becomes brown.

If concentrated sulphuric acid be added to ipurganol, the latter is colored deep reddish brown, while the acid soon acquires a yellow color with a green fluorescence.

In connection with the above description of ipurganol, it may be noted that it appears to be closely related to two substances of alcoholic nature which have quite recently been isolated in these laboratories. One of these was obtained from the resin of *Grindelia camporum*, Greene,[1] and agrees in composition with the formula $C_{23}H_{38}O_4$. It melts at 256–257°, and yields an acetyl derivative melting at 161°. This compound, which was not previously named, may now conveniently be designated as *grindelol*. The other substance was obtained from the resin of watermelon seeds, and has been designated *cucurbitol*. It possesses the formula $C_{24}H_{40}O_4$, melts at 260°, and yields an acetyl derivative melting at 150°. The three substances show slight differences in their color reactions when subjected to the above-mentioned test in chloroform solution with acetic anhydride and concentrated sulphuric acid. Thus grindelol and cucurbitol give at first a blue color, changing to dull green, and finally becoming brown, the intermediate greenish tint being less pronounced in the case of the last-mentioned substance. In view of the composition and character of these three new compounds, it is evident that they are members of a homologous series, which is represented by the general formula $C_nH_{2n-8}O_4$.

Treatment of the Ether Extract with Alkalis.

I. *Extraction with Ammonium and Sodium Carbonates.*—The ethereal solution of the ether extract, from which the ipurganol had been removed, as above described, was successively extracted with solutions of ammonium carbonate and sodium carbonate. This treatment, however, removed only small amounts of black resin. The ethereal liquid was then shaken with several successive portions of water, which removed a quantity of the sodium compound of a resin. These aqueous liquids were united and acidified, when the resin was precipitated, after which it was extracted with ether, the ethereal liquid being dried and the solvent removed. The large quantity (70 grams) of resinous material thus obtained was dissolved in alcohol, treated with animal charcoal, and the filtered liquid concentrated and allowed to stand for some time. As nothing could be separated by this means, the small amount of resin which had previously been extracted by sodium carbonate and treated in the same manner as the last-mentioned product was added to the alcoholic solution of the latter, together with such an amount of sulphuric

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[1] *Proc. Am. Pharm. Assoc.*, **55**, 342 (1907).

acid as to represent about 5 per cent. of the mixture. The whole was then heated in a reflux apparatus for about 6 hours, after which water was added and the alcohol removed. The aqueous, acid liquid, from which a quantity of a soft resin had separated, was subsequently distilled with steam until volatile products ceased to pass over. The distillate, which contained some yellow, oily drops, was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. This alkaline, aqueous liquid was acidified, extracted with ether, and the solvent removed, when a small amount (0.4 gram) of an oily acid was obtained. The latter was converted into an ammonium salt, from which by precipitation with silver nitrate two fractions of a silver salt were prepared, and these were analyzed.

I. 0.2138 of salt gave on ignition 0.0734 Ag. Ag = 34.3
II. 0.1060 of salt gave on ignition 0.0410 Ag. Ag = 38.7
$C_{12}H_{23}O_2Ag$ requires Ag = 35.2 per cent.; $C_{10}H_{19}O_2$ Ag requires Ag = 38.7 per cent.

The ethereal liquid which had been shaken with sodium carbonate was dried, and the solvent removed, when a small quantity (1.5 grams) of a neutral, oily liquid was obtained. This was distilled under diminished pressure, when it passed over between 90 and 160°/15 mm. It gave no coloration with ferric chloride, but responded to the test for furfural.

The above-mentioned distillate, after extraction with ether, was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products of hydrolysis by distillation with steam, as above described, there remained in the distillation flask a reddish-colored, aqueous liquid, and a soft, resinous mass which floated on the surface. The whole was shaken with ether, when the resinous material became completely dissolved. On subsequently extracting the ethereal liquid with sodium carbonate, about 3 grams of amorphous, dark colored resin were removed. The ethereal liquid was then dried, and the solvent evaporated, when 2 grams of a dark reddish-colored oil were obtained, which distilled between 210 and 250° under 15 mm. pressure. This oil separated no solid on standing. It gave a greenish yellow color with ferric chloride, and absorbed bromine in chloroform solution, but no definite product could be obtained from it.

The aqueous liquid which remained in the distillation flask after the removal of the volatile products of hydrolysis, and from which the soft, resinous mass had been separated, was treated with baryta for the removal of the sulphuric acid, and filtered. It then reduced Fehling's solution, but an attempt to prepare an osazone from it was not successful.

II. *Extraction with Sodium Hydroxide.*—After the treatment of the ethereal solution of the ether extract with ammonium and sodium carbonates it was shaken with two successive portions of a 10 per cent. solution of sodium hydroxide, and finally washed with water. The liquids thus obtained, which were dark in color, were acidified and extracted with ether, when it was observed that a small amount of a solid substance was deposited. This was found to consist of ipurganol, for, when treated with acetic anhydride, it yielded diacetylipurganol, melting at 166–167°. On subsequently evaporating the ethereal liquid a quantity (50 grams) of dark colored, resinous material was obtained, which possessed a somewhat disagreeable odor. As nothing could be separated from this resin, it was dissolved in alcohol, and a little water added, together with such an amount of sulphuric acid as to represent about 5 per cent. of its weight. The mixture was then heated in a reflux apparatus for 4 hours, after which water was added, the alcohol evaporated, and steam passed through the mixture until all the volatile products had been removed. The distillate, which contained some oily drops floating on the surface, was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. This alkaline, aqueous liquid was acidified, extracted with ether, and the solvent removed, when a small quantity of an oily acid was obtained. The latter was converted into an ammonium salt, from which a silver salt was prepared and analyzed.

0.2954 of salt gave on ignition 0.1026 Ag. Ag = 34.7
0.0658 of salt gave on ignition 0.0224 Ag. Ag = 34.0
$C_{12}H_{23}O_2$ Ag requires Ag = 35.2 per cent.

The ethereal liquid which had been shaken with sodium carbonate was dried, and the solvent removed, when a small quantity (about 3.5 grams) of a neutral yellowish oil was obtained. This was distilled under diminished pressure, when it passed over between 90 and 180°/20 mm., and was evidently a complex mixture.

The above-mentioned distillate, after extraction with ether, was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products of hydrolysis, as above described, there remained in the distillation flask an aqueous, acid liquid, together with a cake of solid substance. The whole was shaken with ether, when the solid substance became completely dissolved. The ethereal liquid was extracted with sodium carbonate, which removed a quantity of soft, resinous material, after which it was dried, and the solvent removed. A quantity of a light colored oil was thus obtained, which solidified on cooling, and when distilled under diminished pressure passed over for the most part between 200 and 210°/25 mm. In order to ascertain its character, it was heated for a short time with an alcoholic solution of potassium hydroxide, and the liquid poured into water, when about 2 grams of a solid substance separated. This was extracted with ether, the ethereal liquid being dried and the solvent removed, when a residue was obtained which, after several crystallizations from light petroleum, melted at 49–50°.

0.1592 gave 0.4614 CO_2 and 0.2024 H_2O. C = 79.0; H = 14.1.
$C_{16}H_{34}O$ requires C = 79.3; H = 14.1 per cent.

This substance was thus identified as cetyl alcohol, which had also been obtained from the petroleum extract of the resin.

The aqueous liquid which remained in the distillation flask after the removal of the volatile products of hydrolysis, and which had been extracted with ether, was subsequently treated with baryta for the removal of the sulphuric acid. The filtered liquid, when concentrated, yielded a very small amount of a sirup, but this did not reduce Fehling's solution, and therefore contained no sugar.

The ethereal solution of the original ether extract, after being treated with alkalis, as above described, was dried, and the solvent removed. About 10 grams of a light-colored, viscid product were thus obtained, from which a very small amount of a phytosterol was separated.

III. Chloroform Extract of the Resin.

This extract, after the removal of the solvent, was a hard, dark reddish brown mass, which could be reduced to a light brown powder. The amount employed for its investigation was about 350 grams.

Treatment with Sodium Carbonate.
Isolation of β-Methylaesculetin, $C_9H_5(CH_3)O_4$.

As the solution of the extract in chloroform deposited nothing on standing, it was shaken with a solution of sodium carbonate, when a large quantity of a thick, dark brown, tarry product was formed, consisting of the sodium compound of an acidic resin. The chloroform liquid had then become nearly deprived of color, and was found to contain only a small amount of resinous material, while the aqueous, alkaline liquid was dark in color and showed a marked blue fluorescence.

The above-mentioned, tarry product was washed several times with a solution of sodium carbonate. These washings, together with the sodium carbonate extract first obtained, were acidified, when a small quantity of an amorphous, brown solid separated, which was removed by filtration. The acid filtrate was extracted with ether, the ethereal liquid being dried, and the solvent removed, when a small quantity of a sirup was obtained which, after long standing, deposited a crystalline substance. This was collected, and recrystallized from ethyl acetate, from which it separated in nearly colorless needles, melting at 200–202°. The solution of this substance, on the addition of a little ammonia, displayed a fine blue fluorescence. As the amount was too small for analysis, it was heated with acetic anhydride, when it yielded an acetyl derivative melting at 176°. This melting point remained unchanged when the acetylated substance was mixed with acetyl-β-methylaesculetin prepared from the respective compound isolated from the bark of *Prunus serotina*.[1] The identity of the above-described, crystalline substance (m. p. 200–202°) with β-methylaesculetin was therefore definitely established.

Treatment of the Sodium Compound of the Resin with Dilute Alcoholic Sulphuric Acid.

The large quantity of thick, dark brown, tarry product above referred to was dissolved in alcohol, a slight excess of sulphuric acid added, and the mixture poured into water. The liberated resin was then taken up with chloroform, and the solvent removed, after which it was dissolved in alcohol. To this solution some water was added, and such an amount of sulphuric acid that the latter represented about 5 per cent. of the weight of the mixture. This was subsequently boiled in a reflux apparatus for about 12 hours, after which water was added, the alcohol removed, and the mixture distilled with steam until volatile products ceased to pass over. The distillate, which contained some oil floating on the surface, was completely extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate, after which it was dried and the solvent removed. A neutral, oily product was thus obtained, but it was found to be a mixture, and the amount was too small for its further examination.

The above-mentioned sodium carbonate extract of the volatile product was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed, when 1.5 grams of an oily acid were obtained. This distilled for the most part between 174 and 178° under the ordinary pressure, and was analyzed.

0.1258 gave 0.2702 CO_2 and 0.1128 H_2O. C = 58.6; H = 10.0.
$C_5H_{10}O_2$ requires C = 58.8; H = 9.8 per cent.

This acid was dextrorotatory, and was thus identified as *d*-methylethylacetic acid, which is stated to boil at 175°.

The remainder of this liquid, together with a portion of somewhat higher boiling point, was converted into a silver salt. This was obtained in two fractions, both of which were analyzed.

I. 0.3256 of salt gave on ignition 0.1678 Ag. Ag = 51.5
II. 0.4332 of salt gave on ignition 0.2244 Ag. Ag = 51.8
$C_5H_9O_2Ag$ requires Ag = 51.7 per cent.

The above-mentioned aqueous distillate, after extraction with ether, was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products of the acid hydrolysis by distillation with steam, as above described, there remained in the dis-

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[1] *J. Chem. Soc.*, **95**, 256 (1909).

tillation flask an acid liquid, together with a soft, resinous mass. The liquid was decanted from the resin and extracted with ether, which, however, removed only a small amount of an oily product. It was then treated with baryta for the removal of the sulphuric acid, filtered, and concentrated. A sirup was thus obtained, which readily yielded *d*-phenylglucosazone, melting at 210–211°. It was therefore evident that at least a portion of the chloroform extract of jalap resin was glucosidic.

The previously mentioned, soft, resinous mass, which had been separated from the acid, aqueous liquid, as above described, was treated with hot ether, in which the greater portion was soluble. The ethereal solution was separated from the insoluble material, consisting of a black, hard resin, and extracted with a solution of sodium carbonate, after which it was dried, and the solvent removed. About 5 grams of a sirupy product were thus obtained, which was distilled under diminished pressure, when it passed over quite constantly at 210–211° as a lemon-yellow oil. This oil solidified on cooling to a white, crystalline mass, which was first dried on a porous plate and finally in a desiccator, when it melted at 23–25°.

0.0850 gave 0.2204 CO_2 and 0.0926 H_2O. $C = 70.7; H = 12.1$.

$C_{17}H_{34}O_3$ requires $C = 71.3; H = 11.9$ per cent.

This substance was evidently the *ethyl ester of convolvulinolic acid*, $C_{15}H_{29}O_3.C_2H_5$, and its formation during the treatment of the acidic portion of the chloroform extract with alcoholic sulphuric acid may be attributed to the amount of water present not having been sufficient to entirely prevent esterification. It agrees in character with the ethyl convolvulinolate prepared by Hoehnel,[1] which is stated to melt at 22.5°.

The sodium carbonate extract of the ethereal liquid from which the ethyl convolvulinolate was obtained was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed, when it yielded a quantity of a dark colored sirup, which became partially solid on standing. This sirup was dissolved in alcohol, brought onto purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum and ether.

Petroleum Extract.—This was a dark, orange colored sirup, which solidified to a soft, fat-like mass. It was distilled under diminished pressure, and the following fractions collected: (I) Below 220°; (II) 200–225°; (III) 225–230°; (IV) 230–290/15 mm. As no crystalline acid could be obtained from these fractions, they were converted into silver salts, and the latter analyzed.

From these results it is evident that the above-described petroleum extract was a mixture. It undoubtedly contained some convolvulinolic acid, $C_{15}H_{30}O_3$, and apparently also a higher homologue of the latter.

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[1] *Arch. Pharm.*, **234**, 677 (1896).

Fraction I.	0.3474 of salt gave on ignition 0.1124 Ag.	Ag = 32.4
Fraction II (*a*).	0.2032 of salt gave on ignition 0.0572 Ag.	Ag = 28.1
Fraction II (*b*).	0.2094 of salt gave on ignition 0.0594 Ag.	Ag = 28.4
Fraction III (*a*).	0.2780 of salt gave on ignition 0.0752 Ag.	Ag = 27.0
Fraction III (*b*).	0.3588 of salt gave on ignition 0.0978 Ag.	Ag = 27.3
Fraction III (*c*).	0.3017 of salt gave on ignition 0.0830 Ag.	Ag = 27.5
Fraction IV.	0.2442 of salt gave on ignition 0.0648 Ag.	Ag = 26.5

$C_{15}H_{29}O_3$ Ag requires Ag = 29.6 per cent.
$C_{17}H_{33}O_3$ Ag requires Ag = 27.5 per cent.

Ether Extract.—This was a dark red sirup. It was distilled under diminished pressure, when some decomposition occurred, and, although a portion of the distillate became solid, nothing definite could be isolated from it.

IV. *Ethyl Acetate Extract of the Resin.*

This extract, after the removal of the solvent, was a hard, friable, reddish brown mass, which could easily be reduced to a light brown powder.

Treatment with Dilute Alcoholic Sulphuric Acid.

One hundred grams of the dry extract were dissolved in alcohol, and some water added, together with such an amount of sulphuric acid that the latter represented about 5 per cent. of the weight of the mixture. The liquid, which amounted to 1.5 liters, was then heated in a reflux apparatus for about 5 hours, after which the alcohol was removed, water added, and steam passed through the mixture until volatile products ceased to pass over. The distillate, which contained some oily drops floating on the surface, was extracted with ether. The ethereal liquid was shaken with a solution of sodium carbonate, after which it was washed, dried, and the solvent removed. A very small amount of a yellowish oil was thus obtained, which gave a reaction for furfural. The sodium carbonate extract, when acidified and extracted with ether, yielded about 2 grams of a dark yellow, oily acid. This was distilled under the ordinary pressure, when it passed over for the most part between 174 and 178°.

0.1710 gave 0.3682 CO_2 and 0.1494 H_2O. C = 58.7; H = 9.7.
$C_5H_{10}O_2$ requires C = 58.8; H = 9.8 per cent.

An alcoholic solution of this acid was dextrorotatory, which confirmed its identity as *d*-methylethylacetic acid.

The above-mentioned, aqueous distillate, after extraction with ether, was found to contain formic and butyric acids.

After the removal of the volatile products of hydrolysis by distillation with steam, as above described, there remained in the distillation flask a dark red liquid, and a quantity of soft, resinous material which floated on the surface. The aqueous, acid liquid was separated from the resin, and extracted with ether, but this removed only a small amount of an oily product. It was finally treated with baryta from the removal of the sulphuric acid, filtered, and concentrated. A considerable quantity of a sirup was thus obtained, which readily yielded *d*-phenylglucosazone, melting at 206–207°. It was thus evident that at least a portion of the ethyl acetate extract of the resin was glucosidic.

The previously mentioned soft, resinous material, which had been separated from the above described, aqueous, acid liquid, was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum and ether.

Petroleum Extract.—This was a dark orange-colored sirup, which became partially solid on standing, and amounted to 10 grams. It was dissolved in ether, and the ethereal liquid shaken with a solution of sodium carbonate, after which the ether was dried and evaporated, when 2 grams of a dark yellow, oily liquid were obtained. The sodium carbonate extract was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed. A quantity (4.7 grams) of an oily acid was thus obtained, which became solid on standing. The above-mentioned 2 grams of yellow, oily liquid were found to consist of an ester which had been formed by the treatment of the resinous material with alcoholic sulphuric acid. This was therefore hydrolyzed, and the acid thus obtained mixed with the 4.7 grams of acid previously obtained by extraction with sodium carbonate. The whole was then distilled under diminished pressure, when the greater portion passed over between 210 and 230°/12 mm., and formed a light yellow, soft solid. This was neutralized with potassium hydroxide, when a portion of the resulting potassium salt was observed to be sparingly soluble. The acid obtained from this sparingly soluble salt was dissolved in a mixture of light petroleum and ether, from which it separated in the form of a nearly colorless solid, melting at 47–48°.

0.1104 gave 0.2810 CO_2 and 0.1196 H_2O. $C = 69.4$; $H = 12.0$.
$C_{15}H_{30}O_3$ requires $C = 69.8$; $H = 11.6$ per cent.

This substance was thus identified as convolvulinolic acid, a further quantity of which was obtained from the alcohol extract of the resin.

The acid obtained from the more soluble portion of the above-described potassium salt was a soft, fat-like mass. From a portion of it three fractions of silver salt were prepared and analyzed.

I. 0.3118 of salt gave on ignition 0.0868 Ag. $Ag = 27.8$
II. 0.3014 of salt gave on ignition 0.0842 Ag. $Ag = 27.9$
III. 0.0626 of salt gave on ignition 0.0184 Ag. $Ag = 29.4$

$C_{15}H_{29}O_3Ag$ requires $Ag = 29.6$ per cent.
$C_{17}H_{33}O_3Ag$ requires $Ag = 27.5$ per cent.

These results would indicate that the above-described product consisted chiefly of a higher homologue of convolvulinolic acid, having the formula $C_{17}H_{34}O_3$. As previously noted, a similar product was obtained by the acid hydrolysis of the chloroform extract.

Ether Extract.—This was a soft, black, resinous mass, and amounted to 8 grams. It was examined, but nothing of a definite character could be obtained from it.

V. *Alcohol Extract of the Resin.*

This extract, as indicated in the first part of this paper, was the chief constituent of the original crude resin. When quite dry it could readily be reduced to a light brown powder, and on treating it in dilute alcoholic solution with successive portions of animal charcoal, a nearly white product was obtained. The latter, after drying at 110°, melted at 150–160°, and, when heated on platinum foil, it burned with a smoky flame, leaving no residue.

The optical rotatory power of the purified alcohol extract was determined, with the following result:

A solution containing 0.9905 gram of dry substance in 25 cc. of absolute alcohol had α_D —1.47° in a 1 dcm. tube, whence $[\alpha]_D$ —37.1°.

This value is almost precisely the same as that obtained for the purified total resin, namely $[\alpha]_D$ —37.0°, as recorded in the first part of the paper. It also agrees closely with the rotation ($[\alpha]_D$ —36.9°) observed by Kromer[1] for the product designated as "convolvulin," the latter consisting of that portion of jalap resin which is insoluble in ether.

Fusion with Potassium Hydroxide.

Twenty grams of the alcohol extract of the resin were fused with 120 grams of potassium hydroxide in a nickel basin, the temperature of the mixture being kept at about 150° for some time, after which it was slowly increased to 260°, with constant stirring. When the reaction had ceased, and the mass had become pasty, it was allowed to cool, and then dissolved in water. The solution was acidified with sulphuric acid, and distilled with steam until volatile products ceased to pass over. The distillate, which was found to contain only acidic substances, was made alkaline with sodium carbonate, the liquid concentrated, acidified, and extracted with ether, when a quantity of an oily acid was obtained. This was distilled twice under the ordinary pressure, and the following fractions finally collected: (1) Below 165°; (2) 165–175°; (3) 175–185°; (4) 185–245°; (5) 245–280°. Fractions (1), (2) and (3) were analyzed.

It would appear from these results that fraction (1) consisted of a nearly pure butyric acid, while fractions (2) and (3) evidently contained valeric acid. The subsequent fractions consisted of mixtures of acids of higher molecular weight.

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[1] *J. Chem. Soc. Abst.*, **66**, i, 540 (1894).

(1) 0.1940 gave 0.3870 CO_2 and 0.1586 H_2O. C = 54.4; H = 9.1
(2) 0.1732 gave 0.3660 CO_2 and 0.1478 H_2O. C = 57.6; H = 9.5
(3) 0.1862 gave 0.4124 CO_2 and 0.1652 H_2O. C = 60.4; H = 9.9

$C_4H_8O_2$ requires C = 54.5; H = 9.1 per cent.
$C_5H_{10}O_2$ requires C = 54.8; H = 9.8 per cent.
$C_6H_{12}O_2$ requires C = 62.1; H = 10.3 per cent.

The aqueous liquid from which the above-mentioned acids had been extracted by ether was distilled with steam, when the distillate was found to contain formic, acetic, and butyric acids.

After the removal of the volatile products of the potash fusion by distillation with steam, there remained in the distillation flask a yellow, aqueous liquid, which was completely extracted with ether. The ethereal liquid was washed, dried, and the solvent removed. A sirupy liquid was thus obtained, which, after standing for a few days, solidified to a crystalline mass. This was dissolved in water, the solution treated with animal charcoal and concentrated, when a product was obtained which, after further crystallization from water, separated in long, flat needles, melting at 110–111°. As the amount of this acid was small, it was converted into a silver salt, and the latter analyzed.

0.1918 of salt gave on ignition 0.1000 Ag. Ag = 52.1.
$C_{10}H_{16}O_4Ag_2$ requires Ag = 51.9 per cent.

The above-described substance was thus identified as sebacic acid, $C_{10}H_{18}O_4$, and its low melting point was evidently due to a slight impurity. This acid, as will be noted later, had been obtained by Hoehnel by the oxidation of convolvulinolic acid, $C_{14}H_{28}(OH)CO_2H$, but was regarded by him as an isomeride of sebacic acid, and therefore designated "ipomic acid."[1]

The mother liquor from the first crystallization of the sebacic acid was concentrated to a small bulk, when an acid separated in the form of laminae, which, after further crystallization, melted at 103–104°.

0.1082 gave 0.2274 CO_2 and 0.0862 H_2O. C = 57.3; H = 8.8.
$C_9H_{16}O_4$ requires C = 57.4; H = 8.5 per cent.

This substance was thus identified as azelaic acid, which had previously been obtained by the authors in a similar manner from the alcohol extract of the resin of *Ipomoea purpurea*, Roth.[2]

Hydrolysis of the Alcohol Extract of the Resin with Barium Hydroxide.

A quantity (200 grams) of the purified alcohol extract was dissolved in alcohol (1000 cc.), and a cold, saturated solution of barium hydroxide gradually added until the liquid showed an alkaline reaction. The liquid was then kept at a temperature of 35–40°, small portions of solution of barium hydroxide being added from time to time in order to

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[1] *Arch. Pharm.*, **234**, 680 (1896).
[2] *Amer. J. Pharm.*, **80**, 271 (1908).

maintain alkalinity. This treatment was continued until, on testing a small portion of the liquid with water, no turbidity was produced, a condition which was obtained in about 12 hours. The liquid was then allowed to cool, a little water added, and the alcohol removed, after which it was deprived of the excess of barium by means of carbon dioxide and filtering. The barium, which still remained in the filtrate in combination with the acids formed from the resin, was exactly precipitated with sulphuric acid, when, after removing the barium sulphate, a clear, dark red liquid was obtained. This liquid was subjected to distillation with steam in order to remove any volatile acids present. The distillate, which contained some oily drops floating on the surface, was made alkaline with sodium carbonate, concentrated, then acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A quantity (4 grams) of an oily product was thus obtained, which had the odor of valeric acid, and distilled between 174 and 176° as a colorless liquid.

0.1678 gave 0.3614 CO_2 and 0.1524 H_2O. C = 58.7; H = 10.1.
$C_5H_{10}O_2$ requires C = 58.8; H = 9.8 per cent.

The density of the acid was 0.9480 at 16.5°. It was optically active, and a determination of its specific rotatory power gave the following result:

α_D in a 25 mm. tube at 16° = +4° 10′, whence $[\alpha]_D$ +17.58°.

It was thus evident that the above-described liquid consisted of the optically active valeric acid (*d*-methylethylacetic acid, $CH(CH_3)(C_2H_5).CO_2H$), which is recorded[1] as having $[\alpha]_D$ +17.85°.

The liquid from which the valeric acid had been removed by extraction with ether was distilled with steam, when the distillate was found to contain small amounts of formic and butyric acids.

After the removal of the total volatile acids by distillation with steam, as above described, there remained in the distillation flask a clear liquid. This was extracted with ether, which, however, removed nothing. It was then concentrated under diminished pressure to the consistency of a sirup, when it still remained clear, and possessed a dark orange-yellow color. It had a strongly acid reaction, and did not reduce Fehling's solution until after heating with a mineral acid. For the further examination of this product, which may be termed the *hydrolyzed resin*, it was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with the same solvents as had been employed for the extraction of the original mixture of resins. The results were as follows:

Petroleum (b. p. 40–60°) removed nothing.

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[1] *Ber.*, **29**, 52 (1896).

Ether and chloroform extracted 19.3 grams and 9 grams respectively of clear, orange-yellow sirups, which did not solidify.

Ethyl acetate extracted 54 grams of a dark, opaque sirup, which, when perfectly dry, could be reduced to a light brown powder. The latter was extremely hygroscopic, but if kept in a sealed tube, could be preserved unchanged.

Alcohol extracted 88 grams of a product, which formed a hard, brittle mass, and could be reduced to a nearly colorless powder.

Each of the above products from the hydrolyzed alcohol extract of the resin was then subjected to treatment with dilute sulphuric acid.

Ether Extract of the Hydrolyzed Resin.

The entire amount of this extract (19.3 grams) was dissolved in water, and such an amount of sulphuric acid added that the latter represented 5 per cent. by weight of the solution. The whole was then boiled in a reflux apparatus for about 6 hours, when a sirupy product separated which did not become solid on cooling, and the mixture was subsequently distilled with steam. The distillate, which contained a light yellow oil floating on the surface, was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. On evaporating the ether a very small amount of a neutral oil was obtained, which did not respond to the test for furfural and gave no color with ferric chloride. The sodium carbonate liquid was acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when 1.2 grams of a light yellow oil were obtained. This was unsaturated, since it absorbed bromine. It was distilled under diminished pressure, when the following two fractions were collected: (I) 120–140°; (II) 140–160°/15 mm., the latter distilling for the most part at about 160°/15 mm. The first fraction was analyzed with the following result:

I. 0.1480 gave 0.3534 CO_2 and 0.1362 H_2O. C = 65.1; H = 10.2.
$C_7H_{12}O_2$ requires C = 65.6; H = 9.4 per cent.

The remaining portion of this liquid yielded a fraction of silver salt which gave the following result on analysis:

0.1494 gave 0.2342 CO_2, 0.0796 H_2O, and 0.0590 Ag. C = 42.7; H = 5.9; Ag = 39.5.
$C_{10}H_{17}O_2$ Ag requires C = 43.3; H = 6.1; Ag = 39.0 per cent.

Fraction I thus apparently consisted of a mixture of an acid $C_{10}H_{18}O_2$ with one of lower molecular weight.

II. 0.1560 gave 0.3978 CO_2 and 0.1516 H_2O. C = 69.5; H = 10.8.
$C_{10}H_{18}O_2$ requires C = 70.6; H = 10.6 per cent.

From the remainder of this fraction a silver salt was prepared and analyzed.

0.1270 gave 0.2000 CO_2, 0.0746 H_2O, and 0.0492 Ag. C = 43.0; H = 6.5; Ag = 38.7.
$C_{10}H_{17}O_2$ Ag requires C = 43.3; H = 6.1; Ag = 39.0 per cent.

It will be seen from these results that fraction II agrees approximately in composition with a decylenic acid, $C_{10}H_{18}O_2$, but the amount of material available did not permit of its more complete examination. It was therefore impossible to ascertain whether the product was homogeneous.

Hoehnel.[1] by the treatment of so-called "purgic acid" with dilute sulphuric acid, obtained a product (b. p. 176°/135 mm.) which he regarded as decylenic acid, but this conclusion was based only upon the analysis of two amorphous salts and a determination of the iodine value. The latter figure, as found by Hoehnel (82.5), is, moreover, not in agreement with that required for decylenic acid, which is 146. It therefore cannot be considered as definitely established that decylenic acid has been obtained from jalap resin.

The aqueous distillate from which the oily acid had been obtained by extraction with ether was found to contain, furthermore, small amounts of formic and butyric acids.

After the removal of the volatile products by distillation with steam, as above described, there remained in the distillation flask a yellowish liquid, together with a viscid, oily product which floated on the surface. The mixture was extracted with ether, in which the oily product was completely soluble, and the ethereal solution then shaken with a solution of sodium carbonate. On subsequently evaporating the ether, only a very small amount of a neutral, oily liquid was obtained. The sodium carbonate liquid was acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when a quantity of a viscid, dark orange-colored product was obtained, which deposited nothing crystalline. When neutralized with a solution of sodium hydroxide, it formed a gelatinous mass, having the character of a soap. The viscid, oily acid was distilled under diminished pressure, and the following fractions collected: (I) 192–194°; (II) 194–200°; (III) 200–210°; (IV) 210–220°; (V) 220–280°; (VI) 280–310°/15 mm. The total amount of these fractions was 12.2 grams. They were all viscid, yellow, unsaturated liquids, and on analysis gave the following results:

I. 0.1492 gave 0.3520 CO_2 and 0.1398 H_2O. C = 64.3; H = 10.4
II. 0.1372 gave 0.3236 CO_2 and 0.1336 H_2O. C = 64.3; H = 10.8
III. 0.1778 gave 0.4202 CO_2 and 0.1714 H_2O. C = 64.5; H = 10.7
IV. 0.1152 gave 0.2770 CO_2 and 0.1126 H_2O. C = 65.7; H = 10.9
V. 0.1758 gave 0.4294 CO_2 and 0.1678 H_2O. C = 66.6; H = 10.6
VI. 0.1560 gave 0.3904 CO_2 and 0.1496 H_2O. C = 68.2; H = 10.6

The iodine absorption values of fractions I and VI were determined.

I. 0.3176 absorbed 0.0980 I. Iodine value = 30.9
VI. 0.3910 absorbed 0.1986 I. Iodine value = 50.8

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[1] *Arch. Pharm.*, **234**, 668 (1896).

It was evident from these results that the above fractions consisted of a mixture of acids, the identity of which could not be established.

The aqueous, acid liquid contained in the distillation flask, from which the above-described products had been removed by extraction with ether, was treated with baryta for the removal of the sulphuric acid. The filtered liquid was then concentrated under diminished pressure, when a small amount of a sirup was obtained which contained sugar, since it readily yielded *d*-phenylglucosazone, melting at 209–210°. This sirup also contained a small amount of a readily soluble, organic acid.

Chloroform Extract of the Hydrolyzed Resin.

This extract, which amounted to only 9 grams, was subjected to the same treatment with dilute sulphuric acid as has been described in connection with the ether extract of the hydrolyzed resin. On distilling the product with steam, a very small amount of an oily acid was obtained, together with formic and butyric acids. The contents of the distillation flask consisted of an aqueous, acid liquid, on the surface of which there was a small amount of a dark colored, viscid oil. The mixture was extracted with ether, which completely dissolved the oily product, the ethereal liquid being then shaken with a solution of sodium carbonate. On subsequently evaporating the ether, a very small amount of a neutral oil was obtained. The sodium carbonate liquid was acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A small amount of a dark orange-colored oil was thus obtained, from which no solid substance separated. It was therefore mixed with purified sawdust, and the mixture successively extracted with light petroleum and ether, but the resulting products were of an oily nature, and did not solidify. The acids were finally converted by fractional precipitation into a number of silver salts, the analysis of which, however, indicated them to consist of complex mixtures. The above-mentioned, aqueous liquid which had been extracted with ether was finally treated with baryta for the removal of the sulphuric acid, and filtered. It was then found to contain sugar, since it readily yielded *d*-phenylglucosazone, melting at 207–208°. It also contained a readily soluble, organic acid.

Ethyl Acetate Extract of the Hydrolyzed Resin.

This extract, which amounted to 54 grams, was obtained in the form of a dark, opaque sirup. As previously noted, it could be reduced to a powder after thorough drying, but the latter was extremely hygroscopic. It was heated for about 6 hours with dilute sulphuric acid, in the same manner as the two preceding extracts, and the product distilled with steam. The distillate, which contained some oily drops, was extracted with ether, and the ethereal liquid shaken with a solution of sodium carbonate. On subsequently evaporating the ether, only a very small amount of a neutral, oily liquid remained. The sodium carbonate liquid was then acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A quantity (5.2 grams) of an acid was thus obtained, which was distilled under the ordinary pressure, when it passed over for the most part between 174 and 178°.

0.1792 gave 0.3842 CO_2 and 0.1570 H_2O. $C = 58.5$; $H = 9.7$.
$C_5H_{10}O_2$ requires $C = 58.8$; $H = 9.8$ per cent.

The density of the acid was 0.9388 at 17.5°. A determination of its optical rotatory power gave the following result:

α_D in a 25 mm. tube at 17.5° = +4°7,′ whence $[\alpha]_D$ +17.53°.

This acid was thus identified as the optically active valeric acid (*d*-methylethylacetic acid), $CH(CH_3)(C_2H_5).CO_2H$.

The distillate which had been extracted with ether was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products by distillation with steam there remained in the distillation flask a dark colored liquid, together with a solid cake of resin, which was separated by filtration. The clear liquid was extracted with ether, but this removed only a small amount of oily substance, which did not permit of further examination. After extraction with ether the liquid was treated with baryta for the removal of the sulphuric acid, filtered, and the filtrate concentrated under diminished pressure. A sirup was thus obtained which contained sugar, since it yielded *d*-phenylglucosazone, melting at 207–208°. It also contained an organic acid which was readily soluble in water.

The above-mentioned, solid cake of resin, which was separated from the aqueous, acid liquid, was dissolved in alcohol, mixed with purified sawdust, and the mixture successively extracted with light petroleum, ether, and alcohol. The products from the first two solvents were of an oily nature, while the alcohol removed only a small amount of a hard resin. The petroleum and ether extracts were further examined, but they appeared to consist of a complex mixture of acids, of which no constituent could be definitely identified.

Alcohol Extract of the Hydrolyzed Resin.

This constituted the largest portion of the product of the alkaline hydrolysis of the resin. It formed a hard, transparent, light yellow mass, which could be reduced to a nearly colorless powder, and, unlike the ethyl acetate extract, was permanent in the air. It dissolved readily in water, yielding a clear solution, which was strongly acid to litmus. It melted at 110–115°, and with cold, concentrated sulphuric acid gave a deep red color. It was optically active, and a determination of its specific rotatory power gave the following result:

An aqueous solution containing 1.1060 grams of substance in 25 cc. had α_D —1° 29′ in a 1 dcm. tube, whence $[\alpha]_D$ —33.53°.

Hoehnel[1] has recorded for the so-called "convolvulic acid," to which he assigned the formula $C_{45}H_{80}O_{28}$, and which represented that portion of the product of the alkaline hydrolysis of "convolvulin" which was insoluble in ether and not volatile in steam, a specific rotatory power of —34.68°, whereas Kromer[2] had noted for a somewhat similar product $[\alpha]_D$ —31.33°.

For the examination of the above-mentioned extract 100 grams of material were employed. This was dissolved in water, and such an amount of sulphuric acid added that the latter represented 5 per cent. by weight of the mixture. The whole was then heated in a reflux apparatus for 4 hours, and the mixture allowed to cool, when it was observed that a resinous product had separated in the form of a soft, plastic mass. On passing steam through the mixture a slightly acid distillate was obtained, which contained no oily drops. It was made alkaline with sodium carbonate, concentrated, then acidified and extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A very small amount of an oily acid was thus obtained, which was converted into a silver salt, and the latter analyzed.

0.1396 of salt gave on ignition 0.0728 Ag. Ag = 52.1.
$C_5H_9O_2$ Ag requires Ag = 51.7 per cent.

This acid was thus identified as a valeric acid.

The acid liquid which had been extracted with ether was distilled with steam, when the distillate was found to contain small amounts of formic and butyric acids.

After the removal of the volatile products there remained in the distillation flask a dark colored liquid, which was decanted from the mass of resinous material and extracted with ether, but this removed only a small amount of a mixture of acids. The aqueous, acid liquid was finally treated with baryta for the removal of the sulphuric acid, and the filtered liquid concentrated under diminished pressure. A sirup was thus obtained which contained sugar, since it readily yielded *d*-phenylglucosazone, melting at 209–210°. It also contained a readily soluble organic acid.

The resinous material obtained by the above treatment, and which had been separated from the aqueous, acid liquid, was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively with light petroleum, ether, and alcohol.

Petroleum Extract.—This was a light yellow oil, which solidified to a fat-like mass, and amounted to 11.2 grams.

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[1] *Arch. Pharm.*, 234, 662 (1896).

[2] *J. Chem. Soc. Abst.*, **66**, i, 540 (1894).

Ether Extract.—This product was a soft, dark brown mass, and amounted to 9 grams.

Alcohol Extract.—This was a dark resinous mass, and amounted to only 4 grams. No crystalline substance could be obtained from it.

Isolation of Convolvulinolic Acid, $C_{14}H_{28}(OH).CO_2H$.
(Hydroxypentadecylic Acid.)

The above-mentioned petroleum extract, which was strongly acid to litmus, was mixed with water, and carefully neutralized with sodium hydroxide. The solution was then concentrated on a water bath, and, after filtering, was allowed to stand for some time, when a crystalline sodium salt separated. This was collected, dried on a porous plate, then dissolved in water, and the solution acidified with hydrochloric acid, when the organic acid separated in a solid state. It was collected on a filter, dried, and then crystallized three times from a mixture of light petroleum and ether, the solution being cooled in a freezing mixture of ice and salt. The acid then separated in the form of small, fine needles, which melted at 51–52°.

0.1288 gave 0.3284 CO_2 and 0.1416 H_2O. C = 69.5; H = 12.2.
$C_{15}H_{30}O_3$ requires C = 69.7; H = 11.6 per cent.

A portion of the acid was converted into a silver salt, and the latter analyzed.

0.1970 of salt gave on ignition 0.0580 Ag. Ag = 29.4.
$C_{15}H_{29}O_3$ Ag requires Ag = 29.6 per cent.

It is thus evident that the above-described acid possesses the formula $C_{15}H_{30}O_3$, and that it is identical with an acid of the same composition previously described by Taverne[1] as a hydroxypentadecylic acid (m. p. 50.5°) and by Hoehnel[2] as convolvulinolic acid (m. p. 51.5°). The latter designation appears, however, to have been given first by Mayer[3] and subsequently by Kromer,[4] to products obtained from jalap resin by methods analogous to that above described, but to which different formulas were assigned, and which were obviously not pure substances.

Methyl Convolvulinolate, $C_{14}H_{28}(OH).CO_2CH_3$.—One gram of convolvulinolic acid was dissolved in methyl alcohol, and the solution saturated with dry hydrogen chloride. After allowing the liquid to stand over night, it was poured into water, and the mixture extracted with ether, the ethereal liquid being washed with a dilute solution of sodium carbonate, then with water, dried, and the solvent removed. A light

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[1] *Rec. trav. chim. Pays Bas,* **13,** 187 (1894); *J. Chem. Soc. Abst.,* **68,** i, 119 (1895).

[2] *Arch. Pharm.,* **234,** 674 (1896).

[3] *Ann.,* **83,** 121 (1852).

[4] *J. Chem. Soc. Abst.,* **66,** i, 540 (1894).

yellow, viscid product was thus obtained, which was distilled under diminished pressure, when it passed over as a colorless oil. On allowing the latter to stand, it solidified to a mass of small needles, which, after drying on a porous plate, melted at 32–33°.

0.0940 gave 0.2420 CO_2 and 0.1012 H_2O. C = 70.2; H = 11.9.
$C_{16}H_{32}O_3$ requires C = 70.6; H = 11.8 per cent.

This substance was thus quite pure methyl convolvulinolate. It appears to have first been prepared by Taverne,[1] who has recorded its boiling point as 206–208°/15 mm., and its melting point as 35°.

Isolation of Ipurolic Acid, $C_{13}H_{25}(OH)_2.CO_2H$.

The above-mentioned ether extract, obtained from the product of the action of dilute sulphuric acid on the alcohol extract of the hydrolyzed resin, was a soft, dark brown mass. It was mixed with water, and carefully neutralized with sodium hydroxide. The solution was then concentrated on a water-bath, and allowed to cool, when a sodium salt separated in a partially crystalline condition. This salt was twice recrystallized from water, after which it was decomposed by hydrochloric acid, and the resulting acid extracted by means of ether. The solid thus obtained was twice recrystallized at a low temperature from a mixture of ether and chloroform, after which it melted at 94–95°. On subsequently crystallizing twice from the same mixture of solvents, and finally from chloroform, the melting point was raised to 100–101°.

0.1120 gave 0.2648 CO_2 and 0.1094 H_2O. C = 64.5; H = 10.8.
$C_{14}H_{28}O_4$ requires C = 64.6; H = 10.8 per cent.

A silver salt of the acid was also prepared and analyzed.

0.1496 of salt gave on ignition 0.0436 Ag. Ag = 29.1.
$C_{14}H_{27}O_4$ Ag requires Ag = 29.4 per cent.

The above-described substance was thus identified as ipurolic acid, $C_{13}H_{25}(OH)_2.CO_2H$, which was first isolated by the authors from the stems of *Ipomoea purpurea*, Roth.[2] When mixed with the acid obtained from the latter source, the melting point remained unchanged.

Methyl Ipurolate, $C_{13}H_{25}(OH)_2.CO_2CH_3$.—This was prepared by the method previously described.[3] When crystallized from dilute methyl alcohol it separated in fine, colorless needles, melting at 68–69°.

0.1070 gave 0.2562 CO_2 and 0.1056 H_2O. C = 65.3; H = 10.9.
$C_{15}H_{30}O_4$ requires C = 65.7; H = 10.9 per cent.

It may be noted in this connection that Hoehnel[4] has designated that portion of the product of the alkaline hydrolysis of "convolvulin" which is insoluble in ether as "convolvulic acid," and has assigned to it the

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[1] *Loc. cit.*

[2] *Am. J. Pharm.*, **80**, 273 (1908).

[3] *Loc. cit.*, p. 275.

[4] *Arch. Pharm.*, **234**, 684 (1896).

formula $C_{45}H_{80}O_{28}$. He has furthermore assumed that the formation of convolvulinolic acid, $C_{15}H_{30}O_3$, from the last-mentioned product by its acid hydrolysis may be expressed by the following equation:

$$C_{45}H_{80}O_{28} + 5H_2O = 5C_6H_{12}O_6 + C_{15}H_{30}O_3.$$

It has been shown, however, by this investigation that the portion of the product of the alkaline hydrolysis of the resin which was not only insoluble in ether, but which had also been deprived of constituents soluble in chloroform and ethyl acetate, when submitted to the action of dilute sulphuric acid, yielded, besides sugar and convolvulinolic acid, a number of other acids, among which formic, butyric, valeric, and ipurolic acids were identified. A portion of the product, moreover, is apparently not glucosidic, and remains after the treatment with sulphuric acid in the form of an organic acid which is readily soluble in water. It is obvious, therefore, that the formation of all these substances can not be expressed by a simple equation, and that the amorphous product designated as "convolvulic acid" can by no means be regarded as an individual substance, which is capable of being represented by a chemical formula.

Oxidation of the Alcohol Extract of the Hydrolyzed Resin with Nitric Acid.

Ten grams of the previously described alcohol extract of the hydrolyzed resin were dissolved in a little water, and about 100 grams of nitric acid (sp. gr. 1.4) added. A vigorous reaction soon ensued, and when this had subsided the mixture was heated for a time, after which water was added, and the heating continued for about 10 minutes. On allowing the liquid to cool, a quantity of substance was deposited, which was extracted with ether, and the ethereal liquid then shaken with a solution of sodium carbonate. The ether was subsequently dried and evaporated, when only a slight oily residue was obtained. The sodium carbonate liquid was acidified and extracted with ether, the ethereal liquid being dried and the solvent removed, when 1.4 grams of an oily product were obtained, which soon solidified to a perfectly white, crystalline mass. This was repeatedly crystallized from water, when two principal fractions were obtained, melting at 105–106° and 122–125° respectively. The final mother liquor contained a small amount of an acid which was freely soluble in water, and was evidently oxalic acid.

The fraction melting at 105–106° consisted of long, flat needles, and was analyzed with the following result:

0.1072 gave 0.2266 CO_2 and 0.0844 H_2O. C = 57.6; H = 8.7.
$C_9H_{16}O_4$ requires C = 57.4; H = 8.5 per cent.

This substance was thus identified as azelaic acid, the melting point of which has been recorded as 106°.

The fraction melting at 122–125° was obtained in the form of small needles, and gave on analysis the following result:

0.0768 gave 0.1676 CO_2 and 0.0658 H_2O. C = 59.5; H = 9.5.
$C_{12}H_{18}O_4$ requires C = 59.4; H = 8.9 per cent.

This substance was evidently sebacic acid, the melting point of which has been variously stated as 127–128° and 133–133.5°.

By the oxidation of convolvulinolic acid with potassium permanganate, as also with nitric acid, Hoehnel[1] obtained, besides a valeric acid, a crystalline, dicarboxylic acid of the composition $C_{10}H_{18}O_4$ (m. p. 109°), which he has designated as ipomic acid ("ipomsäure"), and regards it as isomeric with sebacic acid. The name of *ipomic* or *ipomoeic* acid was first given by Mayer[2] to a product obtained by the action of nitric acid on that portion of jalap resin which is insoluble in ether, and which he designated "convolvulin." The acid obtained by Mayer was stated to agree with the formula $C_5H_9O_2$, and to melt at 104°. Neison and Bayne,[3] who repeated the experiment of Mayer, have shown, however, that the so-called ipomoeic acid is identical with sebacic acid, for by the oxidation of material designated by them as "jalapin" they obtained an acid melting at 126–127°, and agreeing in all respects with sebacic acid, the melting point of which they record as 127–128°. This fact appears not to have been considered by Hoehnel,[4] who has retained the name of "ipomsäure" for a substance which was evidently somewhat impure sebacic acid. The present investigation has shown, moreover, that the sebacic acid obtained as above described is accompanied by a lower homologue, namely, azelaic acid. A mixture of these two acids was likewise obtained, as already noted, from the product of the fusion of the alcohol extract of the resin with potassium hydroxide.

Summary.

In view of the extended experimental details of this investigation, a summary of the more important results may here be given.

The material employed consisted of an original bale of jalap tubers of good quality. On completely extracting the jalap with hot alcohol, and subjecting the resulting extract to distillation with steam, a small amount of an *essential oil* was obtained. This oil was at first of a pale yellow color, but became very dark on standing. The odor was smoky and disagreeable. It distilled between 80 and 160°/60 mm., had a density of 0.8868 at 20°/20°, and was optically inactive.

The portion of the extract which was soluble in water contained chiefly coloring matter and sugar, the latter yielding *d*-phenylglucosazone

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[1] *Arch. Pharm.*, **234**, 679 (1896).

[2] *Ann. Chem. Pharm.*, **83**, 143 (1852); **95**, 160 (1855).

[3] *J. Chem. Soc.*, **27**, 729 (1874).

[4] *Loc. cit.*

(m. p. 217–218°). The portion of the extract insoluble in water represents the product known as "resin of jalap," which is recognized by most of the national Pharmacopoeias. The amount of this resin contained in the drug, as indicated by a special assay of the latter, corresponded to 9.4 per cent. of its weight, and 11.6 per cent. of it was soluble in ether. The total crude resin, when purified by means of animal charcoal, had a specific optical rotation of —37.0°. On extracting the crude resin successively with (I) light petroleum (b. p. 40–60°), (II) ether, (III) chloroform, (IV) ethyl acetate, and (V) alcohol, a number of products were obtained, the examination of which has shown the resin to be of much more complex composition than has previously been assumed.

I. *Petroleum Extract of the Resin.*—This represented 1.9 per cent. of the total resin. It contained palmitic and stearic acids in a free state, and, after hydrolysis, yielded formic, butyric and higher volatile acids, palmitic acid, and a mixture of unsaturated acids, which appeared to consist chiefly of linolic acid. From the unsaponifiable portion of the extract there were obtained a phytosterol, $C_{27}H_{46}O$ (m. p. 134–135°; $[\alpha]_D$ —32.4°), cetyl alcohol, $C_{16}H_{34}O$, and a small amount of a substance melting at 56–57°, which agrees in composition with the formula $C_{18}H_{36}O$. This *substance*, which appears to be a new compound, yields color reactions similar to those of the phytosterols.

II. *Ether Extract of the Resin.*—This represented 9.7 per cent. of the total resin. From it there was isolated a small amount of a new, dihydric alcohol, which possesses the formula $C_{21}H_{32}O_2(OH)_2$, and is designated *ipurganol.* Ipurganol crystallizes in colorless needles, melting at 222–225°, and has, in pyridine solution, $[\alpha]_D$ —44.9°. It yields color reactions similar to those given by the phytosterols. *Diacetylipurganol*, $C_{21}H_{32}O_4(CH_3.CO)_2$, forms colorless leaflets, melting at 166–167°, and has, in pyridine solution, $[\alpha]_D$ —36.0°. The ether extract, after treatment with alkalis and dilute sulphuric acid, yielded, furthermore, a little phytosterol and cetyl alcohol, small amounts of volatile acids, and a quantity of amorphous products.

III. *Chloroform Extract of the Resin.*—This represented 24.1 per cent. of the total resin. From it there was isolated a very small amount of β-methylaesculetin, $C_9H_5(CH_3)O_4$. After treatment with alkalis and dilute sulphuric acid this extract yielded, furthermore, formic, butyric, and *d*-methylethylacetic acids, together with convolvulinolic acid, $C_{15}H_{30}O_3$, and apparently a higher homologue of the latter. Glucose was also produced by this treatment, thus indicating that a portion of the extract was of a glucosidic nature.

IV. *Ethyl Acetate Extract of the Resin.*—This represented 22 per cent. of the total resin. On treatment with dilute alcoholic sulphuric acid, it yielded formic, butyric, and *d*-methylethylacetic acids, together with convolvulinolic acid, $C_{15}H_{30}O_3$, and apparently a higher homologue of the latter, having the composition $C_{17}H_{34}O_3$. It also yielded, besides indefinite amorphous products, a considerable quantity of a sugar, which was evidence that at least a portion of the extract was of a glucosidic nature.

V. *Alcohol Extract of the Resin.*—This represented 38.8 per cent. of the total resin. After treatment with animal charcoal it was obtained in the form of a nearly white powder, which melted at 150–160°, and had $[\alpha]_D$ —37.1°. When fused with potassium hydroxide it yielded formic, acetic, butyric, valeric, and higher volatile acids, together with azelaic and sebacic acids. When subjected to alkaline hydrolysis with baryta it yielded, besides small amounts of formic and butyric acids, *d*-methylethylacetic acid, $C_5H_{10}O_2$ (b. p. 174–176°; $[\alpha]_D$ +17.55°), together with a quantity of an amorphous product, readily soluble in water, which may be designated as the hydrolyzed resin. This has now been shown to be of very complex composition, for by successive extraction with (*a*) ether, (*b*) chloroform, (*c*) ethyl acetate, and (*d*) alcohol it is capable of being resolved into a number of products.

(*a*) *Ether Extract of the Hydrolyzed Resin.*—This extract, on heating with dilute sulphuric acid, yielded formic, butyric, and other acids, together with sugar.

(*b*) *Chloroform Extract of the Hydrolyzed Resin.*—This extract, like the preceding one, yielded small amounts of formic, butyric, and other acids, together with sugar.

(*c*) *Ethyl Acetate Extract of the Hydrolyzed Resin.*—This extract, on heating with dilute sulphuric acid, yielded formic, butyric, *d*-methylethylacetic, and other acids, together with sugar.

(*d*) *Alcohol Extract of the Hydrolyzed Resin.*—This extract could be obtained in the form of a nearly colorless powder, which melted at 110–115°, and had $[\alpha]_D$ —33.53°. When heated with dilute sulphuric acid it yielded, in addition to sugar, small amounts of formic, butyric, and valeric acids, together with convolvulinolic and ipurolic acids. The last-mentioned acid possesses the formula $C_{13}H_{25}(OH)_2.CO_2H$, and was first obtained by the authors from the stems of *Ipomoea purpurea*, Roth.[1]

By the oxidation of this extract with nitric acid, azelaic and sebacic acids were obtained.

Each of the above-described extracts of the hydrolyzed resin appeared to be only partly glucosidic, and to contain a readily soluble organic acid which was unaffected by the treatment with dilute sulphuric acid.

Physiological Tests.

The extracts obtained by the treatment of the original jalap resin with various solvents, as above described, were kindly tested for us with

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[1] *Am. J. Pharm.*, 80, 273 (1908).

respect to their physiological action by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, and our thanks are due to him for the assistance rendered in this connection.

One gram of each of the extracts was administered to dogs, with the following results:

1. The petroleum extract had no effect.
2. The ether extract produced prompt, but not severe purgation.
3. The chloroform extract caused repeated purgation, lasting for 48 hours.
4. The ethyl acetate extract was similar in its action to the chloroform extract, the purgation lasting 24 hours.
5. The alcohol extract produced repeated and powerful purgation.

Apart from the purgative action of the various extracts no effect was observed, all the animals having remained perfectly well. It was furthermore concluded by Dr. Dale that the apparent differences in the degree of action of the extracts II, III, IV, and V cannot be regarded as of great importance in view of individual differences with respect to the action of drugs, and of purgatives in particular.

The product resulting from the alkaline hydrolysis of the alcohol extract of the resin, consisting of acids readily soluble in water, had no effect when administered to a dog in doses of 1 gram. This result is in accordance with the observations previously recorded respecting an analogous but less completely purified product from jalap resin, which has been designated "convolvulic acid."[1]

Conclusions.

In considering the results of this investigation, some of the more important facts and deductions may specially be noted.

In the first place, it has been shown that the resin of jalap is of much more complex composition than has hitherto been assumed, and that none of the amorphous products obtained from it possess the attributes of a homogeneous substance. It follows that the formulas which have heretofore been assigned to products such as the so-called convolvulin, purgic acid, convolvulic acid, etc., are devoid of any significance or scientific value, and they should therefore no longer be retained in chemical literature. The same considerations will doubtless apply to the various amorphous products obtained from other convolvulaceous resins to which distinctive names and formulas have been assigned.

In the present investigation of jalap resin, as already indicated, a number of substances have been obtained which permitted of definite identification or characterization. It is evident, however, that the formation of these substances, when resulting from the degradation of an

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[1] Compare Husemann, "Die Pflanzenstoffe," 2nd edit., 1882, p. 1141.

amorphous product of the resin, can by no means be expressed by simple chemical equations.

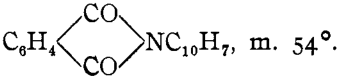
It may finally be observed that the purgative action of jalap resin is not due to any single or well-defined constituent, inasmuch as the products obtained by its successive extraction with various solvents, with the exception of the portion removed by light petroleum, appear to possess about an equal degree of physiological activity.

ACTION OF AMINES ON PHTHALIC ACID. VI.[1]

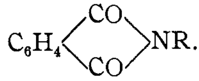
By J. Bishop Tingle and B. F. Parlett Brenton.

Received November 2, 1909.

In the course of the work described in our earlier paper, we studied the interaction of phthalic anhydride on a number of amino derivatives other than those we have already mentioned. The products which we ultimately obtained did not prove to be suitable for our intramolecular rearrangement investigations and consequently we did not carry on the work with them very far. We desire, however, to record the results which we have obtained, because we cannot continue our experiments conjointly.

Camphylamine and phthalic anhydride, when melted together, gave what is probably the *imide*,  $C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NC_{10}H_7$, m. 54°. No solid hydrolysis product (amidic acid) could be obtained from it.

Benzidine and phthalic anhydride, under similar conditions, yielded a highly insoluble compound of great stability.

We made a large number of experiments with the object of "fixing" the mobile amidic hydrogen atom in the amidic acids, $RNHCOC_6H_4CO_2H$. With phosphorus pentachloride, phosphorus trichloride, or thionyl chloride, the only stable product of the reaction was the imide  $C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NR$. We then directed our attention to the preparation of acylated amidic acids, such as $CH_3CONRCOC_6H_4CO_2H$. We attempted to prepare them by the action of acyl chlorides and of acid anhydrides on the amidic acids and also from acyl amines and phthalic anhydride. We found, however, that acetyl chloride or acetic anhydride either failed to react with the amidic acids, or else it transformed them into the imide, behaving in this respect exactly like the phosphorus halides mentioned above. Most of our experiments were made with phthalphenylamidic

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[1] The previous papers bearing on this subject have appeared as follows: Bishop Tingle and Cram, *Am. Chem. J.*, **37**, 596 (1907): Bishop Tingle and Lovelace, *Ibid.*, **38**, 642 (1907); Bishop Tingle and Rolker, This Journal, **30**, 1882 (1908); Bishop Tingle and Brenton, *Ibid.*, **31**, 1157 (1909); Bishop Tingle and Bates, **31**, 1233 (1909).