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CHEMICAL EXAMINATION

OF

LIPPIA SCABERRIMA, *Sonder*

("Beukess Boss")

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CHEMICAL EXAMINATION OF LIPPIA SCABERRIMA, SONDER (" BEUKESS BOSS").[1]

By Frederick B. Power and Frank Tutin.

A South African plant, which is known in its native country as " Beukess Boss," was brought to our notice as being worthy of investigation on account of its reputed medicinal value. It is found in the Orange River Colony, in the neighborhood of Kroonstad, where it is regarded as possessing remarkable hæmostatic properties, together with a slightly tonic and aperient action, and is therefore used in the treatment of hæmorrhoids. Through the kindness of Mr. E. M. Holmes, F.L.S., Curator of the Museum of the Pharmaceutical Society of Great Britain, the plant was identified as *Lippia scaberrima*, Sonder, belonging to the family of *Verbenaceæ*. A botanical description of this species of *Lippia* is contained in *Linnaea*, xxiii (1850), 87. Afr. austr.

With regard to the origin or meaning of the vernacular name " Beukess Boss," we have been informed that " Beukess " is the name of an old Dutch family who formerly prepared a decoction of the plant for medicinal use, whereas " Boss " is a corruption of the Boer name of " Bosch," meaning a bush. Hence in time the plant became known as " Beukess Boss " or " Beukess Bush."

A number of species of the genus *Lippia* have heretofore attracted attention on account of their aromatic properties, which are due to the presence of essential oils. One of the best known of these is the *Lippia citriodora*, Kunth (*Verbena triphylla*, L'Heritier), the so-called

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[1] Translated from a communication to the *Archiv der Pharmacie*, 1907, 245, pp. 337-350, from the Wellcome Chemical Research Laboratories, London.

"lemon-verbena," which affords the genuine verbena oil (compare Gildemeister and Hoffmann, "Die ætherischen Oele," p. 774, and Beilstein's *Handbuch der org. Chemie, Ergänzungsband*, III, p. 380). Some South American species of *Lippia*, which likewise yield aromatic essential oils, have recently been brought to notice, namely: *L. urticoides*, *L. geminata*, and *L. microcephala* (*Ber. d. deutsch. Pharm. Ges.*, **14**, p. 468).

Podwissotzki (*Pharm. Zeit. f. Russl.*, 1882, **21**, 926) has recorded the results of an examination of the leaves and stems of *Lippia mexicana*, from which on distillation with water he obtained an essential oil possessing a sweet taste, reminding of that of Italian fennel, together with a crystalline, camphor-like substance (m. p. 25-30° C.), designated as *lippiol*. Although one analysis was recorded of this substance ($C = 75{\cdot}81$; $H = 12{\cdot}43$; $O = 10{\cdot}20$ per cent.), the figures are evidently quite inconclusive, and no further evidence was afforded of its composition, nor was its chemical character determined. The presence of a small amount of tannin in the plant was likewise noted.

Maisch (AMER. JOUR. PHARM., 1885, **57**, p. 330), in commenting "on some useful plants of the natural order of Verbenaceæ," stated that he was unable to find any reference in botanical works to a plant bearing the name of *Lippia mexicana*, and therefore expressed the opinion that the material examined by Podwissotzki (*loc. cit.*) was either obtained from the labiate plant *Cedronella mexicana*, Benth., which has been admitted into the Mexican Pharmacopœia under the name of *toronjil*, or that it was *Lippia citriodora*, Kunth (compare also *Proc. Amer. Pharm. Assoc.*, 1876, **24**, p. 772). In the "National Standard Dispensatory," 1905, p. 1630, it is stated that "the drug *Lippia mexicana* is the leaves of *L. dulcis*, Trev., var. *dulcis*, of Mexico and Central America."

EXPERIMENTAL.

The material used in this investigation was specially collected for us in South Africa, and consisted of the air-dried stems and leaves of the plant, which was botanically identified as *Lippia scaberrima*, Sonder. The herb possesses an agreeable aromatic odor, reminding of both lavender and sage.

Test for an Alkaloid.—Twenty-five grammes of the finely ground herb were macerated with Prollius' fluid, and the resulting liquid evaporated. The residue left by the latter, when extracted with acidulated water, gave no reaction with alkaloidal reagents.

Quantitative Estimation of the Tannin.—A quantity (17·3 grammes) of the finely ground herb was extracted with successive small portions of boiling water, and the cold filtered liquid diluted to the measure of 500 c.c. 100 c.c. of this liquid, when evaporated, and the residue dried in a water-oven until of constant weight, yielded 0·5402 gramme of extract; 100 c.c. of the same liquid, after treatment with hide powder, yielded 0·3498 gramme of extract. The amount of substance absorbed by the hide powder was therefore 0·1904 gramme, which would correspond to 5·5 per cent. of *tannic matter* in the air-dried herb.

Extraction with Alcohol.—A quantity (7600 grammes) of the dried herb was extracted by continuous percolation with hot alcohol, and the greater portion of the alcohol removed. The resulting thin extract, which had a dark green color and an aromatic odor, was brought into a large flask and distilled in steam until oily drops were no longer visible in the condenser. There then remained in the distillation flask a quantity of resinous substance (*A*) and a dark-colored aqueous liquid (*B*), which were separately examined.

Examination of the Steam Distillate.

The distillate was a milky liquid, on the surface of which a small quantity of a greenish-yellow essential oil had separated. It was extracted several times with ether, the ethereal liquid washed with water, dried with anhydrous sodium sulphate, and the ether removed. The residual oil was distilled under the ordinary pressure, when it nearly all passed over between 220° and 230° C., and amounted to 19 grammes, corresponding to 0·25 per cent. of the weight of dried herb.

This *essential oil* had a brownish-yellow color, an odor resembling that of the herb, and was distinctly camphoraceous. It was readily soluble in 70 per cent. alcohol, and its solution gave a slight brown color with ferric chloride. It possessed the following constants: $d\ 15^\circ / 15^\circ$ C. $= 0{\cdot}9500$; $a_D + 7^\circ 36'$ in a 1 dcm. tube.

The aqueous portion of the distillate, from which the essential oil had been removed by means of ether, contained a small amount of a mixture of acids, which was found to consist chiefly of *formic* and *butyric acids.*

Examination of the Resins (*A*).

The mass of black, tarry resins in the distillation flask was separated from the aqueous liquid, then thoroughly washed with hot water, and dried. It amounted to 275 grammes, corresponding to 3·6 per cent. of the weight of air-dried herb. This crude resin was mixed with purified sawdust, and extracted successively with light petroleum, ether, chloroform, ethyl acetate, and alcohol. All these products were separately examined.

I. Petroleum Extract of the Resins.

This extract, which constituted by far the greater portion of the total resin, was a dark green, soft solid, and amounted to 170 grammes. Having ascertained by a preliminary experiment that it contained nothing of a basic, acidic, or phenolic nature, it was hydrolysed by boiling with an alcoholic solution of 50 grammes of potassium hydroxide. On subsequently removing the alcohol, a dark green mass was obtained, which was mixed with water, and then repeatedly extracted with ether. When shaking with the first portion of ether it was observed that the liquids contained a small amount of a flocculent precipitate. This was removed by filtration, and found to consist largely of the potassium salt of a fatty acid, but the amount of acid (m. p. about 81–83° C.) obtained from it was too small to admit of its being purified. The ethereal extract of the alkaline liquid was washed, dried, and the ether removed, when a semi-solid, yellow residue, weighing 50 grammes, was obtained. This was distilled under 15 mm. pressure, when the following fractions were collected: 140–205°; 205–265°; 265–330° C./15 mm.

Fractions 140–205° and 205–265° C./15 mm.—These fractions were somewhat thick, yellowish oils, but the one of higher boiling point contained a small amount of a crystalline solid. This was collected on a filter, and recrystallized from ethyl acetate, when it was obtained in beautiful leaflets, melting sharply at 59° C.

0·0600 gave 0·1865 CO_2 and 0·0787 H_2O. C = 84·8; H = 14·6.

$C_{27}H_{56}$ requires C = 85·3; H = 14·7 per cent.

This substance agrees in melting point and composition with the hydrocarbon *heptacosane*, and is doubtless identical with it.

The oily liquid from which this hydrocarbon had been separated was then mixed with the fraction of lower boiling point, and the mixture fractionally distilled under 20 mm. pressure, when it was resolved principally into two fractions, boiling at 145-175° and 200-230° C. / 20 mm. respectively. Both these fractions were light yellow, fairly mobile oils, possessing a somewhat fragrant odor. The one of lower boiling point (145–175° C. / 20 mm.) gave on analysis the following result:

0·1130 gave 0·3274 CO_2 and 0·1100 H_2O. C = 79·0; H = 10·8.
$C_{11}H_{18}O$ requires C = 79·5; H = 10·8 per cent.

A portion of this product was boiled with acetic anhydride, the product distilled, and then analyzed.

0·1054 gave 0·2970 CO_2 and 0·0968 H_2O. C = 76·9; H = 10·2.
$C_{11}H_{17} — O — CO — CH_3$ requires C = 75·0; H = 9·6 per cent.

The iodine value of the acetylated product was then determined.

0·2349 absorbed 0·1723 iodine. Iodine value = 73·4.

$C_{11}H_{17} — O — CO — CH_3$, containing one double linking, would have an iodine value of 122·1.

The fraction boiling at 200–230° C. / 20 mm. gave on analysis the following result:

0·0854 gave 0·2513 CO_2 and 0·0916 H_2O. C = 80·3; H = 11·9.
$C_{14}H_{24}O$ requires C = 80·8; H = 11·5 per cent.

It was then acetylated, and the product distilled and analyzed.

0·1057 gave 0·3006 CO_2 and 0·1041 H_2O. C = 77·6; H = 10·9.
$C_{14}H_{23} — O — CO — CH_3$ requires C = 76·8; H = 10·4 per cent.
0·2045 absorbed 0·1991 iodine. Iodine value = 97·4.

$C_{14}H_{23} — O — CO — CH_3$, containing one double linking, requires an iodine value of 101·6.

These results show that the above fractions did not consist of pure substances, but evidently contained *alcohols* which appear to possess the general formula $C_nH_{2n-4}O$, with one double linking. The viscid substances which usually accompany the phytosterols in small amount possess an odor resembling that of the above-mentioned alcohols, and they are probably similar in character. The amount of these fractions was too small to permit of their further purification.

Fraction 265-330° C. / 15 mm.—This fraction was by far the largest obtained. It almost all passed over above 290° C. / 15 mm., and, on cooling, solidified completely. It was crystallized three times from ethyl acetate, when a substance was obtained in the form of silky leaflets, melting at 68° C.

0·0757 gave 0·2356 CO_2 and 0·0986 H_2O. C = 84·9; H = 14·5.
$C_{31}H_{64}$ requires C = 85·3; H = 14·7 per cent.

This substance was thus identified as the hydrocarbon *hentriacontane.*

The first mother liquors from this hydrocarbon were of a dark brown color, and, after standing for some days, deposited a quantity of a substance in the form of crystalline plates. This was separated by filtration, and recrystallized from ethyl acetate containing a little dilute alcohol, when it was obtained in handsome plates, which melted at 134° C., and gave with acetic anhydride and sulphuric acid the color reaction characteristic of the phytosterols.

0·0970, heated at 105° C., lost 0·0048 H_2O. $H_2O = 4·9$.

0·0922 of anhydrous substance gave 0 2813 CO_2 and 0·0978 H_2O. $C = 83·2$; $H = 1·1.8$.

$C_{27}H_{46}O$, H_2O requires $H_2O = 4·5$ per cent.

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

This substance was apparently identical with the *phytosterol* obtained from the fatty oil of the seeds of *Gynocardia odorata*, R. Br. (*Jour. Chem. Soc.*, 1905, **87**, p. 898), as a mixture of the two substances melted at the same temperature (134° C.) at which each separately fused.

Maurenbrecher and Tollens (*Ber. d. deutsch. chem. Ges.*, 1906, **39**, p. 3581) have noted a color reaction, first observed by Rauchwenger and Neuberg, which is stated to differentiate between cholesterol and the phytosterols, and is conducted as follows:—A small portion of the substance to be tested, together with a trace of rhamnose, is dissolved in 1 5 c.c. of absolute alcohol, and concentrated sulphuric acid then cautiously added, when, if the substance be cholesterol, a raspberry-red color is produced at the junction of the two liquids, and afterwards extends throughout the whole. According to Rauchwenger and Neuberg, this reaction is not afforded by phytosterol. It was observed, however, by Maurenbrecher and Tollens (*loc. cit.*) that the substance isolated by them from cacao butter, although having the melting point (137° C.) and other characters of a phytosterol, gave the above-mentioned reaction, and they were therefore unable to decide whether this was not due to some adhering cholesterol. In order to ascertain the value of this test, we have applied it to pure cholesterol (m. p. 144–147° C., from Schuchardt), to the phytosterol from the species of *Lippia* under examination, to that from Gynocardia oil, and also to "rhamnol," $C_{20}H_{34}O$ (m. p. 135–136° C.),—the phytosterol occurring in Kô-sam seeds (*Pharm. Jour* , 1903, **71**, p. 186) and in cascara sagrada (*Proc. Amer. Pharm. Assoc.*, 1904, **52**, p. 299), when a precisely similar color was observed in every case. Furthermore, it was ascertained that the color was produced equally well in the absence of the trace of rhamnose. Since making these comparative tests, we have observed that similar experiments have been conducted by Ottolenghi (*Atti R. Accad. Lincei*, 1906 [V], 15, i, 44–47, and *Jour. Chem. Soc. Abstr.*, 1906, **90**, ii, p. 311), and with the same results. This test must therefore be declared valueless as a means of distinguishing between cholesterol and the phytosterols.

The alkaline, aqueous liquid, from which the above-described alcohols and hydrocarbons had been removed by means of ether, was then concentrated, acidified with sulphuric acid, and distilled in steam. The distillate contained a small quantity of an oily acid, which was extracted with ether and converted into its potassium salt, and from the latter six fractions of silver salt were successively precipitated. These silver salts were dried in a vacuum, and analyzed.

1st	fraction,	0·2703	gave	0·1396 Ag.	Ag = 51·6
2d	"	0·3047	"	0·1585 Ag.	Ag = 52·0
3d	"	0·2830	"	0·1474 Ag.	Ag = 52·1
4th	"	0·2509	"	0·1306 Ag.	Ag = 52·1
5th	"	0·1887	"	0·0988 Ag.	Ag = 52·2
6th	"	0·0947	"	0·0498 Ag.	Ag = 52·6

$C_5H_9O_2$ Ag requires Ag = 51·7 per cent.
$C_4H_7O_2$ Ag " Ag = 55·4 " "

The acid removed by ether from the steam distillate therefore consisted essentially of a *valeric acid*, and, on examining the aqueous liquid from which it had been separated, it was found to contain some *formic acid* together with a little *butyric acid*.

Isolation of a New Crystalline Alcohol, Lippianol, $C_{25}H_{35}O_3$ — *OH.*

The liquid in the distillation flask, from which the above-described volatile acids had been obtained by steam distillation, was shaken with ether, when it was observed that a small quantity of a dark green substance remained undissolved. This was collected on a filter and dried on a porous tile, after which it was dissolved in ethyl acetate and treated with animal charcoal, when, after filtering the liquid, a substance separated in the form of colorless needles. The examination of this substance is described below, as a further quantity of it was subsequently obtained.

The ethereal liquid, from which the above-mentioned solid had been removed, was separated from the aqueous liquid, washed, dried and evaporated. The residue, which consisted of a dark green, sticky mass, was treated with several portions of warm, light petroleum to remove the fatty acids it contained, the residual green, resinous product mixed with a small amount of warm ether, and then allowed to stand. At the end of a few days it had deposited a quantity of a granular solid, and this was separated from the green, uncrystallizable syrup. After solution in alcohol, purification with animal charcoal, and several recrystallizations, this substance was obtained in the form of handsome, white needles, which were found to be identical with those above mentioned. This substance is not an acid, as it was unacted upon by aqueous alkalies. When boiled with acetic anhydride it gave an acetyl derivative, which was obtained in the form of an uncrystallizable syrup. It is evident, therefore, that it is of an alcoholic nature, and, as it is not identical with any substance hitherto described, the name *Lippianol*[1] may appropriately be assigned to it.

Lippianol is sparingly soluble in alcohol, and very sparingly so in ethyl acetate, but crystallizes from both these solvents in colorless needles, which melt, with decomposition, at 300–308° C.

0·0861 gave 0·2361 CO_2 and 0·0712 H_2O. $C = 74·8$; $H = 9·2$.
0·0873 " 0·2391 CO_2 " 0·0724 H_2O. $C = 74·7$; $H = 9·2$.
$C_{25}H_{36}O_4$ requires $C = 75·0$; $H = 9·0$ per cent.
$C_{25}H_{38}O_4$ " $C = 74·6$; $H = 9·5$ " "

It is evident from these analyses that lippianol possesses the empirical formula $C_{25}H_{86}O_4$. It is optically active, and a determination of its specific rotatory power gave the following result:

0·1123, dissolved in 25 c.c. of absolute alcohol, gave $a_D + 0° 35'$ in a 2 dcm. tube, whence $[a]_D + 64·9°$.

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[1] The designation *Lippianol* has been adopted in view of the fact that, as already noted, the name *Lippiol* has previously been given by Podwissotzki (*loc. cit.*) to a crystalline substance of indefinite character and composition obtained by the distillation of the so-called *Lippia mexicana*.

As already stated, lippianol is unaffected by aqueous alkalies, but, when boiled with a strong solution of potassium hydroxide containing some alcohol, it forms a compound with the alkali which does not separate even after the removal of the alcohol, and, on acidifying this liquid, the lippianol is precipitated unchanged. Although obtained from that portion of the resins which was extracted by light petroleum, lippianol is quite insoluble in this solvent, and cannot, therefore, have occurred in the plant in a free state. The fact that it was not obtained in association with the other alcohols already described, is owing to its above-mentioned property of forming a compound soluble in water when treated with alcoholic potash. The amount of lippianol obtained (3·5 grammes) is equivalent to about 0·05 per cent. of the weight of the air-dried plant.

Methyl Lippianol, $C_{25}H_{35}O_3 - OCH_3$.—As the acetyl derivative of lippianol was unsuitable for the purpose of ascertaining the number of hydroxyl groups contained in this alcohol, and as a determination by Zeisel's method showed the absence of methoxyl groups, about 1 gramme of the lippianol was completely methylated by treatment with sodium methoxide and methyl iodide. The number of hydroxyl groups present in the original substance was then ascertained by determining the percentage of methoxyl in the resulting derivative.

Methyl lippianol crystallizes from dilute alcohol in colorless needles, which melt, with decomposition, at about 260° C. An estimation of the methoxyl groups, by means of Perkin's modification of Zeisel's method (*Jour. Chem. Soc.*, 1903, **83**, p. 1367), gave the following result:

0·3034 gave 0·1725 AgI. $CH_3O = 7·5$.
$C_{25}H_{35}O_3 - OCH_3$ requires $CH_3O = 7·5$ per cent.

Lippianol is therefore a monohydric alcohol.

Examination of the Non-volatile Acids.

The light petroleum liquid containing the non-volatile fatty acids, which was separated from the product from which the lippianol was obtained, as above described, was washed, dried and evaporated. The residue, which weighed 50 grammes, was distilled under a pressure of 15 mm., when it passed over between 235° and 265°, and crystallized on cooling. It was then dissolved in a little warm ethyl acetate, and the solution allowed to cool, after which the crystalline acid which had separated was collected on a filter. These crystals first melted at 53° C., but after repeated crystallization from ethyl acetate the melting point was raised to 74° C., after which it remained constant.

0·1015 gave 0·2844 CO_2 and 0·1176 H_2O. $C = 76{\cdot}4$; $H = 12{\cdot}9$.
$C_{20}H_{40}O_2$ requires $C = 76{\cdot}9$; $H = 12{\cdot}8$ per cent.

It is evident that this substance was *arachidic acid.*

The mother-liquors from this arachidic acid were concentrated, when a further quantity of crystals was obtained. This was repeatedly recrystallized from a variety of solvents, but the melting point could not be raised above 54° C. It had the appearance of a mixture, and an analysis indicated that it consisted of *palmitic* and *stearic acids.*

The original filtrate from these solid acids contained a considerable quantity of an oil, which was found to be a mixture consisting largely of unsaturated acids. It was, therefore, converted into the lead salts, and the latter treated with ether and filtered. The ethereal solution thus obtained was shaken with concentrated hydrochloric acid, the mixture filtered, and the separated ethereal liquid washed, dried and evaporated. The unsaturated acids were thus obtained as a light yellow oil, which, on distillation under 15 mm. pressure, passed over between 225° and 245° C.

0·0969 gave 0·2742 CO_2 and 0·1001 H_2O. $C = 77{\cdot}2$; $H = 11{\cdot}5$.
$C_{18}H_{32}O_2$ requires $C = 77{\cdot}1$; $H = 11{\cdot}4$ per cent.
0·3270 absorbed 0·5215 iodine. Iodine value = 159·5.

An acid of the formula $C_{18}H_{32}O_2$, containing two double linkings, requires an iodine value of 181·4.

From these results it is evident that the unsaturated acids consisted largely of *linolic acid*, or of an acid isomeric with the latter.

II. Ether Extract of the Resins.

The portion of the resins soluble in ether was dark green in color, and amounted to 54·5 grammes. It contained a small quantity of a substance which was only very sparingly soluble in ether, and which, when dissolved in warm ethyl acetate, and the solution cooled, separated in the form of a white, amorphous powder, which melted and decomposed at 210–213° C.

The ethereal solution of the readily soluble portion of the extract, which was by far the greater part, was then shaken with a solution of sodium carbonate. This treatment caused the separation of the sodium compound of an acidic resin, in the form of a dark green, slimy mass, which was sparingly soluble in water. On treatment with sulphuric acid, this sodium compound yielded a quantity (40 grammes) of a resin, which, after solution in ethyl acetate, and purification with animal charcoal, was obtained in the form of an uncrystallizable, light-colored varnish. The ethereal liquid which had been extracted with sodium carbonate solution was treated with a 10 per cent. solution of sodium hydroxide, but this afforded only a small quantity of a tarry sodium compound, from which nothing crystalline could be obtained. The portion of the ether extract of the resins devoid of acidic properties still remained dissolved in the ether, and this solution was therefore washed, dried and evaporated. The dark green, resinous residue was allowed to stand for a few days, when it deposited a very small quantity of a granular substance, which, when separated from its solution in ethyl acetate, was yellowish in color, and apparently minutely crystalline. As this substance possessed the properties of a hydrocarbon, it was warmed on a water-bath with concentrated sulphuric acid during half an hour, in order to destroy any resinous impurities contained in it. After this treatment the substance was recovered, and was apparently in a state of greater purity, as it was then colorless. It melted at 80° C., and was doubtless a hydrocarbon of high molecular weight, probably possessing a formula approximating to $C_{39}H_{80}$.

III. Chloroform Extract of the Resins.

This was a dark green, soft solid, and weighed 24 grammes. It was redissolved in chloroform, and extracted with a solution of sodium carbonate. On acidifying the alkaline solution thus obtained, a brown powder was precipitated, which was collected and dried on a porous tile. This substance was then dissolved in alcohol, and purified by means of animal charcoal, when it was obtained in beautiful yellow needles, which melted and decomposed at about 268° C. The total amount obtained was less than 0·1 gramme, but it was analyzed with the following result:

0·0518 gave 0·1110 CO_2 and 0·0265 H_2O. $C = 58·4$; $H = 5·7$.
$C_{22}H_{26}O_{10}$ requires $C = 58·7$; $H = 5·8$ per cent.

The chloroformic liquid, after having been shaken with a solution of sodium carbonate, was treated with potassium hydroxide solution, and this caused the separation of a tarry potassium compound, but nothing crystalline could be obtained from it.

IV. Ethyl Acetate Extract of the Resins.

This was very small in amount, but afforded a minute quantity of a crystalline substance which melted at 123° C.

V. Alcohol Extract of the Resins.

This was a black resin, and amounted to 25 grammes. Nothing crystalline could be obtained from it.

Examination of the Aqueous Liquid (B).

The dark-colored, aqueous liquid which had been decanted from the cake of resins, as previously described, was extracted ten times with ether, and the yellow, ethereal liquid shaken with a solution of sodium carbonate. The alkaline liquid thus obtained was acidified with sulphuric acid, when a yellow solid was precipitated. This was collected on a filter, and crystallized from alcohol, when it was obtained in the form of yellow needles, possessing a silky lustre. This substance melted and decomposed at about 267° C., and on analysis afforded the following results:

0·0756 gave 0·1570 CO_2 and 0·0344 H_2O. $C = 56·6$; $H = 5·0$.
0·0803 " 0·1655 CO_2 " 0·0362 H_2O. $C = 56·4$; $H = 5·0$.

The percentage composition of this substance agrees within the limits of experimental error with that required for several possible empirical formulæ, but, as less than 0·3 gramme of the substance was obtained, it is impossible to decide which of these formulæ should be assigned to it. The substance does not contain nitrogen, and, so far as could be ascertained, it is not identical with any substance heretofore described. The ethereal liquid from which this substance had been removed by shaking with a solution of sodium carbonate only contained a small quantity of green resinous matter.

The aqueous liquid, which had been extracted with ether, was then treated with a slight excess of basic lead acetate, and the copious yellow precipitate collected on a filter. A portion of this precipitate was suspended in water and decomposed with hydrogen sulphide; but on concentrating the filtrate only a dark-colored tarry mass was obtained, from which nothing crystalline could be isolated.

The filtrate from the basic lead acetate precipitate was freed from lead by means of hydrogen sulphide, and, after filtering, was concentrated under diminished pressure. The dark brown syrup thus obtained reduced Fehling's solution, and on treatment with phenylhydrazine acetate gave a small quantity of an osazone melting at 210° C. On allowing the syrupy liquid to stand for some time, a considerable quantity of crystals separated, but these were found to consist only of potassium and calcium sulphates. When warmed with potassium hydroxide it evolved ammonia, but did not give any precipitate with alkaloidal reagents. The syrup was therefore mixed with prepared sawdust, and the mixture dried in a vacuum over sulphuric acid, after which it was extracted in a Soxhlet apparatus with ethyl acetate. This removed a quantity of an uncrystallizable syrup, which did not reduce Fehling's solution until after it had been boiled with a dilute mineral acid, a behavior which indicated the possible presence of a glucoside. A quantity of the syrup removed by ethyl acetate was, therefore, diluted with an equal volume of water, 10 per cent. sulphuric acid added, and the mixture gently heated. When the temperature reached about 50° C. a dark-colored, flocculent substance was precipitated, which soon coalesced to a black resin. The mixture was then heated to the boiling point, diluted with water, and distilled in steam, when a slightly turbid distillate was obtained, from which ether removed a few drops of a liquid having a strongly aromatic odor. The distillation flask then contained a hard, black resin, which was insoluble in all the usual solvents and in alkalies, together with a brown aqueous liquid containing sugar, and this, after the removal of the sulphuric acid, afforded an osazone melting at 211° C. It was evident, therefore, that the ethyl acetate extract of the aqueous liquid contained a *glucoside* which is readily hydrolyzed by sulphuric acid; but the only definite hydrolytic product obtained was a sugar, which appeared to consist chiefly of optically inactive glucose.

SUMMARY.

This investigation has shown that *Lippia scaberrima,* Sonder, contains, besides resins and other amorphous products, the following substances:

(1) About 0·25 per cent. of an aromatic essential oil.

(2) Heptacosane, $C_{27}H_{56}$.

(3) Hentriacontane, $C_{31}H_{64}$.

(4) A very small amount of a paraffin, melting at 80° C.

(5) Phytosterol, $C_{27}H_{46}O$ (m. p. 134° C.).

(6) Unsaturated alcohols, possessing the probable general formula $C_nH_{2n-4}O$, and containing one double linking.

(7) Formic and butyric acids in a free state.

(8) Esters of formic, butyric, valeric, arachidic, linolic and other acids.

(9) A new, colorless, crystalline substance, *lippianol*, $C_{25}H_{36}O_4$, which has the characters of a monohydric alcohol, and was obtained in an amount of about 0·05 per cent.

(10) Two *yellow crystalline substances* in very small amount, both of which melt at about 267°, and also a trace of a crystalline substance melting at 123° C.

(11) A *glucosidal substance* which could not be isolated, and which, besides glucose, yielded only indefinite hydrolytic products.

(12) Glucose (chiefly the inactive form).

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