CHEMICAL EXAMINATION
OF
The Roof of Neriam Odorum (Kanher)

By Shunker Trimbak Gadre.

INTRODUCTION.

Nerium Odorum, Linne (Nat. Order Apocynacœ,) is a large, erect, stout shrub with linear lanceolate, thickly coriaceous, acuminate leaves, with faintly sweet-scented, white, red or showy rose-coloured flowers. It goes by the name Karaveera in Sanskrit, and Kanher in Marathi. It is a very familiar plant in the Western Deccan, and is almost an unfailing associate of water streams and rivers.

In Sanskrit medical works the plant is described as hot and poisonous. Its root is recommended for external application in skin diseases and is a popular remedy for venereal diseases. The oil prepared from the root-bark is recommended for skin diseases of a scaly nature and for Leprosy. It is also stated that the leaves are a counter-poison to serpents. The active principles of Nerium Odorum are powerful heat poisons. [*Pharmacographia Indica*, Vol. II p. 399) M. E. Picszczek (*Archiv. d. Pharm.*, 1890, (iii), *38*, 352] obtained from the bark, a glucoside, which he found to be very poisonous and similar to strychnine in its action. The root is the more toxic part of the plant. The red variety, *i. e.* the one bearing red coloured flowers, is considered the strongest and most fatal.

H. G. Greenish (*Pharm. Journ.*, 1881, p. 873) obtained, by masceration of the bark with cold alcohol, an extract which he separated into two fractions, viz : (i.) Soluble in water, but insoluble in chloroform and (ii.) soluble in chloroform, but insoluble in water. The portion soluble in water was named Neriodorein, and that insoluble in water was called Neriodorin. Both of these were found to be free from nitrogen ; they possessed an intensely bitter taste, Neriodorein producing, in addition, " a numbing sensation lasting for a considerable time ". Both these substances were obtained as amorphous solids. With regard to their chemical nature Greenish suggests that Neriodorein may be a glucoside. Beyond this he was unable to establish either the identity or the chemical entity of the products he obtained.

Bose (*Proc. Chem. Soc.*, 1901, *17*, 92-93) repeated Greenish's work and he differentiated the extract of the root into three portions, viz :

i. a portion soluble in boiling water only—This was named *Neriodorin.*

ii. a portion soluble in cold and boiling water—This was named *Neriodorein.*

iii. a portion insoluble in cold or boiling water, but soluble in ether and benzene. This was named *Karabin.*

Recently, some work was carried out by M. A. Leulier on the bark of an Oleander obtained from Algeria. [*Journ. de Pharm. et de Chemie* 1911, (VII), *4* ; 1912, (VIII), *5*,]. Dubigadoux and Durien had obtained from the latex of the bark, a glucoside, which they supposed to be analogous to Strophantine, and Leulier was able to prove that the glucoside is l-strophantine, $C_{40}H_{66}O_{19}$, M. P. 179°-180°C.

EXPERIMENTAL.

The material employed in the present investigation consisted of the root of the white as well as the red variety of *Nerium odorum.* It was gathered in the Krishna Valley (Bombay Presidency), and was kindly supplied by Mr. K. G. Limaye, B. A., of Sangli to whom my best thanks are due.

A small portion (20 grams) of the finely powdered bark was digested with Prollius' fluid, and the resulting product was subjected to the usual tests for an alkaloid, but with negative results.

Another portion (40 grams) of the powdered bark was completely extracted in a Soxhlet's apparatus with various solvents when the following amounts of extract dried at 100°C. were obtained :—

Solvent.	Weight of extract in grammes.		Per cent of material extracted.
Petroleum Ether (B. P. 60-70.°).	1·80	=	4·5
Ether	0·24	=	0·57
Chloroform	2·4	=	6·0
Ethyl Acetate	3·32	=	8·3
Alcohol	5·00	=	12·5
Total......	12·76	=	31·87

For the purpose of a complete examination, 38 kilograms of the powdered root were completely extracted with hot alcohol by a process of continuous percolation. After removing a greater part of the solvent there remained a viscid, dark-coloured, strongly smelling extract, amounting to 8·2 kilograms.

I. Distillation of the Extract with Steam.

Separation of an essential oil.

The entire extract of the root was mixed with water, and distilled in a current of steam. The distillate which was neutral to litmus, was extracted with ether, the ethereal liquid dried, and the solvent removed, when about 15 grams of an orange-coloured, essential oil was obtained. This oil had a characteristic not unpleasant, ethereal odour, and gave the colour reaction for furfuraldehyde. Distilled at ordinary pressure, a third of its volume distilled over between 50° and 80°C. as a colourless very mobile liquid. Under diminished pressure a fraction distilled at 112°/45 mm. as a colourless liquid, but darkened on exposure to light. There remained in the distillation flask a dark brown resinous material,

The following physical constants of the essential oil were determined :—

i. Specific Gravity $D_{4°}^{30°}=0.8660$

ii. Optical Rotation $[\alpha]_D^{31°}=-4.088°$

(In chloroform solution)

iii. Refractive Index $n_D = 1.40315$ at 25°.5C.

Owing to its small quantity, a further investigation of the oil could not be undertaken.

After steam-distillation, a dark coloured aqueous liquid (A) was left in the flask together with a quantity of a soft dark brown resinous solid (B). The aqueous liquid was syphoned off and the resinous solid washed several times with hot water ; these washings were added to the main aqueous liquid (A). The following approximation of the solubility of the extract in water, wa arrived at.

Per cent of the extract soluble in water=45.

Per cent of the extract insoluble in water=55.

II. Examination of the Aqueous Liquid (A),

The aqueous liquid was filtered and concentrated to about a fourth of its original volume. It was then extracted with ether, chloroform, and amyl alcohol, in the order mentioned.

The ethereal extracts were united, washed, dried and the solvent removed, when about 30 grams of a viscid, brown residue was obtained. The residue was redissolved in other and shaken up successively with aqueous solutions of ammonium carbonate, sodium carbonate, and sodium hydroxide. Each of these alkaline liquids was acidified, extracted with ether, and the solvent evaporated. Nearly 15 grams of the ether extract were removed by this treatment, but only from the sodium hydroxide extract could any definitely crystalline solid be obtained. Two kinds of crystalline solid separated from solution in petroleum ether (B. P. 50—60°): (i) colourless nodular crystals and (ii) yellowish brown small cylindrical needles M. V. 140°—141°C. The latter was recrystallised from water, but its melting point was unchanged. Its dilute aqueous solution gives an intensely red colouration with a drop of a dilute solution of ferric chloride. The amount of this crystalline phenolic compound was too small for analysis.

After the removal of acidic bodies, the ethereal solution was washed with water, dried and the solvent removed, when 16 grams of a yellow, transparent viscous oil was obtained. This neutral product had a very bitter, biting taste, which persisted for some time; crystalline products could not be isolated from it.

2. The aqueous liquid was next thoroughly extracted with chloroform. The chloroform extracts were united, washed, dried and the solvent removed, when 220 grams of a dark-brown sticky solid were obtained. Nearly half of this extract consisted of neutral products, which were resinous and possessed a biting but not bitter, taste.

3. The aqueous liquid was then extracted several times with amyl alcohol. The amyl alcoholic extracts were united, washed, dried and the solvent removed under diminished pressure, when 250 grams of a brown thick resinous semi solid were obtained. This extract contained about 60% neutral products; it did not contain free reducing sugar, but when its aqueous solution was boiled with 5% sulphuric acid for 2—3 minutes, a test for glucose was readily obtained with Fehling's solution. This behaviour points to the presence of a glucoside in the neutral products of the amyl alcoholic extracts. An attempt to isolate the glucoside in a crystalline form did not meet with any success.

4. The aqueous liquid was now treated with a 10% aqueous solution of basic lead acetate for the purpose of precipitating tannins, colouring materials, &c. The precipitate was collected, washed several times with water and filtered. All the filtrates and washings were combined and concentrated under reduced pressure. An aqueous solution of this no longer gave a precipitate with basic lead acetate solution.

After the removal of tannins, &c. the excess of lead was removed by means of hydrogen sulphide, and the filtrate, after removal of lead sulphide, was concentrated under reduced pressure. A quantity, 1450 grams, of a brown viscid material was obtained. This syrup had a smell resembling that of honey and a taste which was both sweet and bitter. It contained 46.23 p. c. free reducing sugar, whose amount was determined with the aid of standard Fehling's solution. A known quantity of the mass was dissolved in water and boiled with 5% aqueous hydrochloric acid. The amount of reducing sugar was again determined by means of standard Fehling's solution.

Per cent of reducing sugar (free) in the syrup	...	46.23
Per cent of reducing sugar after hydrolysis	...	63.4

. • . Percent increase of reducing sugar after hydrolysis=17.17.

The above results show that there is in the syrup a considerable proportion of a glucoside. An attempt was made to isolate the glucoside in a crystalline form, but without success. The other component of the glucoside, beside glucose, could not be obtained in any definitely crystalline form. ,

From the free reducing sugar in the syrup an Osazone was prepared and recrystallised from pyridine. Yellow, cylindrical soft needles were obtained melting at 204°—205°C. The Osazone prepared from pure glucose melted at 205°—206°C. A mixture of the two Osazones gave M. P. 204°—206° G The free reducing sugar in the syrup was therefore glucose.

III. Examination of the Resinous Material (B).

The crude resinous material which had been separated from the aqueous liquid (A) and thoroughly washed with water as previously mentioned was dried in a steam-oven. By this means the resinous material separated into (i) a hard solid resin, (1340 grams) and (ii) a thick oily layer which became a soft rosin on cooling, (728 grams).

1. *Examination of the Hard Resin.*

The entire amount of the dry resin, which represented 4.8 p. c. of the root, was finely powdered, mixed with purified sawdust and the mixture extracted successively in a large Soxhlet's apparatus with various solvents. The weights of the products, dried in the steam-oven were as follows:—

Solvent.	Weight of Extracts in
Petroleum (50°—70°C)	153·5
Ether	159·0
Chloroform	477·0
Ethyl acetate	93·5
Alcohol	160·0
Total ...	1043

The ethyl acetate and alcohol extracts do not represent the whole amounts since part of the mixture of resin and sawdust was removed after its extraction with chloroform.

1.a. *Light Petroleum Extract of Hard Resin.*

After the removal of the solvent from the petroleum extract the residue was dissolved in ether, and the ethereal liquid shaken successively with aqueous ammonium carbonate, sodium carbonate, and sodium hydroxide, when it was found that of the total petroleum extract was soluble in alkalis.

The alkaline extracts of the free acids were acidified and again shaken up with ether. The liberated acids were dissolved by ether leaving behind a grey amorphous solid, insoluble in ether. A further quantity of this grey powder was obtained from the neutral products. Attempts were made to crystallise it from a mixture of ethyl acetate and alcohol but it was always deposited as an amorphous brown solid. The substance could not be obtained in a crystalline form and gave a glucoside reaction. It is sparingly soluble in petroleum ether and ether, easily soluble in ethyl acetate but less soluble in absolute alcohol.

Identification of the Free Fatty Acids.

The acids were liberated from their alkaline solutions and were purified by conversion into their methyl esters which were twice distilled under reduced pressure, when a yellow oil was obtained.

The distilled methyl esters were saponified and the saturated and unsaturated acids obtained were separated by means of their lead salts. The lead salt insoluble in ether gave 3 grams of solid acids which were crystallised three times from alcohol when 1·6 grams of snow-white crystals were obtained melting at 67°—68°C.

Pure Stearic Acid has M. P. 69°

0·1202 gram required 0·42 cc. of Normal Alkali

whence Neutralisation Equivalent = 286.

Stearic Aoid has 284.

The above solid fatty acid was, therefore, Stearic Acid.

The lead-salts soluble in ether, when decomposed, gave a yellow oil.

0·0946 gram absorbed 0·0724 gram Iodine.

∴ Iodine value of the Acid = 76·5.

Oleic Acid requires Iodine value 89.

Neutralisation Equivalent of the Acid was 284

Oleic Acid has 282.

It, therefore, seems to be a mixture of oleic and a little of stearic acid.

Neutral Products from Hard Resin.

The ethereal liquid which had been shaken with aqueous alkalis, as described above, was subsequently evaporated and the residue consisting of neutral products was saponified by boiling with alcoholic potash. The alcohol was then evaporated, water added, and the alkaline mixture was extracted many times with ether, to remove unsaponifiable neutral substances.

Identification of the Combined Fatty Acids.

The aqueous alkaline liquid mentioned above contained the potassium salts of the combined acids. It was acidified and again extracted with ether. The ethereal solution of the acids was washed with a little water and the solvent removed, when a "quantity of a brown soft solid was obtained ; this was distilled in a current of steam. A small amount of volatile acids was obtained; in this (i) formic acid and (ii) butyric acid were identified by means of the ethyl esters and para-toluidides. The quantity of these acids was very small.

The acids remaining in the distillation flask were separated by means of their lead salts. The portion insoluble in ether gave solid fatty acids which were purified by conversion into methyl esters. These on distillation gave two fractions, viz.

(i) B. P. 210°/10mm. and (ii) B. P. 215°-230°/10mm, both of which solidified on cooling.

The first fraction after crystallisation from absolute alcohol gave crystalline tufts, (1·5 grams) melting at 37-38°.

Molecular weight determinations gave the following value.—

0·0718 gram Methyl Ester depressed the freezing point of 13·06 gram Benzene by 0·0942°.

whence M. W. = 291·8.

Pure Methyl Stearate melts at 38°

and has M. W. = 298.

The above ester, therefore, appears to be methyl ester of stearic acid.

The second fraction also gave a large amount of methyl stearate.

The solid combined acid, therefore, consists mainly of stearic acid.

The portion of lead salts, soluble in ether, when decomposed by hydrochloric acid, gave a brown viscous liquid, which was converted into its methyl esters. The esters were distilled under diminished pressure, when 8 grams of a pale yellow oil was obtained. The acid obtained by hydrolysing this ester consisted mainly of *Oleic Acid.*

0·23 gram absorbed 0·18796 gram Iodine whence Iodine value = 81·7.

$C_{18}H_{34}O_2$ requires Iodine value — 89.

The acid gave Neutralisation value = 280.

$C_{18}H_{34}O_2$ requires N. V. = 282.

Unsaponifiable constituents of the Light Petroleum Extract of Hard Resin.

The ethereal liquid, obtained by extracting with ether the hydrolysed light petroleum extract of the resin, as above described, was dried and the solvent removed when about 30 grams of an orange coloured, soft, transparent solid was obtained. An attempt was made to separate the constituents of this material by fractional crystallisation, but without success. The whole mass of the unsaponifiable products was then completely freed from solvent and kept in a desiccator, After some days crystals began to separate in the soft solid and soon spread throughout the mass. The crystalline portion was recovered by crushing the mass under a small quantity of alcohol, filtering and washing with alcohol, A colourless crystalline residue was obtained, most of the oily non-crystalline portion being easily dissolved away by alcohol.

This proved to be identical with the crystalline neutral substance isolated from the soft resin by a similar process, and termed Kanerol (p. 195).

1.b. *Ethereal extract of Hard Resin.*

This extract possessed a bitter biting taste, due to the presence in it of a neutral resinous substance which was soluble in water to some extent.

When redissolved in ether, a small amount of finely divided silvery powder, insoluble in ether, was obtained and a further quantity of the same powder was formed when the ethereal solution was shaken several times with water.

The aqueous extracts were combined and evaporated on the water-bath when 2·5 grams of a resinous non-glucosidic neutral substance was deposited.

The grey amorphous powder could be hydrolysed with dilute sulphuric acid, and yielded after hydrolysis a test for reducing sugar with Fehling's solution.

The ethereal solution of the extract freed in large measure from the grey powder and bitter substance soluble in water, as mentioned above, was extracted several times with aqueous alkalis.

The ethereal solution from which the free acids were removed, was washed with water, dried and the solvent removed when 16·5 grams of an orange coloured oily neutral product was obtained. This neutral product was saponified with 10% alcoholic potash. From the unsaponifiable product a small amount of a colourless crystalline substance was obtained, which after repeated crystallisations from alcohol, was found to be identical with the product obtained from the petroleum ether extract of the hard resin. It melted at 180°-181° (uncor.)

No further examination of the unsaponifiable products mentioned above was undertaken.

From the above saponification experiment, besides the usual solid fatty acids viz. stearic and palmitic there was obtained a small amount of a crystalline aromatic acid. This was collected and twice crystallised from alcohol when colourless, thin small crystalline plates were obtained melting at 243°-245°. The amount of this acid, viz. 0·08 gram was not enough for an analysis.

1.c. *Chloroform Extract of the Hard Resin.*

This extract formed the largest portion of the hard resin being about 47 p. c, of its total weight. In addition to a large quantity of resin acids it contained about 30 p. c. of its weight of neutral products.

1.d. *Ethyl Acetate and Alcohol extracts of the Hard Resin.*

These extracts consisted of acids which were soluble in aqueous sodium carbonate and possessed most of the character of resin acids.

2. *Examination of the Soft Resin.*

From the entire amount of soft resin, viz 728 grams, 342 grams were dissolved in a small quantity of alcohol, mixed with purified saw-dust and the thoroughly dried mixture extracted successively in a large Saxhlet's apparatus with various solvents. The solvent was distilled off from the respective extracts and the recovered products dried in a water-oven when the following weights were obtained:—

Solvent.	Weight of Extract in grams.	%Extract.
Petroleum Ether (50°—70°)	283	82.7
Ether	48	14.03
Chloroform	5	1.46
Ethyl acetate	2	0.58
Alcohol	1.5	0.435
	Total=340	

2.a. *Light Petroleum Extract of the Soft Resin.*
Identification of Free Fatty Acids.

The extract, after removal of the solvent, was dissolved in ether and the acids isolated in much the same manner as described under the hard resin (p. 186). The same grey amorphous powder (7 grams) was obtained as in the case of the hard resin. The acids were transformed into their methyl esters and distilled under diminished pressure, when 37 grams of a pale yellow oil was obtained, this was saponified and the liberated acid converted into their lead salts. From the lead salts insoluble in ether about 8 grams of a soft solid were obtained. This was crystallised three times from alcohol when two fractions were obtained.

Fraction I	·2 grams	M. P. 48°—50°.
Fraction II	3 grams	M. P. 52°—55°.

Fraction I.

0·1867 gram required 9·3 cc. of 0·0738 N Alkali whence Neut. Equiv. = 271·6.

Fraction II.

(i) 0·1268 gram required 6·25 cc. of 0·0738 N Alkali whence Neut. Equiv. = 274·8.

(ii) 0·1632 gram gave 0·4524 gram CO_2, and 0·1908 gram H_2O.

Whence C=75·6 p. c. and H=12·9 p. c.

$C_{18}H_{36}O_2$ requires C=76·06 p. c. ; H=12·7 p. c.

$C_{16}H_{32}O_2$ requires C=75 p. c.; H=12·6 p. c.

Found by analysis C=75·6 p. c. H=12·9 p. c.

Evidently, the above solid acids were a mixture of palmitic and stearic acids.

The lead salts soluble in ether gave a yellow oil, (20 grams).

Analysis :—

(i) 0 0962 gram absorbed 0.1083 grams Iodine whence Iodine value = 112.6%

(ii) 0.1250 gram absorbed 0.1405 gram Iodine whence Iodine value = 112·0%

The acids appeared to be a mixture of unsaturated acids. About 5 grams of this mixture were converted into their bromides. A crystalline bromide M. P. 113°—114°., was obtained.

Linolic tetrabromide has M. P. 114°—115°.

Analysis.

(i) 0.1119 gram gave 0.0559 gram Bromine
whence Br. — 55·3 p.c.

$C_{18}H_{32}Br_4O_2$ requires Br=53·3 p. c.

The liquid bromide from which the above crystalline bromide was removed, was analysed.

(i) 0.2793 gram gave 0.0987 gram Bromine
whence Br — 35.34 p. c.

$C_{18}H_{34}O_2Br_2$ requires Br. =36.2 p. c.

From the above results of analyses the liquid acids appear to be a mixture of oleic and linolic acids.

Examination of the Neutral portion of the light Petroleum Extract of the Soft Resin.

The ethereal solution of the extract from which free acids were removed, was washed with water, dried and the solvent removed, when an orange-red soft mass was obtained. This product was saponified with 10%. alcoholic potash, alcohol evaported, water added, and the alkaline mixture extracted with ether, when a large quantity of unsaponifiable matter was removed.

Identification of the Combined "Fatty Acids.

The acids obtained after saponification were transformed into their methyl esters and about 34 grams distilled at 180°-250° under 4-6 mm. pressure. From the esters, after saponification, 25 grams of unsaturated acids were obtained ; the neutralisation equivalent was found to be 299. These acids were distilled under diminished pressure, when a straw yellow, rather viscous oil passed over.

Analysis :—

(i) 0.1188 gram absorbed 01213 gram Iodine
whence Iodine value=102·1.

(ii) 0·1290 gram absorbed 0·13246 gram Iodine
whence Iodine value=102·7

$C_{18}H_{34}O_2$ requires Iodine value=90· 1
$C_{18}H_{32}O_2$ requires Iodine value=181·4

About 5 grams of the above liquid acids were converted into their bromides. A colourless crystalline product was obtained together with a thick oily orange liquid.

The crystalline product was thrice crystallised from petroleum ether (30°—40°), when a pure product was obtained melting at 114°—115°. Linolic acid tetrabromide melts at 114°—115°.

Analysis:—

(i). 0·1337 gram gave 0·1748 gram CO_2 and 0·0660 gram H_2O.

Whence C=35·68 p. c.; H=5·48 p. c.

(ii). 0·1119 gram gave 0·0592 grain bromine

Whence Br=52·94 p. c.

$C_{18}H_{32}O_2Br_4$ requires

C=36 p. c.; H=5·33 p. c. and Br=53·3 p. c.

The above compound is, therefore, Linolic acid tetrabromide. After the removal of the crystalline bromide, there remained an orange coloured thick liquid. This was analysed with the following results.

(i). 0·2460 gram gave 0·08528 gram Bromine whence Br=34·66 p. c.

(ii). 0·3149 gram required 9·5 cc. of 0 0738 N alkali whence neutralisation equivalent=448.

$C_{18}H_{34}O_2Br_4$ requires neut. equivalent=442 and Br=36·2 p. c.

The liquid bromide, therefore, is mainly Oleic dibromide. The above results indicate that the liquid unsaturated acids consisted chiefly of a mixture of oleic and linolic acids.

About 15 grams of saturated acids were obtained and as these contained a neutral substance, they were dissolved in ether and the ethereal solution was extracted with aqueous sodium carbonate. The alkaline extract was acidified and again extracted with ether. The organic acids thus obtained were transformed into their methyl esters. Prom the solid methyl ester an acid was isolated melting at 62°—64° and boiling at

222°—230° under 4 mm. pressure. When crystallised from ethyl -acetate it gave the following fractions :—

I. melting 74°—75°.
II. ,, 65°—66°.
and III. ,, 66°—69°.

These were analysed with the following results :—

Fraction I—M. P. 74°—75°.

(i). 0·1316 gram required 6·2 cc. of 0·0738 N alkali
Whence neutralisation equivalent=283·5

(ii). 0·1434 gram silver salt gave 0·0395 grain Ag.
Whence equivalent of the Acid=285.

Equivalent of $C_{18}H_{36}O_2$=284.

The above results show that the acid is stearic acid.

The melting point of stoaric acid is, generally, given as 69°; but, according to Saytzew, the melting point lies between 71°—75°.5. (*Monatshefte* 1896, *17*, 530).

A sample of pure stearic acid was prepared (M. P. 69°—69·5.), mixed with a little of the above fraction I, approximately, in equal quantities and the melting point of the mixture redetermined. The mixture melted at 70°—72°.

The above results show that fraction I consists of stoaric acid. only.

Fractions II and III had almost the same melting point and the melting point of their mixture was also not depressed; these were, therefore combined and analysed.

Analysis :—

(i) 0·1246 gram required 6.0 cc. of 0·0738 N alkali
whence neut. equiv. = 282.

(ii) 0·0990 gram silver salt gave 0·0270 gram Ag.
Whence equivalent of the Acid = 288.

$C_{18}H_{36}O_2$ has equivalent — 284.

The above acid is, therefore, stearic acid slightly impure.

The liquid methyal esters, 10 grams, which were filtered off from the solid crystalline ester, as mentioned above, were saponified and the resulting solid acids were crystallised three times from alcohol, when a colourless crystalline solid was obtained, melting at 57°-58°. It was analysed with the following results :—

(i) 0·9898 gram required 4-35 cc. of 0·0738 N alkali.
whence neut. equivalent = 278

(ii) 0·3210 gram silver salt gave 0·0901 gram Ag.
whence equivalent of the Acid = 277.

Stearic acid has equivalent = 282.
Palmitic acid has equivalent = 256.

The above results of analyses indicate that the above solid add (M. P. 57°-58°) is a mixture of stearic and palmitic acids.

Unsaponifiable Constituents of the Light Petroleum Extract of Soft Resin.

The ethereal liquid, obtained by extracting with ether the hydrolysed light petroleum extract of the soft resin, as described above, was dried and the solvent removed, when 90 grams of an orange-coloured soft solid were obtained. On keeping this solid in a desiccator, small colourless crystals were observed to have developed through the entire mass. A small quantity of alcohol was added and the whole mass crushed, when most of the oily non-crystalline portion was dissolved away, hut the crystalline portion remained insoluble in cold alcohol; this was filtered off and the above operation repeated twice with smaller amounts of cold alcohol.

Isolation of a Monohydric Alcohol Kanerol, $C_{30}H_{50}O$.

The crude crystalline product amounting to 12 grams melted between 150°—170°, and contained a certain amount of a vitreous gummy matter. After a number of recrystallisations of the product from a mixture of ethyl acetate and alcohol, 6 grams of a colourless crystalline product was obtained which was finally crystallised from 90% alcohol and obtained in the form of flat feathery needles with a silvery lustre, melting at 185·7-186·2° (corrected). With sulphuric acid and chloroform it gave the characteristic colour reaction of Phytosterols.

Analysis :—

(i) 0·1562 gave 0·1614 water and 0·4866 carbon dioxide.
$C = 84{\cdot}9$ p. c.-; $H = 11{\cdot}5$ p.c.

$C_{30}H_{50}O$ requires $C = 84{\cdot}5$ p. c.-; $H = 11{\cdot}82$ p. c.

Optical Rotation.

(ii) 0·3157 gram dissolved in chloroform and the solution made up to 50 cc, gave, in a 2 dcm. tube, $\alpha_D = +1·012$

$$\text{whence } [\alpha]^{\circ}_{D} = +80·1$$

Acetyl Kanerol.

An acetyl derivative of the above alcohol was prepared by boiling for 3-4 hours a mixture of 1 part of kanerol, 10 parts of acetic anhydride and 1 part of fused sodium acetate. The resulting product was crystallised three times from glacial acetic acid, when a colourless crystalline compound was obtained in prismatic plates, melting at 208°-210° (correct).

Analysis:—

(i) 0·8660 gave 0·0860 water, and 0·2600 carbon dioxide.

$C = 81·9$ p. c.; $H = 11·05$ p. c.

$C_{30}H_{49}O·COCH_3$ requires $C = 82·05$ p. c. and $H = 11·1$ p. c.

The molecular weight of the acetyl derivative was determined by the cryoscopic method in benzene.

0·0376 gram acetyl derivative depressed the freezing point of 17·385 grams of benzene by 0·023°.

whence M. W. = 470.

$C_{30}H_{49}$ 0·COCH$_3$ requires M. W = 468.

Optical Rotation.

(iii) 0·0860 gram in 20 cc. chloroform solution gave $\alpha_D = +0°·73$, in a 2 dcm. tube.

$$\text{whence } [\alpha]^{30^{\circ}}_{D} = +84°·88.$$

Benzoyl derivative.

A benzoyl derivative was prepared by the pyridine method. It was recrystallised twice from acetone, when it was obtained as colourless needles melting at 189°-190° (correct).

N. H. Cohen (*Rec. Travaux Chimiques des Pays Bays*, 1909, *28*, *393*) describes α-Amyrine, which resembles this alcohol in many respects as the following table will show ; but as the two compounds appear to be different, the name Kanerol is suggested for the solid alcohol, obtained in the present investigation.

In addition to Kanerol, several fractions of crystalline unsaponifiable neutral products were obtained, but only in small amounts having melting points ranging from 140°-170°. All these gave colour-reactions for phytosterols.

After removal of the crystalline portion of the unsaponifiable products, a soft resin remained from which nothing of a crystalline nature could be isolated.

The ether, chloroform, ethyl acetate and alcohol extracts of the soft resin were not worked up.

Summary and Conclusion.

The material employed for this investigation consisted of the air-dried roots of Nerium Odorum (called Kanher in Marathi) collected in winter in the Krishna Valley (Bombay Presidency).

An alcoholic extract of the roots (which amounted to 13·7 p, c. of the weight of the roots), when distilled in a current of steam, yielded a small amount of an orange coloured essential oil, which gave the following physical constants :—

(i), $D^{30°}_{4°} = 0·8660$

(ii) $[\alpha]^{31°} = -$

(iii) $n_D = 1·40315.$

45 p. c. of the total extract was soluble in water and the following substances found to be present in it :—(i) a crystalline phenolic compound melting at 140°—141°; (ii) a glucoside in considerable amount, having an intensely bitter taste. It could not bo isolated in a crystalline form ; (iii) Free glucose, which gave an osazone melting at 204°—205°.

The portion of the alcoholic extract which was insoluble in water consisted of a resinous material, amounting to 7·5 p. c. of the weight of the roots. ft was composed of a Hard Resin and a Soft Resin. From the Hard Resin the following compounds were isolated :—

(i) Formic and butyric acids, in traces; (ii) Oleic acid, linolic acid, palmitic acid, and stearic acid; (iii) A new monohydric alcohol $C_{30}H_{50}O$. melting at. 184°—185°. This was found to be identical with Kanerol obtained from the petroleum extract of the Soft Resin. (iv) A small quantity of an aromatic acid melting at 243°—245°.

From the Soft Resin the following compounds were isolated :—(i) Oleic acid, linolic acid, palmitic acid, and stearic acid melting at 74°—75°.

(ii) A monohydric alcohol, Kanerol, $C_{30}H_{50}O$ [M. P. 185°·7—186°·2. (correct) and $[\alpha]_D^{30} = +80°·1$] which yields an acetyl derivative [M. P. 208°—210° and $[\alpha]_D = +84°·88$] and a benzoyl derivative melting at 189°—190°. It gives the colour reactions for phytosterol, and in most respects closely resembles α amyrine.

The acids, free as well as combined, obtained from the soft resin contained a larger proportion of liquid acids, while those obtained from the hard resin contained a larger proportion of solid acids.

The ethyl acetate and the alcohol extracts of the hard resin were found to consist mainly of resin acids.

In conclusion, I wish to express my indebtedness to Dr. J. J. Sudborough for his continued interest and helpful guidance during the course of this investigation.

LABORATORIES OF THE DEPARTMENT OF
GENERAL AND ORGANIC CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

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