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TRANSACTIONS.

I.—*The Constituents of Rumex Ecklonianus.*

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Rumex Ecklonianus, Meisner (*N. O. Polygonaceae*), is an herb indigenous to South Africa, where it is reputed to possess medicinal properties. It is referred to in "A Contribution to South African Materia Medica," by Andrew Smith, 1895, p. 107, and also in the Transactions of the South African Philosophical Society, **18**, part 2, p. 216. A botanical description of the plant will be found in *Linnaea*, 1840, **14**, 493.

The investigation of the above-mentioned plant has resulted in the isolation of a number of crystalline substances, some of which are anthraquinone derivatives, such as have previously been isolated from other members of the *Polygonaceae*. A complete summary of the results obtained will be found at the end of this paper.

EXPERIMENTAL.

The material employed consisted of the entire overground portions of the above-mentioned *Rumex Ecklonianus*, collected at the time of flowering, and was received through the kindness of Mr. G. E. Oliver, of East London, South Africa, who stated that it occurred as a common weed on the banks of rivulets and in

marshy places. It had, however, been incorrectly designated by Mr. Oliver as *Polygonum tomentosum*, var. *glabrum*, but its identity as the first-mentioned plant was ascertained by Mr. E. M. Holmes, F.L.S., who had kindly compared it with specimens in the herbarium at Kew.

A portion (50 grams) of the finely-powdered, dried herb was successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 110°, were obtained :

Petroleum (b. p. 35—50°) extracted	0·77 gram	=	1·54 per cent.
Ether	0·51 "	=	1·02 "
Chloroform	0·69 "	=	1·38 "
Ethyl acetate	0·69 "	=	1·38 "
Alcohol	4·07 "	=	8·14 "

Total = 6·73 grams or 13·46 per cent.

After having ascertained by a preliminary experiment that no alkaloid was present, a quantity (11·733 kilograms) of the dried and ground herb was completely extracted by percolation with cold alcohol. The greater part of the alcohol was removed from the resulting extract, when 1·8 kilograms of a thin extract, containing a quantity of black, tarry matter, were obtained.

The entire amount of the above-mentioned extract was mixed with water and distilled with steam until volatile products ceased to be removed. The distillate, which contained a small amount of oil, and also some solid, was extracted with ether, the resulting ethereal liquid being shaken with a solution of sodium carbonate. This treatment removed from the ether a small amount of a substance, which, after being twice crystallised from ethyl acetate, formed yellowish-brown, slender prisms, melting at 159°. This substance dissolved in concentrated sulphuric acid, yielding a golden-yellow liquid, and its alcoholic solution gave with ferric chloride a green colour, which gradually changed to reddish-brown, but the amount obtained was not sufficient for its further examination. The ethereal liquid which had been treated with sodium carbonate yielded, on evaporation, a small amount of an essential oil, which possessed a dark green colour and an odour closely resembling that of the rhubarb of the *Pharmacopœias*.

The contents of the distillation flask then consisted of a quantity of a dark green resin (A), together with a dark-coloured aqueous liquid. These products were separated while still hot, when, on allowing the liquid to cool, a quantity of a brown resin (B) was deposited. The latter was likewise separated from the aqueous liquid (C).

Examination of the Green Resin (A).

The green resin, which formed a viscid mass, and amounted to 346 grams, was mixed with purified sawdust, and the dried mixture extracted successively in a large Soxhlet apparatus with light petroleum, ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Green Resin.

This extract, after the complete removal of the solvent, amounted to about 100 grams. It was dissolved in 1.5 litres of ether, and the ethereal liquid shaken with several successive portions of a 5 per cent. solution of ammonium carbonate. During shaking with the first portion of ammonium carbonate solution, a quantity of crystalline substance separated from the ether. This was collected, and its examination will subsequently be described. The further treatment with ammonium carbonate resulted in the formation of inseparable emulsions, owing to the gradual formation of a product in the form of an amorphous, black powder. The deposition of the latter was effected by removing the ether from the emulsion by passing air through the mixture, after which the solid was collected, but no crystalline substance could be obtained from it. The combined alkaline liquids were acidified, when a small amount of a product was precipitated in the form of a yellowish-brown powder. This was crystallised several times from ethyl acetate, and finally from ether, when it was obtained in long, deep golden-coloured needles, melting at 176° , but the amount was too small for analysis.

Isolation of Emodin Monomethyl Ether.

The previously-mentioned crystalline product, which separated from the ether during the first extraction with alkali, was re-crystallised several times from ethyl acetate, with the use of animal charcoal, when it formed handsome, golden-coloured plates, melting at 197° :

0.1257 gave 0.3116 CO_2 and 0.0493 H_2O . $\text{C}=67.6$; $\text{H}=4.4$.

$\text{C}_{16}\text{H}_{12}\text{O}_5$ requires $\text{C}=67.6$; $\text{H}=4.2$ per cent.

This substance proved to be emodin monomethyl ether, which has previously been obtained by Perkin and Hummel from *Ventilago madraspatana* (Trans., 1894, **65**, 932). Its identity was confirmed by the preparation of its acetyl derivative, which formed long, pale yellow needles, melting at 185 – 186° . Emodin was methylated by Jowett and Potter (Trans., 1903, **77**, 1330), who obtained a monomethyl ether, melting at 200° . They con-

sidered, however, that the ether prepared by them differed from the naturally occurring compound, inasmuch as it yielded an acetyl derivative melting at 157° . A specimen of the emodin monomethyl ether prepared by Jowett and Potter being available to us, we compared it directly with the analogous compound obtained from *Rumex Ecklonianus*, when the two substances were found to be identical. A quantity of the synthetical compound was then acetylated, when the above-described acetyl derivative, melting at $185-186^{\circ}$, was obtained. It is evident, therefore, that the natural and synthetical emodin monomethyl ethers are identical, and the low melting point found by Jowett and Potter for the acetyl derivative of the synthetical compound must be attributed to incomplete acetylation. In this connexion it may be noted that the conversion of emodin monomethyl ether into its acetyl derivative takes place only very slowly, unless a powerful condensing agent, such as camphorsulphonic acid, is employed. In order further to confirm the identity of the natural and synthetical compounds, emodin, which was subsequently isolated in the present investigation, was methylated, whereby a monomethyl ether was obtained, which proved to be identical with that occurring in the plant.

The ethereal liquid, which had been extracted with ammonium carbonate, was then shaken with several successive portions of aqueous potassium carbonate. This caused the formation of emulsions, which, after standing for some time, were separated from the ether and repeatedly washed with this solvent. In order to ensure the complete freedom of the potassium carbonate extract from substances insoluble in this alkali, the total quantity of emulsion was acidified and the product extracted with much ether, after which it was again treated with potassium carbonate, the emulsion being separated from the ether and washed as before. This process was twice repeated. The alkaline emulsions were finally acidified, and the product extracted with ether, after which the ethereal liquid was concentrated to a small bulk and treated with light petroleum. This caused the precipitation of a quantity of the previously-mentioned black, amorphous powder, which was removed by filtration. The clear, dark green filtrate was concentrated to a small bulk, when a quantity of a substance separated after some time. This was collected and recrystallised several times from glacial acetic acid, after which it formed colourless leaflets, melting at $56-60^{\circ}$. On analysis it was found to consist essentially of palmitic acid.

The original filtrate from this product evidently contained further

quantities of fatty acids, and in order to separate these from any phenolic substances which might be present, the entire product was esterified by means of alcohol and sulphuric acid. The material was then dissolved in ether and washed with water, after which it was shaken with potassium carbonate solution. The first treatment with this alkali removed only a quantity of tarry product, but the alkaline extracts subsequently obtained were deep red in colour, and, on acidification, yielded some emodin, which was afterwards obtained in larger amount. Extraction of the ethereal solution of the esters with potassium hydroxide removed only a small amount of impure emodin monomethyl ether, but on subsequently washing it with water a large amount of chlorophyll was removed.

Isolation of a Phytosterol, C₂₀H₃₄O.

The ethereal solution of the esters which had been freed from substances soluble in alkalis was evaporated, and the residue distilled under diminished pressure. When the greater part of the product had passed over, it was observed that the residue in the distillation flask possessed a very high boiling point, and tended to become solid. The distillation was therefore stopped, and the undistilled material boiled with alcoholic potash. After removing the greater part of the alcohol, water was added, and the mixture extracted with ether. In this way, a substance was obtained which crystallised from a mixture of ethyl acetate and dilute alcohol in colourless plates, melting at 134°:

0.1024, on drying at 110°, lost 0.0048 H₂O. H₂O = 4.7.

0.0976 gave 0.2962 CO₂ and 0.1032 H₂O. C = 82.8; H = 11.7.

C₂₀H₃₄O, H₂O requires H₂O = 5.8 per cent.

C₂₀H₃₄O requires C = 82.8; H = 11.7 per cent.

This phytosterol appeared to be identical with rhamnol, an alcohol which was first isolated by Power and Lees from Kô-sam fruits (*Year Book of Pharmacy*, 1903, 503), and also occurs in the bark of *Rhamnus purshiana* (Jowett, *Proc. Amer. Pharm. Assoc.*, 1904, 299). It is evident, however, that this alcohol must have occurred in the plant in the form of an acid ester, or analogous compound, since the product from which it was obtained was entirely soluble in alkali carbonates.

The esters of the fatty acids, which had been separated from the above-described alcohol by distillation, were examined in connexion with the acids subsequently obtained from the neutral portion of the petroleum extract of the resin.

Isolation of Chrysophanic Acid.

The original ethereal solution of the petroleum extract of the resin, which had been extracted with ammonium and potassium carbonates, was shaken with a solution of potassium hydroxide. This yielded a deep red liquid, which, on acidification, gave a quantity of a yellow powder. The latter was mixed with the material contained in the mother liquors previously obtained during the purification of the emodin monomethyl ether, and the entire product fractionally crystallised many times from a mixture of ethyl acetate and alcohol. A substance was thus obtained which crystallised in deep golden-coloured spangles, melting at 190° :

0.0807 gave 0.2097 CO_2 and 0.0307 H_2O . $\text{C}=70.9$; $\text{H}=4.2$.

$\text{C}_{15}\text{H}_{10}\text{O}_4$ requires $\text{C}=70.9$; $\text{H}=3.9$ per cent.

This substance was thus identified as chrysophanic acid, and its identity was confirmed by the preparation of its acetyl derivative. The latter compound formed bright yellow leaflets, melting at $204-205^{\circ}$.

Dimethyl ether of chrysophanic acid.—It was shown by Jowett and Potter (*loc. cit.*) that chrysophanic acid was not methylated when heated in a sealed tube at 100° with sodium and methyl iodide in the presence of methyl alcohol. It has now been found, however, that methylation does occur if the latter liquid is absent.

Chrysophanic acid (0.2 gram) was dissolved in absolute alcohol, and a solution of 0.04 gram of sodium in the same solvent added. The liquid was then concentrated, when the sodium derivative, which had separated in the form of small, violet-coloured needles, was rapidly collected and dried. This was then heated with dry methyl iodide in a sealed tube at 100° for six hours. After removing the excess of methyl iodide, the residue was acidified with acetic acid and dissolved in chloroform, the solution thus obtained being freed from unchanged chrysophanic acid by means of potassium hydroxide. On removing the solvent, a product was obtained which crystallised from ethyl acetate in yellow prisms, melting at 190° :

0.0956 gave 0.2520 CO_2 and 0.0430 H_2O . $\text{C}=71.9$; $\text{H}=5.0$.

$\text{C}_{17}\text{H}_{14}\text{O}_4$ requires $\text{C}=72.3$; $\text{H}=5.0$ per cent.

Chrysophanic acid dimethyl ether dissolves in cold concentrated sulphuric acid, giving a deep purple solution. It is insoluble in cold aqueous potassium hydroxide, but on boiling with this reagent it slowly dissolves, yielding a red solution, thus indicating that at least one methyl group is gradually removed by the alkali.

The product contained in the mother liquors obtained during

the purification of the chrysophanic acid was found to consist entirely of a mixture of the latter with emodin monomethyl ether, since, after heating at 160° with concentrated sulphuric acid, it was resolved into emodin and chrysophanic acid. The total amount of anthraquinone derivatives present in the petroleum extract of the green resin was 4.5 grams.

Isolation of Ceryl Alcohol.

The ethereal solution of the neutral portion of the petroleum extract of the green resin was evaporated, and the residue boiled with an excess of alcoholic potash. After removing the greater part of the alcohol, water was added, and the unsaponifiable matter extracted with ether. The product so obtained was fractionally distilled under diminished pressure. The portion boiling below $305^{\circ}/20$ mm. was an unsaturated, oily liquid, but the fraction distilling above this temperature gradually solidified. This was crystallised several times from absolute alcohol, when colourless leaflets, melting at 75° , were obtained:

0.0821 gave 0.2466 CO_2 and 0.1031 H_2O . C = 81.9; H = 14.0.

$\text{C}_{27}\text{H}_{56}\text{O}$ requires C = 81.8; H = 14.1 per cent.

This substance therefore appeared to be ceryl alcohol.

Some phytosterol was present in the mother liquors from the above-described product, but no pure substance could be isolated from them.

Isolation of Ipuranol, $\text{C}_{23}\text{H}_{38}\text{O}_2(\text{OH})_2$.

The alkaline liquid, from which the unsaponifiable matter had been removed by means of ether, was acidified and distilled with steam, but no volatile acids were obtained. The contents of the distillation flask were then shaken with ether, when a small amount of flocculent matter collected in the lower portion of the ethereal layer. This was separated by filtration, and purified by crystallisation from dilute pyridine with the use of animal charcoal. It was thus obtained as a colourless, minutely crystalline product, which melted at $285\text{--}290^{\circ}$, and yielded an acetyl derivative crystallising in leaflets, which melted at 162° . A comparison of this acetyl derivative with that obtained from ipuranol (Trans., 1908, **93**, 907) rendered it evident that the two substances were identical.

Identification of the Fatty Acids.

The ethereal solution of the fatty acids from which the above-described ipuranol had been separated was evaporated to a small bulk, and treated with a large volume of light petroleum. This

caused the precipitation of a considerable amount of a black, amorphous powder, which was removed by filtration. The fatty acids contained in the filtrate were then distilled under diminished pressure, after which the saturated and unsaturated constituents were separated by means of their lead salts. A quantity (6 grams) of a mixture of palmitic and stearic acids was thus obtained, which melted at 55—56°, together with 18 grams of liquid acids, which had an iodine value of 173·9.

The previously-mentioned ethyl esters of the acids which had occurred in the plant in the free state were then hydrolysed, and the resulting mixture of acids similarly separated into its solid and liquid components, which amounted to 2 grams and 20 grams respectively. The latter product had an iodine value of 169·5. In order to ascertain the constituents of these mixtures of unsaturated acids, 15 grams of both the free and combined liquid acids were together oxidised with potassium permanganate in the manner described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, **1**, 360). This resulted in the formation of isolinusic acid and di- and tetra-hydroxystearic acids, the last-mentioned compound predominating. The unsaturated acids therefore consisted of linolic acid, together with smaller amounts of isolinolenic and oleic acids.

Ethereal Extract of the Green Resin.

Isolation of Emodin and Kaempferol.

This extract amounted to 62 grams. A portion of it (about 6 grams) was very sparingly soluble in ether, and formed a nearly black, amorphous powder, from which nothing could be isolated. The ethereal solution of the more readily soluble portion of the extract was first treated with a solution of ammonium carbonate, but this removed only resinous products, from which nothing crystalline could be separated. The ethereal liquid was then shaken with six successive portions of aqueous potassium carbonate. The first of these operations caused the precipitation of a small amount of black tarry matter, which yielded nothing crystalline, but the aqueous, alkaline liquids subsequently obtained possessed a deep red colour, and, on acidification, yielded a brown powder. This was collected and submitted to a number of fractional crystallisations from glacial acetic acid, when it was ultimately resolved into two products. One of these formed pale yellow, acicular crystals, melting at 276°:

0·0688 gave 0·1586 CO₂ and 0·0227 H₂O. C=62·9; H=3·7.

C₁₅H₁₀O₆ requires C=62·9; H=3·5 per cent.

Although the total amount of the above-described product did not exceed 0.15 gram, its identity as kaempferol (1:3:4-trihydroxyflavonol) was positively confirmed by the characteristic behaviour of its acetyl derivative. The latter compound, prepared in the usual manner and recrystallised from methyl alcohol, first melted at 121°, then resolidified, and finally fused at 182° (compare Perkin, *Trans.*, 1902, **81**, 587).

The second crystalline compound obtained from the potassium carbonate extract of the portion of the resin soluble in ether formed dark red needles, melting at 255°, and amounted to 1 gram:

0.0803 gave 0.1954 CO₂ and 0.0281 H₂O. C=66.4; H=3.9.

C₁₅H₁₀O₅ requires C=66.7; H=3.7 per cent.

The identity of this substance with emodin was confirmed by the preparation of its acetyl derivative, which formed golden-yellow needles, melting at 190—191°.

Subsequent treatment of the original ethereal liquid with aqueous potassium hydroxide removed about 4 grams of a mixture of chrysophanic acid and emodin monomethyl ether, after which the ethereal liquid contained only small amounts of green resin.

Chloroform, Ethyl Acetate, and Alcoholic Extracts of the Green Resin.

The chloroform, ethyl acetate, and alcoholic extracts of the resin amounted to 60, 50, and 70 grams respectively. They were all examined in an exhaustive manner, but were found to consist entirely of resins.

Examination of the Brown Resin (B).

This resin, which was soluble in hot water, but again separated on allowing its solution to cool, was thoroughly examined, but nothing definite could be isolated from it. In order to ascertain whether it contained a glucoside, a portion of it was submitted to the action of 5 per cent. aqueous sulphuric acid, but no sugar was formed by this treatment.

Examination of the Aqueous Liquid (C).

The original dark-coloured aqueous liquid (C) was evaporated under diminished pressure to about 1.5 litres, and extracted many times with ether. The ethereal liquid thus obtained was treated first with a solution of ammonium carbonate, then with sodium carbonate, and finally with aqueous sodium hydroxide. The first of these reagents removed a small amount of a product in the form of a gum-like mass, but on extracting the latter with suc-

cessive portions of boiling benzene, evidence was obtained of the existence in it of several crystalline substances. The amounts were so small, however, that none of these could be isolated in a state of purity. The sodium carbonate extracts yielded a small amount of emodin, and a little of a compound which formed pale yellow, acicular crystals, melting at 247° . The latter compound appeared to be pure, but the amount was too small for analysis. It dissolved in alkalis, yielding a solution which was at first colourless, but darkened on exposure to the air, whilst its solution in concentrated sulphuric acid exhibited a purple-blue fluorescence. The material removed from the original ethereal liquid by means of alkali hydroxide yielded nothing definite.

In order to search for a glucoside in the aqueous liquid, the latter was further evaporated under diminished pressure, and the resulting syrup submitted to a prolonged process of extraction with absolute alcohol, followed by ethyl acetate, in a manner similar to that successfully employed by Power and Moore for the isolation of *l*-mandelonitrile glucoside from the bark of *Prunus serotina* (Trans., 1909, 95, 257). During this process 80 grams of potassium chloride and a considerable amount of ammonium chloride separated, but no indication could be obtained of the presence of a glucoside. The viscid syrup, representing the organic constituents of the aqueous liquid which were insoluble in ethyl acetate, was then dissolved in water, and treated with an excess of a solution of basic lead acetate. This caused a voluminous precipitate, from which nothing definite could be isolated. The filtrate from the basic lead acetate precipitate was deprived of lead by means of hydrogen sulphide, and concentrated under diminished pressure. The liquid so obtained contained a small amount of a sugar, which yielded *d*-phenylglucosazone (m. p. 214°), and, on keeping for some time, a considerable quantity of ammonium nitrate was deposited, but no other crystalline substance could be obtained from it.

Summary.

The results of the preceding investigation of *Rumex Ecklonianus*, Meisner, may be summarised as follows.

An alcoholic extract of the herb, when distilled with steam, yielded a trace of a substance which formed yellow prisms, melting at 159° , together with a small amount of essential oil. The non-volatile constituents of the extract consisted largely of brown, resinous matter and a product which slowly formed a black, amorphous powder, but the following definite substances were also obtained: Ceryl alcohol; a phytosterol, $C_{20}H_{34}O$, apparently

identical with rhamnol; palmitic, stearic, oleic, linolic, and *iso*-linolenic acids; a small amount of ipuranol, $C_{23}H_{38}O_2(OH)_2$; kaempferol; chrysophanic acid; emodin; and emodin monomethyl ether; together with traces of other crystalline substances and large amounts of inorganic salts. A sugar which yielded *d*-phenylglucosazone was also present in small amount, but no evidence could be obtained of the presence of a glucoside. The emodin monomethyl ether which was isolated was identical with that obtained by Perkin and Hummel from *Ventilago madraspatana* (Trans., 1894, **65**, 932), and with that prepared synthetically by Jowett and Potter (Trans., 1903, **77**, 1330). The *dimethyl ether* of *chrysophanic acid* was prepared, and obtained in yellow prisms, melting at 191° .

The extract from this plant, like many other products containing anthraquinone derivatives, was found to possess a mild purgative action.

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