

CLXXXIX.—*The Resin of Hevea Rubber.*

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THE circumstance that the resin of the rubber from *Hevea brasiliensis* constitutes only a small proportion of the weight of the rubber (on the average, about 2.80%. Compare van Rossem, *Koll.-Chem. Beih.*, 1918, **10**, 52; "The Quality of Plantation Rubber," Imp. Inst., 1922, pp. 13, 27, 88, 95) and is of a sticky, semi-fluid consistency has apparently deterred investigators from subjecting it to chemical examination (compare, *e.g.*, Tschirch and Müller, *Arch. Pharm.*, 1905, **243**, 141), and when the present investigation was begun but little was known concerning its chemical nature.

It has now been shown that, contrary to Hinrichsen and Kindscher's statement (*Z. angew. Chem.*, 1910, **23**, 49), the resin contains several optically active substances (all lævorotatory, with the exception of an amino-acid occurring in very small amounts only) and that sterol substances are present. Hillen's failure to obtain sterol colour reactions (*Arch. Pharm.*, 1913, **251**, 94) was probably due to interference of other substances present in the crude extract. Cohen (*Arch. Pharm.*, 1908, **246**, 520) examined the resin for lupeol, with negative results. Hinrichsen and Kindscher (*loc. cit.*) found the resin to be largely saponifiable, and Dekker (*Koll.-Chem. Beih.*, 1918, **10**, 54), who confirmed this finding, obtained the data shown in the first two columns below. The figures in the third column, which have been added, would seem to suggest that the differences in the percentage of extract unsaponifiable in different forms of *Hevea* rubber are due to differences in the amount of saponifiable matter rather than to differences in the amount of unsaponifiable matter.

Form of rubber.	Acetone extract %.	% extract unsaponifiable.	% unsaponifiable in the rubber.
Fine hard Para .....	3.0	25.4	0.76
Sheet .....	1.8	48.3	0.87
Crêpe .....	3.2	22.0	0.705

A sample of the resin was found by Hinrichsen and Kindscher (*loc. cit.*) to show an iodine absorption of 118%. Beadle and Stevens (*Internat. Cong. Appd. Chem.*, 1912, **24**, 581) reported that the resin was partly water-soluble. The presence in it of nitrogenous material was mentioned by Spence and Kratz (*Kolloid-Z.*, 1914, **14**, p. 268, footnote), and was confirmed by Dekker (*Meded. Delft*, 1916, 506) by an indirect method. Dekker found acetone extraction to reduce the nitrogen content of two samples of *Hevea* crêpe by 0.051 and 0.029%, respectively, and of a sample of *Hevea* sheet by 0.014%.

Working with a sufficiently large amount of the acetone extract of *Hevea* rubber, the present authors have isolated and identified a sterol, a sterol ester, a sterol glucoside, *d*-valine, quebrachitol, and stearic acid and the liquids, oleic and linoleic acids. The amounts and ratios in which the substances occur vary in different rubber samples. The mixture of unsaturated, liquid fatty acids occurs in much larger amount than any of the other constituents. Titration of the acetone extract of twenty-four samples of smoked sheet and pale crêpe rubber showed that the average total acid content was equivalent to 0.272 g. of potassium hydroxide per 100 g. of rubber. Hence, if the mean molecular weight of the acids is taken as 280, the total acid content of average samples of latex *Hevea* rubber is of the order of 1.4% of the weight of the rubber or roughly one-half of the weight of the acetone extract.

The total amount of solid material which it was actually possible to crystallise from the extract was about 0.65% of the weight of the rubber. As the resin content of the crêpe from which most of the resin examined was obtained was 2.71%, it may be said that of this about 1.9 (=1.25 + 0.65) was definitely accounted for. The balance of about 0.8% represented losses together with unidentified constituents of the liquid, uncrystallisable portion of the resin.

The order of magnitude (%) in which the recognised constituents of *Hevea* resin occurred was estimated roughly as follows :

Sterol ester .....	0.075	Quebrachitol .....	very small amount
Sterol glucoside .....	0.175	Stearic acid .....	0.15
Sterol .....	0.225	Oleic acid .....	} 1.25
<i>d</i> -Valine .....	0.015	Linoleic acid .....	

The high proportion of free fatty acid in the resin of *Hevea* rubber makes this resin unique, not only among the resins of rubbers of various botanical origins, but also among resins in general. In *Hevea* resin, fatty acids predominate, and hence it has a softer consistency, a higher saponification value, and a smaller optical activity than have other rubber resins, in which optically active unsaponifiable, crystalline substances predominate. The resins obtained by extracting plants with organic solvents contain free fatty acids in a good many cases, but never in large proportions (Power and his co-workers, J., various papers).

The question of the mode of association of the resin constituents with the hydrocarbon in rubber is of some interest. It is probable that the fatty acids occur in solution in the caoutchouc. Rubber, both raw and vulcanised, swells considerably when placed in oleic acid, linoleic acid, molten stearic acid, or the mixed liquid fatty acids actually isolated from *Hevea* rubber. Thus, for example, a sample of smoked sheet placed in the last-mentioned medium

imbibed 4.04 times its weight after 7 days. The sterol glucoside found in rubber is insoluble in all the usual laboratory solvents, including benzene. It probably occurs, not dissolved in the caoutchouc, but in solution in the fatty acids, for the authors have observed that it will dissolve on warming in fatty acids, except in the lowest members, yielding sols which often gel on cooling.

The resin, and especially the fatty acids which it comprises, influence the behaviour of rubber in several important ways (compare Whitby, *Trans. Inst. Rubber Ind.*, 1925, **1**, 12; Whitby and Jane, *Second Colloid Symposium Monograph*, 1925, 16).

#### EXPERIMENTAL.

Samples of rubber were extracted with acetone in a large, heavily galvanised iron extractor of the Soxhlet type, 3 ft. high and 1 ft. in diameter. The thimble, which is large enough to hold about 4.5 kg. of rubber, is suspended directly in the vapour of the boiling extractant. The condenser, which sits on a flange at the top of the main extraction vessel, consists of a hollow cone and head through which water circulates and a separate, conical coil of block tin round the cone. The metal of the extractor was attacked slightly in the course of time, zinc salts of fatty acids being found in the extract.

The extracts from a number of different samples of rubber (crêpe, smoked sheet, slab crêpe) were examined. The procedure varied somewhat in different cases, as the proportions of the constituents were not identical in different batches, but in general it was as follows: The batch of rubber was extracted for 70 to 100 hours. The solution was concentrated to about 600 c.c. per kg. of rubber and kept for a week or so at or below 0°. The solid which separated (Fraction A) was removed and the solution (and washings) was concentrated to one-third or less of its volume and again kept in the cold for a week. The solid which separated (Fraction B) was removed and washed with a little cold acetone. The solution and washings were then evaporated on the water-bath to remove as much acetone as possible. The viscous liquid residue is called the Liquid Fraction.

#### *Fraction A.*

This fraction (47 g. of a light brown powder from 21.7 kg. of pale latex crêpe) was separated into a chloroform-soluble sterol ester, a water-soluble amino-acid and quebrachitol, and an insoluble sterolin.

*Sterol Ester.*—Chloroform extracted from fraction A about 10 g. of a sterol ester which, after recrystallisation from alcohol, had m. p. 83° and  $[\alpha]_{D}^{25}$  — 11.1°, — 10.8° (0.2145 and 0.2303 g. in 15 c.c.

of chloroform) (Found: C, 83.0; H, 12.6; iodine absorption, 34.3.  $C_{17}H_{33}O_2 \cdot C_{27}H_{45}$  requires C, 82.8; H, 12.4; iodine absorption, 39.6%). The iodine absorption is due to unsaturation of the sterol part of the ester, the acid part being saturated. (The iodine values obtained for sterols are usually somewhat lower than the calculated values.) The *sterol* obtained by hydrolysing the ester with alcoholic potassium hydroxide crystallised from alcohol in fine, white needles, m. p. 133—134°,  $[\alpha]_D^{25} - 23.2^\circ$  (0.3140 g. in 15 c.c. of chloroform) (Found: C, 82.8; H, 11.4.  $C_{27}H_{46}O$  requires C, 83.9; H, 11.9%) and gave the usual colour reactions and also certain new reactions (Whitby, *Biochem. J.*, 1923, **17**, 5). The acetate crystallised from alcohol in matted crystals, m. p. 113—114°, and gave  $[\alpha]_D^{18} - 18.8^\circ$  (0.1707 g. in 15 c.c. of chloroform). The *acid* obtained by hydrolysis of the sterol ester melted at 73—75° after recrystallisation from alcohol and appeared to have the composition  $C_{17}H_{34}O_2$  (Found: C, 74.5; H, 11.2. Calc.: C, 75.6; H, 12.6%. Found for the *silver* salt: Ag, 28.5.  $C_{17}H_{33}O_2Ag$  requires Ag, 28.5%).

The sterol ester isolated from slab rubber and from smoked sheet melted at 102° and 91—93°, respectively, but the amounts isolated were insufficient for careful examination.

*The Aqueous Extract.*—Addition of alcohol to the concentrated aqueous extract of fraction A (derived from 21.7 kg. of crêpe) precipitated 1 g. of an amino-acid; quebrachitol remained in solution. The two substances could also be separated by precipitating the amino-acid with mercuric nitrate or by evaporating the aqueous extract to dryness and extracting the amino-acid with cold alcoholic hydrochloric acid.

The amino-acid, m. p. about 260° (decomp.), gave (a) the ninhydrin reaction, (b) the pine splinter pyrrole reaction, when heated either alone or with zinc dust, and (c) a blue colour with phenol and sodium hypochlorite (Found: C, 52.2; H, 9.42; amino-N, by micro-van Slyke method, 11.7, 11.6.  $C_5H_{11}O_2N$  requires C, 51.3; H, 9.4; N, 11.9%). It had  $[\alpha]_D^{25} + 22.9^\circ$ ;  $[\alpha]_D^{18} + 26.5^\circ$  (0.1888 g. in 25 c.c. of 20% HCl). For a 3% solution of *d*-valine in 20% HCl, E. Fischer (*Ber.*, 1906, **39**, 2325) obtained  $[\alpha]_D^{18} + 28.8^\circ$ . The total amino-nitrogen in an aqueous extract of the original rubber was 0.0015% (micro-van Slyke method). This corresponds to 0.0126% of valine in the rubber or 0.46% of valine in the acetone extract.

Quebrachitol was first noticed as separating in well-formed crystals from the acetone extract of a sample of smoked sheet which had stood for a long time after the separation of a first fraction. It had m. p. 190° and  $[\alpha]_D^{20} - 80.3^\circ$  (0.2800 g. in 14.5 c.c. of water).

It was subsequently always recognised in fraction A, and in several cases was actually isolated from it.

By means of Scherer's test for inositol (*Annalen*, 1852, **81**, 375; compare Boedker, *Ztg. nat. Med.*, **10**, 162) the presence of quebrachitol was detected in forty-five samples of *Hevea* rubber comprising all the usual forms (latex crêpe, lower grade crêpes, smoked sheet, fine hard Para, etc.). For most of these samples the authors are indebted to Dr. O. de Vries. A few grams of the rubber (as little as 1 g. will give a positive result), cut into small pieces, were boiled for 15—30 minutes with glacial acetic acid, which was then evaporated, finally on a water-bath. The material extracted from the residue by a little hot water developed a rose-red colour after the usual nitric acid-calcium chloride treatment.

The isolation of quebrachitol from the latex of *H. brasiliensis* has been recorded by De Jong (*Rec. trav. chim.*, 1906, **25**, 48), and from rubber by Pickles and Whitfield (P., 1911, **27**, 54).

Professor R. P. D. Graham has kindly made crystallographic measurements on some of the crystals which separated from the acetone extract and on larger crystals of quebrachitol which had grown in a sample of evaporated latex serum which had been kept for 9 years. For comparison, there are given below the crystallographic data obtained by Anderson with a sample of quebrachitol isolated by Petrie from *Heterodendron oleæfolium*, Desf. (*Proc. Linnean Soc. N.S. Wales*, 1918, **43**, 857).

*Crystallographic data for l-inositol methyl ether* (by R. P. D. GRAHAM). The crystals were transparent, colourless blades, sometimes attaining a length of 6 mm. or more. *System*: orthorhombic. No cleavage was observed. *Forms and habit*: All the crystals measured exhibited the forms  $a(100)$ ,  $b(010)$ ,  $m(110)$ , and  $q(011)$ . On several of the crystals there were in addition very small facets of the form (101). The crystals were elongated in the direction of the vertical axis, and tabular parallel to  $a$  or  $m$ . The faces of the orthorhombic prism,  $m$ , were heavily striated vertically, with a tendency to curvature; but faces of the other forms were smooth and yielded fair reflexions. A peculiarity of the crystals was that, in nearly all the cases observed, only two opposite faces of the prism  $m$  were developed.

*Angular measurements and axial ratios.*

	Limits.		No.	Mean.	Calc.	Anderson.
$b\ m$	52°	26'—53° 19'	5	52° 47'		52° 44'
$c\ q$	39	10—39 35	6	39 22		39 26
$c$		47° 03'	1	47 03	47° 13'	47 43

Axial ratios  $a : b : c = 0.7595 : 1 : 0.8204$

0.7609 : 1 : 0.8224 (Anderson).

*The Sterolin.*—The residue of fraction A after removal of the chloroform- and water-soluble portions consisted in all cases of sterol glucoside. After purification through its acetate, it had m. p. 285—290° (decomp.) and  $[\alpha]_D^{25} - 41.7^\circ$  (0.2900 g. in 14.6 c.c. of pyridine) (Found: C, 73.0; H, 10.4.  $C_{33}H_{56}O_6$  requires C, 72.3; H, 10.2%). Its behaviour in the sterol colour reactions and in a new test which enables sterolins to be distinguished from sterols has been described elsewhere (Whitby, *Biochem. J.*, 1923, **17**, 5). The *acetate*, prepared by means of hot acetic anhydride, crystallised from alcohol in pearly leaflets, m. p. 165°;  $[\alpha]_D^{25} - 22.4$  (Found: C, 69.1; H, 9.0; Ac, 23.1.  $C_{33}H_{52}O_6Ac_4$  requires C, 68.7; H, 8.9; Ac, 22.5%). The *benzoate* was prepared by treating a pyridine solution of the sterolin with a slight excess of benzoyl chloride, extracting the diluted reaction mixture with ether, and washing the extract with dilute sulphuric acid, dilute potassium hydroxide, and water in succession. The product, recrystallised from ether, had m. p. 198° and  $[\alpha]_D^{25} + 15.7^\circ$ ,  $+ 16.1^\circ$  (0.3256, 0.2637 g., respectively, in 15 c.c. of chloroform).

Hydrolysis of the sterolin by hydrochloric acid in amyl alcohol by Power and Salway's method (J., 1913, **103**, 399) gave glucose (osazone, m. p. 201°) and a sterol. The latter, obtained as lustrous plates after recrystallisation, melted at 134.5° and had  $[\alpha]_D^{25} - 31.7^\circ$ ,  $- 32.1^\circ$  (0.2793 and 0.1268 g., respectively, in 15 c.c. of chloroform) (Found: C, 84.3; H, 12.3.  $C_{27}H_{46}O$  requires C, 83.9; H, 11.9%). The acetate of this sterol melted at 115° and showed  $[\alpha]_D^{25} - 38.6^\circ$  (0.0634 g. in 15 c.c. of chloroform). There is little doubt that the sterolin is sitosterol *d*-glucoside (Power and Salway, *loc. cit.*, p. 1022).

The sterol glucosides are soluble, not only in hot amyl alcohol and in pyridine (Power and Salway, *loc. cit.*, p. 399), but also in amines (piperidine and diethylamine), fatty acids (octoic acid), mustard oils (phenylthiocarbimide), and higher ethers (anisole). In many of such liquids the sols set to gels on cooling.

#### Fraction B.

This fraction usually consisted of a mixture of a sterol or sterols and one or more saturated fatty acids. Separation was effected by treating the mixture with alcoholic potassium hydroxide and then extracting the sterol by ether from the mixture of potassium salt and sterol which came out on cooling. In certain cases, either the sterol or the fatty acid predominated so greatly that recrystallisation was sufficient to obtain it in a pure condition.

*The Sterol.*—A sterol was first isolated from the acetone extract of a batch of 4 kg. of smoked sheet rubber, which, when concentrated to 500 c.c. per kg. and kept in the cold, deposited 9 g. of

almost pure sterol as rosettes of crystals. After recrystallisation six times from alcohol, there was obtained a mass of matted, white leaflets, m. p.  $125^{\circ}$ ,  $[\alpha]_D^{25} - 24.6^{\circ}$  (0.2975 g. in 15 c.c. of chloroform) (Found : C, 83.8; H, 13.0.  $C_{27}H_{46}O$  requires C, 83.9; H, 11.9%).

Fischer's method (*Ber.*, 1913, **46**, 4029) of preparing penta-acyl derivatives of sugars is suitable for the acylation of sterols, including cholesterol. The *benzoate* : The sterol described above was treated in chloroform solution with a slight excess of benzoyl chloride and an equivalent amount of quinoline. After a short time, the solution was washed successively with dilute sulphuric acid, dilute sodium hydroxide solution, and water, dried over calcium chloride, and the chloroform evaporated. The residue crystallised from alcohol-chloroform in lustrous plates, m. p.  $144-145^{\circ}$ ;  $[\alpha]_D^{25} - 20.7^{\circ}$  (0.1340 g. in 14.6 c.c. of chloroform) (Found: C, 83.9; H, 9.9.  $C_{27}H_{45} \cdot O \cdot CO \cdot C_6H_5$  requires C, 83.3; H, 10.2%). The *propionate*, prepared by a similar method, crystallised from alcohol in lustrous white plates, m. p.  $98^{\circ}$ ;  $[\alpha]_D^{25} - 29.4^{\circ}$  (0.2005 g. in 17 c.c. of chloroform). The *acetate*, prepared by treating the sterol with an excess of acetic anhydride, was obtained as white plates or leaflets, m. p.  $114-115^{\circ}$ ;  $[\alpha]_D^{25} - 30.6^{\circ}$  (0.3169 g. in 14.6 c.c. of chloroform).

A sample of sterol obtained, in the case of a batch of 21.7 kg. of pale latex crêpe, by extracting a mixture of potassium soap and sterol with ether was freed from potassium salt by converting this into the silver salt and extracting the sterol with ether. After several recrystallisations from ether, the sterol was obtained as lustrous plates, m. p.  $134-135^{\circ}$ ;  $[\alpha]_D^{25} - 21.4^{\circ}$  (0.3278 g. in 15 c.c. of chloroform). The *benzoate* had m. p.  $144.5^{\circ}$ , and  $[\alpha]_D^{25} - 12.5^{\circ}$  (0.2393 g. in 15 c.c. of chloroform) (Found : C, 83.1; H, 10.2.  $C_{34}H_{50}O_2$  requires C, 83.3; H, 10.2%).

From the acetone extract of a sample of slab rubber, not quite the whole of the sterol separated when the extract was kept at a suitable concentration. The extract was then saponified, and from the unsaponifiable material ether removed a sterol, m. p.  $133-134^{\circ}$ .

*The Fatty Acid.*—The main fatty acid present in fraction B, previously regarded as a  $C_{20}$  saturated fatty acid and named "heveic acid" (Whitby, *Brit. Assoc. Rep.*, 1923, 432), has now been identified as stearic acid. A sample (equiv., 291) isolated from slab rubber melted at  $65.5-66.5^{\circ}$  after recrystallisation from alcohol and at  $68.5^{\circ}$  after recrystallisation from aqueous acetic acid, benzene, aqueous acetone, and light petroleum in succession. It was then mixed with further quantities of solid acid obtained from crêpe rubber, recrystallised until its melting point was  $67.5-68.5^{\circ}$ , and converted, by treatment of the silver salt with ethyl

iodide in benzene, into the ethyl ester. This after purification had m. p. 32.5—33.5° and  $n_D^{40}$  1.4292. The acid regenerated therefrom had m. p. 68—69° (alone or mixed with stearic acid),  $n_D^{70}$  1.4332,  $n_D^{80}$  1.4300 ( $n_D^{70}$  for stearic acid in the same apparatus, 1.4328). A sample of the ester prepared from the solid acid derived from another sample of rubber had, after distillation and recrystallisation from chloroform, m. p. 31.5° (Found: *M*, 314. Calc.: *M*, 312).

Another sample of the chief solid acid was isolated from the acetone extract of a sample of latex crêpe rubber as follows: The mixture of the crystallisable substances which separated on allowing the extract, slightly diluted with acetone, to stand for several months was extracted with chloroform. The residue left on removal of the chloroform was separated by several crystallisations from alcohol and ethyl acetate into (a) a sterol ester (less soluble) and (b) a fatty acid (more soluble). The latter after several recrystallisations melted at 67—69° and had an equivalent weight of 295. It was purified further through its barium salt and then, after recrystallisation from acetone, aqueous acetic acid, and chloroform, had m. p. 68.5—69.5° (Found: equiv. by titration, 293, 289).

#### *The Liquid Fraction.*

This fraction was distilled with steam, which removed the last traces of acetone and also mesityl oxide, evidently formed from the acetone during the extraction. No essential oil was present. After removal of the non-volatile oil with ether, the aqueous layer contained a small amount of nitrogenous material precipitable by alkaloidal reagents; phosphomolybdic acid precipitated 2.5 g. (from 21.7 kg. of crêpe rubber) and in the case of slab crêpe, the precipitate given by platinic chloride contained 24.0% of platinum and did not melt at 295°. Both precipitates gave the pyrrole test on ignition.

The Liquid Fraction consisted preponderantly of unsaturated fatty acids, although some evidence was obtained of the presence of a magnesium salt. After steam distillation the fraction was esterified by hydrogen chloride in methyl alcohol at 0°, the ester mixture distilled, and the fraction, b. p. 195°/9 mm.—185°/5 mm., saponified. The free acid thus obtained had, after removal of a little crystalline material, a mean molecular weight (by titration) of 317 and an iodine absorption (Hübl) of 140, 141. *Hydrogenation.* 8.63 G. were treated with purified hydrogen in ether in presence of platinum-black carried on finely-divided barium sulphate. Unfortunately, some of the alkaline sodium hyposulphite solution over which the hydrogen was stored was sucked into the reaction flask, and in consequence only 619 c.c. of hydrogen were taken up



instead of the 1100 c.c. corresponding to the iodine value. Nevertheless, pure stearic acid was isolated in such good yield and so easily that it may be considered certain that only  $C_{18}$  unsaturated acids were present in the liquid submitted to hydrogenation. The crystals obtained after evaporation of the ether had m. p.  $68.5^{\circ}$  after recrystallisation from ethyl acetate and  $69-69.5^{\circ}$  after further recrystallisation from alcohol and from chloroform (Found : equiv., 281, 284). A total of 3.66 g. of stearic acid was isolated and the final mother-liquor left on evaporation 2.34 g. of impure stearic acid. *Oxidation.* The potassium soaps from 3 g. of the mixed acids were oxidised in aqueous solution with 3 g. of potassium permanganate. That part of the product which was soluble in cold ether was extracted with carbon tetrachloride. The portion thus extracted melted at  $60^{\circ}$  after recrystallisation, and was probably impure saturated acid. The portion (0.05 g.) unextracted by the carbon tetrachloride melted at  $124-126^{\circ}$ , had a molecular weight by titration of about 320, and was probably dihydroxystearic acid (*vide infra*). (A sample of dihydroxystearic acid prepared from Kahlbaum's oleic acid melted at  $128^{\circ}$  after several recrystallisations.) That part of the product which was insoluble in cold ether amounted, after recrystallisation from aqueous alcohol, to 0.42 g. and melted at  $160-170^{\circ}$ . By extracting it with boiling water, crystals were obtained, m. p.  $155-156^{\circ}$ , having an equivalent weight (by titration) of 356 and probably representing sativic acid. *Bromination.* A sample of the mixed acids was brominated in cold ethereal solution by Muggenthaler's method. No ether-insoluble bromide was obtained, and hence linolenic acid was absent. A small amount of a bromide melting, after recrystallisation from light petroleum, at  $112^{\circ}$  was obtained. (Linoleic acid tetrabromide melts at  $113-114^{\circ}$ .)

In order to identify the liquid acids with greater certainty, the solvent was removed from the acetone extract of 11 kg. of latex crêpe rubber, and the residue was boiled with water, in order to eliminate any mesityl oxide and to extract water-soluble constituents. The material was then boiled with 5% potassium hydroxide solution in excess of the amount equivalent to the acid known to be present in the rubber, and, after most of the material had gone into solution, the liquid was evaporated and distributed on pumice. This was then dried on a steam-bath and extracted with light petroleum, which removed, in addition to sterol and other unsaponifiable material, some potassium linoleate. This salt separated on cooling and after recrystallisation was obtained as a pale yellow powder (21 g.), which rapidly became brown in the air. Oxidation with potassium permanganate converted it

into sativic acid, insoluble in light petroleum or ether, melting at  $165^{\circ}$  after one recrystallisation from alcohol, and having an equivalent weight of 338 (sativic acid, 348). The pumice was now boiled with water and the acids liberated from the soap solution thus obtained were washed and dried [Found: *M* (mean), 340, 340. Iodine absorption, 144, 145%]. The potassium salts derived from 19 g. of the acids gave, on oxidation with permanganate: (a) 0.95 g., soluble in light petroleum, melting at  $45-60^{\circ}$  after two recrystallisations, and probably representing impure saturated acid; (b) 0.85 g. of dihydroxystearic acid (white crystals, m. p.  $128-130^{\circ}$ . Found: C, 67.8; H, 11.8%); (c) 2.7 g. of sativic acid. The last was separated by fractional crystallisation into portions, m. p.  $169.5^{\circ}$  and  $154^{\circ}$ , respectively. Nicolet and Cox (*J. Amer. Chem. Soc.*, 1922, **44**, 144) have shown that the two *dl*-mixtures of tetrahydroxystearic acids formed by the oxidation of linoleic acid can be separated by fractional crystallisation, the melting point of one being  $171^{\circ}$  and of the other  $153^{\circ}$ .

The zinc salt of a fatty acid was left on the pumice after the extraction of the soaps. It melted at  $123^{\circ}$ , and was probably impure zinc stearate derived from the zinc of the galvanised iron extractor and the stearic acid of the resin. A specimen of the zinc salt prepared from a somewhat impure sample of the solid acid isolated from the resin (m. p.  $67-69^{\circ}$ ), by heating the acid in cymene solution with zinc oxide, melted at  $123^{\circ}$ .

Hence the presence of oleic and linoleic acids in the Liquid Fraction can be regarded as established; and, since further only  $C_{18}$  acids are present, it seems safe to assume that the higher liquid fatty acids in rubber consist of oleic and linoleic acids exclusively. The purest sample of the mixed liquid fatty acids isolated showed an iodine absorption of 140 (*vide supra*). As this sample probably contained a small amount of solid acid as impurity, it is probable that the amount of linoleic acid present is considerably more than twice that of oleic acid. This conclusion is supported by the relative yields of dihydroxy- and tetrahydroxy-stearic acids obtained on oxidation.

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