196. *The Liquid Acids of Sapucainha Oil.*

By Humphrey Paget.

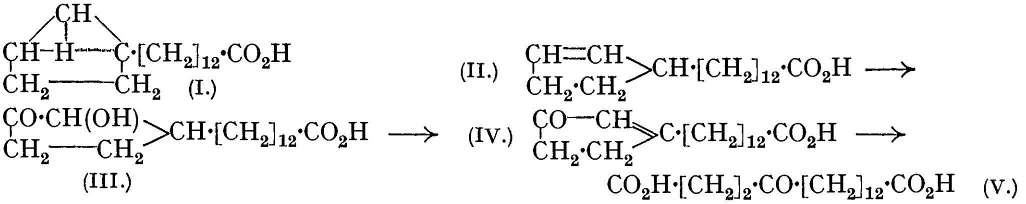
SAPUCAINHA oil is derived from the seeds of *Carpotroche brasiliensis*, Endl., and is used in Brazil for the treatment of leprosy. It resembles closely chaulmoogra and hydnocarpus oils, which are extensively used for the same purpose in other parts of the world, and it has been shown (da Silva, *Rev. Brasil. med. pharm.*, 1926, **2**, 627; Rothe and Surerus, *Rev. Soc. brasil. Chim.*, 1931, **2**, 358; Kariyone and Hasegawa, *J. Pharm. Soc. Japan*, 1934, **54**, 28) to yield the same characteristic acids, chaulmoogric and hydnocarpic, described by Power and his colleagues (J., 1904, **85**, 838; 1905, **87**, 884).

In addition to the crystalline components, the acids from these oils comprise a considerable liquid fraction, the composition of which has not been fully determined. Dean and Wrenshall (*J. Amer. Chem. Soc.*, 1920, **42**, 2626; *U.S. Pub. Health Bull.*, 1924, **141**, 15) obtained from the acids of chaulmoogra oil, by repeated distillation and by the solubility of the lead salts in ether, a liquid acid having an iodine absorption value 180·4, $[\alpha]_D + 53{\cdot}1°$, *M*, 278·9. It gave no solid bromide, but yielded dihydrochaulmoogric acid on hydrogenation. They concluded that an acid, $C_{18}H_{30}O_2$, corresponding to chaulmoogric acid, but with a second ethylenic linkage, was present; from the manner in which it absorbed iodine they considered that the second ethylenic linkage was in the side chain. Hashimoto (*J. Amer. Chem. Soc.*, 1925, **47**, 2325) fractionated under 0·05 mm., in a specially designed apparatus, the final 10—15% of the ethyl esters of chaulmoogra oil which remained after removal of ethyl chaulmoograte and hydnocarpate, and which decomposed during distillation under 1—3 mm. He isolated taraktogenic acid, $C_{36}H_{60}O_6$, m. p. 113·5°, *iso*gadoleic acid, $C_{20}H_{38}O_2$, m. p. 65·6—66°, a lactone-like substance, $C_{18}H_{32}O_2$, m. p. — 11·6°, and other less definite products, which included a considerable amount of tarry matter.

The present work deals with the liquid acids from sapucainha oil, but the conclusions apply equally to the corresponding fraction of acids from hydnocarpus oil. In order to minimise decomposition and polymerisation of these rather unstable acids, separation by distillation was avoided as far as possible, and recourse had to crystallisation and to the separation of the copper salts by means of their different solubilities in acetone and in ether. In this way the residual acids from the mother-liquors after crystallisation of the total acids were separated into three principal fractions:

1. Crystalline acids derived from acetone-insoluble, ether-soluble copper salts. These consisted of chaulmoogric, hydnocarpic and palmitic acids.
2. Liquid acids, soluble in light petroleum, derived from acetone-soluble copper salts, and containing chaulmoogric, hydnocarpic, palmitic, *ketochaulmoogric*, *ketohydnocarpic*, oleic and *dehydrochaulmoogric* acids.
3. Tarry acids, insoluble in light petroleum, derived from the copper salts insoluble in acetone and in ether, and from which a small quantity of ketochaulmoogric and ketohydnocarpic acids was isolated.

The liquid acids deposited on standing a small crystalline crust, from which, by fractional distillation of the methyl esters, palmitic acid and a mixture of two optically inactive keto-acids were obtained. The keto-acids were separated with difficulty into ketochaulmoogric acid (IV), $C_{18}H_{30}O_3$, m. p. 116°, and a small amount of an acid, $C_{16}H_{26}O_3$, m. p. 108°, apparently the lower homologue, ketohydnocarpic acid. The first of these gave on catalytic hydrogenation (1·7 mols. of hydrogen) a mixture of dihydrochaulmoogric acid and a *dihydroketo-acid*, and on oxidation γ-keto-*n*-pentadecanedicarboxylic acid (V) in large yield.

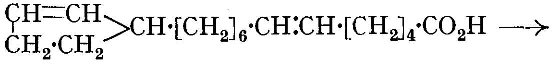

(I.) (II.) (III.) (IV.)

$CO_2H\cdot[CH_2]_2\cdot CO\cdot[CH_2]_{12}\cdot CO_2H$ (V.)

In the course of unpublished work carried out in these laboratories in 1916 on the acids of chaulmoogra oil, Clewer isolated an optically inactive acid, m. p. 114—115°, for which he suggested the formula $C_{18}H_{30}O_3$. His acid was not available for comparison, but from the details of its isolation it is likely that it was identical with ketochaulmoogric acid. Barrowcliff and Power (J., 1907, **91**, 557) found γ-keto-*n*-pentadecanedicarboxylic acid among the products of oxidation of chaulmoogric acid and were thus led to formulate chaulmoogric acid as in a state of equilibrium between two tautomeric forms (I). Perkins (*J. Amer. Chem. Soc.*, 1926, **48**, 1714), while agreeing with Shriner and Adams (*ibid.*, 1925, **47**, 2727) that formula (II) is sufficient to explain Barrowcliff and Power's results, could yet find no intermediate products to account for the production of γ-keto-*n*-pentadecanedicarboxylic acid. Its ready formation from ketochaulmoogric acid (IV), and the fact that the latter has also been prepared by the autoxidation of chaulmoogric acid or its ethyl ester, suggest the above course of oxidation, the keto-acid being a dehydration product of the ketol (III), which, though it has not been isolated, may be supposed to be formed during autoxidation (cf. King, J., 1936, 1788).

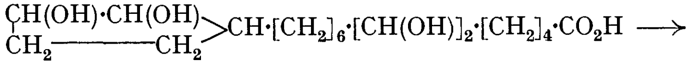
The remainder of the liquid acids, about 16% of the total acids, contained a more highly unsaturated constituent than chaulmoogric acid, and this has been identified as dehydrochaulmoogric acid (VI).

(VI.)



$$\begin{matrix}CH{=}CH\\ CH_2{\cdot}CH_2\end{matrix}\!>\!CH{\cdot}[CH_2]_6{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CO_2H \longrightarrow$$

(VII.)



$$\begin{matrix}CH(OH){\cdot}CH(OH)\\ CH_2\text{———}CH_2\end{matrix}\!>\!CH{\cdot}[CH_2]_6{\cdot}[CH(OH)]_2{\cdot}[CH_2]_4{\cdot}CO_2H \longrightarrow$$

(VIII.) $CO_2H{\cdot}[CH_2]_2{\cdot}CH(CO_2H){\cdot}[CH_2]_6{\cdot}CO_2H + CO_2H{\cdot}[CH_2]_4{\cdot}CO_2H$ (IX.)

Dehydrochaulmoogric acid yielded no crystalline derivative by which it could be isolated, and since further purification involved distillation at a somewhat high temperature and with decomposition, it was not attempted. On the basis of the iodine absorption value and on the assumption that oleic and chaulmoogric are the only other acids present, it constituted about 60% of this fraction of acids. The liquid acids were readily hydrogenated, yielding dihydrochaulmoogric and stearic acids. The products of oxidation by permanganate included (i) dihydroxystearic acid, which with the formation of stearic acid by hydrogenation proved the presence of oleic acid, and (ii) a lævorotatory, water-soluble acid, which for the reasons given below is regarded as *tetrahydroxydihydrochaulmoogric acid* (VII). This acid can exist in a number of stereoisomeric forms and the fact that difficulty was experienced in raising the melting point by crystallisation, and that fractions melting as widely apart as 60° and 113° gave comparable analytical figures and the same products on oxidation, suggests the presence of more than one form. It was rapidly oxidised by cold Beckmann's chromic acid mixture to give adipic acid (IX) and a tribasic acid, $C_{12}H_{20}O_6$, which could not be obtained crystalline but yielded a *trianilide*. The tribasic acid must be n-*nonane-αα'γ-tricarboxylic acid* (VIII), since on oxidation succinic acid and a mixture of adipic and suberic acids were obtained.

In addition to the tribasic acid (VIII) a keto-acid was isolated from the oxidation products of tetrahydroxydihydrochaulmoogric acid, as its *semicarbazone*, $C_{13}H_{23}O_5N_3$. Insufficient was obtained to determine its constitution, but by analogy with δ-keto-*n*-hexadecanedicarboxylic acid, obtained by Shriner and Adams (*loc. cit.*) from *iso*chaulmoogric acid, it is possible that this acid is δ-keto-*n*-decane-αω-dicarboxylic acid, $CO_2H{\cdot}[CH_2]_3{\cdot}CO{\cdot}[CH_2]_6{\cdot}CO_2H$, indicating the presence of a dehydro*iso*chaulmoogric acid in the liquid acid fraction.

The acid fraction (3) from the copper salt insoluble in acetone and in ether resembled the non-crystalline products obtained by autoxidation of sapucainha oil, its acids or their esters. Like other unsaturated long-chain fatty acids, after long exposure to light and air in thin layers they exhibit a rise in acid and saponification values and of specific gravity, and a considerable lowering of iodine absorption value and specific rotation. From the clinical point of view this product is of importance, since it causes great irritation on injection (Paget, Trevan, and Attwood, *Internat. J. Leprosy*, 1934, **2**, 149), and hydnocarpus preparations, intended for clinical use, should be prepared and stored under conditions which will reduce the risk of autoxidation, with the formation of this substance, to a minimum.

The amounts of these constituents in the sample of oil examined were approximately (i) chaulmoogric, hydnocarpic and palmitic acids 65—70%, (ii) oleic acid 4% ,(iii) dehydrochaulmoogric acid 9%, (iv) ketochaulmoogric and ketohydnocarpic acids 4%, and (v) tarry acids 9%.

EXPERIMENTAL.

Isolation of Acids of Sapucainha Oil.—The seeds of *Carpotroche brasiliensis* resembled those of *Hydnocarpus wightiana* but were smaller, 100 seeds weighing on an average 34 g. They were crushed and extracted completely with carbon tetrachloride. The extract was evaporated, and the residue freed from traces of solvent by steam and dried at 100° in a vacuum. The yield of oil was 41·2% of the whole seed, and it closely resembled hydnocarpus oil.

Oil.	Acid value.	Sapon. value.	Iodine value.	$[\alpha]_D$.	$d^{25°}_{25°}$.
Sapucainha	21·7	199·7	101·3	+54·0°	0·9563
Hydnocarpus	6·0	196·0	95·0	+55·4	0·9656

The oil was hydrolysed by boiling for 30 minutes with a small excess of *N*-alcoholic potash; most of the alcohol was then distilled off, and the residue diluted with water and acidified. The fatty acids were washed with water, dried at 100°, and dissolved in 10 volumes of 80% alcohol. After standing overnight at 10°, a crop of crystalline acids separated (*A*; 56·5%). It has been repeatedly shown that the mixture of crystalline acids isolated from chaulmoogra and hydnocarpus oils consists essentially of chaulmoogric and hydnocarpic acids and small amounts of palmitic acid have also been obtained (Power and Gornall, J., 1904, **85**, 838). The crystalline acids of sapucainha oil have the character of such a mixture, m. p. 44—46°, $[\alpha]_D + 57{\cdot}2°$, and by fractional crystallisation from alcohol of strength gradually increasing from 80 to 95%, and finally from light petroleum, these three components were separated, chaulmoogric acid, m. p. 69°, $[\alpha]_D^{20°} + 62{\cdot}05°$ ($c = 1{\cdot}04$; chloroform); hydnocarpic acid, m. p. 56°, $[\alpha]_D^{20°} + 67{\cdot}7°$ ($c = 0{\cdot}76$; chloroform); palmitic acid, m. p. 62°.

Evaporation of the mother-liquors from the crystalline acids left a soft, light brown solid (43·5%; acid value, 195; iodine value, 129; $[\alpha]_D + 52°$). This was dissolved in alcohol and neutralised by alcoholic potassium hydroxide, and the solution evaporated to dryness at low pressure. The dried potassium salts were extracted with acetone, which removed a small amount of unsaponified oil and a neutral substance crystallising from *iso*propyl ether in leaflets, m. p. 132°; it gave the colour reactions of the phytosterol isolated by Power and Gornall (*loc. cit.*) from chaulmoogra oil, and a mixture with this substance showed no depression of melting point. From the potassium salts, dissolved in water, the copper salts were precipitated by a solution of copper acetate as a plastic mass, which was washed with water, air-dried, and ground with successive quantities of cold acetone until the solvent remained colourless. On evaporation of the acetone, about 75% of the copper salt remained as a sticky, dark green mass (acetone-soluble copper salt). The acetone-insoluble fraction was refluxed with ether, which removed a small amount (ether-soluble copper salt) as a dark green powder on evaporation of the solvent. Finally a lighter coloured solid salt remained, insoluble both in acetone and in ether (insoluble copper salt). Each of these three fractions was decomposed by shaking with a small excess of 10% hydrochloric acid and an equal volume of ether until dissolved, and the acid recovered. The ether-soluble copper salt yielded a mixture of crystalline acids closely resembling (*A*), with which it was mixed, and it need not be further considered.

Acids from the Acetone-soluble Copper Salt.—The acid from the acetone-soluble copper salt was a light brown, rather viscous oil. It was poured into 15 volumes of light petroleum and shaken with charcoal, which eliminated a small amount of tar; after standing for some days at about 4°, the solution was decanted and evaporated, yielding a liquid, golden-yellow acid fraction, which slowly deposited crystalline matter (*B*). When the deposition ceased, the clear liquid acids were decanted and converted into methyl esters, and the latter distilled in a current of carbon dioxide until the b. p. rose to 200°/4 mm.; distillation was then stopped. The distilled fractions (30%; saponification value, 195 to 200; $[\alpha]_D + 40°$ to $+ 50°$) on hydrolysis yielded solid acids, which, after removal of a crop of nearly pure hydnocarpic acid by crystallisation from alcohol, were mixed with (*B*). The undistilled fraction of methyl esters, after hydrolysis and removal of a little crystalline acid, which proved to be mainly chaulmoogric acid, yielded the liquid acid fraction, as a mobile yellow oil, which solidified to some extent below 5° (*C*; 16% of total sapucainha acids; acid value, 198; iodine absorption value, 138; $[\alpha]_D + 45°$).

Acid fraction (B). The crystalline matter (*B*) was converted into the methyl ester and distilled in three fractions: (1) b. p. 145—160°/0·5 mm. (30%); (2) b. p. 160—185°/0·5 mm. (34%); (3) b. p. 185—210°/0·5 mm. (12%), leaving a tar which decomposed on further heating. Fraction (1) solidified and after crystallisation from methyl alcohol was identified by its m. p. (29°) and that of its acid (62°) as methyl palmitate. Fraction (2) was a mixture. The third fraction also crystallised, m. p. about 42°, and yielded on hydrolysis an optically inactive acid, sparingly soluble in ether, m. p. 98—104°. After repeated crystallisation from alcohol, ethyl acetate and finally from acetic acid, it was obtained in slightly yellow, crystalline granules, m. p. 116° (Found: C, 73·5; H, 10·2. $C_{18}H_{30}O_3$ requires C, 73·5; H, 10·2%). It yielded a *semicarbazone*, which crystallised well from alcohol, m. p. 157° (decomp.) (Found: C, 65·3; H, 9·45; N, 11·85. $C_{19}H_{33}O_3N_3$ requires C, 64·95; H, 9·4; N, 11·95%), and on acid hydrolysis gave the original keto-acid, which is shown below to be *ketochaulmoogric acid*.

From the mother-liquors from which this acid was obtained a small amount of another acid separated, m. p. 108°, which appeared to be the lower homologue, *ketohydnocarpic acid* (Found: C, 72·3; H, 9·1. $C_{16}H_{26}O_3$ requires C, 72·2; H, 9·8%), but insufficient was obtained from this source in a pure condition to characterise it beyond the preparation of its *semicarbazone*, m. p. 156° (decomp.) (Found: C, 63·45; H, 8·9; N, 12·5. $C_{17}H_{29}O_3N_3$ requires C, 63·2; H, 9·0; N, 13·0%).

Ketochaulmoogric acid (IV). When shaken vigorously in alcoholic solution with Adams's platinum oxide catalyst in hydrogen, the keto-acid absorbed rather less than the equivalent of two molecules (Found, 1 g. = 130·7 c.c. Calc. for $2H_2$, 152·4 c.c.). The m. p. of the product was indefinite, 74—82°, and by treatment with semicarbazide and refluxing the product with ether it was separated into an insoluble *semicarbazone* (60%), m. p. 164° (from acetic acid) (Found : C, 64·85; H, 10·0; N, 11·7. $C_{19}H_{35}O_3N_3$ requires C, 64·6; H, 9·9; N, 11·9%), and an ether-soluble non-ketonic acid (40%), m. p. and mixed m. p. with dihydrochaulmoogric acid, 72° (Found : C, 76·0; H, 12·0. Calc. : C, 76·6; H, 12·1%). The keto-acid (0·7 g.) in 1% potassium hydroxide solution (20 c.c.) was oxidised at 20° by 1% aqueous potassium permanganate (120 c.c.), and the filtered solution made acid and extracted with ether. It yielded an acid, m. p. and mixed m. p. with γ-keto-*n*-pentadecanedicarboxylic acid 127° (Found: C, 65·1; H, 9·5. Calc.: C, 65·0; H, 9·55%). This identification was confirmed by preparation of the oxime, m. p. 87°.

The liquid acids (C). *Hydrogenation.* On hydrogenation in alcoholic solution in presence of palladium on barium sulphate, the liquid acids absorbed rapidly 40% of the amount of hydrogen required by the iodine value (Found : 48 c.c. per g.; required by iodine value 138, 122 c.c. per g.), yielding (*a*) a crystalline acid, m. p. and mixed m. p. with dihydrochaulmoogric acid 72°, and (*b*) a non-crystalline residue, iodine value 86, $[\alpha]_D$ − 0·6°. The latter rapidly absorbed more hydrogen in presence of Adams's platinum oxide catalyst (Found : 83 c.c. per g.; required by iodine value 86, 76 c.c. per g.), yielding a solid, optically inactive product, which crystallised well from light petroleum in leaflets. Prolonged fractional crystallisation resulted in the isolation of nearly 50% as dihydrochaulmoogric acid, the remaining crops melting between 48° and 65° and being of almost the same empirical composition (Found : C, 76·1; H, 12·3; *M*, by titration, 296·3. Calc. : C, 76·6; H, 12·1%; *M*, 282). They showed no depression of m. p. with a mixture of dihydrochaulmoogric acid (70%) and stearic acid (30%), which melted at 63—64°. No further separation could be effected by distillation of the methyl esters, by lead salt precipitation, or by crystallisation of the *p*-bromoanilides, which melted at 93° to 96° after several crystallisations from light petroleum (Found : C, 66·0; H, 8·85; N, 3·5; Br, 18·4. Calc. for $C_{24}H_{38}ONBr$: C, 66·0; H, 8·7; N, 3·2; Br, 18·35%). The p-*bromoanilide* of dihydrochaulmoogric acid melts at 102° and that of stearic acid at 113°; a mixture in the proportion 70 : 30 melts at about 95—100°.

Oxidation. The liquid acids (50 g.) in 10% potassium hydroxide solution (300 c.c.) and 1 l. of water were oxidised by 4% aqueous potassium permanganate (1 l.), added slowly and with vigorous stirring, about 1 kg. of ice being added during the operation. Sulphur dioxide was passed into the product to decompose the manganese dioxide, and the solution made acid to Congo-red paper and kept. The aqueous layer was separated from water-insoluble acids, which were boiled with 1500 c.c. of water and separated. The water-insoluble acids were dissolved in ether, dried, and diluted with the same solvent; a flocculent precipitate then separated. After crystallisation from ethyl acetate, it had m. p. and mixed m. p. with dihydroxystearic acid, 131° (Found: C, 68·1; H, 11·2. Calc.: C, 68·4; H, 11·4%). The remaining water-insoluble, syrupy product (acid value, 175; iodine absorption value 50, $[\alpha]_D$ + 5°) was not further examined.

The combined aqueous solutions were concentrated till opalescent, and on cooling they deposited a flocculent solid; this was filtered off, and the process repeated, until about 100 c.c. remained, which were extracted with ether. The acid so obtained was sparingly soluble in ether, chloroform or benzene, moderately in water or ethyl acetate and readily in alcohol; by repeated crystallisation from ethyl acetate and finally from water, an *acid* was obtained, m. p. 111—113°, $[\alpha]_D^{18°}$ − 17·9° (*c* = 1·7; absolute alcohol) (Found: C, 62·55; H, 10·1; *M*, by titration, 349·7. $C_{18}H_{34}O_6$ requires C, 62·4; H, 9·8%; *M*, 346). The *methyl* ester, prepared by means of diazomethane, was rather sparingly soluble in ether, but crystallised well from benzene, m. p. 88° (Found : C, 63·2; H, 10·45; OMe, 8·4. $C_{19}H_{36}O_6$ requires C, 63·3; H, 10·0; OMe, 8·6%). On heating a few degrees above the m. p. for some hours, the acid lost 4·8% (H_2O requires 5·2%), forming a glassy lactone, from which the acid was regenerated by long boiling with potassium hydroxide in alcohol. The acid did not react with semicarbazide; attempts to obtain a crystalline benzoate or nitrobenzoate were unsuccessful, the greater part of the acid being recovered apparently as the lactone. The methoxyacetyl derivative of the methyl ester was prepared by heating the ester (1 g.) in dry pyridine (5 c.c.) with methoxyacetic anhydride (5 g.) to boiling for 1 minute : after standing for 2 hours, the product was dissolved in ether and washed several times with 1% sulphuric acid and with 2% sodium carbonate solution. The product, which was a hygroscopic syrup, was dried to constant weight in a vacuum desiccator [Found : C, 57·8; H, 8·1; OMe, 23·1; *M* (by hydrolysis), 657. $C_{19}H_{32}O_6(C_3H_5O_2)_4$ requires C, 57·4; H, 8·0; OMe, 23·9%; *M*, 648]. This is therefore the *tetramethoxyacetyl* derivative of methyl tetrahydroxydihydrochaulmoograte. The *phenylurethane* of the acid, prepared by refluxing with the theoretical amount of phenyl *iso*cyanate in dry benzene solution for 6 hours, crystallised from dilute alcohol, m. p. 145° [Found : C, 67·5; H, 6·6; N, 7·15. $C_{18}H_{30}O_6(C_7H_6ON)_4$ requires C, 67·15; H, 6·6; N, 6·8%].

Oxidation of Tetrahydroxydihydrochaulmoogric Acid (VII).—The acid (2 g.) was heated gently with Beckmann's chromic acid mixture (80 c.c.) for 15 minutes, cooled, and extracted thoroughly with ether. The product was allowed to crystallise from about 3 c.c. of ether, yielding an acid, m. p. 151°, identified as adipic acid (Found : C, 49·75; H, 7·0. Calc. : C, 49·3; H, 6·85%). It was further identified by the dianilide, m. p. 238°, and the bromophenacyl ester, m. p. 154°. The yield of adipic acid isolated was about 35% (calc., 42·2%).

The rest of the oxidation product did not solidify. With an alcoholic solution of semicarbazide, it yielded a very small amount of a *semicarbazone*, m. p. 187° (Found : C, 51·1; H, 7·6; N, 13·9. $C_{13}H_{23}O_5N_3$ requires C, 51·8; H, 7·65; N, 13·95%). The non-ketonic acid was recovered, esterified by diazomethane, and distilled to remove traces of methyl adipate; a fraction was obtained, b. p. 200—217°/15 mm., which did not crystallise [Found : C, 59·85; H, 8·75; OMe, 29·5. $C_9H_{17}(CO_2Me)_3$ requires C, 59·6; H, 8·6; OMe, 30·8%]. The *trianilide* was prepared from the methyl ester by Hardy's method (J., 1936, 398), m. p. 189° (from absolute alcohol) (Found: C, 73·95; H, 7·35; N, 8·85. $C_{30}H_{35}O_3N_3$ requires C, 74·2; H, 7·2; N, 8·65%).

Oxidation of the Tribasic Acid, $C_{12}H_{20}O_6$ (VIII).—The tribasic acid (3 g.) was refluxed for 24 hours with successive amounts of Beckmann's chromic acid mixture (30 c.c.), and the combined liquors extracted thoroughly with ether. A mixture of crystalline acids was obtained in addition to unchanged tribasic acid, and on boiling with chloroform a part was sparingly soluble, m. p. and mixed m. p. with succinic acid 181°; its *p*-bromophenacyl ester melted at 210°; and it gave a sparingly soluble, crystalline barium salt (Found : Ba, 54·75. Calc. for $C_4H_4O_4Ba$: Ba, 54·2%). From the fraction of acids soluble in chloroform was separated, by repeated crystallisation from ethyl acetate, a small amount which, though melting sharply at 122—123°, was apparently a mixture (Found : C, 53·4; H, 7·65; *M*, by titration, 168). A mixture of suberic acid (70%) and adipic acid (30%), fused together and finely powdered, melted at 121—123° (Calc. : C, 53·35; H, 7·65%; *M*, 165·6); admixture with the acid from the oxidation caused no change of m. p.

The Acids from the "Insoluble Copper Salt."—The product from the decomposition of the insoluble copper salt by dilute hydrochloric acid was dark and viscous and represented about 9% of the total acids. It gave a barium salt insoluble in water and had acid value 151, saponification value 226, iodine absorption value 69, $[\alpha]_D$ about + 10°. Neither the acids nor their ethyl esters could be distilled without considerable decomposition; a part of the ethyl esters was soluble in light petroleum but gave no appearance of satisfactory separation. When the acid was boiled with light petroleum, and the solvent decanted hot and kept, a small amount of a mixture of ketochaulmoogric and ketohydnocarpic acids separated, but no other crystalline product was obtained.

Autoxidation of Sapucainha Oil and of Ethyl Chaulmoograte.—Sapucainha oil was exposed in thin layers in glass dishes to sunlight and air for several months. The oil, which was at first limpid, gradually set to a tough and sparingly soluble skin, without darkening in colour. On saponification it at once became very dark, yielding a tarry acid product.

Ethyl chaulmoograte, prepared from pure chaulmoogric acid and distilled in carbon dioxide at 191—193°/0·5 mm., melted at 8°, saponification value, 184·5; iodine absorption value, 82·3; $[\alpha]_D^{20^\circ}$ + 56·3° (*c* = 1·03; chloroform); $d_{15^\circ}^{15^\circ}$ 0·9080. This was freely exposed in the same way throughout the summer months; it then showed an increase in weight of 8·5% (calc. for O_2, 10·4%), and was considerably altered in character [acid value, 27·7; saponification value, 211·6; iodine absorption value, 31·8; $[\alpha]_D^{20^\circ}$ + 3·3° (*c* = 1·17; chloroform); $d_{15^\circ}^{15^\circ}$ 1·002]. The product was hydrolysed by dissolving it in alcohol, and, in an atmosphere of nitrogen, adding the calculated amount of alcoholic potassium hydroxide solution. The solution darkened at once; it was concentrated and acidified, and the syrupy acid product dried and extracted repeatedly with hot light petroleum. The petroleum extract deposited crystals, separating from alcohol in a granular form, m. p. and mixed m. p. with ketochaulmoogric acid from the liquid acid fraction of sapucainha oil, 116°.

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