LXXV. UNSATURATED ACIDS OF NATURAL OILS.

I. HIGHLY UNSATURATED ACIDS FROM ORTICICA OIL (*LICANIA RIGIDA*).

BY WILLIAM BERNARD BROWN
AND ERNEST HAROLD FARMER.

*From the Organic Chemistry Department, Imperial College of Science
and Technology, South Kensington, London.*

(Received January 30th, 1935.)

ORTICICA oil comes into the market from Brazil in two forms, (1) as a fat of melting-point about 20° and (2) as a permanent oil. The botanical source of the oil has been for some years in doubt, being variously ascribed to the fruits of *Couepia grandiflora* (or *grandifolia*), *Licania rigida*, *Moquilea tomentosa*, *Pleragina umbrosissima*, *Arruda camara* and several other trees. The most recent opinion, however, ascribes the oil to the kernels of *Licania rigida*.

The authors' experiments were begun with the intention of investigating the constitution of the most highly unsaturated acid present (as a glyceride) in the oil of *Couepia grandiflora*, which according to the work of Van Loon and Steger [1931] is a conjugated triene acid, $\text{CH}_3 \cdot (\text{CH}_2)_3 \cdot (\text{CH}:\text{CH})_3 \cdot (\text{CH}_2)_7 \cdot \text{CO}_2\text{H}$, isomeric with elaeostearic acid. If the constitution thus assigned were correct the new acid would add a third conjugated isomeride (supposedly of *cis-trans* type) to the two well-known forms (α - and β -) of elaeostearic acid.¹ The new acid, a substance very prone to atmospheric oxidation, has been designated by Van Loon and Steger couepic acid, and its constitution depends on its reputed conversion into stearic acid by catalytic hydrogenation (three double bonds) and its oxidation by ozone to yield valeric acid and azelaic acid. The physical characteristics of the acid are represented as being considerably different from those of α -elaestearic acid: the optical exaltation, in particular, is low (2.3) in comparison with that of α -elaestearic acid (8), a circumstance on which Rossmann [1932] subsequently bases a criticism of the triene constitution assigned by Van Loon and Steger, suggesting in place of the latter the non-conjugated semi-cyclic constitution

This semi-cyclic formula appears to merit no very serious consideration, but the multiplication of the isomerides of the economically important α -elaestearic acid as reported by Van Loon and Steger—especially in view of certain recent experimental observations of Rossmann [1933] to the effect that elaeostearic acid passes on heating to 220° in an atmosphere of carbon dioxide into both a semi-cyclic isomeride and a dimeride—is of very great interest.

¹ Van Loon and Steger [1931] recognise five elaeostearic acids of which three (α -, β - and γ -) are stated to occur in chinawood oil, one (δ -) is obtained synthetically, and the fifth (ϵ -) is couepic acid.

The authors' attempts to obtain the authenticated fruits or oil of *Couepia grandiflora* proved unsuccessful and attention was turned to oiticica oil which appeared probably, although not certainly, to be the material actually employed by Van Loon and Steger. Two varieties of commercial oiticica oil and an adequate supply of oiticica kernels were obtained, the latter being definitely identified as kernels of *Licania rigida*. One of the commercial samples of oil was a semi-solid fat at room temperature, and this resembled the fat extracted by light petroleum from the disintegrated kernels (a faintly yellow oil until cooled); the other sample was permanently an oil and doubtless represented a "polymerised" oiticica oil which is obtained by heating the solvent-extracted or hot-pressed oil at 225° for about an hour. The permanently liquid oil, the heat-modified nature of which was not at first suspected by the authors, yielded on saponification a mixture of unsaturated and saturated acids from which the highly unsaturated component could readily be separated by crystallisation from petroleum. This acid, amounting to about 2 % of the total mixed acids (much of the original highly unsaturated acid having apparently undergone conversion into a petroleum-insoluble material), melted at 96.5° and rapidly absorbed oxygen from the atmosphere: it corresponded in all described characteristics with an acid, M.P. 94°, reported by Wilborn and Löwa [1929] to be isolable from *Couepia grandiflora*, but was apparently different from Van Loon and Steger's couepic acid (highest recorded M.P. 74–75°) in that it yielded on oxidation with permanganate not valeric acid and azelaic acid as principal products, as should a geometrical isomeride of elaeostearic acid, and as was indeed reported by Van Loon and Steger for their acid, but valeric acid and γ -ketoazelaic acid, $\text{HO}_2\text{C} \cdot (\text{CH}_2)_4 \cdot \text{CO} \cdot (\text{CH}_2)_2 \cdot \text{CO}_2\text{H}$. There was formed, however, in addition to the above-mentioned major products, a very small proportion of a dicarboxylic acid of M.P. 205°, doubtless fumarylglucydic acid

apparently derived by the dehydration of racemic acid.

Saponification of the two semi-solid fats yielded in each case a mixture of acids from which the highly unsaturated component could readily be isolated by crystallisation from petroleum. This substance was in each case the same, *viz.* an acid of M.P. 74–75°, which, although similar in general characteristics to the one from permanently liquid oiticica oil, showed a marked depression of melting-point on mixing therewith; furthermore in each case the acid was obtained in not less than 25 % (maximum isolated 33 %) yield, and in each case was unaccompanied by any considerable quantity of petroleum-insoluble acid. There was thus every indication that the semi-solid commercial oiticica oil was in reality licania oil in a state not seriously changed by the processes involved in its preparation. The subsequent observations are mainly concerned with the structure of what must now be regarded as the characteristic highly unsaturated acid of *Licania rigida*, and this acid is henceforth referred to as *licanic acid*. It is to be noted that the saturated and the less highly unsaturated acids of licania or oiticica oil have not been examined.

Licanic acid yielded on oxidation with permanganate valeric acid and a ketoazelaic acid identical with that obtained from the highly unsaturated acid of "polymerised" oiticica oil. These were the major products, but when oxidation was pushed well beyond the stage at which rapid decoloration of permanganate at 0° ceased, there were also obtained some oxalic acid (about $\frac{1}{3}$ mol.) and a quantity of syrupy and gummy acidic material which was susceptible of

further slow oxidation with permanganate at room temperature. It is to be observed, however, that none of the dicarboxylic acid (M.P. 205°) referred to above was formed.

The ketoazelaic acid, which readily yielded a semicarbazone (M.P. 197°) and passed smoothly into azelaic acid on reduction by the method of Clemmensen, must necessarily be either the α - or γ -keto-derivative of the normal-chained dibasic acid, since it neither gave a colour with ferric chloride, as would a β -keto-acid, nor resembled the already-known δ -ketoazelaic acid (M.P. 108–109°; semicarbazone, M.P. 176–177°) synthesised by von Pechmann and Sidgwick [1904]. Its formulation as the γ -acid was confirmed by its degradation in the expected manner with Beckmann's chromic acid mixture; with this reagent it yielded as principal products adipic and succinic acids:

In the presence of platinum licanic acid absorbed three molecular proportions of hydrogen yielding thereby hexahydrolicanic acid—an acid characterised by great stability towards permanganate but capable of forming a semicarbazone and possessing the empirical composition of a ketostearic acid. Thus, since both the two principal oxidation fragments are normal-chained acids, only two formulae offer themselves for the representation of licanic acid, *viz.* (I) and (II), which embody the two ways in which the ketoazelaic acid skeleton can be attached to the valeric acid skeleton whilst retaining triene unsaturation:

The correctness of the normal chain here depicted follows from the smooth conversion of the hexahydrolicanic acid into stearic acid by the method of Clemmensen:

Choice between the two formulae (III) and (IV) for hexahydrolicanic acid was made by oxidising the latter acid with chromic acid in acetic acid. The hexahydro-acid possessed a much higher degree of resistance towards chromic acid than did γ -ketoazelaic acid, but it broke down slowly on boiling with the oxidising mixture into a low-melting mixture of fatty acids and succinic acid; no adipic acid or glutaric acid was formed. The fatty acid product resembled myristic acid, but obviously was not homogeneous: doubtless it consisted of a mixture of myristic acid, $\text{CH}_3 \cdot (\text{CH}_2)_{12} \cdot \text{CO}_2\text{H}$, and pentadecanoic acid, $\text{CH}_3 \cdot (\text{CH}_2)_{13} \cdot \text{CO}_2\text{H}$, but, owing to the great difficulty of separating these acids, the isolation of the pure fatty acid components was not attempted with the amount of material at disposal. The dibasic acid complementary to pentadecanoic acid, *viz.* malonic acid would not survive under the conditions of oxidation. Of the two formulae (III) and (IV), III must therefore represent hexahydrolicanic acid; that is to say, hexahydrolicanic acid, M.P. 96.5°, is γ -ketostearic acid. Confirmation of this conclusion is supplied by the experimental establishment of identity between hexahydrolicanic acid and synthetic γ -ketostearic acid, M.P. 97°, the latter first obtained by Clutterbuck and Raper [1925] as an oxidation product of stearic acid and now obtained by repeating their preparation.

Licanic acid is accordingly γ -keto- $\Delta^{9,11,13}$ -octadecatrienoic acid (4-keto- $\Delta^{9,11,13}$ -octadecatrienoic acid), represented by formula (I), and it is, so far as the authors

are aware, the first ketonic polyene-acid outside the group of carotenoids to be described.

A point of interest arises in connection with the nature of the difference between the two triene acids described above. Both licanic acid and the acid from permanently liquid oiticica oil (*isolicanic acid*) are forms of γ -keto- $\Delta^{8,10}$ -octadecatrienoic acid, and the difference between the two would appear to be one of geometrical configuration about one or more of the double bonds. It is to be noted that only about half the quantity of acid taken readily undergoes degradation to valeric acid and γ -ketoazelaic acid, the remainder doubtless persisting as hexahydroxy-derivatives, which by reason of superior resistance to oxidative attack survive where their stereoisomerides undergo fission. The nature of these and of similar resistant polyhydroxy-acids obtained by oxidation of highly unsaturated acids is at present being investigated, but it is perhaps significant to find that although neither licanic nor *isolicanic acid* yields any appreciable quantity of racemic or mesotartaric acid, *isolicanic acid* gives a very small yield of fumarylglucydic acid (see p. 632).

Although there is nothing to show whether the oxide ring is formed during the oxidation process or subsequently by the dehydration of racemic acid, the appearance of the fumarylglucydic acid suggests that the middle double bond of *isolicanic acid* possesses a *trans*-configuration, in which respect it probably differs from licanic acid, which on further investigation may be found to yield the less-readily isolable maleylglucydic acid corresponding to mesotartaric acid.

It would seem likely that licanic acid is identical with Van Loon and Steger's couepic acid and that the latter authors' constitution for this acid is erroneous. There remains a possibility, however, that the botanical source of their *Couepia grandiflora* oil is a tree distinct from *Licania rigida*.

EXPERIMENTAL.

The triene acid from commercial oiticica oil (liquid). The liquid variety of oiticica oil as imported from Brazil was a dark golden yellow viscous liquid which from its permanent liquidity, comparatively high specific gravity (0.9898) and low iodine value (108.2) doubtless represented the so-called "polymerised" variety of oiticica oil, obtained by heating commercially expressed (or solvent-extracted) oil at 225°. The "polymerised" nature of the oil was not, however, known to the authors at the beginning of the work. The oil was saponified in the following way:

100 g. of oil were boiled under reflux for 5 hours with a solution made by dissolving 50 g. of caustic potash in the minimum quantity of water and diluting the product with 200 ml. of rectified spirit. The alcoholic solution of the potassium salts was made up to 500 ml. with cold water and then cooled in ice, cautiously acidified with 100 ml. of 45 % sulphuric acid (by weight) and finally shaken with 150 ml. of ether. The ethereal solution of fatty acids thus obtained was washed with water, dried with anhydrous sodium sulphate and gently warmed to remove the bulk of solvent; the free fatty acids were obtained by removing the residual solvent at reduced pressure without further heating.

The saponification product was immediately mixed with petroleum (B.P. 40–60°): at first a homogeneous solution was obtained, but on further addition of the solvent two layers separated, the lower layer consisting apparently of the partially oxidised or "polymerised" components of the commercial oil. This portion was twice extracted with petroleum but not further utilised. The combined upper layer and petroleum extracts were concentrated to a bulk of

300–400 ml. and allowed to cool to room temperature: a highly unsaturated acid crystallised out which was only sparingly soluble in petroleum. This acid was collected and twice extracted with 150 ml. of boiling petroleum (B.P. 40–60°), the extracts being rapidly filtered, united and allowed to cool. The crystals which then separated were collected, washed with petroleum and stored under petroleum to prevent atmospheric oxidation, which rendered them somewhat sticky in the course of several hours and ultimately converted them into a liquid material. One further recrystallisation was always carried out before the acid was used: in this way colourless flaky crystals of M.P. 96.5° were obtained. The maximum yield of acid was 1.3 g. from 100 g. of oil. Owing to the rather rapid absorption of oxygen the acid was troublesome to analyse but gave figures showing it to be an octadecatatrienoic acid (C, 73.8, 73.4; H, 9.6, 9.65 %. $C_{18}H_{28}O_3$ requires C, 73.7; H, 9.65 %). On exhaustive hydrogenation at room temperature and atmospheric pressure, in an alcoholic medium and using a platinum catalyst, the acid took up three molecules of hydrogen and yielded a saturated acid which did not decolorise permanganate even on boiling. This saturated acid which crystallised from rectified spirit in colourless flakes of M.P. 96° (C, 72.95; H, 11.5 %. $C_{18}H_{34}O_3$ requires C, 72.75; H, 11.8 %) proved to be identical with the hexahydrolicanic acid described below; moreover the semicarbazone of the acid (M.P. 126°) and its methyl ester (M.P. 49.5°) proved on direct comparison to be identical with the corresponding derivatives of hexahydrolicanic acid described below.

On oxidation with approximately 3 % permanganate at 0° the unsaturated acid took up readily 7.3 atoms of oxygen. At this stage of oxidation the principal products were a volatile fatty acid recognised as valeric acid (B.P. 180–185°; *p*-bromophenacyl ester, M.P. 64°, mixed M.P. 64°) and a solid acid which after several recrystallisations from chloroform melted at 108–109°; there were also obtained some oxalic acid and a quantity of partly oxidised material. The acid of M.P. 108–109° had the composition and basicity of a ketoazelaic acid, subsequently identified as γ -ketoazelaic acid (C, 53.35; H, 6.9 %; mol. wt. (dibasic), 204. $C_9H_{14}O_5$ requires C, 53.4; H, 6.9 %; mol. wt., 202), and yielded a *semicarbazone* of M.P. 197° (C, 46.0; H, 6.6 %. $C_{10}H_{17}O_5N_3$ requires C, 46.3; H, 6.6 %). All the above-named oxidation products were also obtained from commercial oiticica fat and from the fat from *Licania rigida* kernels and are more fully described below; another oxidation product, however, was isolated from the crude ketoazelaic acid in very small yield, and this has been obtained from neither of the other varieties of oil studied. This substance, which differed greatly from ketoazelaic acid in respect of its sparing solubility in ether, its high M.P. (205° with decomp.), and high oxygen content, appears from its composition, basicity and general properties to be the fumarylglucidic acid described by Lossen [1906] (C, 36.75, 36.65; H, 3.25, 3.2 %; equiv., 65.9. $C_4H_4O_5$ requires C, 36.35; H, 3.05 %; mol. wt., 132). The further study of the liquid form of oiticica oil has been postponed.

The triene acid from commercial oiticica fat. The commercial fat was a cream-coloured solid consisting of a mixture of glycerides. Like the liquid variety of oil it was readily saponifiable by boiling for 5 hours with strong alcoholic potash, the resulting potassium soap yielding on cautious acidification with dilute sulphuric acid and extraction as described above a partly solidifiable mixture of fatty acids. From this mixture, which set on cooling to a pale yellow waxy solid, the highly unsaturated component was isolated by dissolving the former in boiling petroleum (B.P. 60–80°) and filtering off the crystals which separated on cooling. These crystals melted at once at 73–74°, the highest M.P. attainable

even after numerous recrystallisations from petroleum being 74–75°. The crystals absorbed oxygen on exposure to the air yielding a sticky liquid; consequently it was convenient to preserve the once-crystallised acid under petroleum and crystallise it still once more immediately before use. The yield of this acid, which is henceforth designated *licanic acid*, amounted to 33 %.

On analysis *licanic acid* gave figures indicating that it possessed the empirical composition $C_{18}H_{28}O_3$ (C, 72.85; H, 9.65 %; mol. wt., ebullioscopic, in alcohol, 277; equiv., 291.5. $C_{18}H_{28}O_3$ requires C, 72.9; H, 9.65 %; mol. wt., 292) and on hydrogenation at room temperature and atmospheric pressure (platinum catalyst) in an alcoholic medium took up 3 mols. (experimental figure, 3.05 mols.) of hydrogen to yield a saturated acid of M.P. 96°. This *hexahydrolicanic acid* crystallised in colourless flakes from alcohol, the purest specimens obtainable melting at 96.5°; it possessed ketonic properties, yielding a well-defined *semi-carbazone* which crystallised from aqueous alcohol in colourless flattened needles, M.P. 126° (C, 64.1; H, 10.25 %. $C_{18}H_{37}O_3N_3$ requires C, 64.15; H, 10.5 %); moreover its analytical figures pointed to the empirical formula $C_{18}H_{34}O_3$ (C, 72.70; H, 11.55 %; equiv., 295. $C_{18}H_{34}O_3$ requires C, 72.75; H, 11.8 %; mol. wt., 298). On esterification with methyl alcoholic hydrogen chloride, the hexahydro-acid yielded the corresponding *methyl ester* which crystallised from alcohol in colourless plates, M.P. 49–50° (C, 73.1; H, 11.6 %. $C_{19}H_{36}O_3$ requires C, 73.1; H, 11.6 %).

Thus *licanic acid* is a keto-octadecatrienoic acid, and direct comparison of this acid with the isomeric acid of M.P. 96.5° obtained from the permanently liquid variety of oiticica oil showed the two substances to be quite different: on the other hand the hexahydro-acids derived from the two triene acids proved to be identical in M.P. and in the characteristics of their derivatives; moreover there was no depression of M.P. on mixing the two hexahydro-acids, their *semi-carbazones* or their esters, and both acids yielded identical products on oxidation with chromic acid (see below).

Reduction of hexahydrolicanic acid by Clemmensen's method. 0.7 g. of the hexahydro-acid, dissolved in 15 ml. of concentrated hydrochloric acid, was boiled for 4 hours with 6 g. of zinc amalgam, during which operation hydrogen chloride was passed into the boiling solution. The product, on precipitation with water and filtration, yielded a mixture of two acids, the components of which were readily separable by fractional crystallisation from petroleum (B.P. 60–80°) into unchanged hexahydrolicanic acid (M.P. 96°; mixed M.P. 96°) and stearic acid; the latter was identified by comparison with an authentic specimen (M.P. 69.5–70°; mixed M.P. 69.5–70°) and by conversion into its methyl ester (M.P. 36°; mixed M.P. 38°). Thus hexahydrolicanic acid is a ketostearic acid.

Oxidation of licanic acid. 19.5 g. of the acid dissolved in a solution of 10 g. of sodium carbonate in 100 ml. of water were oxidised at 0° with 1320 ml. of 4.85 % permanganate (9.1 atoms of oxygen). The manganese mud was filtered off and extracted three times with boiling water, the filtrate and aqueous extracts so obtained being united, concentrated to a bulk of 200 ml. and then acidified with slight excess of concentrated hydrochloric acid. The acidic product was extracted four times with 125 ml. portions of ether and the aqueous liquor first freed from ether and then from oxalic acid by precipitation with calcium chloride in presence of free ammonia; finally the ammoniacal filtrate was evaporated to dryness, the residue taken up in a little water and the filtered solution cautiously acidified and re-evaporated to dryness. From the final residue 3.2 g. of syrupy and viscous acidic material were extracted by ether and acetone used successively; a portion of this material esterified with methyl alcoholic hydrogen

chloride yielded an oil which decomposed on distillation. On removal of the solvent the ethereal extract yielded a partly crystalline residue: the liquid portion of this yielded 4.6 g. of pure valeric acid of B.P. 184° ($86-88^{\circ}/15$ mm.), the identity of which was confirmed by the preparation of the corresponding *p*-bromophenacyl ester of M.P. 64° (mixed M.P. with an authentic specimen, 64°); the rather sticky solid residue yielded on crystallisation from chloroform 6.1 g. of the γ -ketoazelaic acid (M.P. $108-109^{\circ}$; semicarbazone, M.P. 197°) previously obtained by the oxidation of permanently liquid oiticica oil and 2.9 g. of a syrupy acidic residue. It was remarkable that the crude calcium oxalate obtained from the oxidation product (about 3 g.) contained no considerable quantity of the salts of mesotartaric or racemic acid, although the restriction of the quantity of permanganate to that actually employed might have been expected to lead to their formation.

A similar oxidation carried out with 37.5 g. of licanic acid yielded 12.6 g. of ketoazelaic acid, 5.9 g. of valeric acid, 3.6 g. of calcium oxalate and 4 g. of brown syrupy acid; a portion of the last on re-oxidation with permanganate yielded a further small quantity of ketoazelaic acid.

Constitution of ketoazelaic acid. 1 g. of ketoazelaic acid was boiled for 4 hours with 10 g. of amalgamated zinc and 15 ml. of concentrated hydrochloric acid through which hydrogen chloride was bubbled continuously. On extraction with ether the cooled product yielded an acid which on crystallisation from water formed colourless prisms, M.P. $105-106^{\circ}$. This acid was different from the original acid, depressing the melting-point thereof and yielding no semicarbazone: it was identified as azelaic acid (mixed M.P. $105-106^{\circ}$).

3.5 g. of ketoazelaic acid were boiled gently with 45 ml. of Beckmann's chromic acid mixture until the latter was completely reduced. On exhaustive extraction of the cooled product with ether 4.2 g. of dry acids were obtained. Preliminary examination of this mixture by fractional crystallisation showed it to contain succinic acid, probably adipic acid and a substance melting below 100° . The mixture was therefore dissolved in water, rendered alkaline with ammonia and the boiling solution treated with calcium chloride; from the calcium succinate precipitated 0.2 g. of pure succinic acid, M.P. 185° (mixed M.P., 185°), was obtained. The dry mixed acids (3.2 g.) recovered from the ammoniacal liquor consisted mainly of adipic acid and yielded on crystallisation from ether-chloroform slightly impure adipic acid which on one further recrystallisation from the same medium attained the M.P. of 148° and gave no depression of M.P. with an authentic specimen of adipic acid. The small acidic residue (M.P. $95-100^{\circ}$) recovered from the solvent yielded no glutaric anhydride on treatment with acetic anhydride and appeared to be somewhat impure ketoazelaic acid.

From the above evidence it follows that the ketoazelaic acid obtained from licanic acid is the γ -keto-compound, a conclusion which is in agreement (a) with the observation that this ketoazelaic acid gave no colour with ferric chloride in aqueous or alcoholic solution, and (b) with the fact that this acid differed in melting-point and in the melting-point of its semicarbazone from the δ -ketoazelaic acid described by von Pechmann and Sidgwick [1904].

Oxidation of hexahydrolicanic acid. 2.8 g. of the hexahydro-acid were dissolved in 25 ml. of glacial acetic acid and thereto 5.12 g. of chromic oxide (twice the calculated quantity) were added. The mixture was boiled for 3 hours on a sand-bath and then cooled. After diluting somewhat and filtering off unchanged acid the filtrate was saturated with sulphur dioxide, boiled to expel excess of this reagent, diluted and treated with excess of ammonia. The chromium

hydroxide precipitated on boiling the alkaline liquor was filtered off and the filtrate evaporated to dryness. The residue was acidified with slight excess of concentrated hydrochloric acid and the product extracted several times with ether; the aqueous liquor was evaporated to dryness and the residue extracted first with ether and then with acetone. From the first ethereal extract, after evaporation of the solvent and the acetic acid contained therein, there was obtained a semi-solid mass, from which light petroleum removed a low-melting solid acid, leaving a small quantity of unchanged hexahydrolicanic acid; the low-melting acid (m.p. 25–30°), doubtless largely myristic acid contaminated with some proportion of pentadecanoic acid, was not further examined owing to the improbability of its complete purification being effected with the amount of material at disposal. The second ethereal extract and the acetone extract both yielded nearly pure succinic acid, melting at 185° on recrystallisation (mixed m.p. 185°). Since no trace of adipic acid was isolated the ketone group of hexahydrolicanic acid must be in the γ -position, the hexahydro-acid being accordingly γ -ketostearic acid.

The triene acid from the oil of Licania rigida kernels. The disintegrated kernels on extraction with petroleum (b.p. 60–80°) in a Soxhlet apparatus gave a 26.3 % yield of a clear golden yellow oil; when extracted with ether a 35.8 % yield of a rather turbid pale yellow oil was obtained. Both products when cooled in ice set to a faintly yellow-coloured fat which retained its solidity at room temperature. On saponification of the oil with alcoholic potash licanic acid, m.p. 74–75°, was obtained in a yield rather less than that from commercial oiticica fat. The identity of this acid with the acid from the commercial oil was fully confirmed by its behaviour on oxidation and hydrogenation and also by the identity of the corresponding derivatives of the two acids.

Preparation of hexahydrolicanic acid from stearic acid. By repetition of the oxidative procedure described by Clutterbuck and Raper [1925] γ -ketostearic acid was obtained in the form of colourless flakes, m.p. 96°; this acid yielded a semicarbazone of m.p. 126°. The acid and its semicarbazone were found by direct comparison to be identical respectively with the hexahydro-acid derived from each of the above-mentioned specimens of oiticica oil and its semicarbazone.

SUMMARY.

Two specimens of commercial oiticica oil have been examined in respect of the most highly unsaturated acid contained therein. Oiticica fat yields by saponification a solid triene acid (m.p. 74–75°), the constitution of which has been shown by degradative and synthetic methods to be γ -keto- $\Delta^{6\kappa\mu}$ -octadecatrienoic acid, $\text{CH}_3.(\text{CH}_2)_3.(\text{CH}:\text{CH})_3.(\text{CH}_2)_4.\text{CO}.\text{CO}_2\text{H}$. This acid is found to be identical with that obtainable by saponification of the freshly extracted oil from the kernels of *Licania rigida*. Thus the source of oiticica oil, which has long been in doubt, is almost certainly *Licania rigida*, and the name licanic acid is now applied to the above-mentioned acid.

From the second or permanently liquid variety of oiticica oil another form of γ -keto- $\Delta^{6\kappa\mu}$ -octadecatrienoic acid (m.p. 96.5°) has been obtained in small yield. This appears to differ from its isomeride in geometrical configuration only and is designated *isolicanic acid*. Since the permanently liquid oil appears to have been heat-altered during its commercial preparation, the *iso*-acid is probably all that remains of the original licanic acid, the remainder having been oxidised, cyclised or polymerised.

Licanic acid appears to be the first naturally-occurring ketonic unsaturated

acid to be described. It is in all probability the same compound as the "couepic acid" of van Loon and Steger.

The authors desire to thank the Government Grant Committee of the Royal Society for a grant to one of them, and also the Director of the Imperial Institute for valuable assistance in the identification of botanical specimens.

REFERENCES.

- Clutterbuck and Raper (1925). *Biochem. J.* **19**, 385.
Lossen (1906). *Liebig's Ann.* **348**, 261.
von Pechmann and Sidgwick (1904). *Ber. deutsch. chem. Ges.* **37**, 3817.
Rossmann (1932). *Rec. Trav. Chim. Pays-Bas*, **51**, 248.
—— (1933). *Fettchem. Umschau*, **40**, 96, 117.
Van Loon and Steger (1931). *Rec. Trav. Chim. Pays-Bas*, **50**, 936.
Wilborn and Löwa (1929). *Farben-Ztg.* **35**, 388.