322. *The Doubly Conjugated System in α- and β-Licanic Acids.*

By Robert S. Morrell and W. R. Davis.

In a previous communication (Morrell and Samuels, J., 1932, 2251) the compounds formed by the combination of maleic anhydride and α- and β-elæostearic acids were described. The discovery and identification of a new acid, containing the triply unsaturated conjugated system, suggested the application of the Diels–Alder synthesis (cf. Farmer, *Ann. Reports*, 1930, 86) as a possible means of obtaining easily identifiable crystalline derivatives of this compound. Licanic acid, occurring as its glyceride in the oil (oiticica) from the fruit of *Licania rigida*, was identified by Brown and Farmer (*Biochem. J.*, 1935, **29**, 631) as a

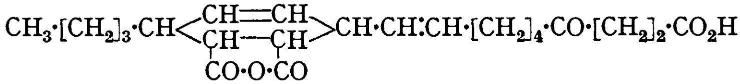
4-keto-$\Delta^{9:11:13}$-octadecatrienoic acid occurring naturally as its α-form, but isomerisable by light to a β-modification. Prior to the work of Brown and Farmer the 4-keto-group remained undetected and van Loon and Steger (*Rec. trav. chim.*, **1931**, **50**, 936) considered the acid an isomeride of the elæostearic series.* The maleic anhydride addition *complexes* of α- and β-licanic acids herein described are of interest, therefore, in that they support the structure assigned to the acid by Brown and Farmer.

Both acids combine with maleic anhydride to form crystalline derivatives, that from the α-acid melting at 79° and that from the β at 97°. The reaction in both cases is markedly exothermic and the transitory development of a yellow colour during the combination, as observed with the elæostearic acids, was noticed.

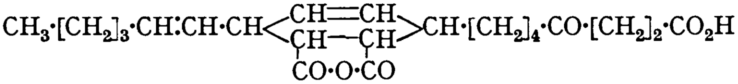
The addition complexes show a much greater stability towards atmospheric oxidation than do the free α- and β-licanic acids, which are, indeed, extremely sensitive.

Ozone or alkaline permanganate oxidation of the two compounds and an examination of the breakdown acids decided at which two of the three ethenoid linkages the addition had occurred. The α-compound gave γ-ketoazelaic acid in 34% of the calculated yield with only a trace of valeric acid, and the β-compound gave 87% of the calculated yield of valeric acid with no identifiable γ-ketoazelaic acid. The smaller yield of γ-ketoazelaic acid in the α-oxidation is ascribed to further breakdown of the acid by oxidation at the ketone group. The maleic anhydride compound of α-licanic acid is accordingly given formula (I) and that from the β-acid formula (II).

(I.)



$$\mathrm{CH_3{\cdot}[CH_2]_3{\cdot}CH}\Big<\begin{array}{c}\mathrm{CH{=\!=}CH}\\ \mathrm{CH{-\!-}CH}\\ \mathrm{CO{\cdot}O{\cdot}CO}\end{array}\Big>\mathrm{CH{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H}$$



$$\mathrm{CH_3{\cdot}[CH_2]_3{\cdot}CH{:}CH{\cdot}CH}\Big<\begin{array}{c}\mathrm{CH{=\!=}CH}\\ \mathrm{CH{-\!-}CH}\\ \mathrm{CO{\cdot}O{\cdot}CO}\end{array}\Big>\mathrm{CH{\cdot}[CH_2]_4{\cdot}CO{\cdot}[CH_2]_2{\cdot}CO_2H}$$

(II.)

In addition to the above-mentioned breakdown acids, both compounds gave on oxidation a considerable quantity of tar, representing, no doubt, the remaining oxidised six-membered ring section of the molecule. In the oxidation of the α-complex, where alkaline permanganate at 0° was employed as the oxidising agent, 11 atoms of oxygen were required to bring the process to completion.

(I) and (II) have been reduced by hydrogen in the presence of a platinum oxide catalyst, and crystalline saturated *derivatives*, m. p. 111° and 73°, respectively, obtained; as in the case of the hydrogenated products of the corresponding elæosteric acid compounds the α-derivative has the higher melting point. Both compounds absorbed 4 atoms of hydrogen each as is required by the doubly unsaturated structures assigned to them; the ketone radical, however, was not capable of reduction under the conditions employed and, indeed, showed comparative inactivity. The hydrogenation products would not form crystalline semicarbazones or 2 : 4-dinitrophenylhydrazones, although the ketone oxygen atom is clearly shown by analysis. The γ-ketoazelaic acid when split from the α-complex formed a semicarbazone with readiness.

The conjugated double bonds taking part in the maleic anhydride addition are the same with the licanic acids as with the elæostearic system (cf. Morrell and Samuels, *loc. cit.*); thus the two furthest from the carboxyl radical in the case of the α- and the two nearest in the case of the β-, are employed. There exists, therefore, a similarity in the *cis–trans* arrangements of these linkings in the two pairs of acids, and the probable X-*trans-trans–cis*-Y·CO$_2$H structure for the α- and X-*cis-cis–trans*-Y·CO$_2$H for the β-, deduced for the elæostearic acids from steric considerations (Morrell and Davis, *Trans. Faraday Soc.*, **1936**, **32**, 209), is equally applicable to α- and β-licanic acids.

The iodine value estimations of unsaturation on (I) and (II) were unreliable, as abnormally high figures were given. This was due, no doubt, to the enolisation of the ketone radical, previously observed with the free acids and glycerides by Kappelmeier (*Fettchem-*

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* The occurrence of elæostearic acid as well as of licanic acid in oiticica oil will be discussed in another paper.

ische Umschau, **1935**, **42**, 145), since the fully saturated products from (I) and (II) also showed a marked iodine value.

EXPERIMENTAL.

To minimise oxidation the freshly prepared mixture of α- or β-licanic acid and the other acids in the oil was combined with maleic anhydride and subsequently treated for the isolation of the maleic anhydride compound, in preference to the isolation of the licanic acid in a pure state before combination. In consequence a large number of crystallisations (usually 5 or 6) were necessary to purify the product and the final yield in each case was relatively small (10—20% of the calculated value).

General Method of Preparation.—(1) *For the α-compound.* Oiticica oil, freshly extracted from the fruit of *Licania rigida* in an atmosphere of carbon dioxide, was saponified in nitrogen. The mixed fatty acids obtained from the alkali salts by acidification were treated with a slight excess of maleic anhydride (1 mol. anhydride : 1 mol. $C_{18}H_{28}O_3$). Combination was carried out in dry carbon dioxide at 85°. The reacting mixture developed a yellow colour and its temperature rose 20° above that of the heating bath. When the combination was complete the yellow colour had practically disappeared. Excess of maleic anhydride was removed at 90° under reduced pressure in a stream of carbon dioxide. The resulting syrup was dissolved in a small volume of benzene and added dropwise to 10 times its volume of light petroleum (b. p. 40—60°) maintained at 40° and rapidly agitated. The fatty acids in the mixture not reacting with maleic anhydride were extracted by this means and the petroleum-insoluble maleic anhydride compound collected as a syrup at the bottom of the vessel. The petroleum solution was decanted and the syrup after five or six recrystallisations from ether gave the pure α-licanic acid–maleic anhydride compound (I).

(2) *For the β-compound.* For the preparation of the β-complex a 25% petroleum solution of oiticica oil was treated with 0·01% of iodine and kept in sunlight. The precipitate of β-licanin thrown down was rapidly filtered off in carbon dioxide and treated as the oil in (1) to give eventually the pure β-licanic acid–maleic anhydride compound.

The α-Licanic Acid–Maleic Anhydride Compound.—The *compound* crystallised from ether in needles, m. p. 79° [Found : C, 67·6, 67·8; H, 8·0, 7·9; I val. (48 hours Wijs), 165·1 (cf. p. 1482). $C_{22}H_{30}O_6$ requires C, 67·7; H, 7·7%; I val., 130·2]. On catalytic hydrogenation in acetic acid at room temperature and pressure, 4·08 atoms of hydrogen were absorbed per mol. The hydrogenation *product* crystallised from acetone–light petroleum in needles, m. p. 111° [Found : C, 67·1; H, 8·4; I val. (65 hours Wijs), 55·1. $C_{22}H_{34}O_6$ requires C, 67·0; H, 8·6%; I val., zero].

Oxidation. 8 G. of the α-licanic acid–maleic anhydride compound were dissolved in 40 ml. of water containing 4 g. of sodium carbonate and oxidised at 0° with 5% potassium permanganate solution. After 496 ml. of this had been added (11·5 atoms of oxygen per mol. of compound) reduction of the permanganate was practically complete. The mixture was filtered from the manganese dioxide, which was re-extracted with boiling water. The filtrate and washings were combined, evaporated to 150 ml., acidified, and extracted with ether (5 × 70 ml.), the dried extract was evaporated, and the residual syrup steam-distilled. Only traces of rancid-smelling steam-volatile acids were obtained from the distillate. The non-steam-volatile syrup was extracted with cold water, which was filtered from a little insoluble tar. After evaporation of the water the product was crystallised three times from chloroform, giving 1·4 g. of white crystalline γ-ketoazelaic acid (cf. Brown and Farmer, *loc. cit.*), m. p. 108·5° (34% of the calculated yield) (Found : C, 53·3; H, 6·8. Calc. for $C_9H_{14}O_3$: C, 53·5; H, 6·9%). The semicarbazone had m. p. 194—195° (decomp.) (Found : C, 46·55; H, 6·5. Calc. for $C_{10}H_{17}O_5N_3$: C, 46·3; H, 6·6%).

The β-Licanic Acid–Maleic Anhydride Compound.—The *compound* crystallised from ether in needles, m. p. 97—98° [Found : C, 67·6; H, 7·7; I val. (24 hours Wijs), 188·0, (48 hours) 205·2. $C_{22}H_{30}O_6$ requires C, 67·7; H, 7·7%; I val., 130·2]. On catalytic hydrogenation in acetic acid at room temperature and pressure, 3·92 atoms of hydrogen were absorbed per mol. of compound. The hydrogenation *product* crystallised from ether in needles, m. p. 72—73° [Found : C, 67·2; H, 8·9; I val. (48 hours Wijs), 28·3. $C_{22}H_{34}O_6$ requires C, 67·0; H, 8·6%; I val., zero].

Ozonisation of the β-Licanic Acid–Maleic Anhydride Compound.—In an attempt to restrict the breakdown to the double bonds in the molecule, ozone was employed as a means of fission. Ozonised oxygen was passed through 4·5 g. of the compound, dissolved in 90 ml. of chloroform, for 25 hours, the whole being maintained at 0°. The solvent was then removed in a current of air at 50°, and the ozonide carefully warmed with 100 ml. of water and finally refluxed at 100° for 2 hours to complete the decomposition. The aqueous solution was oxidised below 20° with 138 ml. of 5% permanganate solution to convert any aldehydic products into acids. The acid products were separated from manganese dioxide as before and worked up to give a mixed acidic syrup, which was steam-distilled. The non-steam-volatile tar was extracted with hot chloroform, from which 0·12 g. of an unidentified white solid was obtained, m. p. 99—105°. The steam-volatile fraction yielded 1·02 g. of a rancid-smelling oil, identified as valeric acid (87% of the calculated yield) by conversion into its p-*bromophenacyl* ester (Hann, Reid, and Jamieson, *J. Amer. Chem. Soc.*, 1930, **52**, 819), m. p. 73° (Found : C, 52·1; H, 5·0. $C_{13}H_{15}O_3Br$ requires C, 52·2; H, 5·0%). Authentic valeric acid gave a *p*-bromophenacyl ester, m. p. 73° (Found : C, 52·2; H, 4·9%).

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