BIOGENESIS OF CYCLOPROPENE ACIDS

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Received July 27, 1964

Amongst the unusual fatty acids that have not been investigated biogenetically are those containing cyclopropene rings. Of these, sterculic acid (I) could clearly arise by addition of a one-carbon unit to a C_{18} acid unsaturated at $C_{(9)}$. Such an origin could parallel the formation of a saturated analogue, lactobacillic acid, from *cis*-Δ^{11}-octadecenoic (vaccenic) acid and methionine (Hofmann and Liu, 1960). Sterculic acid is the major cyclopropene acid of *Sterculia foetida*, but in the related Malvaceae it is largely replaced by the lower homologue (II), malvalic acid. If (I) and (II) originated by parallel routes, then (II) would require an odd-numbered C_{17} acid for its precursor; this seemed sufficiently unusual to warrant investigation.

As in our studies of polyacetylenic acids (Bu'Lock and Smith, 1963), we used the technique originated by Newcomb and Stumpf (1953), that of incubating newly-germinated seedlings with ^{14}C-acetate; under such conditions there is usually some ^{14}C incorporation into the reserve lipids even though there is no nett synthesis. We used seedlings of *Hibiscus syriacus*

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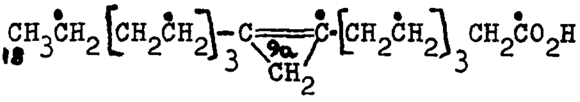
("Rose of Sharon"), the seed-fat of which contains about 3.4% of (I) and about 16.5% of (II) (Wilson et al., 1961); four-day-old seedlings were placed in solutions containing 1-^{14}C-acetate for a further one to six days.

The crude labelled lipid was converted into a mixture of methyl esters, and after controlled oxidation with permanganate-periodate (6 minutes at pH 8) the β-diketone fraction corresponding to (I) and (II) was obtained, containing about 2% of the total lipid ^{14}C. The homologous diketones were separated by reversed-phase chromatography and purified to constant radioactivity by crystallisation of the copper-chelates.

Sterculic acid

C atom no.	1+9	2-8	9a	10	11-18
% total ^{14}C, found (± 0.3)	21.8	33.7	0.1	0.1	44.6
% total ^{14}C, theory*	22.2	33.3	0	0	44.4

*for structure:



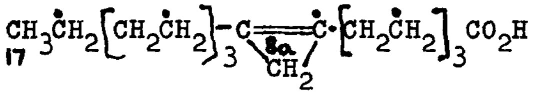
$\underset{18}{C}H_3\dot{C}H_2\left[CH_2\dot{C}H_2\right]_3-\underset{\underset{CH_2}{9a}}{C{=}\dot{C}}\cdot\left[CH_2\dot{C}H_2\right]_3CH_2\dot{C}O_2H$

(I); $\dot{C} = {}^{14}C$

Malvalic acid

C atom no.	1+8	2-7	8a	9	10-17
% total ^{14}C, found (± 0.5)	12.7	37.2	0.1	0.1	50.1
% total ^{14}C, theory*	12.5	37.5	0	0	50

*for structure:



$\underset{17}{C}H_3\dot{C}H_2\left[CH_2\dot{C}H_2\right]_3-\underset{\underset{CH_2}{8a}}{C{=}\dot{C}}\cdot\left[CH_2\dot{C}H_2\right]_3CO_2H$

(II); $\dot{C} = {}^{14}C$

Each diketone was then further oxidised by permanganate-periodate (24 hours at pH 9), giving on subsequent treatment with acid a quantitative yield of CO_2 from the central carbon, together with nonylic acid, and azelaic (from I) or suberic (from II) acids. These acids were separated chromatographically and subjected to Schmidt degradation. The results of these degradations are summarised in the Table.

As shown, the labelling pattern of the n-octylcyclopropenyl portion is identical in both acids, with alternate labelling along the straight chain and with an extra unlabelled carbon atom as the CH_2 group of the cyclopropene ring. In the azelaic acid, from (I), 5 of the 9 C atoms were labelled; in the suberic acid, from (II), 4 of the 8. Excluding the extra CH_2 group, the labelling of (I) was precisely that expected for an n-C_{18} acid. We conclude therefore that the CH_2 group of the cyclopropene ring in sterculic acid (I) has been introduced by an alkylation reaction similar to that leading to cyclopropane acids. The labelling of malvalic acid (II) is that of sterculic acid minus the carboxyl-carbon and shows no sign of any incorporation of propionate or similar precursor in the odd-numbered chain. We conclude that at some stage in the biogenesis of malvalic acid, either before or after formation of the cyclopropene ring, there has been a process of chain-shortening by an α-oxidation mechanism similar to that found in the groundnut (Martin and Stumpf, 1959).

If the alkylation step is strictly analogous to that leading to lactobacillic acid, then the precursor of (I) would be octadec-9-ynoic (stearolic) acid. This is not known as a natural product but its occurrence would not be unexpected either from structure-comparisons or on taxonomic grounds. This and other extensions of our work are under active investigation.

References

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