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New Ring Opening Oxidation of Methyl Sterculate and Malvalate

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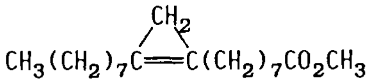
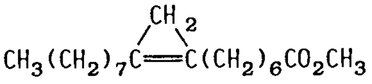
Air oxidation of cyclopropene fatty acid methyl esters, methyl sterculate and malvalate, resulted in the cleavage of cyclopropene ring, respectively, to afford a pair of conjugated enones containing a terminal methylene group.

In early studies on the seed germination inhibitors from *Hibiscus*,$^{1)}$ we have isolated two new fatty acid methyl esters, methyl 10-octyl-9-oxo-10-undecenoate (1-a) and 9-octyl-8-oxo-9-decenoate (**2-a**), possessing a methylenic double bond conjugated with a carbonyl group. In continuation of our studies, we isolated two cyclopropene acid methyl esters, methyl sterculate (1)$^{2)}$ and malvalate (2),$^{3)}$ as the active constituents and found out that they were gently oxidized to a pair of conjugated enones with a methylenic double bond, respectively, by air. These results strongly supported our biogenetic aspect$^{1)}$ on the production of **1-a** and **2-a**. We wish to report this new ring opening oxidation of the cyclopropenoids **1** and **2** in this communication.


$CH_3(CH_2)_7\overset{CH_2}{\overbrace{C{=}C}}(CH_2)_7CO_2CH_3$

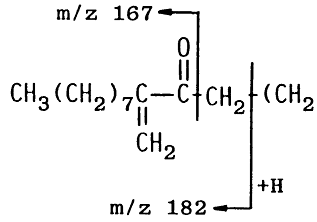
methyl sterculate (1)


$CH_3(CH_2)_7\overset{CH_2}{\overbrace{C{=}C}}(CH_2)_6CO_2CH_3$

methyl malvalate (2)

Both the compounds **1** and **2** were sensitive to air or temperature, and therefore, by blowing air through their solutions or at 50 °C, they polymerized to give complex mixtures.$^{4)}$ But, without the bubbling air, they were slowly oxidized at room temperature to afford a pair of 1 : 1 mixture of conjugated enones **1-a** and **1-b** (50%), and **2-a** and **2-b** (48%), respectively, with a complex mixture after 3 days. After a week, they completely changed to give the enones in 71 and 68% yields, respectively.

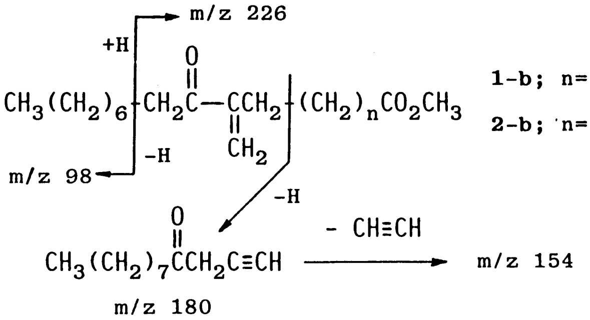
The high-resolution mass spectra of **1-a** and **1-b** both indicated same molecular formula of $C_{20}H_{36}O_3$ and their IR and UV spectra also resembled each other to show the presence of a conjugated enone group [ν_{max} 1670 and 1620 cm^{-1} and λ_{max} 228 nm(ε 4800)], along with an ester carbonyl group (1730 cm^{-1}), which showed **1-a** and **1-b** to be isomers. Signals in the ^1H and ^{13}C NMR spectra of **1-a** suggested the presence of a disubstituted methylenic double bond [δ 5.69(1H, br s) and 5.95(1H, s), and δ 149.1(s) and 123.3(t)] and two carbonyl groups [δ 202.5 and 176.9]. From these data, **1-a**, having a conjugated enone system containing a terminal methylene group, was identified to be same compound as one isolated previously from *Hibiscus*.[1] A comparison of the ^1H and ^{13}C NMR spectra of **1-b** with those of **1-a** indicated that the two compounds had nearly identical structures and differed from one another only in the location of the enone system.



$CH_3(CH_2)_7\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_2-(CH_2)_nCO_2CH_3$

1-a; n= 6

2-a; n= 5



$CH_3(CH_2)_6-CH_2\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_2}{\|}}{C}CH_2-(CH_2)_nCO_2CH_3$

$CH_3(CH_2)_7\overset{\overset{O}{\|}}{C}CH_2C{\equiv}CH \xrightarrow{-\ CH{\equiv}CH}$ m/z 154

1-b; n= 6

2-b; n= 5

Unequivocal support for their structures, **1-a** and **1-b**, were obtained from their EI mass spectra. The position of the CO group in **1-a** has been assigned to C-9 as the significant α- and β-fission ions were obtained at m/z 167 and 182, respectively. On the other hand, **1-b** showed a different fragmentation to obtain a characteristic rearranged peak at m/z 180 (41%) and a peak at m/z 154 (41%) due to a successive loss of CH≡CH, along with β-cleaved ion peaks to the CO group at m/z 226 (9%) and 98 (27%).

The remaining isomers, **2-a** and **2-b**, having a same molecular formula of $C_{19}H_{34}O_3$, exhibited similar IR, UV, and NMR spectra to those of **1-a** and **1-b**, which proposed their structures, **2-a** and **2-b**. Their mass fragmentations also established them in a similar manner as above.

These two enone isomers would have been produced by an oxygen attack to either of the two olefinic carbons of cyclopropene rings in **1-a** and **1-b**, respectively.

References

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4) F. L. Carter and V. L. Frampton, Chem. Rev., 64, 497(1964).

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