

SHORT COMMUNICATION

Epoxy Oleic Acid in *Quamoclit* Seed Oils

C.D. Daulatabad*, V.A. Desai, K.M. Hosamani and V.B. Hiremath

Department of Chemistry, Karnatak University, Dharwad 580 003, India

Quamoclit phoenicea Choisy and *Quamoclit coccinea* Moench. (Syn. *Ipomoea coccinea* Linn), belonging to the Convolvulaceae plant family, was found to contain palmitic (22.2%, 33.3%), stearic (11.3%, 1.7%), oleic (13.5%, 14.6%), linoleic (40.1%, 30.8%), vernolic (6.4%, 10.2%), arachidic (3.5%, 6.8%) and behenic (3.8%, 2.6%) acids, respectively.

KEY WORDS: Convolvulaceae, 12,13-epoxy-*cis*-octadec-9-enoic, fatty acids, *Quamoclit*, seed oils.

Seed oils rich in epoxy acids are of potential interest as stabilizers in plastic formulations (1) and in the preparation of other long-chain compounds (2). Epoxy compounds have also attracted much attention on account of their co-carcinogenic properties (3). *Quamoclit phoenicea* and *Quamoclit coccinea* are moderate sources of oil, and show sufficient promise for their exploitation as alternative commercial oils. New and interesting unusual fatty acids present in high concentration in certain seed oils are being exploited for commercial use. These acids of unusual structure are highly important to the chemical industry as raw materials for the production of oleochemicals (4).

Quamoclit phoenicea is an annual twiner with ovate-cordate leaves and salver-shaped, crimson flowers. It is cultivated in gardens throughout India (5). *Quamoclit coccinea* is a scandent, twinning, slender vine reaching a length of several meters. The flowers are erect and red. It is distributed in Tropical South and Central America, and is cultivated in India as an ornamental plant (6).

The present paper describes the occurrence of vernolic acid along with other normal fatty acids. This is the first report on these seed oils.

EXPERIMENTAL PROCEDURES

The air-dried seeds of *Quamoclit phoenicea* and *Quamoclit coccinea* were powdered and then extracted separately with light petroleum ether (b.p. 40–60°C) in a Soxhlet apparatus. The infrared spectra of the oils and methyl esters showed weak absorption bands at 825 cm⁻¹, due to an epoxy functional group. The oils gave a positive picric acid thin-layer chromatography test (7), indicating the presence of epoxy fatty acids. However, the oils did not give 2,4-DNP thin-layer chromatography (TLC) (8) and Halphen (9) tests, indicating the absence of keto and cyclopropanoid fatty acids, respectively. Direct TLC of the oils revealed the absence of hydroxy fatty acids when using castor oil as a reference standard. The Durbetaki titration (10) of *Quamoclit phoenicea* and *Quamoclit coccinea* seed oils at 3°C indicated 6.5% and 10.3% of epoxy fatty acids, respectively. The analytical values of the oils obtained were determined according to AOCS (11) methods and are listed in Table 1.

TABLE 1

Analytical Data of *Quamoclit* Seed Oils

| | <i>Quamoclit phoenicea</i> | <i>Quamoclit coccinea</i> |
|-----------------------|----------------------------|---------------------------|
| Oil content | 14.0% | 18.0% |
| Unsaponifiable matter | 2.0% | 2.2% |
| Iodine value | 90.3 | 77.7 |
| Saponification value | 200.6 | 201.8 |
| Halphen test | — ^a | — ^a |
| Picric acid TLC test | + ^a | + ^a |
| 2,4-DNP TLC test | — ^a | — ^a |
| HBr equivalent at 3°C | 6.5% | 10.3% |
| Infrared (IR) | 825 cm ⁻¹ | 825 cm ⁻¹ |

^a+ Indicates positive response to the test. — Indicates negative response to the test.

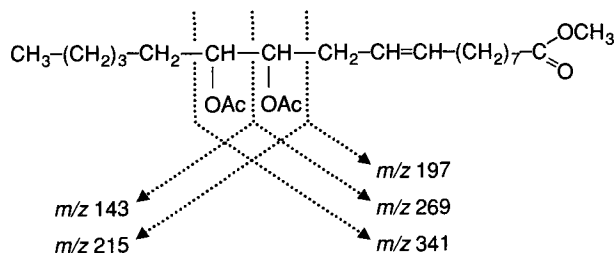
Acetolysis of each epoxide group was effected by treatment of the oils (20 g) with glacial acetic acid and 10% sulfuric acid (5:2, v/v) at room temperature, following the procedure of Wilson (12). The acetolyzed products were saponified separately by stirring overnight with 0.8 N alcoholic potassium hydroxide at room temperature. The nonsaponifiable matter was removed. The saponified products were acidified to pH 5 with 0.5 N sulfuric acid. The liberated mixed fatty acids of each oil were separated into oxygenated and nonoxygenated fractions by preparative TLC and were examined for the characterization of individual fatty acids. The yield of corresponding dihydroxy acids of *Quamoclit phoenicea* and *Quamoclit coccinea* were equivalent to 6.4% and 10.2% of the total oils, respectively.

The methyl esters were prepared by transesterification with absolute methanol containing 1% sodium methoxide. The reaction was allowed to proceed by refluxing the solution for half an hour, and the methyl esters were extracted with ether. The ether solution was washed with distilled water and dried over anhydrous sodium sulfate. The solvent was removed in a stream of nitrogen.

The infrared (IR) spectra were taken on a Hitachi 270-30 Model (Tokyo, Japan) instrument and nuclear magnetic resonance (NMR) spectra were recorded on a Varian T-60 Model (Palo Alto, CA) instrument with tetramethylsilane as internal standard. The mass spectra were recorded on a Joel-JMS-D-300 Model (Japan) instrument. The gas-liquid chromatographic (GLC) analyses were carried out on a Perkin-Elmer Sigma Unit (Norwalk, CT) with a stainless steel column (2 m × 3 mm) coated with 15% DEGS on Chromosorb W, 45–60 mesh. The temperature of the injection port, detector port and oven were 240, 240 and 190°C, respectively. The nitrogen flow and chart speed were 30 mL/min and 1 cm/min, respectively. The machine directly recorded the weight percent of individual peaks. The peaks were identified by comparing their retention times with those of standard reference samples under similar conditions.

*To whom correspondence should be addressed.

SHORT COMMUNICATION



SCHEME 1

RESULTS AND DISCUSSION

The IR spectrum of the dihydroxy esters had a strong absorption band at 3450 cm^{-1} for hydroxyl functional groups. The unsaturated dihydroxy acids on hydrogenation (13) separately furnished 12,13-dihydroxyoctadecanoic acid (14), m.p. $96-7^\circ\text{C}$. The unsaturated dihydroxy acids were cleaved separately with permanganate periodate reagent (15). GLC analysis of the resulting products as their methyl esters showed that the cleavage fragments were hexanoic and azelaic acids by using *Cassia siamea* (16) seed oil as standard reference.

The unsaturated dihydroxy acids had the same R_f value as *threo*-12,13-dihydroxy oleic acid obtained by acetolysis of *Vernonia anthelmintica* seed oil.

The NMR spectrum of the unsaturated dihydroxy esters gave signals at δ 5.46 (2H, $-\underline{\text{CH}}=\underline{\text{CH}}$), 3.66 (3H, $-\text{COOCH}_3$), 3.35 (4H, $2\text{H}(-\underline{\text{CH}}-\text{O}) + 2\text{H}(-\underline{\text{OH}})$), 2.24 (2H, alpha to the carbonyl function), 2.9 (protons alpha to the double bond), 1.3 (shielded methylene protons), 0.88 (3H, terminal $-\underline{\text{CH}}_3$). After shaking the samples with D_2O , the signal at δ 3.35 was reduced and integrated for two protons only (2H, $-\underline{\text{CH}}-\text{O}-$), indicating that the hydroxyl proton signal was merged with the signal of $-\underline{\text{CH}}-\text{O}-$.

The mass spectra of the diacetyl derivatives of the unsaturated dihydroxy fatty esters showed a small molecular ion peak at m/z 412. The allylic cleavage (m/z 197) established the double bond at C(9) and C(10). Alpha cleavage on either side of two acetate groups gave signals at m/z 341, 269, 215, 143, and placed the acetate groups at C(12) and C(13). This can be seen in Scheme 1. Thus, the epoxy fatty acids obtained from *Quamoclit phoenicea* and *Quamoclit coccinea* were characterized as 12,13-epoxy-*cis*-octadec-9-enoic (vernolic) acid.

Quamoclit phoenicea and *Quamoclit coccinea* seed oils thus contain a minor amount of vernolic acid (6.4% and 10.2%, respectively). The two seed oils also contain appreciable amounts of palmitic (22.2%, 33.3%), stearic (11.3%, 1.7%), oleic (13.5%, 14.6%), linoleic (40.1%, 30.8%),

TABLE 2

Fatty Acid Compositions of *Quamoclit* Seed Oils

| Fatty acids | <i>Quamoclit phoenicea</i> | <i>Quamoclit coccinea</i> |
|-------------|----------------------------|---------------------------|
| Palmitic | 22.2% | 33.3% |
| Stearic | 11.3% | 1.7% |
| Oleic | 13.5% | 14.6% |
| Linoleic | 40.1% | 30.8% |
| Vernolic | 6.4% | 10.2% |
| Arachidic | 3.5% | 6.8% |
| Behenic | 3.0% | 2.6% |

arachidic (3.5%, 6.8%) and behenic (3.0%, 2.6%) acids, respectively. These results are given in Table 2.

ACKNOWLEDGMENT

One of the authors (K.M.H.) is indebted to the Council of Scientific and Industrial Research, New Delhi, for the award of a Senior Research Fellowship.

REFERENCES

1. Riser, G.R., J.J. Hunter, J.S. Ard and L.P. Witnauer, *J. Am. Oil Chem. Soc.* 39:226 (1962).
2. Bharucha, K.E., and F.D. Gunstone, *J. Chem. Soc.*, 1611 (1956).
3. Swern, D., R. Wieder, M. McDonough, D.R. Meranze and M.B. Shimkin, *Cancer Res.* 30:1037 (1970).
4. Osman, S.M., F. Ahmad and I. Ahmad, in *Oil Seeds and Their Utilisation*, edited by R.K. Suri and K.C. Mathur, Rohini Publishing House, Dehradun, 1984, p. 113.
5. *The Wealth of India: Raw Materials*, Vol. V, C.S.I.R., New Delhi, 1959, p. 253.
6. Kirtikar, K.R., and B.D. Basu, *Indian Medicinal Plants*, Vol. III, Allahabad, India, 1933, p. 1713.
7. Fioriti, J.A., and R.J. Sims, *J. Chromatography* 32:761 (1968).
8. Davis, E.N., L.L. Wallen, J.C. Goodwin, W.K. Rohwedder and R.A. Rhodes, *Lipids* 4:356 (1969).
9. Halphen, G., *J. Pharm.* 6:390 (1897).
10. Harris, J.A., F.C. Magne and E.L. Skau, *J. Am. Oil Chem. Soc.* 40:718 (1963).
11. *Official and Tentative Methods of the American Oil Chemists' Society*, 3rd edn., edited by W.E. Link, American Oil Chemists' Society, Champaign, IL, 1973, Methods Da 15-48 and Da 16-48.
12. Wilson, T.L., C.R. Smith, Jr. and K.L. Mikoljczak, *J. Am. Oil Chem. Soc.* 38:696 (1961).
13. Vogel, A.I., *A Textbook of Practical Organic Chemistry*, 3rd edn., Longmans, Green and Co., London, England, pp. 866 and 950.
14. Hilditch, T.P., and P.N. Williams, *The Chemical Constitution of Natural Fats*, 4th edn., Chapman and Hall, London, 1964, p. 618.
15. Von Rudloff, E., *Can. J. Chem.* 34:1413 (1956).
16. Daulatabad, C.D., K.M. Hosamani and A.M. Mirajkar, *J. Am. Oil Chem. Soc.* 65:952 (1988).

[Received April 24, 1991; accepted September 23, 1991]