

Synthesis of 12-Phosphonooleic Acid and Surfactant Properties of its Sodium Salt¹

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Methyl ricinoleate (9-*cis*, 12-hydroxyoctadecenoate) was transformed to 12-bromo/iodo-oleate via methyl 12-mesyloxyoleate by homoallylic displacement reaction. The halooleate was reacted with triethyl phosphite to give methyl 12-diethyl phosphonooleate via the Michaelis-Arbuzov reaction under modified conditions. The phosphonooleate was hydrolyzed to 12-phosphonooleic acid using conc. hydrochloric acid. The compounds were characterized by phosphorus estimation and a combination of IR, ¹H-NMR and ¹³C-NMR spectroscopic techniques. The 12-phosphonooleic acid was neutralized to its sodium salt, and the salt was then studied for its surfactant properties. The sodium phosphonooleate was found to be superior to sodium salts of sulfate and phosphate esters of castor oil, and comparable to sodium lauryl sulfate in wetting ability, emulsifying power and in lowering of surface tension. The sodium phosphonooleate, being a poor foamer, could be used for machine laundry washing, dish washing and cosmetics.

Organophosphorus compounds are used in formulations of detergents, oil additives, pesticides, plasticizers, gasoline additives, corrosion inhibitors, flotation agents and flame proofing agents (1). Investigations on phosphorus derivatives of castor oil have been restricted to phosphate and phosphite esters (2,3). The phosphate and phosphite esters are easily hydrolyzed (4), but a phosphonate group containing a carbon-phosphorus bond at the alpha carbon of a fatty acid or vinyl carbon of its vinyl ester has been reported to resist hydrolysis (5). Such derivatives of several fatty acids have been prepared and evaluated for surfactant properties (6). No information exists on the synthesis and properties of phosphonates of ricinoleic (9-*cis*, 12-hydroxyoctadecenoic) acid, which constitutes ca. 90% of castor oil fatty acids.

The preparation of a phosphonate involves the reaction of dialkyl phosphite with either a Grignard reagent or an organolithium derivative of the corresponding hydroxy compound and subsequent oxidation (7). These reactions are unsuitable for the synthesis of phosphonates from hydroxyolefinic fatty acids. Phosphonic acid derivatives of non-hydroxy olefinic substrates have been prepared by the free radical addition of dialkyl phosphite to the double bond in the presence of peroxides or ultraviolet radiation (8). The phosphonates of hydroxyolefins can be synthesized via their alkyl halides by either the Michaelis (9) or the Michaelis-Arbuzov (10) reaction. The Michaelis reaction has been reported to yield a small amount of diphosphonate. By the addition of dialkyl phosphite to the double bond in addition to monophosphonate, which is formed by reaction with alkyl halide. The

Michaelis-Arbuzov reaction, on the other hand, has been found to be very selective. In the present work, we synthesized 12-phosphonooleic acid from methyl ricinoleate by the selective substitution of the hydroxy group with a phosphono group, while retaining the olefinic center at the ninth position, via the Michaelis-Arbuzov reaction. Methyl ricinoleate was transformed via methyl 12-mesyloxyoleate to 12-bromo/iodo-oleate by homoallylic displacement reaction. The halooleate was reacted with triethyl phosphite to give methyl 12-diethyl phosphonooleate, which on hydrolysis yielded phosphonooleic acid. Sodium salt of the phosphonooleic acid was evaluated for surfactant properties.

MATERIALS AND METHODS

Methanesulfonyl chloride (Fluka) was purchased. Methyl esters of castor oil were prepared by refluxing the oil with methanolic sodium methoxide as described by Schneider *et al.* (11). Methyl ricinoleate was isolated in 85% yield by column chromatography (silica gel 60-120 mesh) using hexane-ether (80:20, v/v) and found to be 99% pure by gas-liquid chromatography on EGS column (12). Triethyl phosphite was prepared by the reaction of phosphorus trichloride with dry ethanol in the presence of N,N-dimethylaniline at 0°C (13). For comparison, the sodium salt of sulfate ester of castor oil (Turkey Red Oil) was obtained from Bharat Chem Industries, Bombay, and the phosphate ester of castor oil was prepared by reaction with phosphorus oxychloride, subsequent hydrolysis (14) and neutralization.

Infrared (IR) spectra were recorded on a Perkin-Elmer 283 B unit. ¹H- and ¹³C-Nuclear Magnetic Resonance (NMR) spectra were recorded on a JEOL FX 90Q FT NMR spectrometer at 90 MHz and 22.5 MHz, respectively.

The phosphorus contents of the compounds were determined by the method of Harris and Popat (15). A DuNouy Tensiometer was used for determining surface tension. The Draves-Clarkson's method as described in the Indian Standard Specification (16) was used to determine the wetting ability. Emulsification power was determined by giving 10 downward strokes to a mixture of surfactant solution (40 ml) and liquid paraffin (40 ml) taken in an Erlenmeyer flask (500 ml), followed by pouring the emulsion in a measuring cylinder (100 ml). Next, we determined the time needed for the separation of aqueous phase (10 ml) (17). Foaming ability was determined using a Ross-Miles pour-foam apparatus (18).

Preparation of methyl 12-mesyloxyoleate. Methyl 12-mesyloxyoleate was prepared from methyl ricinoleate by the reaction of methanesulfonyl chloride (1:1 mole) in the presence of pyridine at 10°C in a 3-necked flask equipped with a reflux condenser, an addition funnel, a thermowell and a stirrer (19). The liquid product, obtained in 50% yield, solidified at 5°C.

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Preparation of methyl 12-bromooleate. Methyl 12-mesyloxyoleate (0.2 mole), dry ether (100 ml) and anhydrous magnesium bromide (0.6 mole) were stirred together for 24 hr at room temperature in a 3-necked, round bottom flask equipped with a reflux condenser, an inlet tube for nitrogen and a magnetic stirrer. After the addition of cold water, the product was extracted twice with ether. The ether extract was dried over anhydrous sodium sulfate and the solvent evaporated off to give a low melting solid (m.p. 20°C). The 12-bromooleate was purified by preparative TLC (hexane-ether, 70:30, v/v; Rf 0.8; yield 60%).

Preparation of methyl 12-iodooleate. Methyl 12-mesyloxyoleate (0.2 mole), dry ether (50 ml), acetonitrile (5 ml) and potassium iodide (0.6 mole) were stirred together at 50°C for 24 hr in a 3-necked, round bottom flask equipped with a reflux condenser, an inlet tube for nitrogen and a magnetic stirrer. The 12-iodooleate was extracted and purified as before (Rf 0.8, yield 68%, m.p. 24°C).

Methyl 12-diethyl phosphonooleate. A mixture of methyl 12-halooleate (0.25 mole), triethyl phosphite (0.75 mole) and acetonitrile (50 ml) was refluxed in a round bottom flask. At the end of four hr a small amount of water (0.5 ml) was added to facilitate the cleavage of quasiphosphonium ion intermediate and the mixture was refluxed for another four hr period. The reaction mixture was then poured into cold water and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the solvent evaporated off to give yellow colored viscous liquid. The compound methyl 12-diethylphosphonate was purified by preparative TLC (hexane-ether, 60:40, v/v; Rf 0.4) and it had 6.2% phosphorus content, (theoretical 6.9%, yield 70%).

Preparation of 12-phosphonooleic acid. Methyl 12-diethyl phosphonooleate (0.013 mole) and conc. HCl (4 ml) were placed in a round bottom flask and refluxed for one hr on a steam bath. 12-Phosphonooleic acid was extracted as before (yield 86.2%, phosphorus content 7.5% vs. theoretical 8.0%).

Preparation of sodium salt of 12-phosphonooleic acid. Standardized alcoholic sodium hydroxide solution (17 ml) of 0.5 N was added dropwise to an alcoholic solution of 12-phosphonooleic acid (4.0 g, 0.012 mole). The contents of the flask were refluxed for one hr on a steam bath. The solvent was distilled off. The trisodium salt thus obtained was washed with ether to remove any unreacted phosphonooleic acid. The sodium salt was dried in a china dish on a steam bath and stored in a desiccator (faint yellow colored solid, decomposed at 320°C).

DISCUSSION

Among the organophosphorus derivatives of castor oil known so far, only phosphoric acid esters have been exploited for the surfactant properties (e.g., their ammonium salts) (2). The phosphoric acid esters are prone to hydrolysis, unlike phosphono esters (4). In the present work, 12-phosphonooleic acid was synthesized with the intention of evaluating the surfactant properties of its sodium salt in comparison with the sodium salt of phosphate ester, sulfate ester of castor oil and so-

dium lauryl sulfate. 12-Phosphonooleic acid was prepared from methyl ricinoleate via mesyloxy and halo derivatives.

Methyl 12-mesyloxyoleate, a reactive intermediate was prepared from methyl ricinoleate using methanesulfonyl chloride in the presence of pyridine. The 12-mesyloxy group on reaction with anions (bromo/iodo), in proper solvent underwent homoallylic substitution to give the corresponding methyl 12-halooleate. Methyl 12-chlorooleate was obtained only in poor yield, when potassium chloride in ether and acetonitrile were used. The bromide ion substitution was effectively carried out with magnesium bromide in the presence of dry ether at room temperature, while the iodo substitution using potassium iodide was found to occur in dry ether and acetonitrile at 50°C. This is so probably because of the higher lattice energy of KI as compared to that of MgBr, due to the higher electronegative value of the former. The bromo- and iodo-oleates showed the same spectral characteristics in ¹H- and ¹³C-NMR, except for the chemical shift value of twelfth carbon in ¹³C-NMR spectrum. The twelfth carbon in the iodooleate was found to be very much upfield (26.05) as compared to that in the bromooleate (57.09) due to the lower electronegativity and larger atomic size of iodine.

There have been several investigations (10,20,21) on the Michaelis-Arbuzov reaction, and it was generally believed that secondary halides do not give the phosphonate product in quantitative yields. However, Goodell *et al.* (22) have shown that the polar solvents facilitate the faster dissociation of phosphorane intermediate in the Arbuzov reaction, and thereby enhance the yield of phosphonate product. In the present investigation, methyl 12-halooleate bearing a secondary halide was reacted with triethyl phosphite at different temperatures (10,25,60, and 100°C) but methyl 12-diethyl phosphonooleate was formed in negligible quantities. However, when the above reaction was carried out in the presence of acetonitrile at each of the above temperatures and monitored on TLC plates at frequent intervals, it was observed that the intensity of the spot corresponding to ricinoleate slowly decreased and became negligible after 4 hr. But the product at this stage was found to contain only a trace amount of the phosphonate, thus explaining that the methyl 12-halooleate could have reacted with triethyl phosphite to give a quasiphosphonium ion intermediate. However, the polarity of the solvent may not be sufficient to help in the Arbuzov reaction. Dissociation of the above intermediate is one of the crucial steps in the Arbuzov reaction, which is reported to be rather sluggish in the synthesis of secondary phosphonates. In order to overcome this, the above experiment was modified, wherein 0.5 ml of water was added after four hours of reaction and refluxing was then continued for another four hour period. In the case of 12-iodooleate the reaction was relatively fast and the overall reaction was completed within four hours.

Methyl 12-diethyl phosphonooleate was hydrolyzed using conc. HCl according by the procedure described by Kosolapoff *et al.* (23). The spectral characteristics of the 12-phosphonooleic acid and its intermediates are given in Table 1. The IR spectrum of 12-phosphonooleic acid showed bands at 960 & 1250 cm⁻¹, indicating

SYNTHESIS AND SURFACE ACTIVITY OF SODIUM 12-PHOSPHONOOLEATE

TABLE 1

Spectral Data of 12-Substituted Methyl Oleate/Oleic Acid ($\text{CH}_3(\text{CH}_2)_5\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOR}$)

| Compound | IR, ν in cm^{-1} | $^1\text{H-NMR}(\text{CDCl}_3, \delta)$ | | | | | Others |
|----------------------|-----------------------------------------------------------------------------------------|-----------------------------------------|------------------|-------------------------|----------------|-------------------------------|--------|
| | | $-\text{CH}_3$ | COOCH_3 | $-\text{CH}=\text{CH}-$ | $-\text{CH-X}$ | | |
| R, CH_3 | 1740 (s, C=O); | 0.8 | 3.6 | 5.5 | 4.7 | 3.0 (s, S- CH_3) | |
| X, mesyloxy | 1345,1368,1175 (m,-S-O); 1328 (m, S- CH_3) | (t) | (s) | (m) | (m) | | |
| R, CH_3 | 1740 (s, -C=O) | 0.8 | 3.6 | 5.2 | 4.0 | — | |
| X, bromo | | (t) | (s) | (m) | (m) | | |
| R, CH_3 | 1740 (s, -C=O) | 0.8 | 3.5 | 5.0 | 4.0 | — | |
| X, iodo | | (t) | (s) | (m) | (m) | | |
| R, CH_3 | 1740 (s, -C=O) | 0.8 | 3.6 | 5.8 | 3.1 | 4.1 (q, PO CH_2) | |
| X, diethyl phosphono | 1250 (s, -P=O) 1160 (s, -COP) 960 (m, pentavalent P) 1020 (s, -COOCH $_3$) | (t) | (s) | (m) | (m) | | |
| R, H | 1710 (s, -C=O) | 0.8 | — | 5.8 | 3.1 | — | |
| X, phosphono | 1250 (s, -P=O) 960 (m, pentavalent P) | (t) | | (m) | (m) | | |

| Compound | IR, ν in cm^{-1} | $^{13}\text{C-NMR}(\text{CDCl}_3, \text{ppm})$ | | | | | | |
|----------------------|-----------------------------------------------------------------------------------------|------------------------------------------------|--------------|-----------------|-----------------|-----------------|------------------|--------------------------------|
| | | C_1 | C_9 | C_{10} | C_{12} | C_{18} | COOCH_3 | Others |
| R, CH_3 | 1740 (s, C=O); | 178.04 | 122.93 | 133.60 | 83.33 | 13.97 | 51.40 | 71.30 (S- CH_3) |
| X, mesyloxy | 1345,1368,1175 (m,-S-O); 1328 (m, S- CH_3) | | | | | | | |
| R, CH_3 | 1740 (s, -C=O) | 174.00 | 124.07 | 131.80 | 57.09 | 13.62 | 51.42 | — |
| X, bromo | | | | | | | | |
| R, CH_3 | 1740 (s, -C=O) | 174.00 | 123.92 | 130.92 | 26.05 | 13.54 | 51.40 | — |
| X, iodo | | | | | | | | |
| R, CH_3 | 1740 (s, -C=O) | 174.00 | 125.02 | 131.57 | 60.24 | 14.02 | 51.45 | 65.00 (P-O- CH_2) |
| X, diethyl phosphono | 1250 (s, -P=O) 1160 (s, -COP) 960 (m, pentavalent P) 1020 (s, -COOCH $_3$) | | | | | | | |
| R, H | 1710 (s, -C=O) | 212.00 | 125.00 | 132.68 | 62.25 | 14.05 | — | — |
| X, phosphono | 1250 (s, -P=O) 960 (m, pentavalent P) | | | | | | | |

that the C-P bond remained inert during the hydrolysis. Further evidence was also obtained from ^1H - and ^{13}C -NMR spectra. The multiplet signal at 3.1 δ in ^1H -NMR spectrum of methyl 12-diethyl phosphonooleate corresponding to -CH- proton at the twelfth position was found to appear at the same chemical shift value in the ^1H -NMR spectrum of 12-phosphonooleic acid. The ^{13}C -NMR also showed the signal at 62.25 ppm, confirming the presence of a phosphono group at the twelfth position in 12-phosphonooleic acid. The presence of a peak at 1710 cm^{-1} in IR spectrum and a characteristic signal at 212.00 ppm in ^{13}C -NMR spectrum of the compound indicated the conversion of the methyl ester to the corresponding carboxylic acid during hydrolysis of methyl 12-diethyl phosphonooleate. The resulting 12-phosphonooleic acid was neutralized with alcoholic sodium solution to give the trisodium salt.

Surfactant properties. Surfactant properties of the sodium salts prepared from 12-phosphonooleic acid as well as sulfate and phosphate esters of castor oil were determined with reference to sodium lauryl sulfate.

At room temperature, aqueous solutions of sodium salts of 12-phosphonooleic acid, sulfate ester of castor oil and lauryl sulfate were clear at 0.5% concentration, while that of the phosphate ester of castor oil was slightly turbid. The surfactant properties, namely surface tension, foaming power, emulsifying power and wetting ability were determined, and are tabulated in Table 2.

It is obvious from the Table 1 that sodium 12-phosphonooleate is a good wetting, emulsifying and surface tension lowering agent. Except for the foaming power, the phosphonate is comparable to sodium lauryl sulfate in surfactant properties. It has been reported earlier (2) that neutralized phosphate ester of castor oil was superior to sulfate esters in surface activity. The present investigation shows that the phosphonate is superior even to the phosphate ester in surfactant properties. Phosphonates could be the choice of surfactants in machine laundry washing, dish washing, cosmetics, etc., where the properties such as surface tension reduction, emulsification and wetting abilities are required, but the foaming power is not.

TABLE 2

Surfactant Properties of Sodium Salt of 12-Phosphonooleic Acid

| | Surface tension ^a (dynes/cm) | | Foaming power height in cm | | Emulsification power (sec) | | Wetting ability (sec) |
|------------------------------------|--------------------------------------------|-------|-------------------------------|-------|-------------------------------|-------|--------------------------|
| | 0.5% | 0.25% | Initial | Final | 0.5% | 0.25% | 0.25% |
| Sodium salt | | | 0.5% | | | | |
| 12-Phosphonooleic acid | 40.5 | 37.0 | 0.0 | 0.0 | 172.0 | 91.0 | 3.5 |
| Phosphate ester of castor oil | 52.0 | 59.2 | 3.5 | 0.0 | 53.0 | 41.5 | 52.8 |
| Sulfate ester of castor oil | 42.5 | 57.5 | 0.0 | 0.0 | 67.0 | 13.2 | 30.0 |
| Sulfate ester of lauryl alcohol | 37.5 | 37.5 | 11.3 | 8.0 | 124.8 | 94.0 | 3.3 |

^aSurface tension of water is 72 dynes/cm at room temperature.

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REFERENCES

- Boenig, I.A., M.M. Crutchfield, C.W. Heitsch, in *Kirk-Othmer Encyclopedia of Chemical Technology Vol. 15*, edited by A. Standen, 3rd Ed., John Wiley & Son Inc., New York, New York, 1982, p. 491-537.
- Bayer, A., U.S. Patent, 2,252,479 (1941).
- Diamond, M.J., T.H. Applewhite, R.E. Knowles and L.A. Goldblatt, *J. Am. Oil Chem. Soc.* **41**:9 (1964).
- Jungermann, E., and H.C. Silberman in *Anionic Surfactants*, Part 2 edited by W.M. Linfield, Marcel Dekker, Inc., New York, New York, 1976, pp. 511.
- Ackerman, B., T.A. Jordan, C.R. Eddy and D. Swern, *J. Am. Chem. Soc.* **78**:4444 (1956).
- Jungermann, E., and H.C. Silberman in *Anionic surfactants*, Part 2, edited by W.M. Linfield, Marcel Dekker, Inc. New York, New York, 1976 pp. 518-529.
- Crofts, P.C., *Quart. Rev.* **12**:341 (1958).
- Ackerman, B. in *Fatty Acids*, Part 4, edited by K.S. Markey, Interscience Publishers John Wiley & Sons, New York, New York 1967, pp. 2669-2670.
- Griffin, C.E., *J. Org. Chem.* **25**:665 (1960).
- Bhattacharya, A.K. and G. Thyagarajan, *Chem. Rev.* **81**:415 (1981).
- Schneider, E.L., S.P. Loke, and D.T. Hopkins, *J. Am. Oil Chem. Soc.* **45**:585 (1968).
- Lakshminarayana, G., M.M. Paulose and B. Neeta Kumari, *Ibid.*, **61**:1871 (1984).
- Aksnes, G., and D. Aksnes, *Acta Chem. Scand.* **19**:898 (1965).
- Cooper, R.S., *J. Am. Oil Chem. Soc.* **40**:642 (1963).
- Harris, W.D., and P. Papat, *Ibid.* **31**:124 (1954).
- IS:1185 (1957) First Method, Bureau of Indian Standards, New Delhi.
- Subrahmanyam, V.V.R. and K.T. Achaya, *J. Chem. Eng. Data* **6**:38 (1961).
- Ross, J., and G.D. Miles, *Oil and Soap* **18**:99 (1941).
- Baumann, W.J., and H.K. Mangold, *J. Org. Chem.* **29**:3055 (1964).
- Buck, F.C. and J.T. Yoke, *Ibid.* **27**:3675 (1962).
- Aksnes, G. and D. Aksnes, *Acta Chem. Scand.* **18**:38 (1964).
- Goodell, J.L. and J.T. Yoka, *Can. J. Chem.* **47**:2461 (1969).
- Kosolapoff, G.M., *J. Am. Oil Chem. Soc.* **67**:1180 (1945).

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