Preparation and Surface-Active Properties of the Sodium Soaps, Mono- and Diethanolamides and Diol and Triol Sulfates of Cycloaliphatic C_{21} Di- and C_{22} Tricarboxylic Acids[1]

P. Vijayalakshmi, R. Subbarao and G. Lakshminarayana*
Regional Research Laboratory, CSIR, Hyderabad 500007, India

Cycloaliphatic C_{21} di- and C_{22} tricarboxylic acids were prepared by the Diels-Alder reaction of dehydrated castor oil (DCO) fatty acids (containing 48% conjugated and 42% nonconjugated dienes) with acrylic and fumaric acids, respectively. The reaction temperature, time, catalyst concentration, and mole ratio of reactants were varied to get maximum yields of the di- and tricarboxylic acids. The unreacted DCO fatty acids were removed from the products by partition between aqueous methanol and n-hexane. The products were converted to methyl esters and characterized as the substituted cyclohexene derivatives before and after dehydrogenation with Pd/C in xylene, hydrogenation with Pd/C in decalin and oxidation with periodate-permanganate reagent and by mass and proton nuclear magnetic resonance spectrometry. The acids were converted to sodium soaps, mono- and diethanolamides and the corresponding diol and triol sulfates, and the resulting products were evaluated for their surface-active properties. The sodium soaps showed better calcium tolerance and poorer foaming power than sodium oleate. The diethanolamides were inferior to lauroyl diethanolamide in wetting and emulsifying power. The monoethanolamides were better than the respective diethanolamides and lauroyl diethanolamide in wetting property. The diol and triol sulfates were poorer in wetting and emulsifying ability and better in calcium tolerance than sodium lauryl sulfate.

KEY WORDS: **C_{21} diacid, C_{21} diol, C_{22} triacid, C_{22} triol, ethanolamides, soaps, sulfates, surfactant properties.**

Soaps of cycolaliphatic C_{21} di- and C_{22} tricarboxylic acids are reported to be excellent hydrotropes for solubilizing nonionics in alkaline solutions and disinfectants in cleaner formulations (1). The preparation of C_{21} di- and C_{22} tricarboxylic acids by the Diels-Alder reaction of conjugated *trans, trans*-octadecadienoic acids with suitable dienophiles (2-5) and of tall oil fatty acids with acrylic and fumaric acids, respectively, in the presence of iodine has been reported (6,7). In the present investigation, dehydrated castor oil (DCO) fatty acids containing about 48% conjugated and 42% nonconjugated dienes (8) were used to prepare the cycloaliphatic C_{21} di- and C_{22} tricarboxylic acids as intermediates for surfactants—namely sodium soaps, mono- and diethanolamides and sodium salts of the corresponding diol and triol sulfates.

EXPERIMENTAL PROCEDURES

DCO fatty acids were prepared by decomposition of the estolides derived from split castor oil and had the following composition (8): 16:0, 2.7%; 18:0, 2.6%; 18:1, 5.2%; 18:2-conjugated *cis, trans* (*trans, cis*), 34.4%; 18:2-conjugated *trans, trans,* 3.9%; 18:2-conjugated *cis, cis,* 9.7%; 18:2-9-cis, 12-*trans,* 29.8%; 18:2-9-*trans,* 12-*cis,* 2.3%; and 18:2-9-*cis,* 12-*cis,* 18.4%. Acrylic acid and fumaric acid were laboratory reagents (BDH, Poole, U.K.). Palladium on carbon (10%) was prepared in the laboratory (9). Silica gel G was obtained from ACME Synthetic Chemicals (Bombay, India). Tetrahydrofuran (THF) was distilled over lithium aluminum hydride (LAH). Other chemicals were of analytical grade.

Infrared (IR) spectra were recorded in CCl_4 solution using a Perkin-Elmer 283-B unit (Perkin-Elmer, Norwalk, CT). Proton nuclear magnetic resonance (^1H-NMR) spectra were recorded in $CDCl_3$ solution in a Jeol FX-90 Q spectrometer (JEOL Ltd., Japan) using tetramethylsilane as internal standard. Mass spectra were recorded in a Micromass 7070 H unit (VG Analytical Ltd., Manchester, U.K.). Gas-liquid chromatography (GLC) was done on an HP5840A unit (Hewlett Packard, Palo Alto, CA, U.S.A.) equipped with a data processor, hydrogen flame ionization detector (FID) and a stainless steel column (2.4 m × 3.2 mm) packed with 15% EGSS-X/Gas Chrom Q (100-120 mesh). The column, injection port and detector were maintained at 210, 260 and 260°C respectively. The flow rate of carrier gas, nitrogen, was 40 mL/min.

C_{21} dicarboxylic acid. A 0.5-L stainless steel autoclave was charged with DCO fatty acids (190 g), acrylic acid (48.9 g) and iodine (0.19 g). The contents were flushed with nitrogen and heated to attain a temperature of 225°C in about 40 min and maintained at that temperature for 1 hr. After the reaction the bomb was taken out and the contents were cooled. Unreacted acrylic acid was removed by washing an ethereal solution of the product with distilled water. The product was freed of iodine by washing it with an aqueous solution of potassium iodide and sodium thiosulfate acidified with acetic acid. The unreacted fatty acids were removed by partition between aqueous methanol (80% methanol) and n-hexane (10). Polymeric material (5) was precipitated using a solvent mixture of n-hexane and diethyl ether (60:40, v/v). The final product (70 g) was refluxed with aqueous potassium hydroxide solution (6N, 400 mL) for 4 hr to convert lactones (11) into acids. The acid value was determined before and after saponification. The acid was esterified with an ethereal solution of diazomethane containing methanol and purified for characterization by silica gel G TLC using n-hexane- diethyl ether (80:20, v/v).

C_{22} tricarboxylic acid. DCO fatty acids (190 g), fumaric acid (78.7 g) and iodine (0.57 g) were charged into a 0.5-L stainless steel autoclave. The contents were flushed with nitrogen and heated to 200°C in 1 hr and at 200°C for 2 hr and then cooled. Unreacted fumaric acid was removed by precipitation from benzene. The tricarboxylic acid was thereafter purified as described for the C_{21} dicarboxylic acid.

Dehydrogenation, hydrogenation and oxidation. The esters of di- and tricarboxylic acids were dehydrogenated by

---

[1] RRL(H) Communication No. 2327.
*To whom the correspondence should be addressed.

refluxing them with Pd/C and xylene (2), and hydrogenated with Pd/C in decalin, which served as a solvent as well as the hydrogen donor (12). The esters were oxidized with periodate-permanganate (13), and the resulting products were esterified with an ethereal solution of diazomethane containing methanol and purified by TLC on silica gel using n-hexane-diethyl ether (70:30, v/v). Mass and ^{1}H-NMR spectra of the products were recorded.

Sodium soaps. Mono- and disodium soaps of the C_{21} dicarboxylic acid, and mono- and trisodium soaps of the C_{22} tricarboxylic acid were prepared by neutralizing the acids with the calculated amounts of alcoholic solution of sodium hydroxide. The soaps obtained as solids were washed with diethyl ether and dried in a vacuum desiccator. Sodium oleate was prepared in a similar way for reference purpose.

Mono- and diethanolamides. Diethanolamides and monoethanolamides were prepared using the procedure described by Gast *et al.* (14) for diethanolamides. Diethanolamine (4.2 g, 0.04 mole) was placed in a round bottom flask fitted with a stirrer, thermometer, nitrogen inlet tube and a dropping funnel. Sodium methoxide (0.026 g) was added and the flask was heated to 110-115°C. The dicarboxylic acid methyl ester (3.8 g, 0.01 mole) prepared using methanol and sulfuric acid was added drop by drop over a period of 15 min. The reaction was carried out for 3 hr at 115°C. The product was cooled, dissolved in diethyl ether, washed with aqueous sodium chloride (15%) and dried over anhydrous sodium sulfate. The solution was filtered and the solvent was removed under vacuum. The product, a viscous material, was washed with hexane to remove the unreacted ester and dried in a vacuum desiccator (yield, 78%). Similarly, diethanolamides of C_{22} tricarboxylic acid (yield, 74%) and lauric acid (yield, 96%), and monoethanolamides of C_{21} di- (yield 82%) and C_{22} tricarboxylic acids (yield, 76%) were prepared with appropriate ratios of reactants. The final products were analyzed for hydroxyl, amine and acid values, and nitrogen and ester contents (Table 1).

C_{21} diol and C_{22} triol sulfates. The dicarboxylic acid was reduced with LAH to a diol (15). The dicarboxylic acid (7.04 g, 0.02 mole) dissolved in THF (200 mL) was added dropwise to a slurry of LAH (1.9 g, 0.05 mole) in THF (100 mL) over a period of 1 hr. The contents were then refluxed for 3 hr and cooled. The excess of LAH was destroyed with ethyl acetate. The product was isolated from the reaction mixture by treating it with cold dilute sulfuric acid and extracting it with diethyl ether. The ethereal solution was washed with dilute alkali to remove unconverted acid. The diol (yield, 91%) was sulfated with chlorosulfonic acid as follows. Cold chlorosulfonic acid (2.56 g, 0.022 mole) was added dropwise in 20 min to the diol (3.24 g, 0.01 mole) dissolved in CCl_4 (50 mL) and cooled to 0°C, while stirring the mixture with a magnetic stirrer and maintaining the temperature at 0°C. The contents were diluted with butanol and neutralized with aqueous sodium hydroxide solution. The water-butanol solvent mixture was removed in a rotary evaporator and the residue was dried in a vacuum oven at 80°C. The sulfate was extracted with butanol, freed of solvent under vacuum and of unreacted diol by washing it with diethyl ether, and was dried in a vacuum desiccator (yield, 84%). The tricarboxylic acid was reduced to triol (yield, 86%) and its sulfate (yield, 78%) was similarly prepared, with appropriate ratios of reactants. The sulfur content (Table 2) of the sulfates was determined by the microanalytical method of Fritz *et al.* (16). Sodium lauryl sulfate used for reference was a laboratory reagent (BDH).

TABLE 1

Analysis and Surfactant Properties of Di- and Monoethanolamides of Cycloaliphatic C_{21} Dicarboyxlic and C_{22} Tricarboxylic Acids

Surfactant	Ester content (%)	Amine value	Hydroxyl[a] value	Nitrogen[a] content (%)	Acid value	Surface tension (dynes/cm at 25°C)		Emulsifying power[b] (seconds)		Wetting power (seconds)		Foaming power (mm)			
Surfactant concentration (%)						0.1	0.3	0.1	0.3	0.05	0.1	0.1		0.3	
												Initial	After 5 min	Initial	After 5 min
Diethanolamide of															
Lauric acid	0.0	1.6	394.1 (390.9)	4.9 (4.9)	1.2	28.5	28.0	331	720	26	17	60	52	68	60
C_{21} Dicarboxyic acid	2.2	3.0	411.1 (426.6)	5.2 (5.3)	1.6	37.5	37.0	261	566	140	95	60	40	80	50
C_{22} Tricarboxylic acid	4.0	3.3	498.3 (512.3)	6.0 (6.4)	2.5	39.5	39.5	161	261	276	138	80	20	82	20
Monoethanolamide of															
C_{21}Dicarboxylic acid	2.5	2.5	250.0 (256.2)	6.3 (6.4)	1.4	36.5	36.0	178	295	18	12	45	42	70	61
C_{22} Tricarboxylic acid	3.0	2.8	310.0 (320.6)	7.8 (8.0)	2.0	39.0	38.5	162	230	22	14	55	40	75	50

[a] Theoretical values are given in parentheses.

[b] Time for separation of 10 mL surfactant solution.

TABLE 2

Sulfur Content and Surfactant Properties of Sodium Salts of Sulfates of Cycloaliphatic C_{21} Diol and C_{22} Triol

Surfactant concentration (%)	Sulfur[a] content (%)	Surface tension (dynes/cm at 25°C)			Emulsifying power[b] (seconds)			Wetting power (seconds)		Foaming power (mm)				Calcium tolerance[c] (mL)
		0.1	0.3	0.5	0.1	0.3	0.5	0.05	0.1	0.05		0.1		0.5
										Initial	After 5 min	Initial	After 5 min	
Sodium lauryl sulfate	11.3 (11.1)	41.5	41.0	40.5	50	92	110	29	8	83	71	99	80	2.4
Sodium salt of C_{21} diol sulfate	11.6 (12.1)	41.0	40.5	38.5	46	67	69	70	40	87	80	110	100	Clear[d]
Sodium salt of C_{22} triol sulfate	12.8 (14.6)	40.5	39.5	39.0	56	69	78	126	53	68	53	80	63	Clear[d]

[a] Theoretical values are given in parentheses.
[b] Time for separation of 10 mL surfactant solution.
[c] Volume in mL of 1% calcium acetate solution.
[d] Turbidity was not observed even with 5% solution.

TABLE 3

Preparation and Analysis of Reaction Products of Dehydrated Castor Oil (DCO) Fatty Acids and Acrylic Acid

Reaction conditions				Product composition[a] (wt. %)			Composition of unreacted fatty acids[d] (wt. %)	
Temp. (°C)	Time (hr)	DCO Fatty acids: acrylic acid (Mole ratio)	Catalyst (wt% based on DCO fatty acids)	Unreacted fatty acids[b]	C_{21} dicarboxylic acid[c]	Polymer	18:2 (non-conjugated)	18:2 conjugated)
175	2	1:1.1	0.1	61.3	35.3	3.4	46.3	33.0
175	2	1:1.1	0.2	56.2	44.0	3.8	46.6	29.4
200	1	1:1.1	0.1	52.0	44.4	3.6	45.8	28.5
200	2	1:1.1	0.1	43.6	52.7	3.7	57.3	13.5
200	1	1:1.1	0.2	48.6	48.0	3.4	49.2	23.9
200	2	1:1.1	0.2	38.5	57.8	3.7	54.0	12.2
225	0.5	1:1.1	0.1	28.4	67.8	3.8	50.7	0.0
225	1	1:1.1	0.1	25.4	70.6	4.0	41.3	0.0
225	0.5	1:1.25	0.1	26.3	66.7	7.0	47.9	0.0
225	1	1:1.25	0.1	23.6	69.0	7.4	43.2	0.0

[a] C^{21} acid was estimated by partition between aqueous methanol and n-hexane, and the polymer by precipitation from ether-n-hexane mixture.
[b] Contained 1.5-2.5% of C_{21} dicarboxylic acid as determined by preparative silica gel G TLC using n-hexane-ether (30:70, v/v).
[c] Contained 2-3% of the unreacted fatty acids as determined by preparative Silica gel G TLC.
[d] The DCO fatty acids used for the reaction contained 41.5% nonconjugated 18:2 and 48.0% conjugated 18:2. The remainder of unreacted fatty acids consisted of 16:0, 18:0 and 18:1.

Surface-active properties. Surfactant solutions (0.05-0.5%) were prepared in distilled water and the properties were determined at room temperature (25°C). Surface-tension measurements were made using a Du Nouy tensiometer. For emulsifying properties, surfactant solution (40 mL) and liquid paraffin (40 mL) were taken in a stoppered conical flask (500 mL) and shaken vigorously. The resulting emulsion was poured in a measuring cylinder (100 mL). The emulsifying power was determined as the time taken for the separation of 10 mL of the aqueous phase (17). Foaming properties were determined using a Ross-Miles pour-foam apparatus (18). Wetting tests were carried out by the method of Draves-Clarkson as modified by the Indian Standards Institution (19). Calcium tolerance was determined by a modified Harts method in which surfactant solution (0.5%, 50 mL) was titrated with 1% calcium acetate solution until the turbidity just obscured a strip of printed paper fastened to one side of the beaker (20).

RESULTS AND DISCUSSION

C_{21} di- and C_{22} tricarboxylic acids were prepared by the Diels-Alder reaction of dehydrated castor oil fatty acids with acrylic and fumaric acids, respectively, under various experimental conditions (Tables 3 and 4). Increases in temperature, reaction time and catalyst concentration in-

TABLE 4

Preparation and Analysis of Reaction Products of Dehydrated Castor Oil (DCO) Fatty Acids and Fumaric Acid

Reaction conditions				Product Composition (wt.%)[a]		Composition of unreacted fatty acids[d] (wt. %)	
Temp. (°C)	Time (hr)	DCO fatty acids: fumaric acid (mole ratio)	Catalyst (wt% based on DCO fatty acids)	Unreacted fatty acids[b]	C_{22} tri-carboxylic acid[c]	18:2 (non-conjugated)	18:2 (conjugated)
175	2	1:1.1	0.1	67.1	32.9	51.7	24.7
175	2	1:1.1	0.2	54.7	45.3	48.8	20.7
175	4	1:1.1	0.2	35.6	64.4	37.4	22.5
175	6	1:1.1	0.2	30.2	69.8	22.2	18.2
175	2	1:1.1	0.3	45.8	54.2	43.0	22.9
200	2	1:1.1	0.1	23.6	76.4	36.9	0.0
200	3	1:1.1	0.1	20.0	80.0	28.0	0.0
200	2	1:1.1	0.2	19.1	80.9	26.7	0.0
200	2	1:1.1	0.3	17.8	82.2	22.5	0.0
175	4	1:1.5	0.2	28.9	71.1	21.1	18.0
200	2	1:1.5	0.1	20.0	80.0	26.0	0.0

[a] Determined by partition between aqueous methanol and n-hexane.

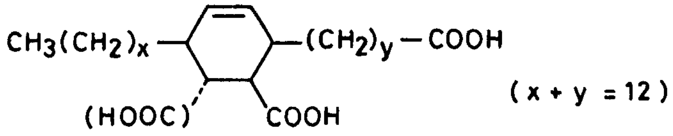
[b] Contained 2-3% of C_{22} tricarboxylic acid as determined by preparative silica gel G TLC using n-hexane-ether (30:70, v/v).

[c] Contained 0.5-1.5% of the unreacted fatty acids as determined by preparative silica gel G TLC.

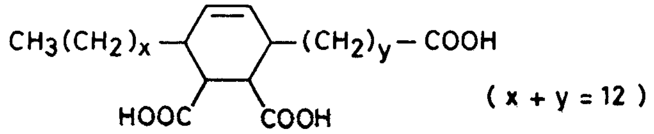
[d] The DCO fatty acids used for the reaction contained 41.5% nonconjugated 18:2 and 48.0% conjugated 18:2. The remainder of unreacted fatty acids consisted of 16:0, 18:0 and 18:1.

creased the yield of di- and tricarboxylic acids. Use of higher molar proportion of acrylic acid resulted in a slightly lower yield of C_{21} diacid and a higher proportion of polymeric material, while increases in the mole proportion of fumaric acid increased the yield of C_{22} triacid. GLC analysis of the unconverted DCO fatty acids showed that conjugated dienoic acids reacted relatively faster than the nonconjugated dienoic acids. The conditions found for maximum yield of the C_{21} dicarboxylic acid (70.6%) and C_{22} tricarboxylic acid (82.2%) were: temperature, 225°C, 200°C; reaction time, 1 hr, 2 hr; molar ratio of the reactants, 1:1.1, 1:1.1; and catalyst concentration, 0.1%, 0.3%; respectively. The acid value of the dicarboxylic acid before and after saponification and subsequent acidification was 297 and 312 (calc. 317), and that of the tricarboxylic acid was 381 and 398 (calc. 425). An increase in the acid value after saponification indicated the formation of lactones in the reaction (11).

The mass spectra of di- and tricarboxylic acid methyl esters showed the presence of molecular ions $(M)^+$ at *m/z* 380 and 438, respectively. The retro Diels-Alder fragmentation of the acids gave a fragment at *m/z* 294, indicating the acids as the products of Diels-Alder reaction. The IR spectra of the esters showed a weak band at 655 cm-1, which is characteristic of a C-H group of a *cis*-disubstituted double bond in a cyclohexene moiety (11). The ^{1}H-NMR spectra of the esters showed a signal at δ 5.65 characteristic of protons attached to a double bond in a cyclohexene moiety, indicating that the acids were formed through the Diels-Alder reaction. The dehydrogenated esters showed a multiplet at δ 7.1 to 7.3 indicating formation of benzenoid protons. The hydrogenated esters did not show any signal at δ 5.65 showing complete saturation of the double bond (12). ^{1}H-NMR spectra of the methyl esters of the oxidation products obtained from the di- and the tricarboxylic acids did not show any signal at δ 5.65, but showed signals at δ 3.65 corresponding to four and five ester groups, respectively, in comparison with the intensity of the terminal methyl group protons. The structures of the C_{21} di- and C_{22} tricarboxylic acids arrived at on the basis of the above spectral data, are given in Scheme 1.



C21 Cycloaliphatic dicarboxylic acid



C22 Cycloaliphatic tricarboxylic acid

Scheme 1. Cycloaliphatic acids.

Sodium soaps, mono- and diethanolamides of C_{21} di- and C_{22} tricarboxylic acids and the sodium salts of the sulfates derived from the corresponding diol and triol were evaluated for their surface active properties in comparison with standard materials.

Surface tension values of sodium oleate solutions were lower compared to those of di- and trisodium soaps of di- and tricarboxylic acids (Table 5). Solutions of di- and trisodium soaps were clear and had lower surface tension than the corresponding monosodium soaps, which were turbid. Emulsifying power of monosodium soap of tricarboxylic acid was the best of all the soaps examined. In wetting power the trisodium soap was inferior to disodium soap, but

TABLE 5

Surface-Active Properties of Sodium Soaps of Cycloaliphatic C_{21} Dicarboxylic and C_{22} Tricaboxylic Acids

Surfactant	Surface tension (dynes/cm at 25°C)			Emulsifying power (seconds)[a]		Wetting power (seconds)		Foaming power (mm)				Calcium tolerance (mL)[b]
Surfactant Concentration (%)	0.1	0.3	0.5	0.1	0.3	0.1	0.3	0.1		0.2		0.5
								Initial	After 5 min	Initial	After 5 min	
Sodium oleate	28.5	28.2	–	94	124	16	3	85	75	90	85	0.5
Monosodium soap of dicarboxylic acid	42.5	38.5	37.5	48	65	–	–	–	–	–	–	–
Disodium soap of of dicarboxylic acid	36	32	31.5	27	66	20	7	18	7	30	15	0.95
Monosodium soap of tricarboxylic acid	40.5	38.5	38	148	330	–	–	–	–	–	–	–
Trisodium soap of tricarboxylic acid	37.5	36	35	26	37	38	20	13	3	28	11	1.85

[a] Time for separation of 10 mL surfactant solution.
[b] Volume of 1% calcium acetate solution.

both were inferior to sodium oleate. The di- and trisodium soaps were inferior to sodium oleate in foaming properties. In calcium tolerance, the trisodium soap was better than the disodium soap which, in turn, was better than sodium oleate.

The analytical characteristics and surface-active properties of mono- and diethanolamides of C_{21} di- and C_{22} tricarboxylic acids are given in Table 1. Aqueous solutions of these diethanolamides were clear. A comparison of surfactant properties showed that diethanolamide of the dicarboxylic acid was better than the diethanolamide of the tricarboxylic acid in emulsifying and wetting properties. Diethanolamides of the di- and tricarboxylic acids were poorer than the diethanolamide of lauric acid in wetting and emulsifying powers. Initial foaming powers of the diethanolamides were slightly better than that of diethanolamide of lauric acid but the foam was not stable. In wetting power, the monoethanolamides of the di- and tricarboxylic acids were far better than the respective diethanolamides and the diethanolamide of lauric acid.

The C_{21} di- and C_{22} tricarboxylic acids were reduced with LAH to the corresponding diol and triol, and had hydroxyl values of 341.0 (calc. 346.3) and 457.3 (calc. 475.4), respectively. The diol and triol were sulfated and the sodium salts of sulfates were evaluated for their surfactant properties. The sulfates were comparable to sodium lauryl sulfate in reduction of surface tension (Table 2). The foaming power of the sulfate of the diol was slightly better than that of lauryl sulfate while the emulsifying and wetting powers were poorer. In wetting and foaming powers, the sulfate of the diol was better than the sulfate of the triol. The sulfates of the diol and the triol were vastly superior to lauryl sulfate in regard to calcium tolerance.

ACKNOWLEDGMENT

P.V. thanks the Council of Scientific & Industrial Research for a Research Fellowship.

REFERENCES

1. Ward, B.F., C.G. Force, A.M. Bills and F.E. Woodward, *J. Am. Oil Chem. Soc. 52*:219 (1975).
2. Teeter, H.M., J.L. O'Donnell, W.J. Schneider, L.E. Gast and M.J. Danzig, *J. Org. Chem. 22*:512 (1957).
3. Danzig, M.J., J.L. O'Donnell, E.W. Bell, J.C. Cowan and H.M. Teeter, *J. Am. Oil Chem. Soc. 34*:136 (1957).
4. Teeter, H.M., E.W. Bell, J.L. O'Donnell, M.J. Danzig and J.C. Cowan, *Ibid. 35*:238 (1958).
5. Sastry, G.S.R., B.G.K. Murthy and J.S. Aggarwal, *Ibid. 48*:686 (1971).
6. Ward, B.F., and S.C. Charleston, U.S. Patent 3,753,968 (1973).
7. Powers, J.R., M. Pleasant, F.C. Miller and S.C. Charleston, U.S. Patent 4,081,462 (1978).
8. Lakshminarayana, G., R. Subbarao, Y.S.R. Sastry, T. Chandrasekhara Rao, V. Kale and P. Vijayalakshmi, *J. Am. Oil Chem. Soc. 59*:238 (1982).
9. Vogel, A.I., *A Text Book of Practical Organic Chemistry Including Qualitative Organic Analysis,* Longmans, Green and Co., London, 1948, p. 843-845.
10. Gunstone, F.D., *J. Chem. Soc.* 1611 (1954).
11. Firestone, D., *J. Am. Oil Chem. Soc. 40*:247 (1963).
12. Vijayalakshmi, P., R. Subbarao and G. Lakshminarayana, *Ibid. 65*:939 (1988).
13. Youngs, C.G., *Ibid. 38*:62 (1961).
14. Gast, L.E., W.J. Schneider and J.C. Cowan, *Ibid. 43*:418 (1966).
15. Brown, W.G., in *Organic Reactions,* Vol. 6, edited by Roger Adams, John Wiley and Sons, New York, 1951, p. 469.
16. Fritz, J.S., and S.S. Yamamura, *Anal. Chem. 27*:1461 (1955).
17. Subrahmanyam, V.V.R., and K.T. Achaya, *J. Chem. Eng. Data 6*:38 (1961).
18. Ross J., and G.D. Miles, *Oil and Soap 18*:99 (1941).
19. Indian Standards Institution, New Delhi, IS:1185, 1957, First Method.
20. Harts, R., *Am. Dyestuff Reporter 23*:646 (1934).

[Received February 6, 1989; accepted July 24, 1990]