

## DISCUSSION

The term "phytate" is not well defined when it is applied to the organic phosphorus compounds in natural products determined by the acid ferric iron precipitation method. Many inositol phosphate esters are precipitated under the conditions commonly used. These compounds include the polyphosphates of inositol isomers other than *myo*-inositol. In this study it was shown that all of the *myo*-inositol phosphates from the di- through the hexaphosphate form insoluble iron complexes. However, the mono-, di-, and triphosphates are appreciably soluble and are not quantitatively precipitated. The monophosphate did not precipitate at the concentrations tested in this study. Mollgaard (1946) stated that inositol mono- and diphosphates are not measured analytically by the iron precipitation method. The present results agree that the diphosphate is not quantitatively precipitated. Whether or not a precipitate is observed depends on concentrations.

Although the effects of penta-, tetra-, and triphosphates on nutrient availability are not known, it appears that the lower phosphates do not occur at detectable concentrations in mature plant seeds of commerce. From the present study, it is clear that they might arise during processes which involve prolonged heat treatment. Enzyme hydrolysis will also give rise to a series of inositol polyphosphates. Tomlinson and Ballou (1962) treated phytic acid with phytase from wheat bran and isolated the *myo*-inositol 1- and 2-monophosphate, 1,2-diphosphate, 1,2,3-triphosphate, and 1,2,5,6-tetraphosphate. The pentaphosphates were present but were not characterized.

Phytate can be readily extracted from corn germ and soybean flakes but it is tightly bound in sesame meal and to isolated soybean protein. Water extraction does not offer a promising practical method of removing phytate from foodstuffs, but it will remove phytate from some products during processes in which water is added and then removed. For example, phytate is removed from corn products during the wet milling process.

These results confirm the usual assumption that the iron precipitable phosphorus in plant seeds is chiefly *myo*-inositol hexaphosphate. It is also apparent that the usual cooking procedures will not destroy an appreciable proportion of phytate in natural foodstuffs. Neither is it likely to materially change the nature of the "phytate". Some food-

stuffs subjected to water extraction may lose appreciable quantities of phytate. The rate of destruction of inositol hexaphosphate by heat is low when it is associated with proteins and/or cations in natural products. The cations naturally associated with the phytate are not known, but as pointed out previously (O'Dell et al. 1972), phytate could not possibly exist in cereal grains totally as phytin, the calcium-magnesium salt, because there is not sufficient calcium present to account for the necessary stoichiometry.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge gifts of the corn samples by Pioneer Hi-Bred Corn Co., Johnston, Iowa, rice by the Arkansas Rice Growers' Cooperative, Stuttgart, Ark., and sesame meal by the John Kraft Sesame Corp., Paris, Tex. We acknowledge the advice and consultation of G. Inglett, USDA Northern Regional Laboratory, Peoria, Ill., and thank him for supplying the soybean flakes. We are also indebted to W. R. Wichser and The Quaker Oats Co., Barrington, Ill., who dry milled the corn samples.

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## Synthesis and Flavor Properties of Some Alkyl-Substituted $\alpha$ -Pyrone Derivatives

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A general synthesis of 6-alkyl- $\alpha$ -pyrones has been achieved in ca. 40% overall yield by acylation of methyl 3-butenate under Friedel-Crafts conditions followed by cyclization of the intermediate unsaturated keto esters at 490°C. The gas chro-

matographic retention indices ( $I_E$  values), ir, NMR, and mass spectral data for 6-alkyl- and 6-alkyl-4-methyl- $\alpha$ -pyrones are presented. The organoleptic properties of these alkyl-substituted  $\alpha$ -pyrones and related compounds are discussed.

Lactones are of considerable significance to the fragrance and food industries due to their potent organoleptic characteristics which may convey either desirable or objectionable qualities. Much of this information has been summarized by Forss (1972).

Although the odor and taste properties of the saturated  $\gamma$ - and  $\delta$ -lactones are well known, less organoleptic information is available on the unsaturated lactones, particularly the  $\delta$ -lactones containing double bonds in the ring. (Although Chemical Abstracts classifies the six-membered  $\delta$ -lactones as derivatives of 2(*H*)-pyran-2-one, the older terms  $\alpha$ -pyrone and  $\delta$ -lactone, preferred by most authors, are used in this paper.) Nobuhara (1968, 1969a,b) reported multistep syntheses of alkyl-substituted unsaturated  $\delta$ -lactones in which the position and number of double bonds

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Table I. GC and Spectral Properties of 6-Alkyl- $\alpha$ -pyrone Derivatives

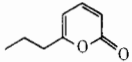
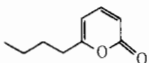
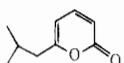
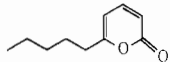
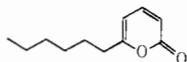
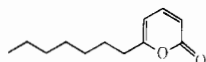
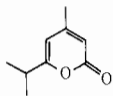
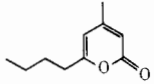
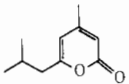
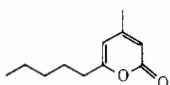
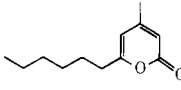
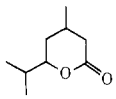
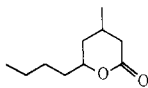
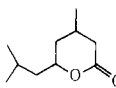
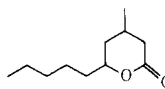
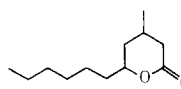
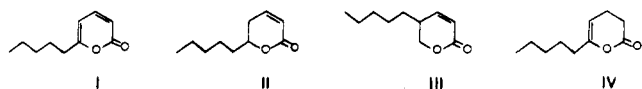
Pyrone	Retention index ( $I_E$ )		Ir, $\text{cm}^{-1}$	Mass fragmentation $m/e$ (%)	NMR, ppm
	CBW	SE-30			
	13.31	8.56	2960, 2935, 2875, 1725, 1630, 1555, 1465, 1455, 1430, 1375, 1355, 1335, 1205, 1170, 1100, 1075, 975, 895, 835, 795	95 (100), 39 (90), 81 (47), 27 (35), <u>138</u> (28), 110 (23) <sup>a</sup>	0.94 (t, 3 H), 1.66 (m, 2 H), 2.44 (t, 2 H), 6.02 (d of d, 2 H), 7.24 (d of d, 1 H) <sup>c</sup>
	14.36	9.55	2960, 2935, 2875, 1725, 1635, 1555, 1465, 1430, 1400, 1375, 1350, 1210, 1170, 1070, 975, 935, 890, 865, 845, 795	95 (100), 39 (97), 81 (42), 27 (42), 82 (29), <u>152</u> (26) <sup>a</sup>	0.92 (t, 3 H), 1.50 (m, 4 H), 2.48 (t, 2 H), 6.02 (d of d, 2 H), 7.22 (d of d, 1 H) <sup>c</sup>
	13.47	9.07	2960, 2930, 2875, 1730, 1635, 1560, 1465, 1430, 1405, 1385, 1365, 1355, 1325, 1285, 1220, 1170, 1105, 1080, 1045, 980, 895, 795	39 (100), 95 (81), 110 (70), 81 (39), 27 (35), <u>152</u> (33) <sup>a</sup>	0.92 (d, 6 H), 2.06 (m, 1 H), 2.32 (d, 2 H), 6.00 (d of d, 2 H), 7.24 (d of d, 1 H) <sup>c</sup>
	15.38	10.51	2950, 2930, 2870, 2860, 1730, 1630, 1555, 1465, 1455, 1375, 1350, 1205, 1170, 1105, 1060, 1045, 970, 795	95 (100), 110 (51), 39 (47), <u>166</u> (41), 81 (39), 82 (30) <sup>b</sup>	0.82 (t, 3 H), 1.30 (m, 4 H), 1.64 (m, 2 H), 2.40 (t, 2 H), 6.04 (d of d, 2 H), 7.24 (d of d, 1 H) <sup>c</sup>
	16.36	11.59	2960, 2930, 2860, 1725, 1630, 1560, 1555, 1465, 1430, 1375, 1350, 1210, 1170, 1105, 1085, 1045, 975, 895, 845, 795	95 (100), 39 (78), 110 (43), 27 (38), 81 (33), 82 (32), <u>180</u> (19) <sup>a</sup>	0.86 (t, 3 H), 1.28 (b, 6 H), 1.64 (m, 2 H), 2.46 (t, 2 H), 6.00 (d of d, 2 H), 7.22 (d of d, 1 H) <sup>c</sup>
	17.40	12.64	2960, 2930, 2860, 1735, 1725, 1630, 1560, 1550, 1460, 1080, 975, 795	95 (100), 39 (75), 110 (52), 27 (38), 82 (36), 41 (35), <u>194</u> (17) <sup>a</sup>	0.86 (t, 3 H), 1.30 (b, 6 H), 1.64 (m, 2 H), 2.46 (t, 2 H), 6.00 (d of d, 2 H), 7.23 (d of d, 1 H) <sup>c</sup>
	14.04	9.38	2970, 2930, 2870, 1720, 1640, 1555, 1460, 1440, 1405, 1380, 1370, 1360, 1340, 1305, 1220, 1115, 1075, 1065, 1015, 935, 870, 830	109 (100), 53 (53), 27 (35), <u>152</u> (20), 39 (19) <sup>a</sup>	1.21 (d, 6 H), 2.10 (s, 3 H), 2.70 (m, 1 H), 5.80 (s, 1 H), 5.90 (s, 1 H) <sup>c</sup>
	15.68	10.89	2960, 2935, 2880, 1730, 1642, 1560, 1465, 1440, 1400, 1375, 1220, 1145, 1130, 1095, 1025, 965, 940, 850, 825	109 (100), 53 (92), 95 (85), 27 (78), 29 (47), 138 (47), <u>166</u> (46) <sup>a</sup>	0.90 (t, 3 H), 1.26-1.74 (m, 4 H), 2.10 (s, 3 H), 2.42 (t, 2 H), 5.82 (s, 2 H) <sup>c</sup>
	14.85	10.20	2960, 2930, 2870, 1720, 1640, 1560, 1465, 1440, 1405, 1385, 1375, 1365, 1335, 1320, 1225, 1145, 1130, 1095, 1020, 965, 890, 835	95 (100), 109 (90), 53 (85), 27 (64), 124 (53), <u>166</u> (50) <sup>a</sup>	0.93 (d, 6 H), 1.98 (m, 1 H), 2.10 (s, 3 H), 2.24 (t, 2 H), 5.80 (s, 1 H), 5.90 (s, 1 H) <sup>c</sup>
	16.67	11.74	2950, 2935, 2860, 1730, 1640, 1565, 1465, 1440, 1405, 1380, 1335, 1220, 1150, 1130, 1100, 1025, 958, 875, 835	109 (100), 53 (84), 27 (75), 95 (73), 29 (50), 41 (46), <u>180</u> (38) <sup>a</sup>	0.88 (t, 3 H), 1.34 (m, 4 H), 1.64 (m, 2 H), 2.10 (s, 3 H), 2.42 (t, 2 H), 5.81 (s, 1 H), 5.87 (s, 1 H) <sup>c</sup>

Table I (Continued)

Pyrone	Retention index ( $I_E$ )		Ir, $\text{cm}^{-1}$	Mass fragmentation $m/e$ (%)	NMR, ppm
	CBW	SE-30			
	17.84	12.91	2955, 2930, 2860, 1725, 1640, 1560, 1460, 1435, 1400, 1370, 1215, 1140, 1125, 1095, 1020, 960, 950, 840	109 (100), 53 (68), 95 (63), 27 (50), 41 (34), 96 (34), <u>194</u> (21) <sup>a</sup>	0.86 (t, 3 H), 1.28 (m, 6 H), 1.63 (m, 2 H), 2.09 (s, 3 H), 2.42 (t, 2 H), 5.79 (s, 1 H), 5.88 (s, 1 H) <sup>c</sup>
	12.70	8.78	2960, 2930, 2870, 1725, 1465, 1455, 1435, 1375, 1280, 1240, 1190, 1170, 1085, 1050, 1040, 1025, 1000, 910	113 (100), 69 (70), 41 (52), 85 (30), 43 (28), 56 (24), <u>156</u> (10) <sup>b</sup>	0.98, 1.00, 1.06, 1.24 (d, d, d, and m, 10 H), 1.80–2.18 (m, 4 H), 2.61 (m, 1 H), 4.08 (m, 1 H) <sup>d</sup>
	14.29	10.32	2960, 2930, 2875, 1730, 1460, 1440, 1380, 1280, 1240, 1165, 1095, 1085, 1045, 1015, 990, 920	113 (110), 69 (47), 41 (45), 56 (44), 85 (25), 29 (25), <u>170</u> (10) <sup>b</sup>	0.83 and 1.06 (t and d, 6 H), 1.20–2.10 (m, 10 H), 2.55 (m, 1 H), 4.20 (m, 1 H) <sup>d</sup>
	13.56	9.64	2950, 2930, 2875, 1720, 1710, 1465, 1450, 1435, 1365, 1315, 1280, 1230, 1160, 1140, 1125, 1090, 1040, 1010, 980, 920	113 (100), 41 (84), 69 (66), 56 (66), 43 (48), 29 (40), 85 (30), <u>170</u> (5) <sup>b</sup>	0.94 (d, 6 H), 1.04 (d, 3 H), 1.22–2.08 (m, 7 H), 2.63 (m, 1 H), 4.36 (m, 1 H) <sup>d</sup>
	15.31	11.38	2960, 2930, 2870, 1735, 1460, 1380, 1285, 1240, 1205, 1165, 1100, 1045, 1025, 995, 920	113 (100), 41 (55), 69 (49), 56 (42), 29 (30), 55 (28), 43 (24), 85 (23), <u>184</u> (5) <sup>b</sup>	0.90 (t, 3 H), 1.03 (d, 3 H), 1.20–1.60 (m, 8 H), 2.00 (m, 4 H), 2.62 (m, 1 H), 4.30 (m, 1 H) <sup>d</sup>
	16.42	12.30	2960, 2930, 2860, 1725, 1450, 1375, 1280, 1235, 1195, 1155, 1090, 1045, 995, 915	113 (100), 69 (59), 41 (55), 56 (41), 85 (33), 43 (32), <u>198</u> (1) <sup>b</sup>	0.90 (t, 3 H), 1.04 (d, 3 H), 1.20–1.60 (m, 10 H), 1.98 (m, 4 H), 2.62 (m, 1 H), 4.24 (m, 1 H) <sup>d</sup>

<sup>a</sup> CEC 21 103C. <sup>b</sup> AEI MS 9. <sup>c</sup> HA 100. <sup>d</sup> XL 100.

were varied as well as the length and position of the alkyl substituent(s) on the ring. He concluded that of the lactones he had evaluated, 6-pentyl- $\alpha$ -pyrone (I) and 2-deceno- $\delta$ -lactone (II) had strong butter, butter-cake flavor while 5-hydroxy-4-pentyl-2-pentenoic acid lactone (III) and 4-deceno- $\delta$ -lactone (IV) had the least desirable flavor (Nobuhara, 1969b).



We wish to report a new general two-step synthesis of 6-alkyl- $\alpha$ -pyrones and to present a comparison of the flavor properties of homologous series of 6-alkyl- and 6-alkyl-4-methyl- $\alpha$ -pyrones with the corresponding saturated  $\delta$ -lactones.

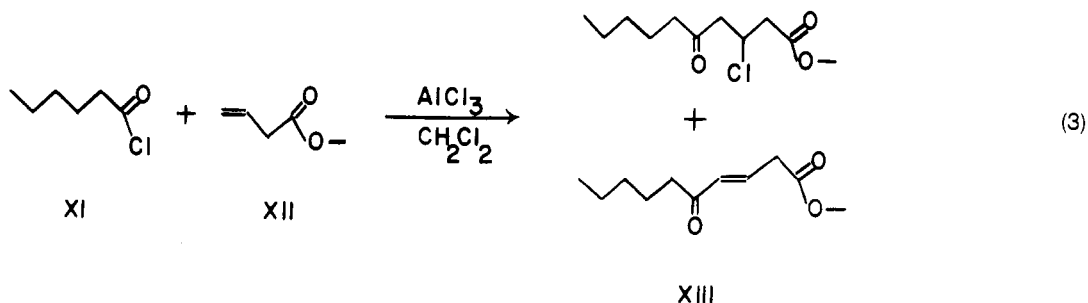
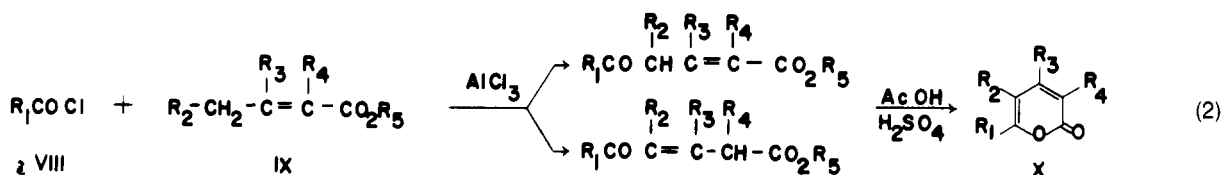
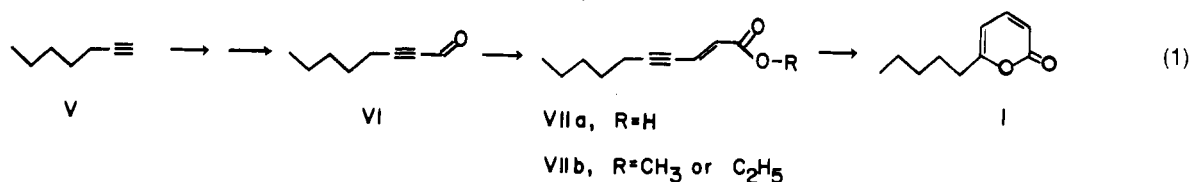
#### EXPERIMENTAL SECTION

**Chemicals.** Methyl 3-butenolate was prepared from crotonyl chloride in 80–85% yield (Kyowa Yuka Co., 1968). Ethyl 3-methyl-2-butenolate was obtained by esterification of 3,3-dimethylacrylic acid obtained from Aldrich Chemical Co., Milwaukee, Wis.

**Methods.** The 6-alkyl-4-methyl- $\alpha$ -pyrones were prepared in 70–80% yield by the method of Lohaus et al. (1967) involving the acylation of ethyl 3-methyl-2-butenolate followed by lactonization of the intermediate ester(s).

Hydrogenation of the 6-alkyl-4-methyl- $\alpha$ -pyrones to the corresponding 6-alkyl-4-methyltetrahydro- $\alpha$ -pyrones was achieved essentially quantitatively at room temperature (ca. 25°C) using a 10% palladium-on-charcoal catalyst and hydrogen at 50 psi.

The general method for the preparation of 6-alkyl- $\alpha$ -pyrones is illustrated by the following procedure for the synthesis of 6-pentyl- $\alpha$ -pyrone. To a stirred, cooled mixture of 800 g of anhydrous aluminum chloride and 1200 ml of dichloromethane was added a mixture of 300 g of methyl 3-butenolate and 405 g of hexanoyl chloride at such a rate to maintain mild reflux. After an additional 3 hr of heating under reflux, the mixture was cooled and decomposed by pouring it into excess ice-water. The lower (organic) layer was collected and the aqueous layer extracted with 2 × 500 ml of dichloromethane. The combined organic solutions were dried (anhydrous magnesium sulfate) and the low-boiling components removed by distillation at 10 mm pres-



sure to a final pot temperature of 75°C. The crude ester mixture (610 g) was obtained as a dark brown oil. This material was then diluted with 1000 ml of cyclohexane and passed slowly (6 hr) in a nitrogen atmosphere through a vertical quartz tube (24 in. × 1.25 in.) packed with protruded copper packing (0.24 in. size) heated at 490 ± 5°C. The condensed reaction products were successively washed with water, saturated sodium bicarbonate solution, and water. After drying (anhydrous magnesium sulfate) the solvent was evaporated and the crude product fractionally distilled to yield 210 g (40% overall yield) of product with a purity of 95% by GC. Extraneous odors were removed by chromatography on silicic acid deactivated by 5% (w/w) water and elution with 20–50% ether in hexane, followed by evaporation of the solvent and distillation of the product under reduced pressure (bp 92°C (0.5 mm)). The pyrones were obtained as colorless liquids which gradually turned orange at room temperature on prolonged exposure to light.

IR spectra were obtained on neat samples using a Beckman IR4 spectrophotometer. NMR spectra were recorded in CDCl<sub>3</sub> solution on either a Varian HA 100 or XL-100 spectrometer using a field sweep of 1000 Hz. Chemical shifts are reported in parts per million downfield from a tetramethylsilane internal standard. Mass spectra were determined on either a CEC 21 103C or an AEI MS-9 mass spectrometer using an ionizing voltage of 70 eV and an inlet temperature of 150°C. The relative abundances of the most intense ions are given; parent ions are underscored (see Table I).

Retention indices (*I<sub>E</sub>* values) were determined on packed Carbowax 20M and SE-30 columns using temperature programmed GC and ethyl esters of *n*-alkanoic acids as standards (van den Dool and Kratz, 1963).

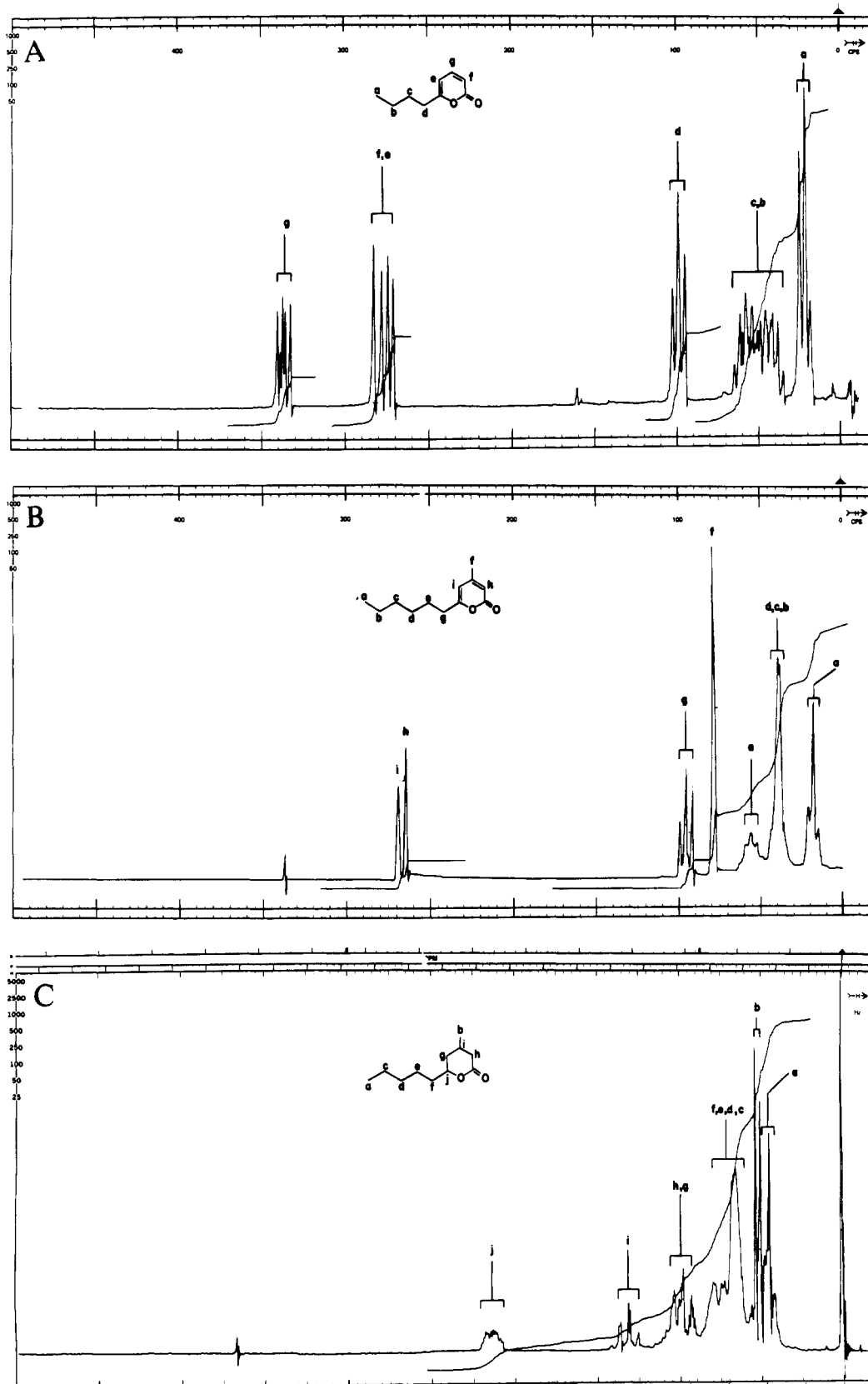
**Organoleptic Data.** The samples of alkyl- $\alpha$ -pyrones used for organoleptic evaluation were freshly distilled and were at least 95% pure by GC analysis (Aerograph 1700 equipped with a 10 ft × 0.25 in. 10% Carbowax column operated isothermally at 220°C); the major impurities present were the corresponding uncyclized unsaturated keto esters. The alkyl- $\alpha$ -pyrones and alkyltetrahydro- $\alpha$ -pyrones were evaluated by expert flavorists. The chemicals were smelled on blotters and the majority of them were tasted in water at 1–10 ppm; a few of the pyrone derivatives were tested at

higher concentrations due to their weak flavor properties; these were 6-heptyl- $\alpha$ -pyrone (15 ppm) and 6-isopropyl- and 6-isobutyl-4-methyl- $\alpha$ -pyrones (20 ppm).

## RESULTS AND DISCUSSION

In our quest for a convenient general method for the preparation of 6-alkyl- $\alpha$ -pyrones we reinvestigated Nobuhara's route B (Nobuhara, 1969b) with the object of reducing the number of steps in the synthesis and increasing the yield (the overall yield from acetylene is about 10%). One approach, illustrated in eq 1, was to prepare 2-octynal (VI) by a Bouveault aldehyde synthesis (Jones et al., 1958) from commercially available 1-heptyne (V), and convert it to dec-2-en-4-ynoic acid (VIIa) or its ester (VIIb) by means of a Doebner, Perkin, modified Knoevenagel, or an Emmons reaction. Cyclization of VIIa or VIIb would yield 6-pentyl- $\alpha$ -pyrone (I), thus eliminating the final decarboxylation step of Nobuhara's synthesis. The yields of  $\alpha$ -pyrone were not encouraging due to the difficulty of cyclizing compound VIIa or b where the double bond exists preferentially in the trans configuration (Crombie, 1955).

A two-step synthesis of alkyl- $\alpha$ -pyrones was reported by Lohaus et al. (1967) involving a Friedel-Crafts acylation of  $\beta,\beta$ -dialkyl acrylates (IX) and cyclization of the intermediate unsaturated keto esters to the alkyl-substituted  $\alpha$ -pyrones (X) (eq 2). Although this method provided an excellent route to the 4-methyl-6-alkyl- $\alpha$ -pyrones ( $R_1$  = alkyl;  $R_2, R_4$  = H; and  $R_3$  = CH<sub>3</sub>) attempts to acylate methyl crotonate ( $R_2, R_3, R_4$  = H) with hexanoyl chloride (VIII,  $R_1$  = pentyl) under a variety of experimental conditions proved unsuccessful. It was concluded that successful acylation occurs only when  $R_3$  is a methyl group. Lohaus et al. postulated that the reaction proceeded via an allylic shift of the double bond of the  $\beta,\beta$ -dialkyl acrylate. We therefore anticipated that much higher yields of the keto esters could be achieved by treating hexanoyl chloride (XI) with methyl 3-butenate (XII) rather than methyl crotonate. This indeed proved to be the case and estimated yields of about 55–65% of the crude keto esters (XIII) were obtained (eq 3). A GC separation and NMR analysis of this mixture showed that the material was composed of the chloro- and unsaturated ketoesters. Attempts to lactonize the crude esters in a hot mixture of acetic and sulfuric acids to the 6-



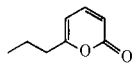
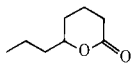
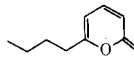
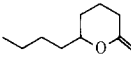
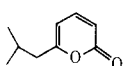

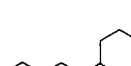


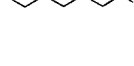
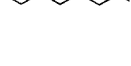
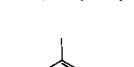
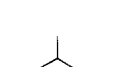
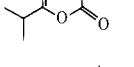
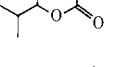
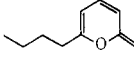
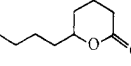
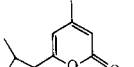
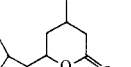


**Figure 1.** NMR spectra of 6-alkyl- $\alpha$ -pyrone derivatives: (A) 6-butyl- $\alpha$ -pyrone; (B) 4-methyl-6-hexyl- $\alpha$ -pyrone; (C) 4-methyl-6-pentyltetrahydro- $\alpha$ -pyrone.

alkyl- $\alpha$ -pyrones resulted in poor conversions, although these experimental conditions worked well in the production of 6-alkyl-4-methyl- $\alpha$ -pyrones. However, passage of the crude ester mixture through a quartz column packed with protruded copper, maintained at a temperature of 490°C, resulted in its conversion to the corresponding  $\alpha$ -

pyrones in 70–80% yield. This procedure was used to produce a series of 6-alkyl- $\alpha$ -pyrones in overall yields from methyl 3-butenolate of about 40%. The final products were further purified and freed of extraneous odors by chromatography on deactivated silicic acid.

The analytical data for the alkylated  $\alpha$ -pyrone deriva-

Table II. Comparative Organoleptic Properties of Pyrones and Tetrahydropyrone Derivatives

Compd	Aroma	Flavor	Compd	Flavor
	Sweet, coumarin, creamy, buttery	Coumarin, coconut, bitter		Coconut, hay, goaty, animal, wine <sup>a</sup>
	Sweet, coconut, coumarin	Coconut, creamy, coumarin, sweet		Fatty, creamy, milk, oily, buttery <sup>a</sup>
	Sweet, dairy	Sweet, coconut, creamy, coumarin, green		
	Coconut, peach-like, lactonic, green	Sweet, coconut, peach, lactonic, milk		Creamy, sweet, coconut, peach, milk <sup>a</sup>
	Sweet, coconut, fatty, green	Mushroom, bitter		Creamy, fatty, peach <sup>a</sup>
	Green, fatty, waxy	Waxy, floral, jasmine		Pear, peach, plum <sup>a</sup>
	Sweet, green, lovage	Walnut		Musty, fatty, unpleasant
	Sweet, celery, foenu-greek, fatty, coumarin	Celery, fatty, nut, spicy		Oily, goaty, chemical
	Sweet, floral, terpenic, fruity	Terpenic, green, solvent-like		Musty, earthy, sour
	Celery, lovage, foenu-greek	Celery, dill, green vegetable, lovage		Oily, goaty, woody, waxy
	Lovage, celery, spicy, waxy, musty	Lovage oil, celery, calamus		Sweet, fatty, musty

<sup>a</sup> Forss (1972).

tives that we synthesized are listed in Table I. The infrared spectra of the unsaturated lactones show absorptions at 1720–1740  $\text{cm}^{-1}$  (C=O), and 1630–1640 and 1550–1560  $\text{cm}^{-1}$  (C=C) characteristic of  $\alpha$ -pyrones (Nakanishi, 1962). The most notable aspect of the NMR spectra of the 6-alkyl- $\alpha$ -pyrones is the spin-spin coupling of the ring protons giving rise to a doublet of doublets at about 6.00 and 7.23 ppm (see Figure 1A); in the case of the 6-alkyl-4-methyl- $\alpha$ -pyrones, the ring protons appear as singlets at about 5.80 and 5.90 ppm (see Figure 1B). A characteristic feature of the NMR spectra of the 6-alkyl-4-methyltetrahydro- $\alpha$ -pyrones is the multiplet for the C-4 proton which resembles a diffuse triplet centered at about 2.60 ppm (Figure 1C). The most abundant ions of the mass spectra of  $\alpha$ -pyrone derivatives arise from cleavage adjacent to the ring oxygen. In the case of the 6-alkyl- $\alpha$ -pyrones, the major ions are  $m/e$  95 ( $\alpha$  cleavage of the side chain), 110 ( $\beta$  cleavage with hydrogen transfer), and 39 ( $\text{C}_3\text{H}_3^+$ ). Similarly, the 6-alkyl-4-methyl- $\alpha$ -pyrones have major ions of  $m/e$  95 and 109 arising from  $\alpha$  cleavage of the C-6 alkyl group with or without the loss of the C-4 methyl group, respectively, and  $m/e$  53 ( $\text{C}_4\text{H}_5^+$ ) and  $m/e$  27 ( $\text{C}_2\text{H}_3^+$ ). The base peak ( $m/e$  113) of the 6-alkyl-4-methyltetrahydro- $\alpha$ -pyrones again results from loss of the alkyl side chain. Such fragmentations are characteristic of satu-

rated  $\delta$ -lactones (Budzikiewicz et al., 1967). The significantly higher retention indices ( $I_E$  values) obtained for the alkyl- $\alpha$ -pyrone derivatives on Carbowax 20M compared with the SE-30 GC columns are a reflection of the polar nature of these compounds.

The organoleptic properties of the alkyl- $\alpha$ -pyrones are given in Table II; in most cases the flavors of the corresponding saturated  $\delta$ -lactones are given for comparison. The 6-alkyl- $\alpha$ -pyrones show a smooth progressive change in flavor character with increasing molecular weight. The lower homologs are coumarin-coconut, while the higher members of the series are waxy, green, and floral. Of the 6-alkyl- $\alpha$ -pyrones evaluated, the 6-pentyl- $\alpha$ -pyrone was considered to have the most pleasant flavor which was described as being coconut, peach-like, and lactonic rather than "butter-like" (Nobuhara, 1969b). Samples of this pyrone isolated from natural sources have also been reported as "coconut" or "lactonic" (Sevenants and Jennings, 1971; Collins and Halim, 1972). From the summarized data (Forss, 1972) for the saturated  $\delta$ -lactones of comparable carbon number, there is a less marked transition of organoleptic properties with increasing molecular weight; however, the lower homologs are creamy-coconut, and the higher ones are more fruity.

The 6-*n*-alkyl-4-methyl- $\alpha$ -pyrones have characteristic

celery, lovage, foenugreek flavors; the 6-butyl-4-methyl- $\alpha$ -pyrone was judged to have the best quality. The presence of branching within the alkyl chain of these derivatives tends to produce weaker, less characteristic, less desirable organoleptic properties. By contrast, the 6-alkyl-4-methyl-tetrahydro- $\alpha$ -pyrones which we synthesized have unpleasant oily, musty, chemical flavors, totally different from either the corresponding 6-alkyl-4-methyl- $\alpha$ -pyrones or the 6-alkyltetrahydro- $\alpha$ -pyrones.

From our results and those reported by Nobuhara (1968, 1969a,b), a number of conclusions may be drawn concerning the flavor properties of the 6-alkyl- $\alpha$ -pyrones and related compounds so far evaluated. The compounds with the most desirable qualities are the C<sub>10</sub> lactones with one or two double bond(s) in conjugation with the carbonyl group and an unbranched alkyl substituent at position 6 on the ring. The alterations in the organoleptic quality created by homologating the 6-alkyl side chain are less significant than the marked changes brought about by the addition of alkyl substituents in the 4 or 5 positions of the ring or by the degree and position of any unsaturation in the lactone ring.

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## Volatile Constituents of Tamarind (*Tamarindus indica* L.)

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The volatile constituents of tamarind have been investigated by the combined technique of gas chromatography-mass spectrometry with 61 major components identified and confirmed. Five additional compounds identified as artifacts appeared to originate from the vacuum steam distillation apparatus during isolation of the volatiles.

Several pyrazines and thiazoles, normally formed during roasting of a variety of foods, were found in tamarind. The results of this study suggest that the overall aroma of tamarind consists of citrus notes and warm spice-like flavors with some roast-character.

Tamarind (*Tamarindus indica* L.), a native fruit of Africa and cultivated in India since prehistoric times, grows well in other parts of tropical Asia, South America, and southern Florida. The fruit, ranging from 3 to 7 in. long and about 1 in. in breadth, is a slightly curved, plump, brownish pod, having a brittle shell. The brown edible pulp is high in sugar (ca. 20%) and minerals, particularly calcium and phosphorus (Mowry et al., 1967). It is rich in thiamine but contains virtually no vitamin A or ascorbic acid (Miller and Bazole, 1945). Because of its pleasant acid taste and rich aroma, tamarind has been used in many commercial products such as meat sauce and more recently in beverage drinks (Benero et al., 1974).

Although the biochemistry, the general composition, and the utilization of tamarind have been published and subsequently reviewed by Lefevre (1971), its volatile constituents have not been investigated. This paper describes the isolation and characterization of the major volatile components of tamarind by the combined technique of gas chromatography-mass spectrometry.

#### EXPERIMENTAL SECTION

**Isolation of Volatiles.** The pulp (ca. 600 g) obtained from shelled samples of tamarind was diluted with 2 l. of water and heated at 33 °C with stirring for 15 min to facilitate dispersing of the sticky mash adhered to the seeds. The seeds were removed to yield a puree by straining the pulp directly through a cheesecloth or by straining through a cheesecloth after maceration in a Waring Blendor for about 45 sec. In either case, subsequent analysis showed no significant variation in the volatile composition of the puree. An aliquot fraction (1 l.) of the resulting puree was further diluted to 2 l. and vacuum steam distilled (ca. 20 mmHg) in a Buchi Rotavapor or a Rinco Rotavaporator at 40 °C for 3 hr. Two 500-ml portions of the distillate trapped in liquid nitrogen were collected; an equal amount of water was added to the distilling flask during the steam distillation. The total distillate, having a distinct tamarind aroma, was thawed and saturated with sodium chloride prior to solvent extraction with 4 × 25 ml of Nanograde methylene chloride. The organic solution was washed with 5% sodium bicarbonate, dried over anhydrous sodium sulfate, and concentrated by slow distillation with a short fractionating column to ca. 0.5 ml for GC-MS analyses. The freshly prepared residue, still possessing the tamarind aroma, was analyzed immediately and again after being

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