

Registry No. Vanillin, 121-33-5; [methyl-¹³C]vanillin, 86884-84-6; ¹³C, 14762-74-4; lignin, 9005-53-2.

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Pyrolysis of Tropical Vegetable Oils

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Pyrolysis products of babassu (*Orbignya martiana*), piqui (*Caryocar coriaceum*), and palm oils (*Elaeis guineensis*) were analyzed by GC/MS using library search programs. The chief products of pyrolysis were straight-chain alkanes and 1-alkenes. Small amounts of cyclic hydrocarbons were detected in triglycerides constituted by oleic acid as the major moiety. Pyrolysis of oleic acid was also studied. A pathway for the cracking reactions involved with the decomposition of the saturated fatty acids is proposed.

Edible oils are essential for the human diet and therefore their use for other purposes has thus far not received much attention. However, during and after World War II several studies on the pyrolysis of vegetable oils were carried out for using the products thus obtained as fuel (Otto, 1945; Chang and Wan, 1947; Hsu et al., 1950). The studies concerning the chemical composition of the volatile compounds produced were not complete due to instrumental limitation and the analytical methods thus used (Hsu et al., 1950). Reports on the thermal cracking of behenic acid by Jurg and Eisma (1964) showed that C₃-C₆ hydrocarbons were chiefly produced when betonite was used as the catalyst. However, Traitler and Kratzl (1980) obtained *n*-alkylbenzenes from pyrolysis of fatty acids using lignin as the catalyst. Craveiro et al. (1981a,b) obtained long-chain methyl ketones when babassu oil was pyrolyzed in the presence of CaO.

On the basis of these studies it is clear that the pyrolysis products from fatty acids or glycerides are highly dependent on the nature and amount of catalyst used. For this reason we decided to investigate cracking reactions, carried out in the absence of catalyst, of three vegetable oils extracted from native or acclimated plants largely dispersed in northern and northeastern Brazil: *Orbignya martiana* (babassu), *Caryocar coriaceum* (piqui), and *Elaeis guineensis* (palm).

EXPERIMENTAL SECTION

Samples. Crude oil samples of babassu and piqui oils were obtained from industries in the state of Ceará, and the palm oil was a commercial sample originated from Bahia State.

Pyrolysis. Cracking reactions were carried out at 300-500 °C (atmospheric pressure) in a glass apparatus with internal and external temperatures being measured

Table I. Fatty Acid Composition of Babassu, Palm, and Piqui Oils

fatty acid	yields, %		
	babassu ^a	piqui ^b	palm ^c
capric	5.0		
lauric	48.5		2.8
myristic	20.0		1.5
palmitic	11.0	48.0	45.6
oleic	10.0	49.0	34.4
stearic	3.5	2.7	8.8
linoleic			5.5

^a *O. martiana*; 72% of oil in the seed (Ruskin, 1975).

^b *C. coriaceum*; 47.4% (yield determined as w/w) in the mesocarp. ^c *E. guianensis*; 30-70% of oil in the fruits (Heiduschaka and Agsten, 1930).

by a thermometer and pyrometer. The percent yields of volatiles so obtained were in the range 60-80 (v/v). Hydrogenation reactions were carried out on a Parr hydrogenation apparatus at 60-70 psi by using Pt as the catalyst over a period of 3 h. CO₂ evolution was detected as CaCO₃.

Gas Chromatography and Gas Chromatography/Mass Spectrometry. Analytical chromatograms were obtained on a FID Varian instrument equipped with fused silica capillary column (30 m × 0.20 mm i.d.) by using methyl silicone as the stationary phase, N₂ as the carrier gas (1 mL/min) at 40-250 °C, and 4 °C/min programmed temperature conditions. The separation and analysis of the cracked samples were made on a HP 5995 mass spectrometer coupled to GC equipped with a glass open tubular column (SP 2100, 30 m × 0.25 mm i.d.) using He as the carrier gas (1 mL/min) and the temperature programmed as above. Chromatographic retention times and peak areas were used to calculate Kovat's indexes and compound percentages, respectively.

Compound Identifications. Compound identifications involved library search programs (Craveiro et al., 1981a,b) and visual comparison with published mass spectra (Stenhagen et al., 1974; Heller and Milne, 1978). Com-

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Table II. Chemical Composition of Cracked Babassu, Piqui, and Palm Oils

compound	M_r	Kovat's indexes	yields, % (v/v)		
			babassu	piqui	palm
1-hexene	82	584		1.68	
<i>n</i> -hexane	84	600	1.03		4.44
1-heptene	98	686		3.57	
<i>n</i> -heptane	100	700	2.64	5.30	2.62
1-octene	112	788	1.77	3.39	
<i>n</i> -octane	114	800	2.49	4.01	3.70
1-nonene	126	855	2.95	2.08	1.63
<i>n</i> -nonane	128	900	6.27	2.98	3.81
1-decene	140	987	6.29	1.23	1.14
<i>n</i> -decane	142	1000	5.84	1.92	1.44
1-undecene	154	1086	4.32	1.71	1.17
<i>n</i> -undecane	156	1100	18.44	1.93	1.66
1-dodecene	168	1188	6.78	2.02	1.63
<i>n</i> -dodecane	170	1200	7.29	2.93	3.90
1-tridecene	182	1288	3.91	3.66	4.83
<i>n</i> -tridecane	184	1300	14.50	4.67	10.08
1-tetradecene	196	1389		4.35	6.31
<i>n</i> -tetradecane	198	1400	3.55	5.43	14.51
1-pentadecene	210	1488		2.60	2.82
<i>n</i> -pentadecane	212	1500	5.36	8.03	23.80
<i>n</i> -hexadecane	226	1600		2.27	3.41
<i>n</i> -heptadecane	240	1700		2.02	2.65
<i>n</i> -octadecane	254	1800		0.42	
total accounted for			94.46	68.20	95.55

pounds with unpublished mass spectra were tentatively identified on the basis of the mass spectra of their homologues along with their calculated Kovat's indexes.

Computer Programs. Computer programs for calculation of Kovat's indexes and mass spectra comparisons were either developed in our laboratory or were derived for HP 9825A calculator software.

RESULTS AND DISCUSSION

The fatty acid content of babassu and palm oils are well-known (Costa, 1967; Heiduschka and Agsten, 1930). The composition presented in Table I for these oils as well as for piqui oil was derived from GC/MS analysis (as Me esters) carried out in our laboratory. Pyrolysis of the crude oils were performed in a Pyrex apparatus and was accompanied by the evolution of gas due to decarboxylation reactions. This afforded a mixture of *n*-alkanes and 1-alkenes as the major products (94.46% for babassu, 68.20% for piqui, for 95.55% for palm oils; see Table II). Noteworthy differences in the cracking patterns (Table II) seem to be associated with the unsaturated fatty acid content (mainly oleic acid) in the original oils, which is likely to generate more volatile molecules than their saturated counterparts. Furthermore, it is possible to make an association between the major saturated fatty acid present in the original oil and the chief saturated hydrocarbon in the pyrolysis product, the latter being generated by decarboxylation of the former.

Triglycerides constituted by oleic acid as the major moiety produced in addition to straight-chain hydrocarbons cycloparaffins and cycloolefins in small amounts. The formation of these cyclic hydrocarbons may be probably related to cyclizations in which the 9-10 double bond of oleic acid plays an important role.

The absence of oxygenated compounds among the volatiles identified in Table II suggests that the elimination of CO_2 and $\text{CH}_2=\text{CO}$ were dominant steps in the cracking reactions of triglycerides and fatty acids, at least in the absence of catalyst.

The formation of a complete series of *n*-alkanes and 1-alkenes (Table II) is consistent with the generation of

Table III. Pyrolysis Products of Oleic Acid and Piqui Oil (Minor Constituents)

compound	M_r	Kovat's indexes	yields, % (v/v)	
			oleic acid	piqui oil
methylcyclohexane	98	715	0.71	0.31
ethylcyclopentene ^a	96	755		0.23
methylcyclohexene ^a	96	760	0.71	0.31
ethylcyclohexane	112	825	0.31	0.20
ethylcyclohexene ^a	110	860	0.39	0.20
<i>n</i> -propylcyclohexane	126	922		0.15
<i>n</i> -propylcyclohexene ^{a,b}	124	938		0.13
<i>n</i> -butylcyclopentene ^a	124	940	4.18	
<i>n</i> -butylcyclohexane	140	1028	0.28	0.13
<i>n</i> -amylcyclopentane ^c	140	1031		0.15
<i>n</i> -amylcyclopentene ^{a,c}	138	1038	0.47	
<i>n</i> -butylcyclohexene ^{a,b}	138	1042	0.23	0.21
<i>n</i> -amylcyclohexane ^b	154	1122	0.20	
<i>n</i> -amylcyclohexene ^{a,b}	152	1135		0.12
<i>n</i> -hexylcyclopentane ^{a,b}	154	1132	0.25	0.21
<i>n</i> -hexylcyclopentene ^{a,c}	152	1137	0.20	
<i>n</i> -hexylcyclohexane ^b	168	1229	0.63	0.17
<i>n</i> -heptylcyclopentene ^{a,c}	166	1240	0.25	
<i>n</i> -hexylcyclohexene ^a	166	1242	0.36	0.18
<i>n</i> -octylcyclopentane ^b	182	1337		0.35
<i>n</i> -octylcyclohexane	196	1437	0.98	
<i>n</i> -nonylcyclohexane ^b	210	1535	1.12	0.89
total accounted for			11.27	3.94

^a Chromatographic retention times and mass spectra fragmentation were insufficient to ascertain the position of the double bond in the ring. ^b No published MS. Tentative identification. ^c Tentative identification based on particular peaks in the MS (Talvari et al., 1974).

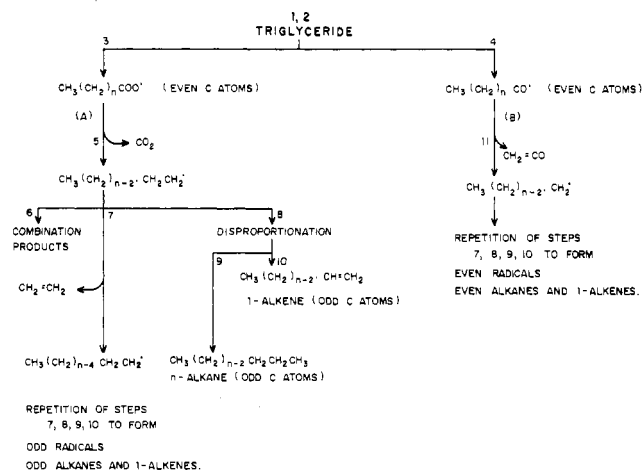
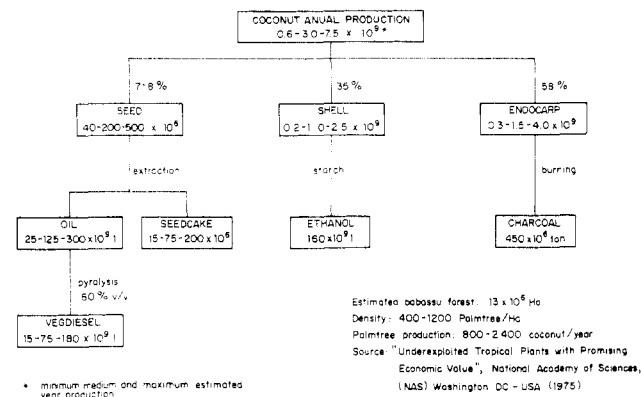


Figure 1. Scheme showing some probable pathways of decomposition of the saturated moieties of triglycerides during cracking reactions.

the radicals $\text{RCOO}\cdot$ (A) and $\text{RCH}_2\text{CO}\cdot$ (B) from the triglyceride molecule (Figure 1). Radical A on decarboxylation would lead to the formation of R. This radical, on disproportionation and successive eliminations of ethylene molecules, would be responsible for the odd series of *n*-alkanes and 1-alkenes present in the mixture. Radical B, by loss of ketene ($\text{CH}_2=\text{CO}$), disproportionation, and successive eliminations of ethylene molecules, would generate the *n*-alkanes and 1-alkenes with an even number of carbon atoms.

A scheme showing the probable decomposition pathway of saturated moieties of triglycerides during cracking reactions is depicted in Figure 1 and was based on pyrolysis mechanisms originally proposed by Chang and Wan (1947) and Greensfelder et al. (1949).

Chart I. Estimated Potential of Babassu Palm (*Orbignya spp.*)



The presence of alkylcyclopentanes and alkylcyclohexanes in the pyrolysis of oils with high oleic acid content indicates that ring formation may occur with the assistance of the double bond through a mechanism similar to that proposed in Figure 1.

The high potential of one of these palms as renewable resource of energy is illustrated in Chart I, which is an overview of the major products obtained from babassu nut; this palm tree grows wild throughout more than 35 million acres in the Brazilian northeastern states.

Registry No. 1-Hexene, 592-41-6; *n*-hexane, 110-54-3; 1-heptane, 592-76-7; *n*-heptane, 142-82-5; 1-octene, 111-66-0; *n*-octane, 111-65-9; 1-nonene, 124-11-8; *n*-nonane, 111-84-2; 1-decene, 872-05-9; *n*-decane, 124-18-5; 1-undecene, 821-95-4; *n*-undecane, 1120-21-4; 1-dodecene, 112-41-4; *n*-dodecane, 112-40-3; 1-tridecene, 2437-56-1; *n*-tridecane, 629-50-5; 1-tetradecene, 1120-36-1; *n*-tetradecane, 629-59-4; 1-pentadecene, 13360-61-7; *n*-pentadecane, 629-62-9; *n*-hexadecane, 544-76-3; *n*-heptadecane, 629-78-7; *n*-octadecane, 593-45-3; methylcyclohexane, 108-87-2; ethylcyclopentene, 2146-38-5; methylcyclohexene, 1335-86-0; ethylcyclohexane, 1678-91-7; ethylcyclohexene, 27138-39-2; *n*-propylcyclohexane, 1678-92-8; *n*-propylcyclohexene, 31620-24-3; *n*-butylcyclopentene, 50984-85-5; *n*-butylcyclohexane, 1678-93-9; *n*-amylcyclopentane, 3741-00-2; *n*-amylcyclopentene, 29031-90-1; *n*-butylcyclohexene, 31620-25-4; *n*-amylcyclohexane, 4292-92-6; *n*-amylcyclohexene, 31620-32-3; *n*-hexylcyclopentane, 4457-00-5;

n-hexylcyclopentene, 87156-78-3; *n*-hexylcyclohexane, 4292-75-5; *n*-heptylcyclopentene, 87156-79-4; *n*-hexylcyclohexene, 31620-26-5; *n*-octylcyclopentane, 1795-20-6; *n*-octylcyclohexane, 1795-15-9; *n*-nonylcyclohexane, 2883-02-5; oleic acid, 112-80-1.

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Effects of Various Anions on the Rheological and Gelling Behavior of Soy Proteins: Thermodynamic Observations

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The effects of neutral salts on the gelation of soy protein isolate and the 7S and 11S protein fractions were studied. The relative effects of salts on the viscosities of progel and gel followed the lyotropic series for anions, i.e., $\text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- < \text{SCN}^-$. NaSCN, which is a protein structure destabilizer, profoundly increased the melting temperature as well as viscosity of the gel, whereas NaCl, which is a protein structure stabilizer, decreased the gel viscosity but increased the melting temperature. However, the ΔH° of gelation was unaffected by the type of the salts used and exhibited a value of about 1 kcal/mol. On the basis of the results, we invoke that the major forces involved in the gelation of soy protein is hydrogen bonding and van der Waals interactions; the contribution of hydrophobic and electrostatic interaction is negligible.

The possession of a range of functional properties has considerably extended the potential use of soy proteins in

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food applications. Properties such as water binding, emulsifying, whipping, thickening, flavor binding, and the ability to form films and gels have been successfully realized in many food formulations and in new product development in recent years (Kinsella, 1979). The ability of gels to act as a matrix for holding water, lipids, sugars, flavors, and other ingredients is important in comminuted