tion rather than the solvent separation and hydrophilification techniques used in the West. Resulting from this is a product with a titer of ca. 29 C rather than the 6-8 C normally associated with oleic acid (Table VI). This is almost certainly due to the high stearic acid content of 8% but, in spite of the high titer, this oleic acid is successfully being used for food esters where its vegetable origin is an advantage.

MARKETS AVAILABLE TO MALAYSIAN OLEOCHEMICALS

Malaysia has a design capacity of 150,000 metric tons of fatty acids. Thus, with a home market of only 2,000 metric tons, Malaysia has sufficient capacity to supply more than 10% of world consumption – a world consumption that already has more locally available capacity than it requires. Malaysia owns no markets, has no unique technology, but has abundant raw materials.

ADDITIONAL DERIVATIVES PLANNED AND POTENTIAL

There is considerable interest in Malaysia for the production of fatty alcohols and, to date, 6 companies have obtained Government licences for their production (Table VII).

The current economic depression and reduction in petrochemical prices have slowed progress, but it is virtually certain that as world economy improves at least one of the licences will reach the commitment stage.

Fatty acids are the first and poorest relation of the oleochemical industry. Most oleochemical companies view their fatty acids as raw materials to be computed into their more sophisticated operations at cost rather than market price. As a result of this policy, the sole fatty acid manufacturer must look "downstream," be it to esters, dimer acids, fatty amines or whatever. Fatty acids, dimer acids, metal stearates, etc., can be produced to supply local ASEAN and South East Asian Markets.

Nitrile could be produced to ship to the major markets of Europe, the USA and Japan, while a portion could be reserved for conversion to the whole range of cationics, nonionics and amphoterics for the small but rapidly increasing local markets.

TABLE VII

Approved Fatty Alcohol Licences in Malaysia

Company	Capacities (metric tons/yr)
Henkel (J.V. with Jomalina & Socoil)	40,000
Albright & Wilson	30,000
Kao Corporation	30,000
Unichema	30,000
Palmco	18,000
Comcraft	10,000
Total	158,000

PROBLEMS

The Malaysian oleochemical manufacturers must learn that finished products and the cost of producing them bear a direct relation to the quality of the raw materials.

Malaysia must learn that, for oleochemicals, it is competing with different raw materials to those it competes with in the food industry. The Malaysian Government must ensure that Malaysian raw materials are preferentially available to Malaysian manufacturers.

The world wants Malaysia's alkyl chain. Should it take it as the triglyceride, the acid group, the methyl ester, the alcohol, the nitrile or whatever?

Malaysia would like to add as much value as possible and export as complex a molecule as possible. The rest of the world would prefer to finish its own raw materials. Fatty acids could be shipped in bulk to the major ports in the USA, Europe and Japan.

The West eventually must reliquish its simpler operations to be carried out at the raw material source.

Structural Determination and Uses of Jojoba Oil

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ABSTRACT

The predominating molecular species in jojoba oil is *cis*-13-docosenyl *cis*-11-eicosenoate (erucyl jojobenoate), ranging from 31% to 45% of the extracted seed oil. Other alcohol/acid combinations contribute to the C_{42} molecular chain length so that this fraction constitutes a low of 41% to a high of 57% of the total wax esters. The positions of the exclusively *cis* ethylenic bonds in the alcohol and acid moieties of the wax esters are 99% ω-9 and 1% ω-7. Only 2% of the alcohol and acid moieties were saturated when analyzed after saponification of the oil. Triglycerides were detected by gas chromatography in all of the more than 200 natural jojoba oil samples tested, a few of which had substantially more than the normal 1%. Among the many uses of jojoba oil cited here, the two most promising are the sulfurized oil as extreme-pressure/extreme-temperature lubricant additive and the natural or refined oil formulated into cosmetic products.

INTRODUCTION

Jojoba (*Buxus chinensis* [Link 1822], *Simmondsia californica* [Nuttal 1844], or *Simmondsia chinensis* [Schneider 1907]) oil is a liquid wax ester mixture extracted from seeds of a desert shrub native to Arizona, California, Northwestern Mexico and Baja California (1-9). Composition and molecular structure of the oil were determined by gas liquid chromatography (GLC), gas chromatography-mass spectrometry (GC-MS), reversed-phase high pressure liquid chromatography (HPLC), ozonolysis and other analytical techniques (10,11).

Many uses for jojoba have been proposed over the past three decades, and those that are interesting and have been experimented on by this author are listed in the last section of this article.

EXPERIMENTAL PROCEDURES

Extraction of Oil

Jojoba seeds were ground in a Laboratory Wiley Mill, either individually or as a batch, and placed in a Butt extraction system for reflux with petroleum ether (pentane/hexane) solvent (bp 33-57 C). After 8 hr, the solvent was removed from the extract by heating and evaporating under a stream of nitrogen. Yields of nonvolatile oil ranged from 40% to 62% of the ground meal. An additional 24-hr extraction of the meal increased the yield only 0.1-0.4%. Whenever the second extraction was performed, composition of the oil from the second was always found identical to the initial extraction when analyzed by GLC.

GLC of Jojoba Wax Esters

Samples of jojoba oil were injected, on-column, into a Hewlett Packard 5880A FID gas chromatograph with a Hamilton 10-microliter GC syringe. Experimental conditions were as follows: 3% OV-1 on Gas Chrom Q, acid-washed, silylated, 100-120 mesh; glass column 0.2-cm id, 0.25-in. od, 100 cm long; helium carrier gas, 50 mL/min, 60 psig; programming rate 1, 2 or 4 C/min from 200 to 350 C.

GLC of Jojoba Alcohols and Acids Derived from Jojoba Oil

A one-gram sample of jojoba oil was refluxed with 10 g of 5% HCl in anhydrous ethanol and 1 g of anhydrous benzene. The system was refluxed for 8 hr to ensure complete ethanolysis. On removal of the solvents and the HCl, half of the ethanolysis product was saponified in 10.0 mL of 0.1M KOH in ethanol with 1.0 mL of water added to accelerate the hydrolytic potassium carboxylate formation. The alcohols were isolated from the acids by repetitive ether extractions from aqueous alkaline solutions, and the free fatty acid fraction was treated with diazomethane to prepare the methyl esters for GLC analysis. Direct gas chromatographic analysis of the alcohols gave the same results as the analyses of trimethylsilyl (TMS) and trifluoroacetyl ethers of the alcohols, which validated the direct analysis of fatty alcohols with nonpolar Apiezon L and polar Resoflex 446 columns. The conditions for GLC analyses were as follows.

Nonpolar apiezon L. Twenty percent liquid phase on Chromosorb W, acid-washed, silylated, 100-120 mesh; stainless-steel column 0.2-cm id, 0.32-cm od, 100 cm long; helium carrier gas, 50 mL/min, 60 psig; isothermal at 250 C; Hewlett Packard 5880A FID.

Polar Resoflex 446. Five percent liquid phase on Chromosorb W, acid-washed, silylated, 100-120 mesh; stainless-steel column 0.2-cm id, 0.32-cm od, 200 cm long; helium carrier gas, 50 mL/min, 60 psig; isothermal at 175 C; Hewlett Packard 5880A FID.

Alcohol/Acid Combinations of Wax Esters in Jojoba Oil

Multiple reversed-phase HPLC columns (two or more μ-Bondapak C_{18}, Waters Associates) were used to separate the wax esters in jojoba oil according to chain length. Each fraction was saponified and the isolated alcohols and acids were derivatized into TMS ethers and methyl esters before GLC analysis. By matching the alcohols and acids so that their GLC chain length sum was equal to the chain length of the HPLC fraction, and by halving the sum of the GLC area percentage of the matching alcohol and acid, the composition within each HPLC chain length fraction was determined.

Each alcohol/acid combination was then multiplied by the percentage of its chain length fraction within the total wax esters, which had been determined accurately by GLC, thereby obtaining the percentage of each wax ester species in jojoba oil.

The alcohol/acid combination and its percentage within each chain length were also determined by a faster alternative GC-MS method described below.

GC-MS of Jojoba Oil

The GC-MS apparatus and its computerized data acquisition and reduction system were reported earlier by Spencer et al. (12) and were utilized for these jojoba analyses with minimal changes. For the determination of alcohol/acid combinations of the wax esters using only GC-MS, jojoba oil was hydrogenated in toluene/ethanol (1:10) with palladium on charcoal catalyst, and the solid product was dissolved in toluene (10% solution) before injection into the GC-MS system.

Molecules with a given chain length (or carbon number) were separated as a group from others of different chain length by the GC section of the instrument, and on their entrance into the mass spectrometer were subjected to cleavage at their ester linkage. The positively ionized masses of R_1COOH, R_1COOH_2 and R_2-1 that add up to the proper chain length were identified as one molecular species among several having the same chain length. Composition of these species in the total jojoba oil was calculated as described in the subsection above.

Positions of ethylenic bonds in the fatty acid moieties of the wax esters were determined by GC-MS of the methoxy derivative of methyl esters, which were separated according to chain length and cleaved into positively charged methyl ethers of the methyl end backbone and into positively charged methyl ethers of the carboxymethyl end backbone of the fatty acid derivative. Matching the proper fractionation products gave the position of fracture, which in turn was interpreted as the position of the double bond.

Ozonolysis-GC for Ethylenic Bond Determination in Alcohol Moiety

Because TMS ethers prepared from jojoba fatty alcohols were not as stable as methyl esters of jojoba fatty acids, the methoxylated TMS ethers gave inconclusive results when analyzed by GC-MS for ethylenic bond position. Nevertheless, excellent results for double bond position were obtained when initial separation of the primary alcohols according to chain length, by use of preparative HPLC, was followed by derivatization into TMS ethers, then by ozonization of the ethylenic bonds in the fatty alcohol backbone and finally by cleavage of the ozonides and separation of their fractionation products by the ozonolysis-GC technique (13).

RESULTS AND DISCUSSION

Composition of Jojoba Oil

Figure 1 shows a gas chromatogram of jojoba oil obtained by utilizing GC techniques of the mid-60s, when samples were flashed on-column with a solvent such as toluene and the attenuation adjusted to facilitate both the visual comparison and the quantitative integration of component peaks.

The use of computers or dedicated computerized integrators with extended dynamic range have altered the GLC techniques somewhat, but the print-outs are similar to the "curves" of yesteryear and compositional results are extraordinarily simple to obtain and highly reproducible. Figure 2 illustrates the composition of oil from mature jojoba seed. Unlike jojoba oil extracted from immature beans that possess high acid value, i.e., 1.0-2.5, mature seeds show very low free acid/free alcohol content. Every fresh natural jojoba oil from mature seed contains 0.5-2% of triglyceride.

Composition of a typical jojoba oil is listed in Table I, in which the components are given as individual molecular species within a particular chain length. The major compo-

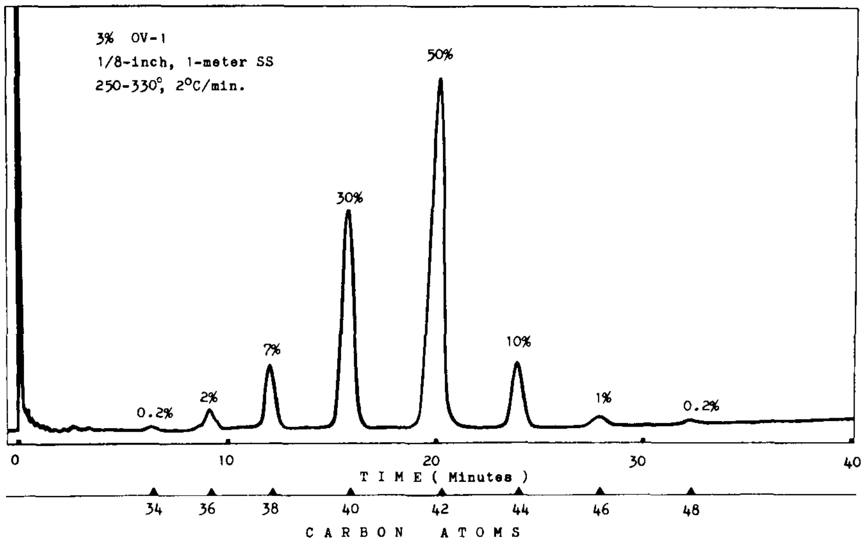

FIG. 1. Gas chromatogram of jojoba liquid wax esters. (Value on each peak is its percentage of the sum of integrated peak areas.)

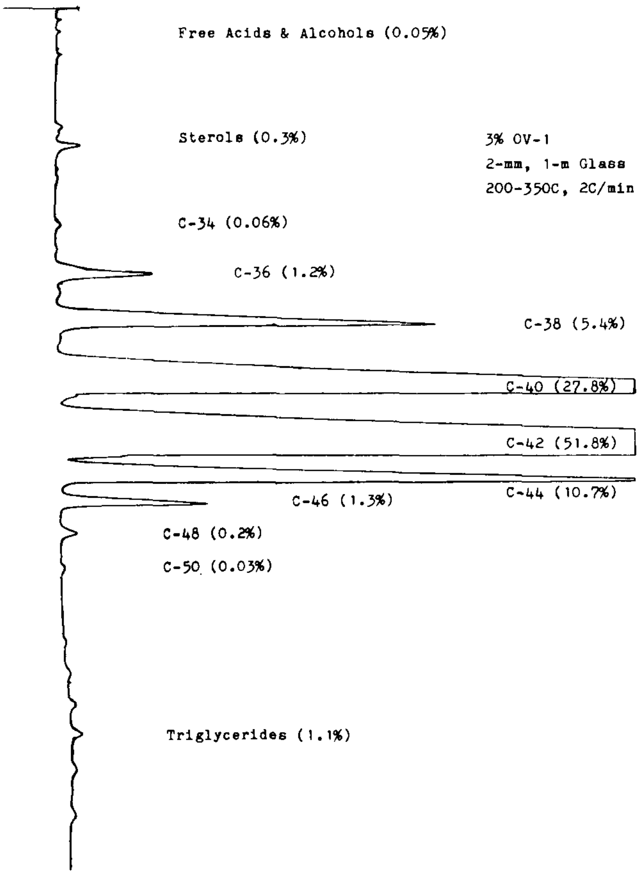

FIG. 2. Gas chromatogram of natural expeller-pressed jojoba oil. (Values are retention time in minutes and area percentage of total oil.)

nent (37%) is *cis*-13-docosenyl *cis*-11-eicosenoate or by trivial name, erucyl jojobenoate, followed by jojobenyl jojobenoate (24%) and jojobenyl erucate (10%). As seen in Table II, *cis*-11-eicosenoic (jojobenoic) acid is the major acid (71%) followed by erucic (14%) and oleic (10%) acids. The major alcohol is erucyl (45%), followed closely by *cis*-11-eicosenyl (jojobenyl) alcohol (44%). In the case of the lowest average molecular weight jojoba oil (11), the major component was jojobenyl jojobenoate (36%) and the major alcohol was jojobenyl (46%) instead of erucyl (42%).

TABLE I

Jojoba Oil Wax Ester Composition

Wax ester chain length	Alcohol/acid combination	Percentage by GLC and GC-MS
34	18/16	0.1
36	18/18	0.1
	20/16	1.8
38	16/22	0.2
	18/20	1.0
	20/18	5.4
	22/16	0.2
40	16/24	0.6
	18/22	1.5
	20/20	24.3
	22/18	3.6
	24/16	0.3
42	18/24	1.5
	20/22	10.5
	22/20	37.0
	24/18	1.0
44	20/24	0.9
	22/22	2.1
	24/20	7.0
46	24/22	0.8
48	24/24	0.1
50	26/24	0.02

Structure of Jojoba Oil

The double bond positions in jojoba oil were almost exclusively ω-9, i.e., the ethylenic bond was between the 9th and 10th carbon atoms when counting from the methyl or terminal end of the backbone carbon chain. A small quantity of the ω-7 homologs hexadec-9-enoic (0.2%) and octadec-11-enoic (1%) acids were found. Absence of absorption at the 10.36-micron *trans* position in infrared absorption spectrophotometry would indicate that all ethylenic bonds were *cis* in geometric configuration.

One seed sample had as much as 7% saturation in its alcohols and 3% saturation in the acids, but most samples contained only 2% saturation in both the alcohols and the

TABLE II

Composition and Structure of Fatty Alcohols and Fatty Acids Derived from Jojoba Oil (Analysis by GLC, Ozonolysis-GC and GC-MS)

Alcohols	(%)	Acids	(%)
Tetradecanol	tr[a]	Dodecanoic	tr
Hexadecanol	0.1	Tetradecanoic	tr
Heptadec-8-enol	tr	Pentadecanoic	tr
Octadecanol	0.2	Hexadecanoic	1.2
Octadec-9-enol	0.7	Hexadec-7-enoic	0.1
Octadec-11-enol	0.4	Hexadec-9-enoic	0.2
Eicosanol	tr	Heptadecenoic	tr
Eicos-11-enol	43.8	Octadecanoic	0.1
Hecos-12-enol	tr	Octadec-9-enoic	10.1
		Octadec-11-enoic	1.1
Docosanol	1.0	Octadecadienoic	0.1
Docos-13-enol	44.9	Octadecatrienoic	tr
Tetracos-15-enol	8.9	Nonadecenoic	tr
Hexacosenol	tr	Eicosanoic	0.1
		Eicos-11-enoic	71.3
		Eicosadienoic	tr
		Docosanoic	0.2
		Docos-13-enoic	13.6
		Tricosenoic	tr
		Tetracosanoic	tr
		Tetracos-15-enoic	1.3

[a] "tr" denotes 0.01-0.05%. Absence of absorption at 10.36 microns in infrared spectrophotometry indicates all ethylenic bonds to be *cis* in geometric configuration.

acids, thereby allowing the conclusion that jojoba wax ester molecules are generally 98% *cis*-monounsaturated at the ω-9 position at both ends of the molecules.

INDUSTRIAL USES OF JOJOBA OIL

Cosmetics

Among the many uses for jojoba oil that have been proposed over the past decades (4,14), the ones that have shown most promise as profitable commercial commodities are the cosmetic products. Jojoba oil has been shown to be completely nontoxic to the human skin (15), and a few cosmetic products formulated by the author to contain 20% jojoba oil have enjoyed favorable comments in their preliminary marketing tests. Jojoba cosmetic products currently on the market are: bath oil, body oil, cleansing cream, cleansing pad, cleansing scrub, facial nourishing cream, facial oil, hair conditioner, hair oil, hair shampoo, hand lotion, lip gloss, make-up remover, moisturizer, shaving cream, skin cleaner, soap bar, soft soap, sun tan lotion, swimmer's hair shampoo/conditioner and vanishing cream.

Lubricants

Potentially the single most extensive and outstanding industrial use of jojoba oil could be the sulfurized derivative formulated into extreme-pressure/extreme-temperature lubricants. Sulfurized products from refined jojoba oil have been shown (16,17) to be equal to or better than sulfurized sperm whale oil, and if available in sufficient supply, the sulfurized jojoba oil might be used extensively in the automotive industry. Adhesion to metallic surfaces by the sulfurized oil and its stability at high temperatures allow continuous provision of a thin-film lubricating boundary, which is crucially needed in reducing frictional wear and temperature rise, the latter characteristic helping directly to prolong the life span of the lubricating oil and indirectly to safeguard the automobile parts.

When cost of jojoba oil is reduced to a level substantially lower than the present, lubricants produced from jojoba oil for cutting, molding and continuous casting metals may become widely used industrially.

Surfactants

Jojoba may become a major source of linear monounsaturated liquid fatty primary alcohols, which are still rare commodities for industrial use. The long alkenyl (jojobenyl, erucyl) alcohols, derived by hydrolysis, can be combined with surface-active polyethylene glycol chains to tailor-make surfactants with desired hydrophile-lipophile balance. In addition to emulsifiers, these surfactants may provide the basis for functional and profitable water evaporation retardants, which are in critical need in many parts of the world.

Other Uses

The heat-stable, nontoxic, skin-compatible, frction-reducing and penetrating characteristics of jojoba oil will allow it to be utilized in many industrial and consumer products, the extent of usage depending on the stability in supply and cost of the oil. Some other uses are discussed in the first volume of the monograph series, Jojoba (18). A few of these are: lamp oil to replace sperm whale oil, solid wax to mix with and improve paraffin candles, microporous polyethylene film from microencapsulation of oil, and fatty acid amides as lubricant for polyethylene film extrusion.

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