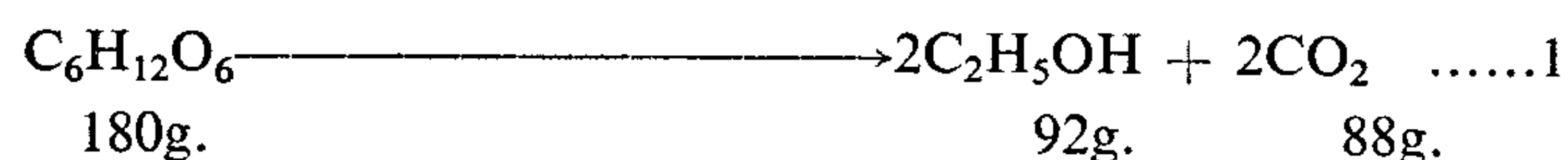


## BIOCHEMISTRY OF FERMENTATION IN TODDY AND PRODUCTION OF ARRACK

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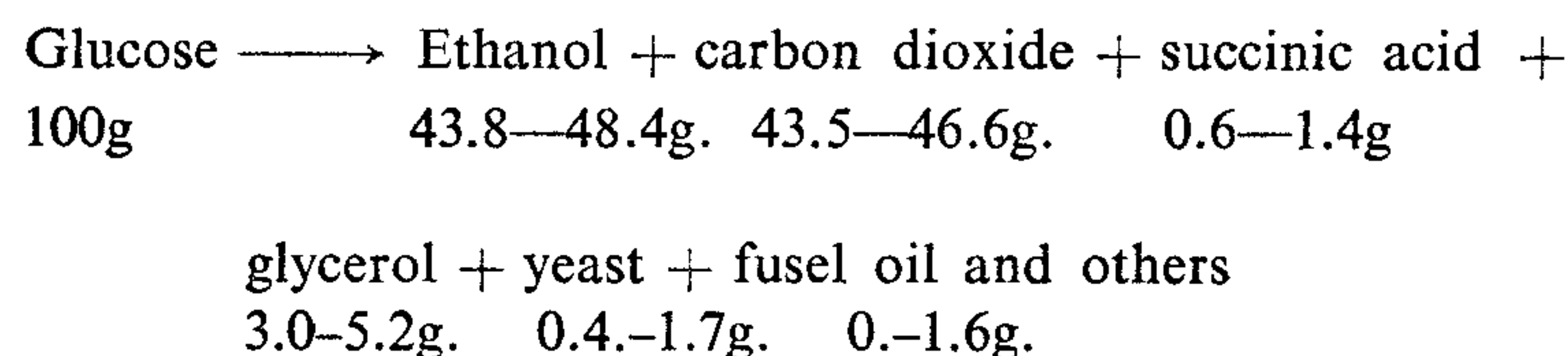
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In alcoholic fermentation a sugar, such as glucose, fructose, or sucrose, in solution is converted to ethyl alcohol and carbon dioxide. The process can be approximated for a hexose by the equation ;



This represents a theoretical yield for ethanol of 51% w/w based on the sugar used ; the balance being evolved as carbon dioxide.

The equation is, however, only an approximation since, in addition to ethanol and carbon dioxide, sugar is consumed by yeast growth and in the production of small amounts of other compounds. Detailed mass balances of alcoholic fermentation have been performed by several workers and reported by Oura (1977). These suggest that, using a selected yeast in pure culture, an ethanol yield of 90—95% as predicted by equation 1 is obtainable and that yields for other products fall in the ranges given in equation below.



### Congeners in Alcoholic Beverages

Ethanol in its pure form has little flavour and none of the character of the popular self-flavoured spirits such as rum, brandy, whisky and arrack. It is the 1% or thereabouts of other compounds that give a liquor its character. They are present individually in the order of parts per million. Some are produced during the fermentation while others originate from the raw material used: sugar cane molasses, grapes, malted barley or palm sap. The non-volatile congeners are largely eliminated by distillation while those that are volatile are concentrated or eliminated to varying extents depending on the type of distillation employed. Maturation of the crude spirit in wooden barrels leads to further changes in composition through mechanisms such as extraction, evaporation, oxidation and esterification.

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Two of the most important groups of congeners present in potable spirits are the ethyl esters of a variety of fatty acids and the group of three to five carbon alcohols known as fusel oil. Table 1 presents a list of compounds reported in fermented alcoholic beverages and Table 2 lists those present in the distilled spirit, rum.

**TABLE 1**  
Aroma compounds reported in alcoholic beverages (Kahn, 1969)

<i>Type</i>	<i>Number</i>	
Alcohols	38	C <sub>1</sub> to C <sub>16</sub> , matsutakeol, menthol, octen-3-ol
Acids	80	formic to hexacosanoic (C <sub>20</sub> ) lauric, palmitic, stearic
Esters	118	many combinations of above acids and alcohols
Carbonyl compounds	41	formaldehyde to many substituted compounds
Acetals	17	diethoxymethane to triethoxpropane
Phenols	41	vanillin, syringaldehyde contributed mostly from wood
Hydrocarbons	11	benzene, naphthalene etc.
Nitrogen compounds	18	amines, pyrazines
Sulphur compounds	11	methyl, ethyl and pentyl sulphides
Lactones	17	butyrolactone to dodecalactones
Sugars	4	fructose etc.
Unclassified compounds	11	Lignins etc.
<b>Total</b>	<b>407</b>	

**TABLE 2**  
Aroma compounds reported in rum (Lethonen and Suomalainen, 1977)

<i>Type</i>	<i>Number</i>	
Alcohols	20	Methanol to Heptanols, Octen-3-ol and menthol
Acids	31	Acetic to decanoic, lauric, palmitic, myristic to palmitolic
Esters	73	Combinations of above acids and alcohols
Phenolic compounds	24	Phenol, vanillin, syringaldehyde etc. constituents from wood
Nitrogenous compounds	15	Pyrazine derivatives
Sulphur compounds	6	Methyl and ethyl sulphides
Lactones	7	Octa and dodecalactones
Carbonyl compounds and acetals	82	Substituted products of many aldehydes
Miscellaneous products	7	
<b>Total</b>	<b>265</b>	

**Congeners in Arrack**

Arrack is produced by the maturation of coconut toddy distillates. The toddy is produced by an uncontrolled, spontaneous fermentation of coconut sap in the collecting pot. Many species of microorganisms are present in these pots and the microbiology of the fermentation has been described in a previous paper (Vidanapathirana *et. al.* 1982).

The arrack industry in Sri Lanka uses two types of still, the patent and the pot for toddy distillation. The congeners present in the toddy are eliminated from, or concentrated in, the distillate to different extents by the two types of still.

Figure 1 shows gas chromatographic traces obtained from three toddy distillates prior to blending. The height of individual peaks is an indication of the concentration of that particular component. The first two traces are of coconut toddy distillates from a patent still and from a double distillation in a pot still. The third is a single pot distillate from fermented palmyrah, (*Borassus flabellifer*) sap. A consistent feature in all these distillates is the presence of ethyl lactate. This compound, found occasionally in Western spirits and also reported in an African gin, is thought to originate from the lactic acid produced by bacteria in the fermenting sap (Nordstrom, 1962). It is present in substantial amounts in the pot still single distillate and the patent still distillate but is largely removed by double distillation from a pot still. It is interesting to note that the quality of arrack which has been double distilled is widely regarded as being superior.

**TABLE 3**

**Congeners in the toddy distillates from pot stills in the different areas in Sri Lanka  
(ppm of absolute alcohol)**

	<i>Seeduwa</i>	<i>Dankotuwa</i>	<i>Wadduwa</i>	<i>Kalutara</i>	<i>Jaffna</i>
Ethanol % .. ..	19	39	58	61	66
Methanol .. ..	7	6	9	13	31
Propanol .. ..	80	56	885	339	1181
2 Methyl Propanol ..	273	286	270	346	325
Amyl Alcohol (Principally 3-methyl butanol) .. ..	1182	1223	1261	1336	1458
Acetaldehyde .. ..	15	11	111	73	40
Ethyl Acetate .. ..	35	69	2824	1796	5082
Ethyl Lactate .. ..	1160	1223	270	487	512
Butanol-2 .. ..	N.D.	N.D.	N.D.	N.D.	+
3-Ethoxy Propanol ..	N.D.	N.D.	N.D.	N.D.	+
Isoamyl Acetate .. ..	N.D.	N.D.	N.D.	N.D.	+

N.D. — not detected < 5 ppm.

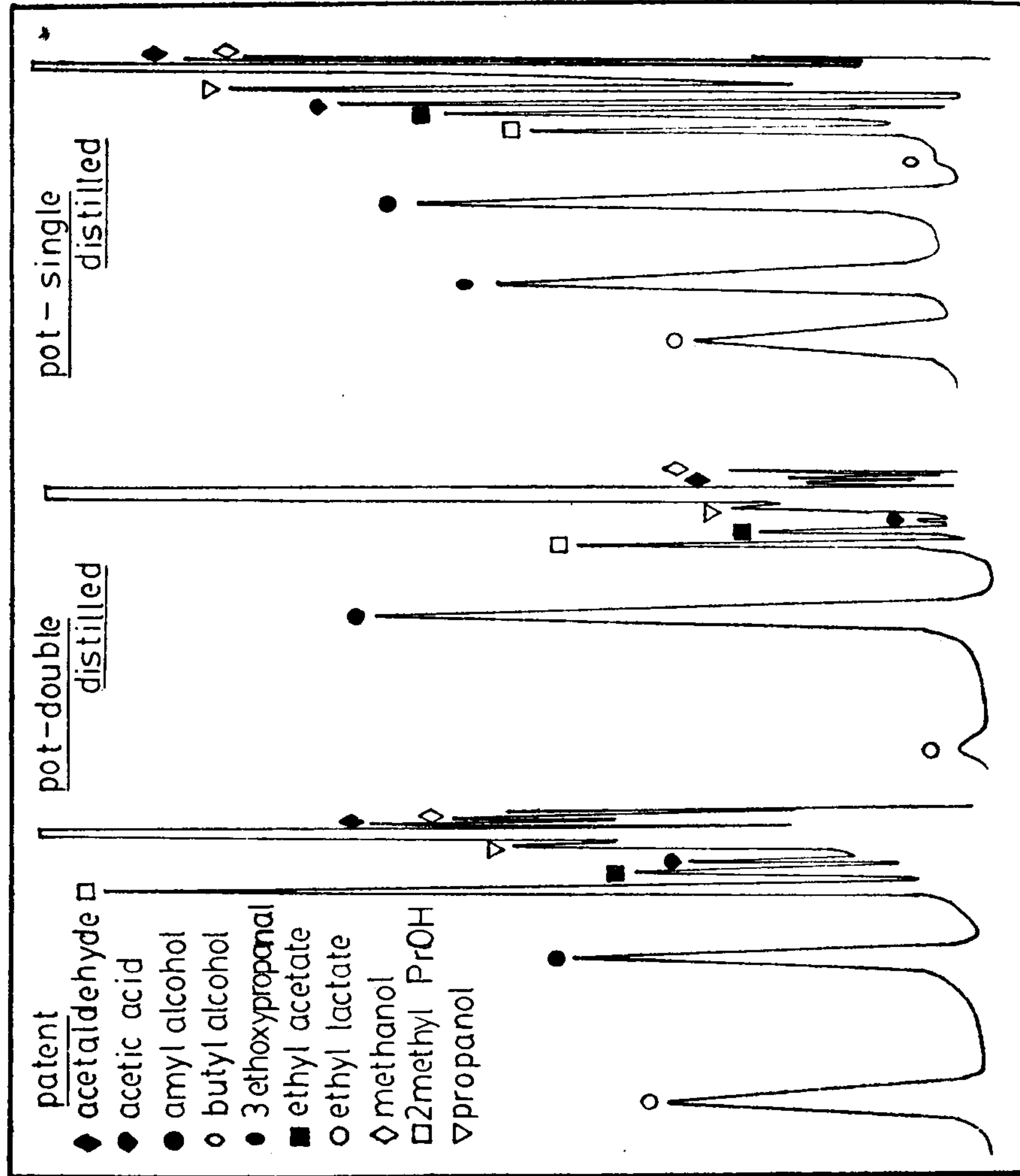


Figure 1. Gas chromatographic traces of commercial coconut sap and palmyrah sap distillates from pot and patent stills.

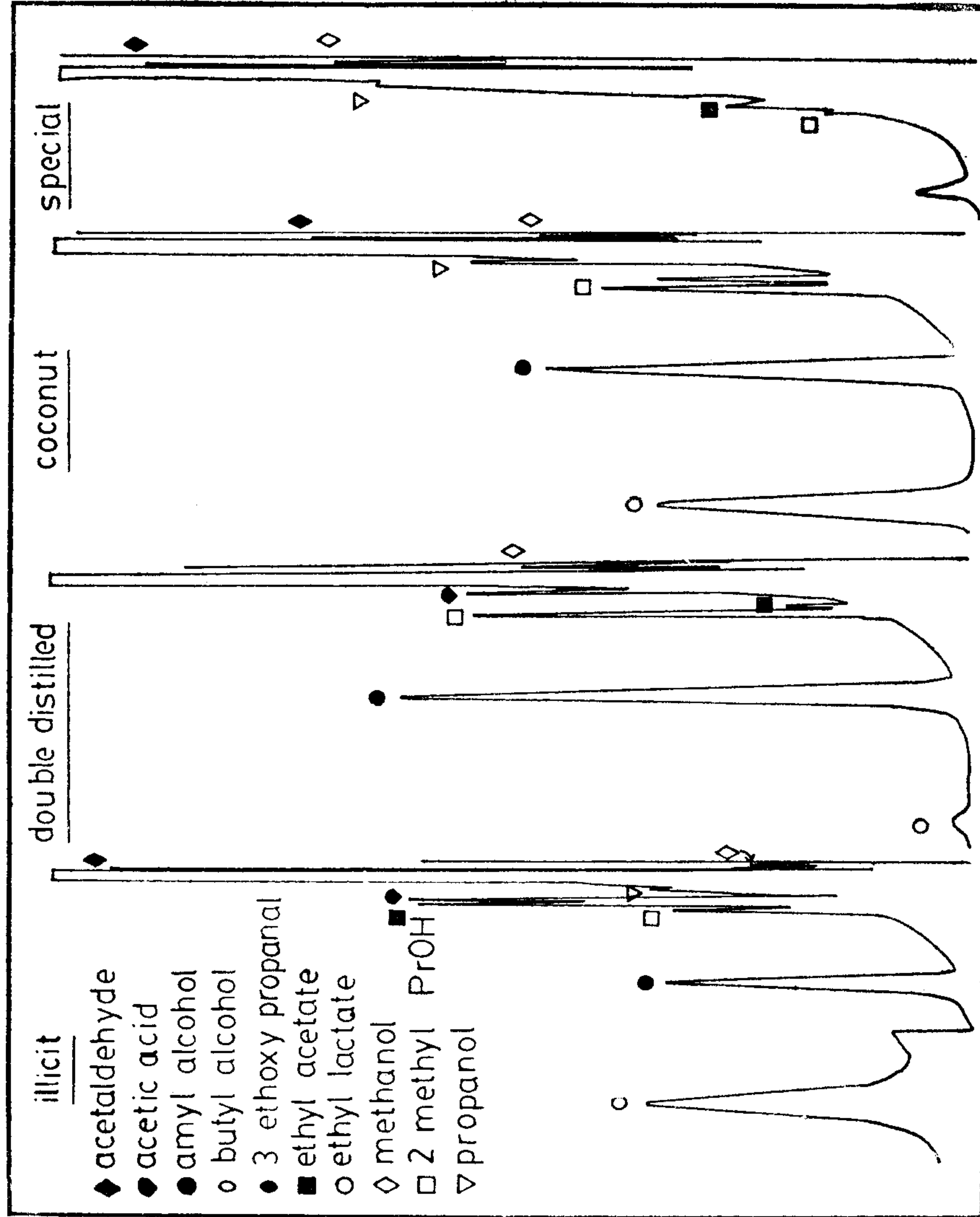


Figure 2. Gas chromatographic traces of three commercial brands of Arrack and Illicit arrack.

The concentrations of congeners in single pot distillates from five localities in the country are given in Table 3. Distillates from Jaffna (where fermented palmyrah sap is distilled, see Figure 1 also) is markedly different from the others having a greater quantity and variety of congeners. The compound 3 Ethoxypropanal, present in large amounts in the Jaffna distillate, is thought to arise from the bacterial decomposition of glycerol (Dubois *et. al.*, 1973) suggesting that it is the differences in microflora that are largely responsible for differences in the product quality. This is supported by evidence from other areas where only the coconut palm is tapped. Distillates from pot stills in the coconut triangle, Dankotuwa and Seeduwa, contain 15—30 times more ethyl lactate than ethyl acetate, whereas similar distillates from other areas, Wadduwa and Kalutara, show completely the opposite, with 3—10 times more ethyl acetate than ethyl lactate. This may be a reason why the distillates from Wadduwa and Kalutara, which are close to each other are supposed to be of better quality.

The Gas Chromatographs of several commercial brands of arrack are presented in Figure 2. The "Special arrack" contain little congeners and has very little flavour. "Coconut arrack" has Gas Chromatographic traces similar to those shown in Figure 1 for patent still and single pot distillate suggesting that it is either one of these or some blend of them. "Double distilled arrack" is richer in fusel alcohols than most other brands but has little ethyl lactate. The illicit arrack obtained from a small home made pot still has comparable levels of congeners (based on ethanol) to "coconut arrack", but has far lower alcohol content. Generally the ratio of esters, ethyl acetate to ethyl lactate, is less in the arracks (Table 4) than in the unaged and unblended distillate samples examined (Samarajewa *et. al.*, 1981).

TABLE 4  
Congeners in different brands of arrack  
in ppm of absolute alcohol

	Coconut	Double Distilled	Old Seeduwa	Special	Illicit	Jaffna
Ethanol%	31	32	40	29	18	35
Methanol	9	16	14	26	8	22
Propanol	90	120	106	2	43	623
2 Methyl Propanol	360	397	336	20	282	331
Amyl Alcohol (Principally 3-methyl butanol)	1083	1472	1351	60	1346	1314
Acetaldehyde	28	10	79	38	194	95
Ethyl Acetate	208	70	570	105	565	1482
Ethyl Lactate	706	49	108	43	1066	320
Acetic Acid	N.D	N.D	tr.	N.D	+	tr
Butanol -2	tr.	tr.	tr.	tr.	tr.	tr.
3 Ethoxy Propanol	N.D	N.D	N.D	tr.	tr.	+

N.D. — not detected < 5 ppm.

tr. — traces

+

The relative amounts of isoamyl and isobutyl alcohols found in arracks are compared with those in whiskies in Figure 3 (Otsuka *et. al.* 1979). The isoamyl alcohol content of arrack is less than that of Bourbon whisky, a beverage with good body, and Scotch malt whisky, a mellow beverage, and its isobutyl alcohol content is less than that of Scotch malt and Scotch blended whiskies. The gradient of the graph is, however, quite close.

This presents the interesting possibility of manipulating the fermentation and distillation of arrack to increase the levels of these compounds so that the product resembles more closely, at least in this respect, to Bourbon and Scotch whisky.

#### **Separation of congeners during distillation of arrack**

During the simple pot distillation of arrack, the initial fractions of distillate contain the highest concentrations of ethanol. Some congeners such as the fusel alcohols and ethyl acetate show a similar behaviour, appearing in higher concentrations at the start of distillation (Figure 4). Ethyl lactate distils in larger concentrations in the later fractions. The distillation regime used will, therefore, have a profound effect on the distillate quality. The separation of a large foreshots fraction will remove higher alcohols at a time when they are being carried over in relatively high concentrations and similarly, by terminating the main fraction at an appropriate stage, the carry over of a large proportion of the ethyl lactate can be avoided.

#### **Congener production by yeasts**

Yeasts play an important part in the production of the congeners found in alcoholic beverages (Suomalainen and Nykanen, 1966). Some of the yeasts found in spontaneously fermenting sap produce little or no alcohol but do produce other compounds.

Figure 5 gives a comparison of the total amounts of major congeners found in distillates of a synthetic sweet toddy (containing lactic acid) which had been fermented with pure cultures of yeasts isolated from fermenting coconut sap. The area of each circle represents the total amount produced and the percentage of ethanol in the distillate is given along with the yeast species used. The mixed culture produced the highest ethanol and congener concentrations though individual cultures of the *Saccharomyces* spp. isolated also produced high levels of both. *Candida sake* produces little alcohol but considerable amounts of congeners. Others species appear to contribute less to either ethanol or congener content of fermented toddy.

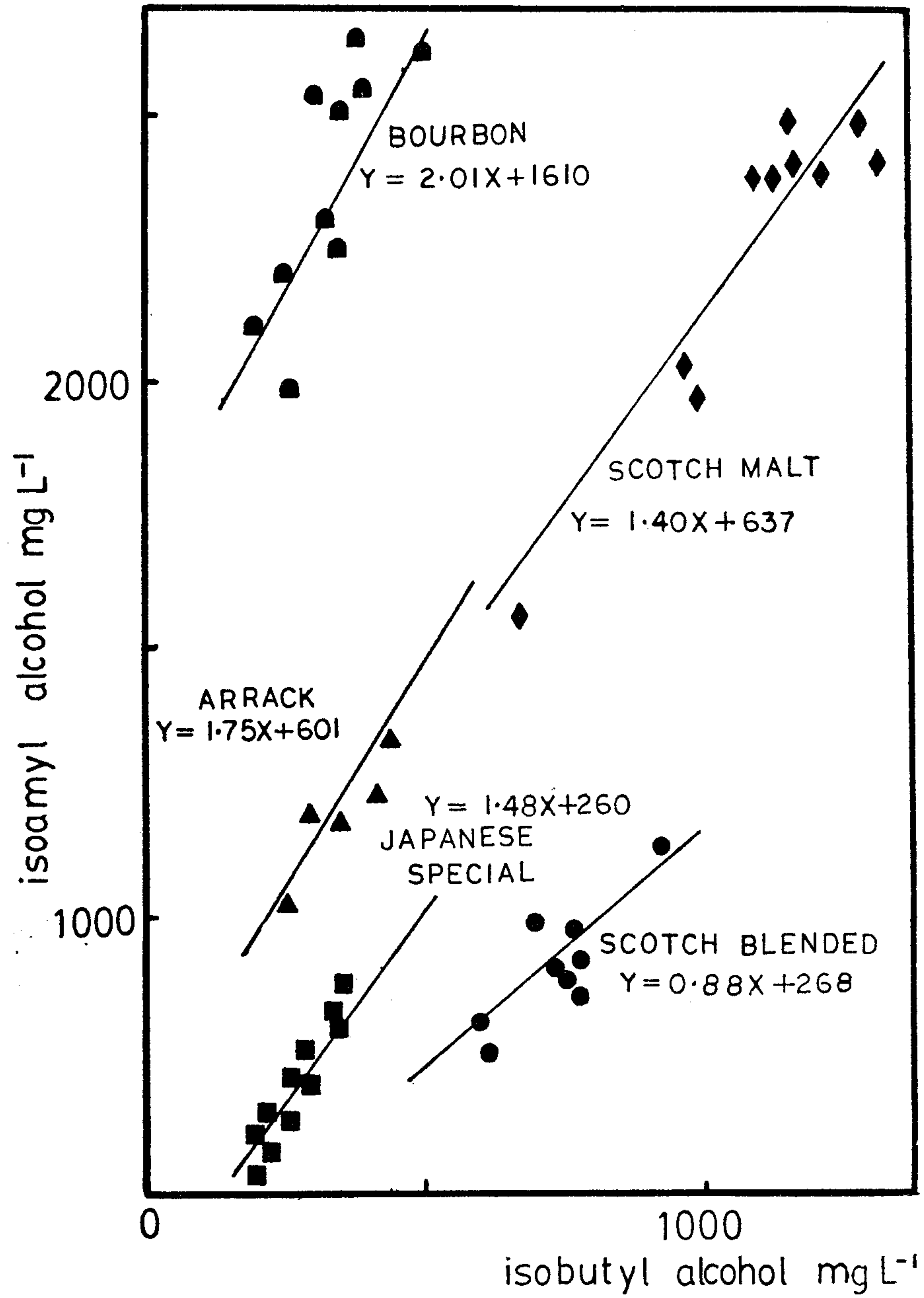


Figure 3. The ratio of isoamyl alcohol to isobutyl alcohol in four brands of whisky and arrack.



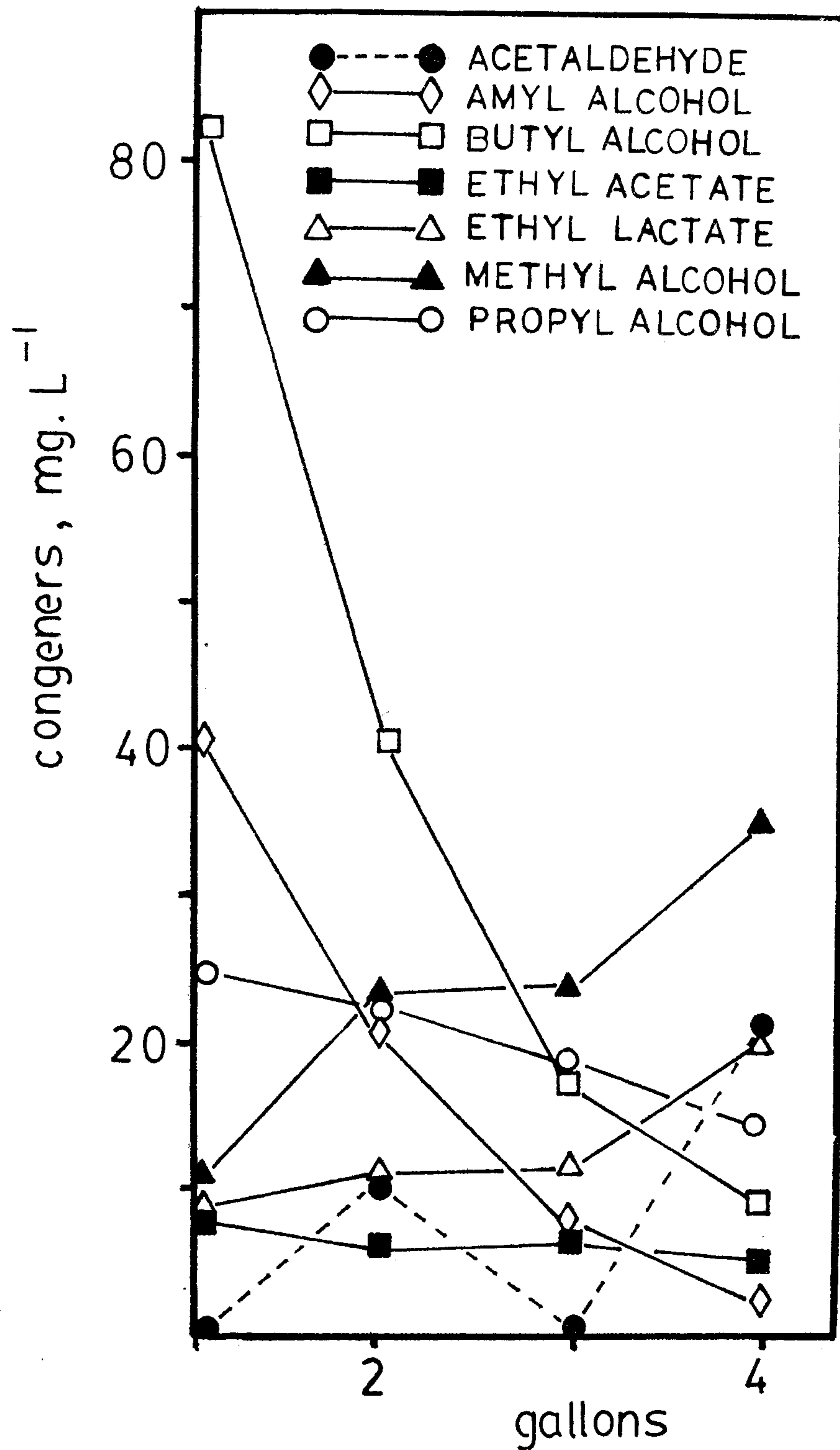


Figure 4. Separation of volatiles into different fractions of the distillate during pilot plant (25 gal.) distillation of Coconut Toddy.

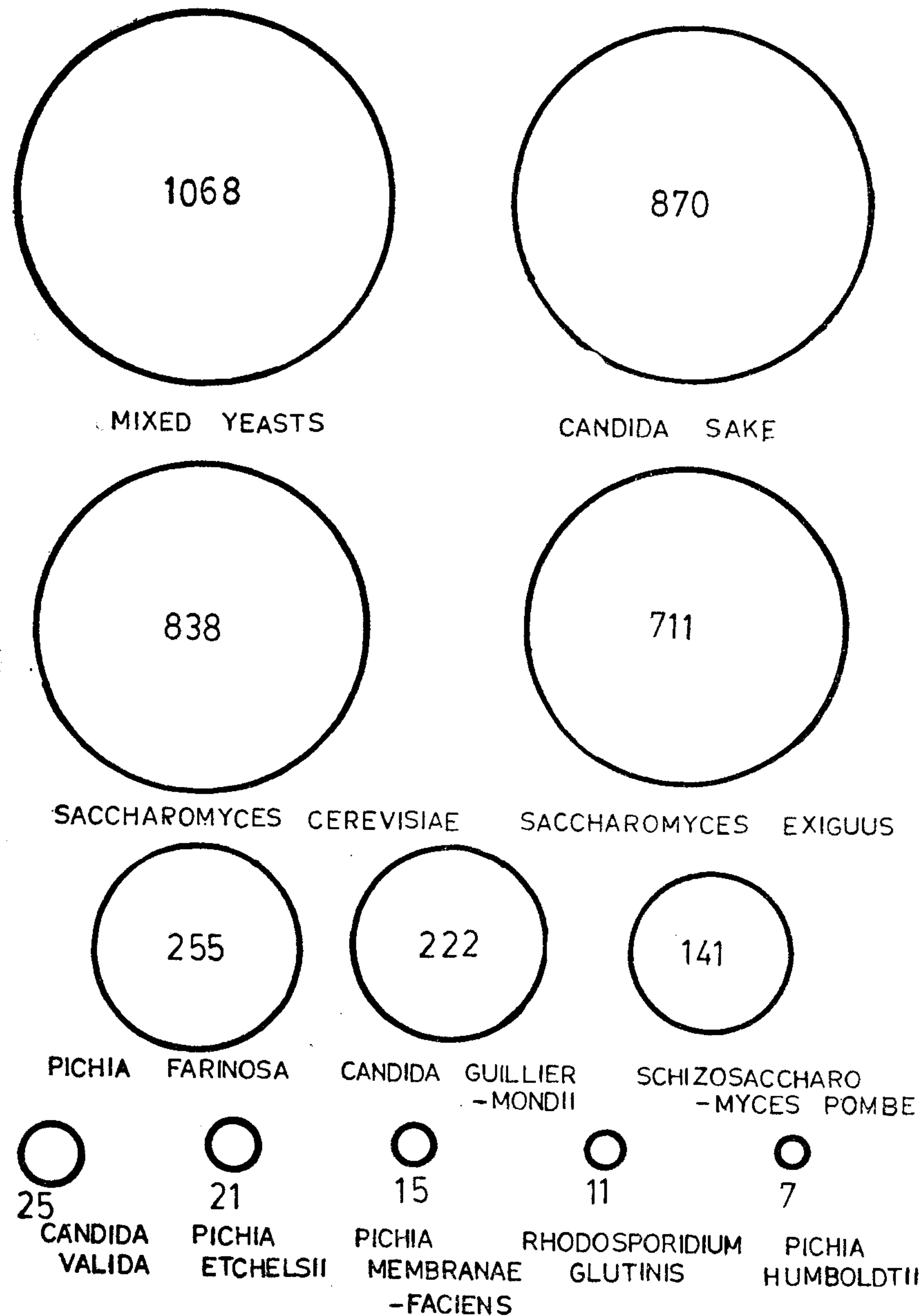


Figure 5. The amounts of volatiles (mg per litre) and ethly alcohol (w/v %) appeared in the distillates from a synthetic toddy fermented using pure and mixed yeast cultures.

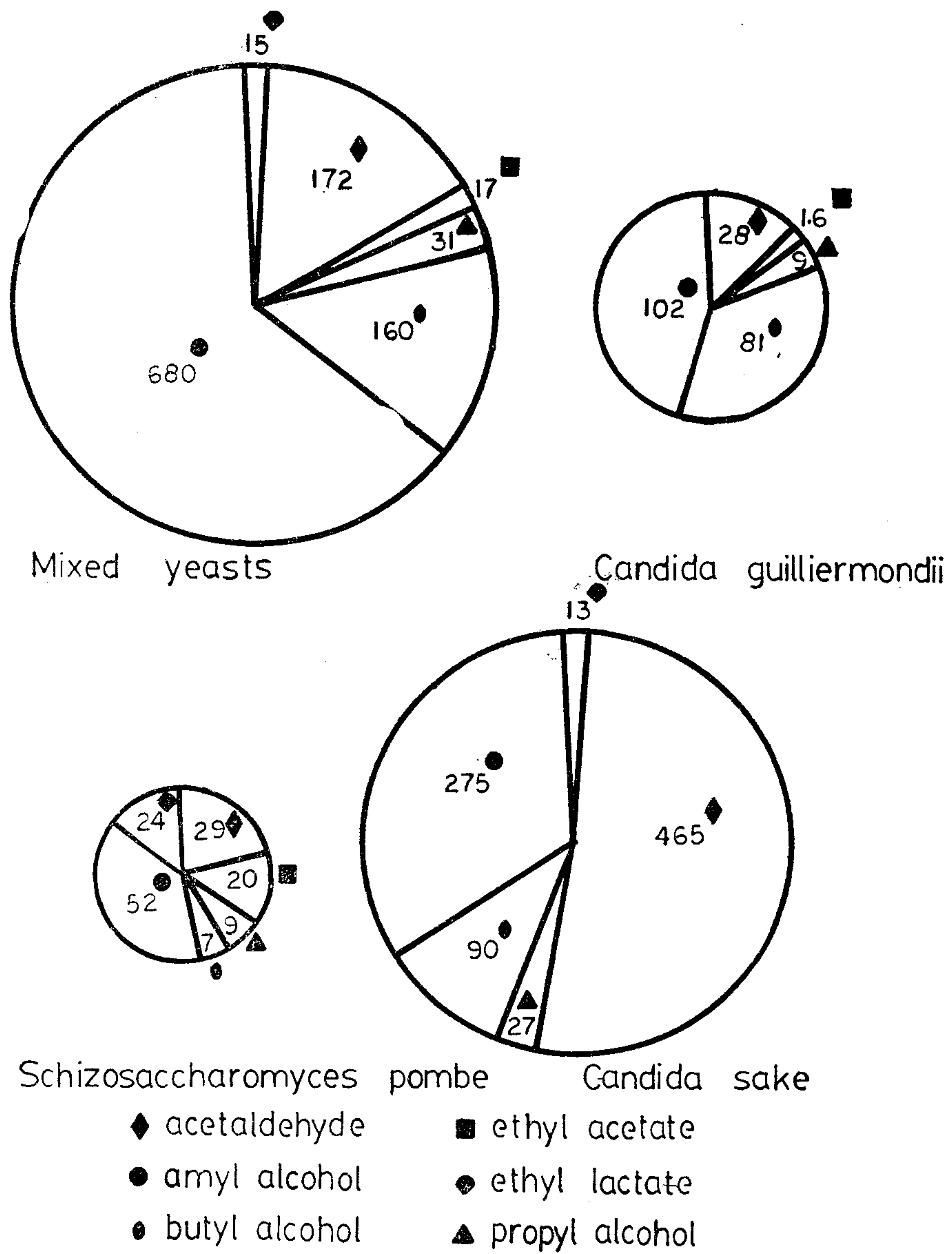


Figure 6. The amount of individual volatiles (mg per litre) appeared in the distillates from a synthetic toddy fermented using pure and mixed yeast cultures.

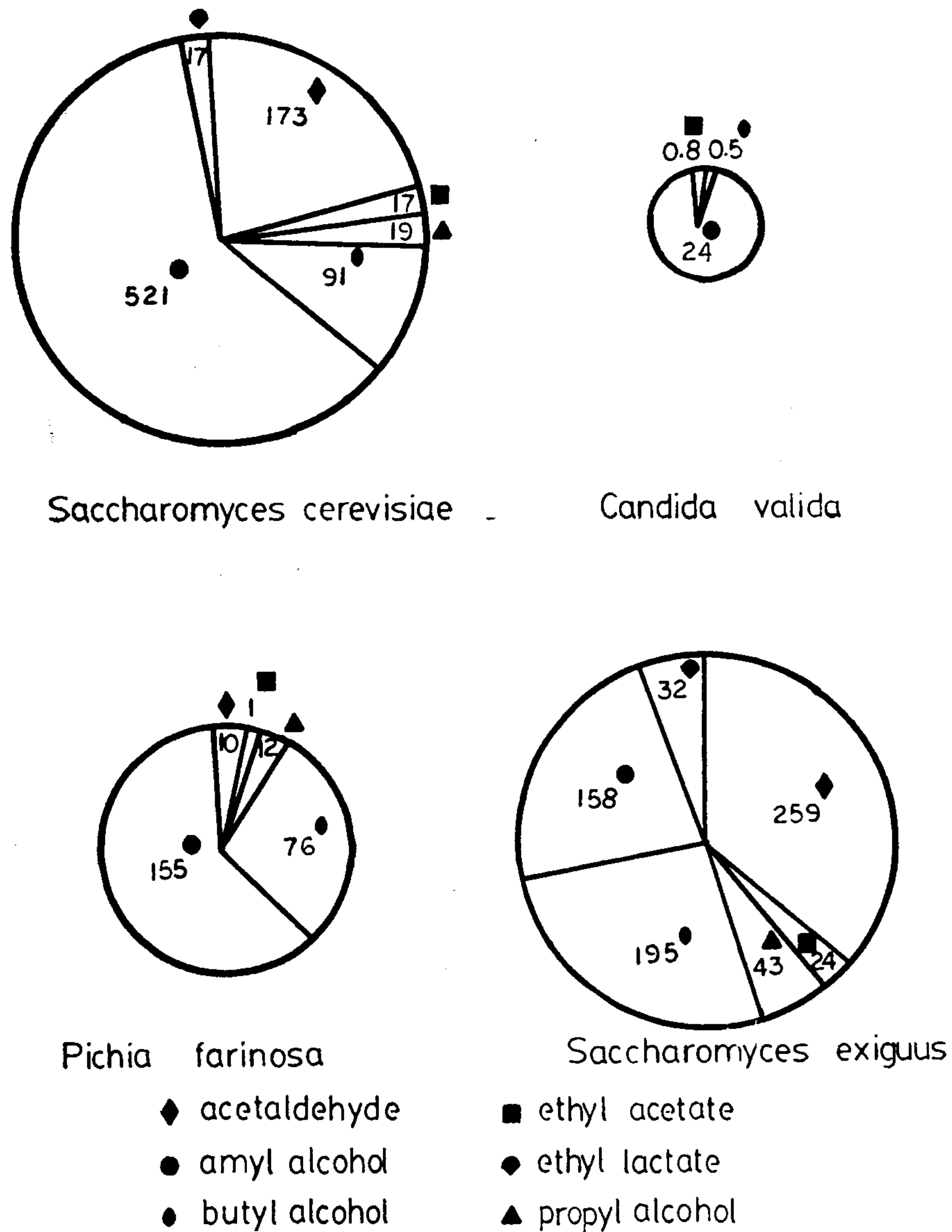


Figure 7. The amount of individual volatiles (mg per litre) appeared in the distillates from a synthetic toddy fermented using pure yeast cultures.

The relative amounts of the different congeners produced by different yeasts vary (see Figure 6 and 7). The ratios of amyl alcohol to isobutyl alcohol as shown are :

Mixed yeasts	4:1
<i>Saccharomyces cerevisiae</i>	5:1
<i>Saccharomyces exiguus</i>	1:1
<i>Candida sake</i>	3:1

In arrack the ratio is around 4:1 ; the same as in the mixed yeast culture. If a pure culture of *S. cerevisiae* were to be used in arrack production this would be likely to shift arrack to a position closer to that of Bourbon whisky in Figure 3. It may, therefore, be possible by the selection of microorganisms for toddy fermentation to change the pattern of congeners found in arrack and thus modify its character to suit different tastes.

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