

Fig. 3. Correlation of chromatographic losses with cup losses.

The correlation coefficient (r) for nondegummed oils was .751, and the multiple correlation coefficient (R) for degummed oils was .642.

These data show, as in the case of the curve constructed by values obtained from class intervals, that, although there are only slight differences from the standard errors of estimate between degummed and nondegummed oils, the correlation coefficients (r , R) indicate a definitely better correlation for the nondegummed samples than for the degummed samples. Nevertheless, as perfect correlation exists when r or $R = 1$, the correlation coefficient value of .642 and .751 are significant and considered to be good.

It should be pointed out that, at least in the types of oils analyzed in this investigation, the shape of the multiple regression curve for degummed oil is very shallow. The minimum point at .77% chromatographic loss is therefore just a theoretical and not a sharply defined point. In view of this and the $\pm .3\%$ standard deviation of cup losses from the mean, the following should be said in case the chromatographic losses are below or in the neighborhood of 1.0%: although it is possible to predict the approximate value of cup losses within the range indicated by the standard error of estimate (S_y , $S_{y_{12}}$), it is not possible to predict the trend which will be followed by one variable when the other variable is changing in one direction.

Summary

It can be concluded, on the basis of our experiments, that chromatographic loss determinations can be well correlated with A.O.C.S. Cup Refining determinations. This correlation is good for samples above 1% chromatographic losses and somewhat less accurate for samples below 1.0%.

Most of the discrepancy in correlation is inherent in the Cup Loss method because it is less precise in general than the chromatographic determination.

On the other hand, the chromatographic loss is an accurate, easily obtainable index for unavoidable losses resulting from the nonneutral oil fraction of the oils. In the majority of cases the degumming of the oil to levels below 1% chromatographic loss is not indicated by a parallel decrease in cup losses. Thus, in these cases, as long as premiums are paid on the basis of the A.O.C.S. Cup Loss method, the processor is placed in a very disadvantageous position.

It should be pointed out that all our determinations were made on the oils from the 1956 crop during the summer months. The possibility that different crop years will result in different correlation curves might exist, and we are planning to do further work in the future.

It is hoped that by presenting statistically significant figures on this subject, enough interest will be stimulated for more collaborative work, which might result in a review of the industry's present method for the determination of refining losses in soybean oil.

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The Synthesis of 2-Heptenal

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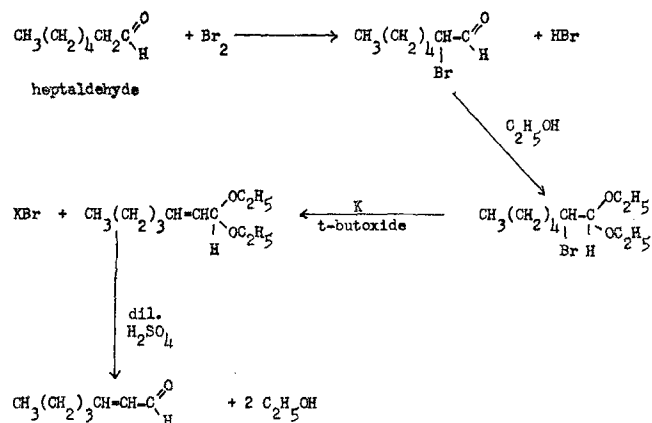
DURING A STUDY on the reversion of soybean oil undertaken some years ago it became necessary to prepare some pure 2-heptenal. Several methods for preparing this α - β unsaturated aldehyde are recorded in the literature. Delaby and Guillot-Allégre (3) and Martin, Schepartz, and Daubert (6) have described the chromic acid oxidation of the corresponding unsaturated alcohol. More recently Bedoukian (1) reported the preparation of a series of α - β unsat-

urated aldehydes by bromination of the appropriate enol acetate, followed by the debromination of the resulting dimethyl bromoacetal.

The yields of 2-heptenal obtained by previous workers were low. Delaby and Guillot-Allégre (3) do not record all of their yields; however, from the data given, the over-all yield of 2-heptenal appears to be about 7-10%. Several attempts to prepare pure 2-heptenal according to the method of Martin *et al.* (6)

gave low yields and products of doubtful purity. The constants for 2-heptenal are not in agreement, particularly the refractive index. The synthesis of Bedoukian (1) is straightforward, but the presence of impurities in the finished aldehyde is admitted. Moreover the over-all yield of 2-heptenal by this procedure is only 9.1%.

The following synthesis is based on the direct bromination of the free aldehyde, followed by a rapid conversion to the diethyl acetal of the α -bromoheptaldehyde. Dehydrobromination with potassium *t*-butoxide and a subsequent acid hydrolysis gave a pure 2-heptenal in a 40.8% yield. Only two products are actually purified and isolated, the diethyl acetal of α -bromoheptaldehyde and 2-heptenal.



Experimental

Diethyl Acetal of α -Bromoheptaldehyde. Efforts to produce this compound through direct bromination of the diethyl acetal of heptaldehyde resulted in the formation of a mixture of compounds. Following the procedure of Freundler and Ledru (4), a pure compound was made by brominating the aldehyde and then converting to the acetal by the addition of ethyl alcohol to the cold reaction mixture to retain the catalyst, HBr. A solution of 93.5 g. (.818 mole) of freshly distilled heptaldehyde (b.p. 51–58°C. at 18 mm.) in 60 ml. of dry carbon tetrachloride was introduced into a 1-liter, 3-neck flask equipped with a stirrer, thermometer, and dropping funnel. The aldehyde solution was cooled to -8°C ., and 126 g. (.79 mole) of bromine were added slowly, keeping the temperature at -5°C . to -10°C . while stirring vigorously. Stirring was continued for 1 hr. after the addition of bromine was complete. The temperature was allowed to rise slowly to 5°C . when the mixture was poured into 275 ml. of commercial absolute ethyl alcohol previously cooled to -5°C . During mixing the temperature was kept below 10°C . The reaction mixture was then stirred at room temperature overnight. When the stirring was stopped, the solution separated into two layers almost immediately. The mixture was poured into 550 g. of ice-water and extracted with ether. The ether extracts were washed twice with water, three times with dilute sodium bicarbonate, and dried with anhydrous sodium sulfate; the solvents were removed by distillation. A net yield of 215.7 g. of crude bromoacetal was obtained.

Purification was achieved by two vacuum, fractional distillations through a 40-cm. Vigreux column.

a) 14 mm., b.p. 102–128°C., yield 173.0 g.

b) 14 mm., b.p. 120–124°C., yield 156.5 g. or 74.3% of theory.

The constants of the diethyl acetal of α -bromoheptaldehyde were $n_D^{20} 1.4451$, $d_4^{20} 1.118$. Percentage bromine: theory 29.95, found 29.95.

2-Heptenal. The removal of halogen acid with potassium *t*-butoxide to produce unsaturation in acetals was initiated by Beyerstadt and McElvain (2). The improved procedure of Johnson, Barnes, and McElvain (5) was used.

To 640 g. of *t*-butyl alcohol were added 34 g. (0.87 mole) of potassium metal. These were heated at reflux until all the potassium had dissolved. To this solution 155.0 g. (0.58 mole) of the diethyl acetal of α -bromoheptaldehyde were added, and the mixture was refluxed for 3 hrs. After the solution had cooled, the product was ether-extracted and water-washed five times. After solvent removal an attempt to vacuum-distill the product was stopped because of foaming.

Washing with 550 g. of ice-cold dilute sulfuric acid (followed by water and sodium bicarbonate washes) sufficed to hydrolyze the acetal to the free aldehyde.

A total of 44.0 g. of crude 2-heptenal, b.p. 63–73°C. (12 mm.) was obtained after re-treating initial distillation residues with potassium *t*-butoxide, followed by cold dilute sulfuric acid. Fractionation through a 40-cm. Vigreux column gave pure 2-heptenal, b.p. 61–63°C./12 mm., weight 35.7 g. (54.9% yield). The over-all yield based on heptaldehyde was 40.8%.

Anal. calcd. for $\text{C}_7\text{H}_{12}\text{O}$: C, 74.93; H, 10.79.

Found: C, 74.86; H, 10.84.

In the following table the constants of the 2-heptenal prepared by the three methods are presented.

Constants	Radlove	Delaby and Guillot-Allégre (3)	Martin <i>et al.</i> (6)
Boiling point ($^\circ\text{C}$).....	61–63/12 mm.	165–167/atm.	80–85/14 mm.
Refractive index.....	$n_D^{20} = 1.4419$	$n_D^{17} = 1.4468$	$n_D^{20} = 1.4314$
n_D^{20}	1.4445 ^a	1.4457 ^a	1.4314
M.P. of 2,4-dinitrophenylhydrazone ($^\circ\text{C}$).....	133–133.5	131.5–132
M.P. of semicarbazone ($^\circ\text{C}$).....	168–168.5	169	168–168.4

^a A correction factor of .0004 per degree was used in order to compare all refractive indices at the same temperature.

Discussion

The analysis, constants, and derivatives of the 2-heptenal prepared by this procedure supports the purity of the 2-heptenal prepared by Delaby and Guillot-Allégre. The discrepancy in refractive index between the 2-heptenal of Martin *et al.* and the other two values indicated that Martin *et al.* did not have pure 2-heptenal but a mixture from which they isolated pure derivatives.

Summary

A new synthesis for the preparation of 2-heptenal which should be applicable to other α - β unsaturated aldehydes is described. The constants of the 2-heptenal prepared by this procedure support the data presented by Delaby and Guillot-Allégre.

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