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### Artefacts found during alumina chromatography

During a recent analysis of lovage root oil\*, we encountered some interesting artefacts originating from preliminary column chromatography.

The oil was first fractionally distilled through a 12 theoretical plate, silvered, vacuum jacketed, glass fractionating column, packed with 0.5 cm diameter glass rings. During the distillation, the pot temperature was maintained at 130–150° and the pressure was varied from 3.5 to 0.02 cm Hg. Under these conditions only twelve fractions (50 g) were collected. Consequently, to try and fractionate the remaining 400 g of residue according to polarity, we were obliged to use a rather crude, large-scale, column chromatographic technique. In order to conserve our adsorbent (Fischer Alumina No. 1), 600–700 g batches were packed under petroleum ether (30–60°) into 1 l separatory funnels. The glutinous residue was then added to a funnel and the system was further eluted with petroleum ether. From this separation, a petroleum ether extract (PE<sub>1</sub>) was obtained together with a sludge which was removed. PE<sub>1</sub> was evaporated and rechromatographed under similar conditions, eluting with petroleum ether, diethyl ether, acetone and methanol. Thus, fractions PE<sub>2</sub>, DIET<sub>2</sub>, ACET<sub>2</sub> and MEO<sub>2</sub> were obtained. Further rechromatography of PE<sub>2</sub> under similar conditions yielded fractions PE<sub>3</sub>, DIET<sub>3</sub>, ACET<sub>3</sub> and MEO<sub>3</sub> (see flow chart).

After the solvent had been distilled from each of the fractions, it was found that MEO<sub>3</sub> was larger than MEO<sub>2</sub>. GLC of MEO<sub>3</sub> over SE-30 showed that there were four major components present. The mixture was then distilled through a 35 theoretical plate 90 cm Podbielniak Spinning Band Column to obtain enriched fractions which could be separated by preparative GLC (see Table II for GLC conditions). The four peaks were collected<sup>1</sup> and their infrared spectra were recorded. From a careful comparison of these spectra with standard infrared spectra of authentic compounds, three of the four peaks were positively identified as: (1) (CH<sub>3</sub>)<sub>2</sub>C = CHCOCH<sub>3</sub>, mesityl oxide; (2) (CH<sub>3</sub>)<sub>3</sub>C(OH)CH<sub>2</sub>COCH<sub>3</sub>, diacetone alcohol\*\*; (3) (CH<sub>3</sub>)<sub>2</sub>C = CHCOCH = C(CH<sub>3</sub>)<sub>2</sub>, phorone. Peak 4 was only tentatively identified as (CH<sub>3</sub>)<sub>2</sub>C = CHCOCH<sub>2</sub>(OH)C(CH<sub>3</sub>)<sub>2</sub>, semiphorone, as no standard spectrum could be obtained. A literature search revealed that CABANI AND CECCANTI<sup>2</sup> had studied the kinetics of the reaction of phorone to semiphorone. We undertook, therefore, to prepare semiphorone in a somewhat similar fashion.

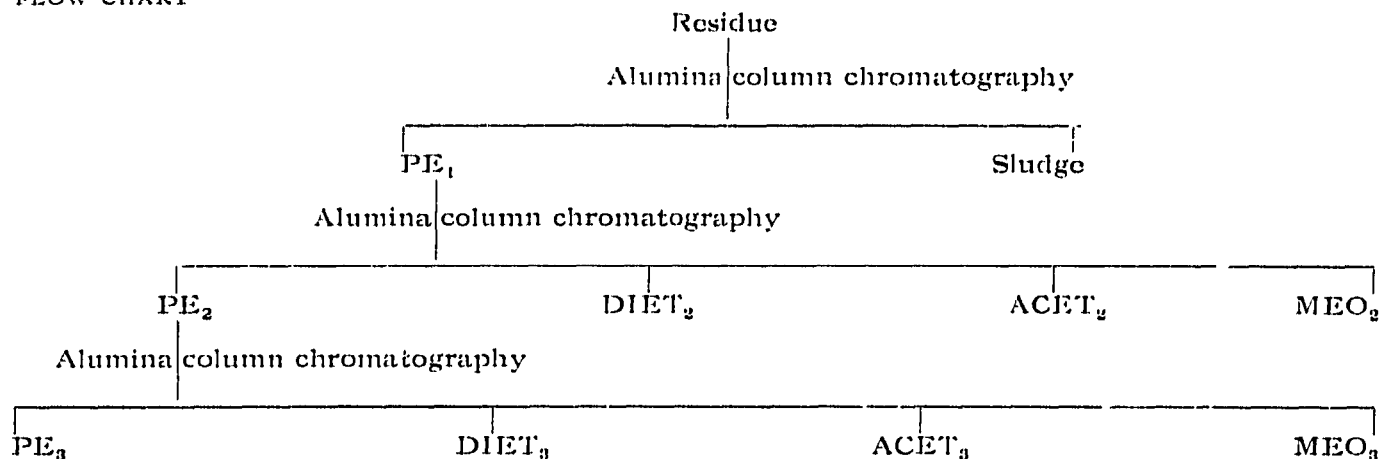
#### *Preparation of semiphorone*

Phorone (0.33 g) was mixed with 10 ml of 1.2 N hydrochloric acid and efficiently stirred for 20 h after which time the solution became homogeneous. The mixture was then neutralized with saturated sodium carbonate and extracted with diethyl ether. The ethereal extract was dried over anhydrous sodium sulphate and subjected to preparative GLC over SE-30. The four peaks separated were found to be: (1) 2,2,6,6-

\* The lovage oil used in this study was obtained from N.V. Chemische Fabriek Flebo, Hoogezand, The Netherlands, and was stated as being the steam distillation product of comminuted roots of Dutch origin.

\*\* Diacetone alcohol<sup>3</sup> has been found before as an artefact during AgNO<sub>3</sub>-alumina column chromatography with acetone as the eluent.

TABLE I  
FLOW CHART



tetramethyl-4-pyrone (87%), (2) phorone (6.1%), (3) semiphorone (6.7%), and (4) a ketodiol (probably triacetone dialcohol) (1.2%). The infrared spectrum of semiphorone, as prepared above, proved that our tentative identification of artefact peak 4 was correct.

It is assumed that the artefacts—mesityl oxide, diacetone alcohol, phorone and semiphorone—were obtained by the dimerization and trimerization of the acetone used as an eluent. Because of their polarity, they were preferentially adsorbed on the alumina and were not eluted until methanol was used as an eluent. When Carbowax 20M was used as the stationary phase in the above analyses, semiphorone dehydrated to phorone. For this reason, SE-30 was used for all GLC separations.

TABLE II  
GAS CHROMATOGRAPHIC CONDITIONS

Instrument: Varian Aerograph Autoprep 700  
 Column: a 12 ft.  $\times$   $\frac{1}{4}$  in. coiled stainless steel column packed with 20% SE-30 on Chromosorb W (60–80 mesh)  
 Flow rate: 60 ml He/min  
 Column temperature: 150–250° ballistically programmed  
 Injector and detector temperature: 270°  
 Detector: thermal conductivity (150 mA bridge current)  
 Recorder: Leeds & Northrup (6 in./h chart speed)

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