

1. Virtanen, A. I. and Lundbom, S. *Acta Chem. Scand.* **7** (1953) 1223.
2. Mozen, M. M., Burris, R. H., Lundbom, S. and Virtanen, A. I. *Acta Chem. Scand.* **9** (1955) 1232.
3. Virtanen, A. I. and Lundbom, S. *Acta Chem. Scand.* **8** (1954) 870.

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On the Rearrangement Products of Humulone

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The main bitter substances of beer are the *isohumulones* formed by rearrangement of the humulone, cohumulone and adhumulone of hops during the wort boiling. They have been isolated from trimethylpentane extracts of beer by counter-current distribution¹. According to Windisch *et al*, however, two products were formed from humulone when rearranged in a buffer solution, as the preformed *isohumulone* (Harzkörper A) was in part degraded to a second compound of similar properties (Harzkörper B)². The latter compound and its analogues have not been observed in beer. When treated with boil-

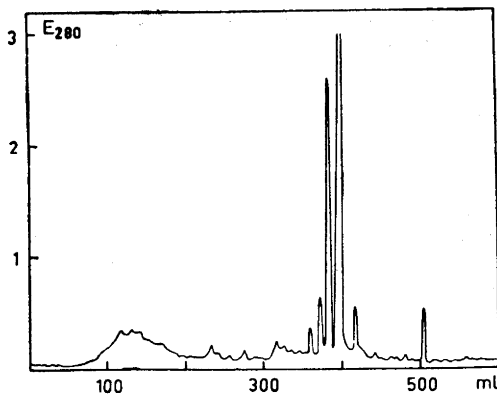


Fig. 1. Distribution diagram for rearrangement products of humulone in an acetate buffer of pH 5.1. The last peak is unreacted humulone.

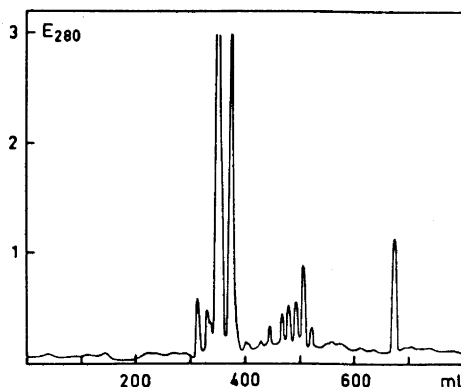


Fig. 2. Chromatographic pattern of the rearrangement products of humulone from alkaline ethanol.

ing alkaline ethanol humulone is stated to give *isohumulone* only³.

We have now tried to study humulone rearrangement products of different origins by reversed-phase partition chromatography. The separations were performed on 800 × 8 mm columns of hydrophobic Hyflo Super Cel with chloroform as the stationary solvent. Gradient elution was accomplished with a buffer solution containing 25% methanol, the pH-value of which was steadily increased. The optical density of the elute was measured continuously by a spectrophotometer connected to a recorder⁴.

When humulone was rearranged at 100°C in a number of buffer solutions of medium pH-value two principal components were always found, which were eluted at pH 5.8–6.0 (Fig. 1). Their ultraviolet absorption spectra were similar to that of the *isohumulones* of beer and to that of humulinic acid. It has been shown earlier⁴ that the chromatographic pattern of the bitter substances of beer was predominated by a five (or six) peaks appearing at pH 5.6–6.2. It seemed probable that the group consisted of six components, two from each of the three humulones.

These results have led us to assume that the two same principal compounds are formed from humulone in beer and in buffer solutions of medium pH-value. A detailed study of the humulone rearrangements in buffer solutions thus is to be desired.

An attempt was also made to prepare *isohumulone* by treating humulone with boiling alcoholic alkali³. However, a rather complex reaction mixture resulted, as was also found by Carson⁵ and by Howard⁶ (Fig. 2). Moreover, none of the main compounds could be identical with the *isohumulone* of beer, though they had resembling ultraviolet absorption curves, as they were eluted already at pH 4.5 and 4.7, respectively. Some minor components only appeared at pH ~ 6 where the *isohumulones* of beer are normally found. The last peak in the chromatogram was formed by unreacted humulone.

1. Rigby, F. L. and Bethune, J. L. *Am. Soc. Brewing Chemists, Proc.* **1952** 98.
2. Windisch, W., Kolbach, P. and Schleicher, R. *Wochschr. Brauerei* **44** (1927) 453, 473, 485, 497.
3. Verzele, M. and Govaert, F. *Intern. Congr. Fermentation Inds. Lectures and Communs. Ghent 1947*, p. 297.
4. Spetsig, L. O., Steninger, M. and Brohult, S. *European Brewery Conv. Proc. Congr. Copenhagen 1957*, p. 22.
5. Carsson, J. F. *J. Am. Chem. Soc.* **74** (1952) 4615.
6. Howard, G. A., Slater, C. A. and Tatchell, A. R. *J. Inst. Brewing* **63** (1957) 237.

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A Stirrer for Flasks Totally Enclosed

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In connection with some fractionation work¹ a stirrer for flasks totally enclosed has been constructed. The design is based on the principle that if one end of a rod, the middle of which is connected to a ball joint, is driven in a circle the other end will also describe a circle, whereas the middle remains fixed. The middle can of course be connected to a flexible membrane instead of a ball joint. In this way it is possible to get a perfect seal. The stirrer is shown in Fig. 1.

It is designed to be used in flasks with joints of Standard Taper 29. The stopper, made of teflon, has been machined so that

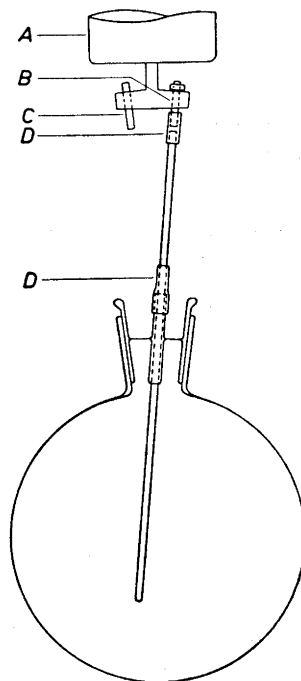


Fig. 1. Stirrer for flasks totally enclosed. A motor, B bearing eccentric to the motor axle, C counter weight, D rubber bushings.

we have a relatively thin-walled cylinder, closed in the center with a plate only 0.5 mm thick, through the middle of which runs a tube that fits tightly around the stirring rod. To obtain a better seal the teflon tube may be pressed against the rod with a thick rubber bushing and in this way we also avoid a slow rotation of the stirrer in the direction opposite to that of the motor. The connection of the motor to the rod, via a bearing eccentric to the motor axle, will be clear from the figure. A length of 30 cm for the rod with a maximum amplitude of 2 cm is adequate.

The simple shape of the rod has proved most satisfactory for fractionate work since very little precipitate becomes attached to the stirrer.

1. Öhrn, O. E. *Arkiv Kemi* **12** (1958) 397.

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