Table 1. Rate of Disappearance of Hydrogen Peroxide (Initial $1 \cdot 9 \times 10^{-3}$ M) from Aqueous Carbohydrate Systems at about 0°

Compound	D-Glucose	D-Glucose	D-Fructose	D-Fructose	D-Xylose	D-Xylose	D-Mannitol	Sucrose	Sucrose	1 : 3-Dihydroxy-propan-2-one
[Sugar] $\times 10^3$ M $-[H_2O_2]$ molecules ml.$^{-1}$ min$^{-1} \times 10^{-12}$	1·22	5·7	1·4	5·7	1·33	7·41	5·6	0·64	2·9	3·8
	1·6	2·5	6·5	7·2	5·7	7·9	4·8	2·7	3·9	4·1

a 256 h post-irradiation period[12]. Rate values quoted in Table 1 further support the previous interpretation[12] of the origin of post-irradiation effects in aqueous solution. Timberlake has also suggested sugar–peroxide interactions to account for the stabilization of ascorbic acid in model systems[13].

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[1] Fenton, H. J. H., and Jackson, H., *J. Chem. Soc.*, 1 (1899).
[2] Salley, D. S., *J. Phys. Chem.*, **38**, 466 (1934).
[3] Schonebaum, C. W., *Rec. trav. chim. Pays-bas*, **41**, 503 (1922).
[4] Löb, W., *Biochem. Z.*, **32**, 43 (1911).
[5] Cross, C. F., Bevan, E. J., and Smith, C., *J. Chem. Soc.*, 815 (1896).
[6] Craik, J., *J. Chem. Soc. Indust.*, **43**, 171 (1924).
[7] Payne, J. H., and Foster, L. M., *J. Amer. Chem. Soc.*, **67**, 1054 (1945).
[8] Souza, A. H. de, *Tribuna Farm.*, **23**, 1 (1955).
[9] Enklewitz, M., *J. Biol. Chem.*, **116**, 47 (1936).
[10] Euler, H. von, and Hasselquist, H., *Z. Naturforsch.*, **11b**, 176 (1956).
[11] Eisenberg, H., *Indust. Eng. Chem. (Anal. Ed.)*, **15**, 327 (1943).
[12] Phillips, G. O., *Advances in Carbohydrate Chemistry*, **16**, 54 (1961).
[13] Timberlake, C. F., *J. Sci. Food Agric.*, **11**, 267 (1960).

Odour of Optical Isomers

The odour differences of optical isomers have been reviewed by Naves[1]. To date, the most that has been observed is a slight difference in the strength or 'noto', and this has often disappeared when the substances were rigorously purified. More important, I know of no cases where one of the enantiomers is odorous and the other is not. These facts have a significance which has so far been overlooked.

It has been suggested by several authors[2–5] that the first stage in the process of smelling is the bringing together of the odour molecules and the olfactory organ in such a way that some metabolic, probably enzymatic, process is thereby retarded or accelerated.

The well-known stereospecificity of enzymes makes it difficult to believe that optical antipodes could so consistently have the same, or nearly the same, odour quality and intensity if their perception depended on any such enzymatic process. If odorous substances can over-ride the stereospecificity of the enzymes, they should be highly and non-specifically toxic—a property which perfumes in general simply do not have. By an extension of the same reasoning, it follows that the primary process of olfaction cannot be an enzymatically controlled transformation of the odorous molecule. It follows, therefore, that the initiation of an olfactory sensation must depend on a physical rather than a chemical interaction, and that enzymes can be involved only in the secondary process of restoring and reactivating the olfactory cells after the odorous molecules have done their work.

The point appears to be general enough to eliminate any 'chemical' or 'enzymatic' theories of olfactory stimulation.

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[1] Naves, Y.-R., in *Molecular Structure and Organoleptic Quality*, 38 (London: Soc. Chem. Indust., Mon. 1).
[2] Alexander, J., *Chem. and Eng. News*, **27**, 2227 (1949); *Proc. Sci. Sect., Toilet Goods Assoc.*, No. 16 (Dec., 1951).
[3] Kistiakowsky, G. B., *Science*, **112**, 154 (1950).
[4] Baradi, A. F., and Bourne, G. H., *Science*, **113**, 660 (1951).
[5] Thompson, H. W., in *Molecular Structure and Organoleptic Quality*, 113.

Preparative Scale Chromatography with Analytical Columns

Two major problems are encountered when using large samples in gas chromatographic separations. First, the charge has to be placed on the column in such a manner that serious band-broadening does not occur due to slow volatilization of the sample. Secondly, the column should be operated so that peak asymmetry, resulting from the non-linear nature of the adsorption isotherm at high levels of concentration, is eliminated or counteracted.

When the second effect was eliminated by suitable operating conditions, satisfactory chromatograms were obtained with heavy loads by placing the charge on the column and allowing a period of five minutes to elapse before the commencement of elution. This procedure is similar to that used by Daniel[1], who used the delayed elution technique to improve the performance of analytical columns. The second problem of counteracting or eliminating the peak asymmetry resulting from solute overload was less simple. In order to explain the method, it is necessary to describe briefly the thermal changes that occur in a column when a solute passes through it[2]. As a solute enters a theoretical plate the heat of solution is evolved and the temperature rises and reaches a maximum near the point of maximum solute concentration. As the solute is eluted from the plate the heat of solution is absorbed and cooling takes place. For charges of a few milligrams the temperature change can be as great as 5° C. This thermal effect will cause the higher concentrations in the peak, where the temperature is greatest, to move more rapidly through the column than the lower concentrations; this relative movement of the different concentrations in the peak results in an asymmetric elution curve opposite in form to that due to column overload. From the equation of the temperature curve of the theoretical plate during the passage of a solute through it[2], it was shown that the temperature increases proportionally with increasing flow rate, producing greater peak asymmetry at higher gas flows. The overloading effect on a column increases with the solubility of the solute in the liquid phase and thus with the retention time or partition coefficient of the substance chromatographed. By the selection of a suitable programme for increasing the flow rate as elution proceeds, the peak asymmetry caused by the two non-ideal effects, thermal changes and column overload, can be made to counteract one another to give a symmetrical peak. The increasing flow rate, however, will cause band-broadening as well as rendering the peak symmetrical. Some loss of resolution would therefore occur which would have to be counteracted by reducing the mean operating temperature and thus increasing the separation ratios.

The experimental work was carried out using the Pye panchromatograph fitted with a molecular entrainer which is, in effect, a splitting device, drawing a small fraction of the column eluate into a macro-argon detector. With this device the column can be flow-programmed without alteration in the base current from the detector. The column used was 5 ft. long, 4 mm in diameter, packed with 25 per cent squalane on 100–120 B.S. mesh 'Celite'. Charges of increasing size were chromatographed while varying the programme time and flow limits until a charge of 175 μl. was satisfactorily resolved. The results obtained are shown in Fig. 1. It is obvious from the chromatogram that very heavy charges can be placed on an analytical column in the manner described and useful separations