injector by which carrier gas enters the column as shown. The back end of the column is connected directly to the instrument's Swagelok fitting by a simple Kovar seal, as in Fig. 1.

The column in Fig. 1 includes the reservoir section because of the report by HUNTER AND WALDEN[1] that this improves the column efficiency and longevity. We confirmed the improved efficiency in the case of poly(diethylene glycol succinate) but there was no effect with Apiezon L. We found that improved separations were obtained with both of the above packings when 0.1 ml of hexamethyldisilazane was slowly injected into the injection zone while the column was maintained at 225°. The reagent, which apparently reacts with OH groups in the column[2], is eluted rather slowly and heating must be continued for several hours at elevated temperatures before samples can be injected.

Since making these columns, we have learned of another application of Kovar seals to glass column chromatography[3]. In this case the adaptation was intended to allow use of long biopsy needles. A basic difference in our applications is that COHEN AND BREWER threaded their Kovar tube so that a flat silicone septum could be attached by means of a retaining nut (like (E) in Fig. 2). Their inlet and outlet connections are of the ordinary type, still subject to temperature limitations.

This work was supported in part by the U. S. Public Health Service research grant NB3192 from the Institute of Neurological Diseases and Blindness.

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Received June 2nd, 1965

J. Chromatog., 20 (1965) 392–394

Gas chromatography of alkaloids with polar stationary liquids

II. The effect of polyvinylpyrrolidone treatment of the support

Coating of the solid support with polyvinylpyrrolidone (PVP) has been used to reduce adsorptive effects in gas chromatography of steroids with polar stationary liquids[1,2]. The PVP treatment has also been shown to produce a preferential affinity of the column for alcohols, and to increase its selectivity for closely related plant sterols. Since adsorption by the support material is a major problem in quantitative gas chromatography of many alkaloids, the present investigation was undertaken to study the effect of PVP treatment.

Experimental

The instrument and the procedure were the same as described previously[3]. Two columns were used, one packed with a dichlorodimethylsilane treated diatomaceous earth (Gas-Chrom Q, 100–120 mesh) coated with 1 % neopentyl glycol succinate (NGS) and the other packed with acid-washed Gas-Chrom P (80–100 mesh) which has been successively coated with 1 % PVP and 1 % NGS. Both columns were operated at 230° and optimum flow rates using helium as the carrier gas.

Results and discussion

Our work confirms earlier observations that PVP treatment of the solid support reduces tailing of the gas chromatographic peaks. More important, however, is the fact that PVP significantly alters the retention characteristics of the stationary liquid. This is apparent from Table I which gives the relative retention times of 22

TABLE I

RELATIVE RETENTION TIMES OF ALKALOIDS

Alkaloid	*Silanized support 1% NGS*	*1% PVP 1% NGS*
Atropine	0.26	0.31
Caffeine	0.15	0.15
Cinchonidine	1.65	2.56
Cinchonine	1.47	2.28
Cocaine	0.18	0.16
Codeine	0.49	0.56
Dihydrocodeinone	0.70	0.77
Heroin	1.12	1.13
Homatropine	0.17	0.18
Hydrastine	8.49	10.3
Laudanosine	1.00	1.00
Morphine	1.78	4.52
Narcotine	9.70	11.1
Neopine	0.53	0.59
Papaverine	3.58	4.27
Pilocarpine	0.66	0.80
Quinidine	3.40	5.21
Quinine	3.64	5.15
Reticuline	3.08	6.61
Scopolamine	0.63	0.86
Strychnine	7.62	8.90
Thebaine	0.83	1.00
Laudanosine time (min)	7.8	11.0

alkaloids on the two columns. Laudanosine is used as the standard because it is not appreciably affected by the PVP undercoating. Alcohols and phenols show the greatest change in retention times. Thus, dihydroxy alkaloids (morphine, reticuline) have their retention times more than doubled by the presence of PVP. It also appears that the aromatic character of the isoquinoline structure in papaverine causes it to be selectively retained by the PVP column, possibly due to a dipole–π bond type of interaction. A similar situation exists in the case of the cinchona alkaloids, in which

the increased retention is due to the combined effects of the secondary alcohol group, the vinyl side chain and the aromatic quinoline structure. Simple esters (cocaine, heroin) are not appreciably affected, whereas lactone alkaloids (narcotine, pilocarpine) exhibit an increase in the relative retention times on the PVP column. Although PVP does not by itself function as a satisfactory stationary liquid[1], it is apparent that the PVP treatment cannot be considered simply as an inactivation of the solid support, and it should, therefore, not be used indiscriminately. Fig. 1 illustrates the adverse effect of PVP treatment on the separation of a number of alkaloids from opium.

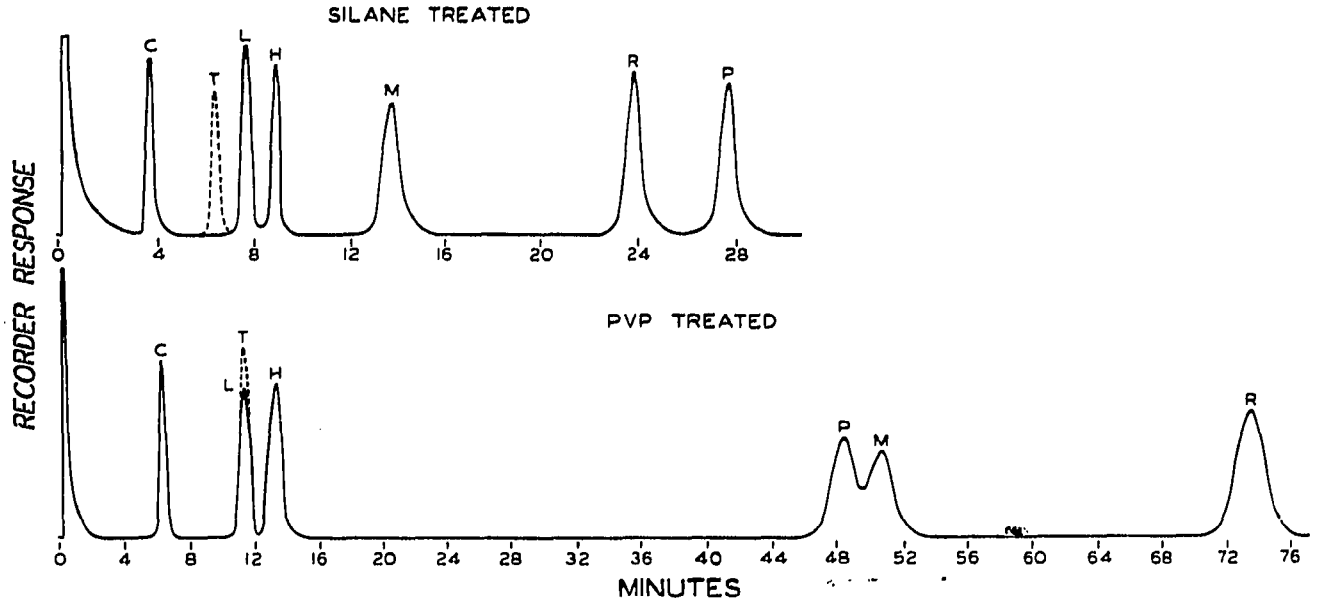

Fig. 1. Gas chromatography of opium alkaloids on silanized and PVP-treated solid supports with NGS as the stationary liquid. C = codeine; T = thebaine; L = laudanosine; H = heroin; M = morphine; R = reticuline; P = papaverine.

Acknowledgement

This work was supported by research grant MH03487 from the National Institutes of Health, U.S. Public Health Service, Bethesda, Maryland.

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Received April 26th, 1965