not be effected by galactose, a sugar known not to inhibit the concanavalin A-carbohydrate interaction.[9]

Electrophoretic analysis in free solution by the revolving tube method of Hjertén [15] revealed that the non-adsorbed Peak 1 contained essentially albumin and γ-globulin and only very small amounts of components of intermediate mobilities (Fig. 2a). The adsorbed material of Peak 2 contained α- and β-globulins together with prealbumin and some fast γ-globulin which according to the behaviour in the ultracentrifuge appears to be IgM (Fig. 2 b). A β-component ($S_{20}=4.4$), probably hemopexin, was found at the rear of Peak 1 which showed a higher carbohydrate content than the leading protein peak. No lipoproteins were found in Peaks 1 or 2.

Relative to protein, Peak 2 contained about 8 times as much carbohydrate as Peak 1. Apparently, concanavalin A-agarose acts as a group specific adsorbent for the serum components of high carbohydrate content. Concanavalin A-agarose and similar adsorbents might therefore be useful for the fractionation of serum proteins.

The fractionation can be improved in several ways. For example: (1) by using concentration gradients of a specific desorbent or even an unspecific desorbent such as hydrogen ions, (2) by the use of selective desorbents specific for different carbohydrate groups, and (3) by using in a sequence adsorbents prepared from different phytohemagglutinins having specific affinities for different carbohydrates.

Biospecific adsorption might thus be generally applicable in the chemistry of carbohydrates and glycoproteins.

After the preparation of this manuscript a paper has appeared [16] in which the synthesis of concanavalin A-agarose is described. The utility of the adsorbent for the fractionation of carbohydrate polymers and hog gastric blood group substance is also illustrated.

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Synthesis of 2,6-Dimethylphenylcarbamoylmethyl Carbamate and a *C*-Methyl Derivative

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Because of their potential pharmacological interest 2,6-dimethylphenylcarbamoylmethyl carbamate (1a) and α-(2,6-dimethylphenylcarbamoyl)ethyl carbamate (1b) have been prepared. The synthesis followed conventional routes. α-Chloro-2,6-dimethylacetanilide (2a) or the corresponding bromopropionanilide derivative (2b) were transformed into the α-hydroxy compounds (4a and b) *via* the acetates (3a and

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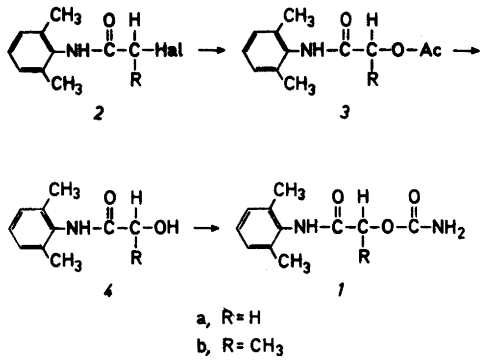

b). The carbamates (1a and b) were prepared from the hydroxy compounds by reaction with sodium cyanate and hydrogen chloride in ethyl acetate.

Experimental. Melting points are corrected. All substances gave IR-spectra consistent with the postulated structures.

α-Acetoxy-2,6-dimethylacetanilide (3a). A mixture of α-chloro-2,6-dimethylacetanilide [1] (100 g) and potassium acetate (200 g) in 1.5 M aqueous acetic acid (2 l) was refluxed for 5 h and kept overnight at 16°. The colourless crystals formed (62 g, m.p. 113.5–115.5) were collected. An analytical sample (m.p. 115.5–116°) was prepared by recrystallization from aqueous ethanol. (Found: C 65.3; H 6.81. $C_{12}H_{15}NO_3$ requires: C 65.1; H 6.83).

Concentration of the mother liquor to 800 ml yielded 4a (35 g, m.p. 91–92°).

α-Hydroxy-2,6-dimethylacetanilide (4a). Hydrolysis of 3a in a mixture of ethanol (1 part) and 0.6 M aqueous orthophosphoric acid (5 parts) provided, after working up, a 70 % yield of 4a, m.p. 91–92°. Recrystallization from aqueous ethanol did not raise the m.p. Löfgren and Widmark [2] report m.p. 90–91°.

A better yield of 4a (90 %) was obtained by controlled lithium aluminium hydride reduction of 3a, following the procedure given below for synthesis of 4b.

2,6-Dimethylphenylcarbamoylmethyl carbamate (1a). 4.3 M ethereal hydrogen chloride (12 ml) was added in four portions during 1.5 h to a stirred mixture of 4a (7.0 g) and sodium cyanate (3.8 g) in dry ethyl acetate (40 ml) at room temperature. Stirring was continued for 20 h. Salts were removed by filtration and washed with hot ethyl acetate. Ether (30 ml) was added to the combined filtrate and washings, which was then neutralized with gaseous ammonia. Norite (0.5 g) was added, the mixture refluxed for 3 min and filtered. Insoluble material was washed with hot ethyl acetate. The combined filtrate and washings were evaporated to dryness and the residue washed several times with warm ether. Pure 1a (4.3 g), m.p. 177–178° (decomp.), was obtained by recrystallization from ethyl acetate. (Found: C 59.6; H 6.21; N 12.4. $C_{11}H_{14}N_2O_3$ requires: C 59.5; H 6.35; N 12.6).

α-Acetoxy-2,6-dimethylpropionanilide (3b). A mixture of α-bromo-2,6-dimethylpropionanilide [1] (90 g), potassium acetate (69 g), and 1-propanol (270 ml) was stirred under reflux for 1.5 h and worked up to give 3b (52 g), m.p. 154–156°. Recrystallization from aqueous propanol raised the m.p. to 156–157°. (Found: C 66.6; H 7.03; N 5.98. $C_{13}H_{17}NO_3$ requires: C 66.4; H 7.28; N 5.95).

α-Hydroxy-2,6-dimethylpropionanilide (4b). A 0.1 M solution of lithium aluminium hydride in ether (350 ml) was added during 1 h to a stirred solution of 0.2 M 3b in ether-tetrahydrofuran (2:1, 213 ml) at room temperature and stirring continued for 3 h. The working up procedure yielded 4b (7.8 g), m.p. 139–141°. Recrystallization from aqueous ethanol raised the m.p. to 141–142°. Shapiro *et al.*[3] report m.p. 139–140°.

α-(2,6-Dimethylphenylcarbamoyl)ethyl carbamate (1b) was prepared in the same manner as 1a with the exception that the temperature was kept at 35° during the reaction and the mole relations of 4b, sodium cyanate, and hydrogen chloride used were 1:3:2.

The yield of 1b, m.p. 184–185° (decomp.) was 35 %. (Found: C 61.2; H 6.51; N 11.7. $C_{12}H_{16}N_2O_3$ requires: C 61.0; H 6.83; N 11.9).

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