The molecule may be considered as built of four main planar or approximately planar groups, *p*-methyl-thiophenyl, prolyl, peptide + pyrrolidine and carboxyl, all of which tend to lie at approximately right angles to one another. In the case of the prolyl ring it would appear that the carbon atom opposite the N–C_α bond does not show any tendency to occupy alternate sites as noted by Leung and Marsh in the analysis of leucylprolylglycine monohydrate.[12] Neither does it maintain the position observed in proline[10] or hydroxyproline,[11] *i.e.*, *trans* with respect to the carboxyl group. In this compound it appears to have swung to the same side as the peptide C=O, providing further evidence of the flexibility of the pyrrolidine ring system in the prolyl group.

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RECEIVED MAY 5, 1958

PHOTOSYNTHESIS OF GALACTOLIPIDS

Sir:

An appreciable portion of the products of brief photosynthesis in $C^{14}O_2$ is lipid in nature.[1] Chromatograms of these products exhibit several separable lipids[2] which had been assumed to be fatty acid-labeled phosphatides. However, we wish to report that the phosphatides constitute but a fraction of these labeled products. We have examined the lipids of *Chlorella* and find that the glycolipid concentration exceeds that of the phospholipids by a factor of four. These glycolipids include the β-D-galactosyl and the α-D-galactosyl-(1 → 6)-β-D-galactosyl monoglycerides which had been identified in wheat flour lipids by Carter, *et al.*,[3] and 3′-*O*-oleyl-glyceryl-1′β-D-galactopyranoside-6-sulfate.[4] Glycerolphosphatides[5] and lesser amounts of a galactotriosyl monoglyceride are observed.

Radiograms of deacylated[5,6] products of five minutes and of thirty seconds of photosynthesis in $C^{14}O_2$ by *Chlorella* revealed that the galactolipids are labeled very rapidly with C^{14}. In five minutes photosynthesis over half of the C^{14} in the lipids was found in the galactose moieties. These lipids had the following C^{14} distribution: fatty acids, 40%; galactosylglycerol, 39%; galactosylgalactosylglycerol, 10%; galactosyl-6-sulfate glycerol, 2%; diglycerophosphate, 3%; glycerol, 4%. The galactolipids were identified by examination of radiograms of the deacylated lipids and then acid hydrolysis of the uniformly-labeled galactosyl glycerols to yield simple ratios of C^{14} in galactose and glycerol. Glyceryl β-D-galactoside and its digalactose homolog cochromatographed precisely with authentic samples generously provided by Professor H. E. Carter. The glyceryl galactotrioside was found in a chromatographic position (R_f = 0.50 in phenol–water and R_f = 0.14 in butanol–propionic acid–water[2]) characteristic of a third member of the homologous series of galactosyl glycerides. Hydrolysis by thirty minutes in 3 *N* hydrochloric acid at 100° of the uniformly labeled unknown formed during eight days of photosynthesis gave galactose and glycerol in an activity ratio of 6.1 to 1, thus indicating that there are three galactose units bound to a monoglyceride in the original lipid.

The only precursor available in appreciable concentration in *Chlorella* for biosynthesis of these glycolipids is uridine diphosphate galactose.[7,8] Biosynthesis of galactosyl glycerides is probably analogous to that of the uridine diphosphate galactose-mediated saccharide syntheses.[9]

We are indebted to Mr. M. S. Brown for valuable assistance. This work was supported by the Atomic Energy Commission and the Pennsylvania Agricultural Experiment Station.

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(2) A. A. Benson, J. A. Bassham, M. Calvin, T. C. Goodale, V. A. Haas and W. Stepka, THIS JOURNAL, **72**, 1710 (1950).

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(6) R. M. C. Dawson, *Biochem. J.*, **59**, 5 (1955).

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(8) V. Ginsburg, P. K. Stumpf and W. Z. Hassid, *ibid.*, **223**, 977 (1956).

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RECEIVED JULY 24, 1958

STEREOCHEMISTRY OF DIELS-ALDER ADDUCTS. I. THE REARRANGEMENT OF 2-*exo*-BROMONORBORNANE-2-*endo*-CARBOXAMIDE

Sir:

A recent communication[1] describing the rearrangement of 2-*exo*-bromonorbornane-2-*endo*-carboxylic acid (I, R = OH) and its methyl ester (I, R = OCH_3) upon catalytic or chemical hydrogenolysis prompts us to report our observations upon the rearrangement of the corresponding carboxamide. 2 - *exo* - Bromonorbornane - 2 - *endo*-carboxamide (I, R = NH_2) does not rearrange upon hydrogenolysis and yields only norbornane-2-*endo*carboxamide (III, R = NH_2), identified by analysis, mixed melting point and comparison of the infrared spectrum with that of an authentic sample. When I (R = NH_2) was heated above its melting point, resolidification took place and a second melting point was observed. The isomeric bromocarboxamide (II, R = NH_2) obtained from the melt gave norbornane-1-carboxamide (IV, R = NH_2) upon hydrogenolysis. The rearrangement of I (R = NH_2) to II (R = NH_2) was also catalyzed by alcoholic alkali. On the basis of Wagner–Meerwein rearrangements undergone by 2,2- disubstituted bicyclo[2,2,1]heptane derivatives[2–4] we have tentatively designated the rearrangement product II (R = NH_2) as 2-*exo*-bromo-

(1) H. Kwart and G. Null, THIS JOURNAL, **80**, 248 (1958).

(2) W. P. Whelan, Jr., Dissertation, Columbia University, 1952.

(3) W. von E. Doering and E. F. Schoenewaldt, THIS JOURNAL, **73**, 2333 (1951).

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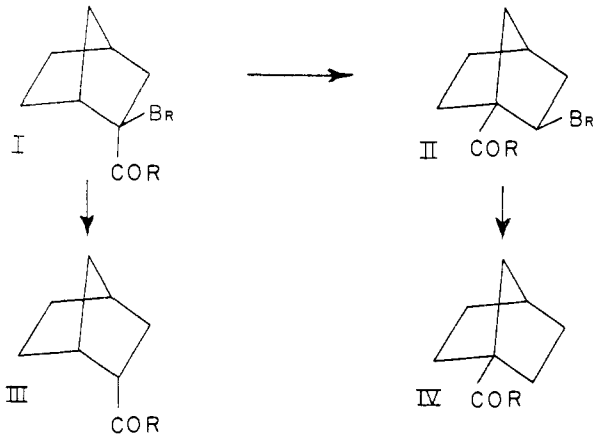
norbornane-1-carboxamide although the position and configuration of the bromine has not been proved.



2-*exo*-Bromonorbornane-2-*endo*-carbonyl chloride (I, R = Cl, b.p. 95–98° (7 mm.)) was prepared by brominating norbornane-2-*endo*-carbonyl chloride (III, R = Cl)[5] in boiling thionyl chloride. Treatment of the bromoacyl halide with anhydrous ammonia in cold ether gave 2-*exo*-bromonorbornane-2-*endo*-carboxamide (I, R = NH_2; m.p. 119.5–121° from toluene. Found: C, 44.34; H, 5.62; N, 6.26; Br, 36.30). Catalytic reduction with zinc and acetic acid[6] gave norbornane-2-*endo*-carboxamide (III, R = NH_2; m.p. 210–211°; reported[7] m.p. 205–206°).

When compound I (R = NH_2) was heated for three minutes at 150–160°, 76% of the isomeric carboxamide (II, R = NH_2; m.p. 173–174° from toluene. Found: C, 44.28, H, 5.62; N, 6.34; Br, 36.76) was obtained. Compound I (R = NH_2), in a solution of 2% potassium hydroxide in 95% methanol, was rearranged quantitatively to II (R = NH_2) in six hours at room temperature. The latter, upon catalytic hydrogenation (Pd-$CaCO_3$) or reduction with zinc and acetic acid,[6] gave norbornane-1-carboxamide (IV, R = NH_2; m.p. 234–236° from water), identified by mixed melting point and by comparison of the infrared spectrum with that of an authentic sample (m.p. 234–236°. Found: C, 68.75; H, 9.25; N, 9.92) prepared from norbornane-1-carboxylic acid (IV, R = OH).[2] Saponification of IV (R = NH_2), gave the free acid IV (R = OH; m.p. 111–112°; reported[2] m.p. 112–113°).

2-*exo*-Bromo-2-*endo*-carbomethoxynorbornane (I, R = OCH_3; b.p. 98–99° (5 mm.), $n^{24.5}D$ 1.5043. Found: C, 46.42; H, 5.36) was obtained from the acid chloride I (R = Cl) by treatment with methanol. Catalytic[8] or chemical[6] hydrogenolysis of this ester gave only 2-*endo*-carbomethoxynorbornane (III, R = OCH_3) which was identified by saponification to norbornane-2-*endo*carboxylic acid (III, R = OH; m.p. 65–66°, reported[5] m.p. 65–66°).

(5) K. Alder, G. Stein, M. Liebmann and E. Rolland, *Ann.*, **514**, 197 (1934).

(6) E. Ott and K. Krämer, *Ber.*, **68**, 1655 (1935).

(7) G. Komppa and S. Beckmann, *Ann. Acad. Sci. Fennicae*, **A39**, No. 7 (1934).

(8) L. F. Fieser and W. T. Huang, THIS JOURNAL, **75**, 4837 (1953).

Bromination[9] of III (R = OH), on the other hand, gave the rearranged bromoacid II (R = OH; m.p. 150–151° from toluene or heptane; (Found: C, 43.58; H, 5.31) which, upon treatment with diazomethane, gave the isomeric methyl ester II (R = OCH_3; b.p. 117–118° (5 mm.), $n^{24.5}D$ 1.5055. Found: C, 46.25; H, 5.72). Hydrogenolysis[7,8] of the latter and saponification of the resulting debrominated ester IV (R = OCH_3) gave IV (R = OH) as the sole product. The acid IV (R = OH) also was obtained by hydrogenolysis[8] of the bromoacid II (R = OH).

It therefore appears highly probable that the bromonorbornanecarboxylic acid and its methyl ester reported by Kwart and Null[1] were rearranged already prior to hydrogenolysis.

(9) Bromination was by the general method of C. S. Marvel in E. C. Horning, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955 p. 523.

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KANAMYCIN. V. THE STRUCTURE OF KANOSAMINE

Sir:

Kanosamine,[1] the remaining unknown moiety of kanamycin,[2] has been shown[3] to be a straight chain 3-amino-3-deoxyaldohexopyranose, which from deamination studies could be either 3-amino-3-deoxy-D-allose or 3-amino-3-deoxy-D-glucose. N-Acetylkanosamine was refluxed in methanolic hydrogen chloride, acetylated (NaOAc, Ac_2O), and recrystallized (ethanol) to give methyl kanosaminide tetraacetate[4], $[\alpha]D$ +105.5° (*c* 0.5, $CHCl_3$), m.p. 172.5–173°. *Anal.* Calcd for $C_{15}H_{23}NO_9$: C, 49.9; H, 6.42; N, 3.88. Found: C, 50.1; H, 6.61; N, 3.78. This product was identical by infrared spectrum and mixed melting point comparison with methyl 3-amino-3-deoxy-α-D-glucopyranoside tetraacetate prepared according to Peat and Wiggins,[5] proving that kanosamine is 3-amino-3-deoxy-D-glucose (3-D-glucosamine). Kanosamine pentaacetate[1] was identical in infrared spectrum and melting point behavior with 3-β-D-glucosamine pentaacetate prepared from the synthetic methyl glycoside tetraacetate by hydrolysis and reacetylation.

The infrared spectrum in KBr pellet of kanamycin base showed bands at 838 and 823 cm.$^{-1}$, with similar bands present at 841 and 821 cm.$^{-1}$ in the spectrum of the sulfate, indicative of two alpha-glycosidic linkages in the kanamycin molecule.[6]

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(2) T. Takeuchi, T. Hikiji, K. Nitta, S. Yamazuki, S. Abe, H. Takayama and H. Umezawa, *J. Antibiotics*, Ser. A, **10**, 107 (1957); M. J. Cron, D. L. Johnson, F. M. Palermiti, Y. Perron, H. D. Taylor, D. F. Whitehead and I. R. Hooper, THIS JOURNAL, **80**, 752 (1958).

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(4) K. Maeda, M. Murase, H. Mawatari and H. Umezawa, *J. Antibiotics*, **A11**, 73 (1958).

(5) S. Peat and L. F. Wiggins, *J. Chem. Soc.*, 1810 (**1938**).

(6) Barker, *et al.* [*J. Chem. Soc.*, 171 (1954); *Methods of Biochemical Analysis*, **3**, 213 (1956)] have considered the 844 ± 8 cm.$^{-1}$ region to be diagnostic of the α-glucopyranose structure. This region must be broadened as shown by the occurrence of bands at 827 cm.$^{-1}$ in melezitose and at 833 cm.$^{-1}$ in N-acetyl-3-α-D-glucosamine.