A solution of 10 g. of sodium in 200 ml. of *t*-amyl alcohol (prepared by 18 hr. refluxing) was mixed with 31 g. of 3,3-dimethyl-1,1-dichlorobutane, then refluxed for 8 hr. The material was washed with water, dried, and distilled, giving 27 g. of pot residue, after products boiling below 120° had been removed.

This residue was washed three times with 50 ml. of water, leaving 20 g. The material was refluxed with 50 ml. of 12 *N* hydrochloric acid, washed with water, dried, and distilled, giving 20 g. of *t*-amyl chloride, b.p. 86–89°, and 2 g. of *t*-butylacetaldehyde, b.p. 108–110°. The 3 g. of pot residue was acid to litmus and smelled like an organic acid.

2,3-Epoxyheptane. A mixture of 9.8 g. of 2-heptene and 325 ml. of ether containing 0.1 mole of perphthalic acid was left in a refrigerator for 5 days. The solution was decanted, washed with sodium bicarbonate solution, ferrous sulfate solution, then twice with water, dried over magnesium sulfate, and distilled, giving 4.0 g. of material, boiling range 125–130°, n^{20}_{D} 1.4080, and 3.0 g., b.p. 135° n^{20}_{D} 1.4119. The yield is 61%.

Anal. of high boiling fraction: Calcd. for $C_7H_{14}O$: C, 73.6; H, 12.3. Found: C, 73.8. H, 12.6.

2,3-Heptanediol. A mixture of 100 ml. of 88% formic acid and 30 ml. of 30% hydrogen peroxide was placed in a three neck flask fitted with a thermometer, a stirrer, and a dropping funnel. After the mixture had been warmed to 40°, 19.6 g. of 2-heptene was added dropwise over a 25-min. period, then the mixture was left overnight. Water and formic acid were removed by distillation at reduced pressure, then the residue was mixed with an ice-cold solution of 16 g. of sodium hydroxide in 30 ml. of water, warmed to room temperature, and left for 2 hr. The mixture was extracted with five 50-ml. portions of ethyl acetate, the extracts were dried over magnesium sulfate and distilled, giving 13 g., b.p. 81° at 3 mm., n^{20}_{D} 1.4420 and 6.5 g., boiling range 91–94° at 3 mm., n^{20}_{D} 1.4445.

Anal. Calcd. for $C_7H_{16}O$ (b.p. 81°): C, 63.6; H, 12.1. Found: C, 65.0; H, 11.7.

Anal. (b.p. 91–94°): Found: C, 63.7; H, 12.0.

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Isolation and Partial Characterization of a Glucoside from *Rivea corymbosa* (L.) Hallier Filius

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Received August 7, 1961

During an investigation of the seed of *R. corymbosa*,[2] in an attempt to isolate the physiologically active constituents, a new glucoside was isolated in 1956. Primary interest was in the alkaloidal constituents of the seed and study of the glucoside was delayed until 1958. The glucoside was isolated from the ethanolic extract of the defatted pulverized seed. The white, crystalline glucoside had a melting point of 241–241.6° and has been assigned the molecular formula of $C_{28}H_{46}O_{12}$.[3] The infrared spectrum of the glucoside indicated the presence of only hydroxyl and ether functional groups. The acetate of the glucoside was prepared and recrystallized to a constant melting point of 247–248°. A determination of the acetyl groups present in the glucoside acetate indicated the presence of seven hydroxyl groups. (The infrared spectrum of the acetate indicated complete acetylation.) The glucoside heptaacetate has been assigned molecular formula $C_{42}H_{60}O_{19}$.

The glucoside gave negative alkoxyl tests, indicating ethers of the cyclic or bridged type. It has been shown that the aglucone is sensitive to low *p*H (*i.e.* a carbonyl is generated as a result of acid hydrolysis of the glucoside). Therefore, it is possible that the aglucone may contain a hemiacetal functional group.

The glucoside was hydrolyzed by suspending it in methanol-water solution with emulsin. The sugar moiety was identified as glucose by paper chromatography and confirmed by the preparation of its phenylosazone and pentaacetate. The aglucone melts at 166–168° and has been assigned the formula $C_{22}H_{36}O_7$. It formed a tetraacetate melting at 206–208°. Analysis indicated the presence of a terminal methyl group.

The absence of unsaturation was confirmed by negative tests with bromine water, ozone,[4] and tetranitromethane.

Dehydrogenation of the glucoside, using 5% palladium on charcoal at 350°, resulted in the isolation and identification of the following compounds: (a) phenanthrene, (b) 2-methylnaphthalene, and (c) 10 methyl-2-ethylphenanthrene.

It is postulated that the carbon skeleton of the aglucone is a hydrogenated pyranonaphthalene which contains four hydroxyls and three bridged ether groups.

When administered to rabbits, the glucoside exhibited about five times the potency as a central nervous system stimulant as did the initial ethanolic extract of *R. corymbosa.* Doses above the level of 31.6 mg./kg. proved fatal to test animals in 5–10 min.

EXPERIMENTAL[5a,b]

Isolation of glucoside. The ethanol soluble extract of *R. corymbosa* was dissolved in warm, distilled water. Concentration of the solution precipitated the glycoside as a white

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(1) (a) Abstracted from the Ph.D. thesis of W. Eugene Keeland, Montana State College, 1960. (b) This research was supported by the Medical Research Foundation, Stanford University, Palo Alto, Calif. (c) Present address: Tift College, Forsyth, Georgia.

(2) The seeds were identified as the seed of *R. corymbosa* by Dr. R. E. Schultes of Harvard University, Cambridge, Mass.

(3) M. C. Perezamador and J. Herran, *Tetrahedron Letters*, No. 7, 30, 1960, reported a compound with similar melting point. The molecular formula, optical rotation, and acetyl analysis differ significantly from that reported here.

(4) Ozonolyses were run by Dr. John Belew, Baylor University, Waco, Tex.

(5) (a) Microanalyses were run by Berkeley Analytical Laboratory, University of California, Berkeley, Calif. (b) Optical rotations were run by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

powder. The crude glycoside was recrystallized from methanol-water to a constant melting point of 241–241.6°.

Anal. Calcd. for $C_{28}H_{46}O_{12}$. C, 58.52%; H, 8.07%. Found: C, 59.08%; H, 8.36%. $[\alpha]^{23}_{D}$ −49.8 ± 0.3 (c = 1.079 mg./ml. in pyridine, 2-dm. tube), negative alkoxyl.

Preparation of glucoside heptaacetate.[6] One gram of the glucoside was dissolved in 10 ml. of dry pyridine. To this solution was added 10 ml. of acetic anhydride. The solution was allowed to stand at room temperature for 24 hr., after which it was poured into 100 ml. of cold water. The product was recrystallized from hot absolute methanol, melting point 247–248°.

Anal. Calcd. for $C_{42}H_{60}C_{19}$: C, 58.05%; H, 6 96%; molecular weight 868.90; acetyl 35.82%. Found: C, 58.21%; H, 7.16%; molecular weight 840 (Rast); acetyl 36.38%.

Hydrolysis of the glucoside. One gram of the glucoside was suspended in 100 ml. of methanol and water (25%/75%). To this solution was added 50 mg. of emulsion. Because of the nonsolubility of the glucoside, this solution was allowed to stand with occasional agitation for one week, after which time the aglucone was recrystallized from methanol and water, melting point 166–168°.

Anal. Calcd. for $C_{22}H_{36}O_7$: C, 64.05%; H, 8.79%; one terminal methyl 3.63%. Found: C, 64.12%; H, 9.07%; terminal methyl, 4.30%; $[\alpha]^{23°}_{D}$ −40.8 ± 0.6° (c = 1.006 mg./ml. in methanol, 2-dm. tube).

Preparation of the aglucone tetraacetate.[6] A 200-mg. sample of the crystalline aglucone was dissolved in 10 ml. of dry pyridine. To this solution was added 5 ml. of acetic anhydride. After 24 hr. the solution was poured into 50 ml. of cold water. The aglucone acetate was recrystallized from methanol, melting point 206–208°.

Anal. Calcd. for $C_{30}H_{44}O_{11}$: C, 62.05%; H, 7.64%; molecular weight, 580.65; four acetyl, 29.65%. Found: C, 62.02%; H, 7.79%; molecular weight, 580 (Rast); acetyl, 28.90%; $[\alpha]^{23.5}_{D}$ −52.4 ± 0.5° (c = 1.132 mg./ml. in pyridine, 1-dm. tube).

Dehydrogenation of aglucone. The aglucone was heated for 6 hr., as an intimate mixture, with an excess of palladium on charcoal (5%) at 350°.[7] During the heating, a stream of dry nitrogen was used to sweep out the hydrogen which was formed. After cooling, the reaction mixture was extracted with cyclohexane followed by benzene. From the cyclohexane extract, there was isolated, by chromatographing on alumina, a white, crystalline product which was characterized as phenanthrene on the basis of its melting point, ultraviolet spectra,[8,9] and infrared spectra.[9] From the benzene fraction there was obtained, by chromatography on silica gel, two other materials. One of the materials was observed to have a tendency to form monoclinic crystals. The ultraviolet spectrum of this material shows a maximum at 225 mμ, which indicates that the dehydrogenation product is a naphthalene derivative.[8,9] The picrate of the naphthalene derivative was prepared and recrystallized to a constant melting point of 115–116°. This is the melting point which has been recorded for 2-methylnaphthalene. A mixed melting point, with the picrate of an authentic 2-methylnaphthalene, showed no depression (mixed melting point 115–115.5°). The second material, which exhibited fluorescence under ultraviolet irradiation, was found to have an ultraviolet spectrum similar to those reported for phenanthrene derivatives:[8,9,11] maxima 299 mμ, 288 mμ, and 277 mμ. The picrate of the phenanthrene derivative was prepared, and recrystallized to a constant melting point of 107–108°. The picrate was yellow and its melting point was that which has been reported for 10-methyl-2-ethylphenanthrene.[10] An authentic sample of 10-methyl-2-ethylphenanthrene was not available for comparison.

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[6] V. C. Mehlenbacher, Chapter 1, Vol. 1, *Organic Analysis* (editors J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskover, and A. Weissberger), Interscience, N. Y., 1953, p. 1.

[7] G. C. Harris and T. F. Sanderson, *J. Am. Chem. Soc.*, **70**, 3870 (1948).

[8] R. A. Friedel and Milton Orchim, *Ultraviolet Spectra of Aromatic Compounds*, J. Wiley and Sons, Inc., N. Y., 1961. Spectrum No. 341.

[9] DK-2 ultraviolet spectrophotometer and IR-4 infrared spectrophotometer were used.

(10) W. E. Bachmann, M. W. Chronyn, and W. S. Struve, *J. Org. Chem.*, **12**, 596 (1947).

(11) F. A. Askew, *J. Chem. Soc.*, 509 (1935).

Polymerization of *N*-Carboxy Anhydrides in Hydrogen Fluoride. Decarbonylation as a Side Reaction

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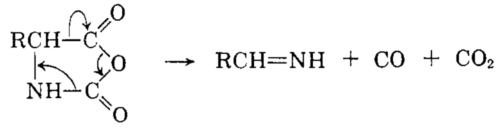
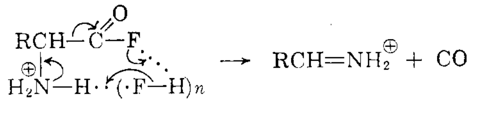
Received August 7, 1961

Solution of amino acid *N*-carboxy anhydrides (NCA) in anhydrous hydrogen fluoride results in the formation of poly-α-amino acids.[1] The path proposed for this reaction, solvolysis of the anhydride and polymerization of the resulting α-amino acyl fluoride, predicts products of high molecular weight. In fact, only relatively short chain lengths (n < 30) have been obtained, in spite of rigorous purification of solvent and starting anhydride to insure the absence of acylatable impurities. Recent investigation of the gaseous products of this reaction has revealed a side reaction which may result in low product molecular weight.

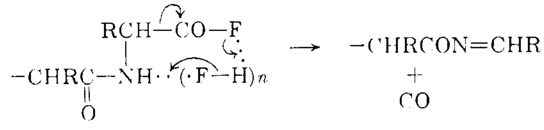
The action of anhydrous hydrogen fluoride on L-leucine NCA at room temperature produces, in addition to the expected carbon dioxide, a 5% yield of carbon monoxide. Treatment of the nonvolatile products of reaction with 2,4-dinitrophenylhydrazine reagent affords isovaleraldehyde dinitrophenylhydrazone. Thus at least one of reactions 1–3 is operative.



$$\mathrm{RCH{-}C(=O){-}O{-}C(=O){-}NH} \rightarrow \mathrm{RCH{=}NH + CO + CO_2} \quad (1)$$



$$\mathrm{RCH{-}C(=O){-}F},\ \mathrm{\overset{\oplus}{H_2N}{-}H\cdot(\cdot F{-}H)_n} \rightarrow \mathrm{RCH{=}\overset{\oplus}{NH_2} + CO} \quad (2)$$



$$\mathrm{RCH{-}CO{-}F},\ \mathrm{{-}CHRC(=O){-}NH\cdot(\cdot F{-}H)_n} \rightarrow \mathrm{{-}CHRCON{=}CHR + CO} \quad (3)$$

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[1] K. D. Kopple and J. J. Katz, *J. Am. Chem. Soc.*, **78**, 6199 (1956).