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ABSTRACTS *

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CONTENTS

1 —	SYN	NTHESIS	232
	1.0	Deuterium compounds	232
		1.0.1 General	232
		1.0.2 Aliphatic compounds	232
		1.0.3 Aromatic compounds	233
		1.0.4 Heterocyclic compounds	234
		1.0.5 Carbohydrates	234
		1.0.6 Peptides, Amino acids, Proteins	234
		1.0.7 Steroids	235
	1.1	Tritium compounds	235
		1.1.1 General	235
		1.1.2 Aliphatic compounds	236
		1.1.3 Aromatic compounds	236
		1.1.4 Heterocyclic compounds	237
		1.1.5 Carbohydrates	237
		1.1.6 Pentides, Amino acids, Proteins	237
		1.1.7 Steroids	238
	12	Carbon-14 compounds	120
	1.2	121 General	239
		122 Aliphatic compounds	239
		123 Aromatic compounds	239
		1.2.4 Heteropyclic compounds	240
		1.2.5 Carbohydrates	242
		1.2.5 Carbonyulates	243
		1.2.7 Staroids	244
			244
	1.3	Halogen labelled compounds	244
	1.4	Phosphorus-32 compounds	245
	1.5	Sulfur-35 compounds	245
	1.6	Oxygen labelled compounds	246
	1.7	Nitrogen-15 compounds	246
	1.8	Miscellaneous	246
	1.0	Carbon 13 compounds	240
	1.9		240

* The references given in this section cover articles drawn from 40 primary periodicals and also from N.S.A. and C.A.

A point is made of singling out information about synthetizing and related problems particularly where the main part of the abstracted article deals with applications.

Author and subject indexes will be published for each volume of this journal.

The results obtained from May 1964 until December 1964 have been published in Euratom reports EUR 2212 e and EUR 2212 e supplement.

2 —	RADIODECOMPOSITION, STABILITY,	STC)RA	GI	Ξ.			•	•		•		·	247
3 —	PURIFICATION, SEPARATION							•				•		247
4 —	ANALYSIS													248
	4.1 Determination of activity													248
	4.2 Apparatus													248
	4.3 Determination of radiochemical pattern					•		•	•	•				250
5 —	MISCELLANEOUS													250

1 - SYNTHESIS

1.0 — Deuterium compounds

1.0.1 - GENERAL

1.0.2 — ALIPHATIC COMPOUNDS

66-169

COPE A. C., KINNEL R. B.

Proximity effects. XLIV. Stereospecific synthesis and solvolysis of cis- and trans-5-phenylcyclooctyl and cis- and trans-5-phenyl-cyclooctyl-1,2,2,8,8-d₅ tosylates.

J. Am. Chem. Soc. 88, 752 (1966)

5-Phenylcyclooctanone (I) in MeOD/ K_2CO_3 , \rightarrow I-2,2,8,8-d₄, + LiAlD₄, + 3,5-dinitrobenzoic acid \rightarrow I-1,2,2,8,8-d₅ 3,5-dinitrobenzoate, hydrolysis, crystallisation \rightarrow cis-5-phenylcyclooctanol-1,2,2,8,8d₅ (II). II \rightarrow corresp. tosylate, boiling in tetraethylammonium acetate, cleavage with LiAlH₄ \rightarrow 21% trans-5-phenylcyclooctanol-1,2,2,8,8-d₅.

66-170

FRITZ H., BUDZIKIEWICZ H., DJERASSI C.

Einfluss behinderter Rotation sowie anderer energetischer Faktoren auf die McLafferty-Umlagerung von Ketonen.

Chem. Ber. 99, 35 (1966)

Addn. of 2-iodobutane-3,3-d₂ to the Mgsalt of N-cyclopentylidene cyclohexylamine \rightarrow 1-sec-butylcyclopentan-2-one-3', 3'-d₂. Yield: 10%.

66-171

GOLD V., KESSICK M.A.

Hydrogen isotope effects in olefin hydration. The relationship of isotope effects to the mechanism of proton transfer from the hydronium ion.

J. Chem. Soc. 1965, 6718 tert.-Butyl alcohol- α -d from isobutene + sulfuryl chloride/99.95% D₂O, 25°, 4 days. 66-172

HART H., COLLINS P. M., WARING A. J.

Preparation, chemistry, and photochemistry of hexaalkyl-2,4-cyclohexadienones.

J. Am. Chem. Soc. 88, 1005 (1966)

2,3,4,5,6,6-Hexamethyl-2,4-cyclohexadienone-3-(methyl-d₃) (I) by exchange in MeOD/ NaOD. I + K-t-butoxide/dimethyl sulfoxide-d₆ \rightarrow corresp. 3,5-dimethyl-d₆ labeled deriv. (II). II + MeOH/NaOH \rightarrow the 5methyl-d₃ labeled deriv.

66-173

JERKUNICA J. M., BORCIC S., SUNKO D. E.

Base catalyzed deuteration of norcamphor and dehydronorcamphor.

Tetrahedron Letters **1965**(49), 4465. CA **64**, 8241c (1966)

Norcamphor and soln. of D_2O , methan ol-d, and NaOMe, 12 hrs. at 100° in a sealed ampul $\rightarrow 50\%$ of 2 atoms D per mol, 65% after a second exchange. Dehydronorcamphor in a single D exchange $\rightarrow 95\%$ of 2 atoms D per mol.

66-174

KLOOSTERZIEL H., TER BORG A. P.

Kinetic protium-deuterium isotope effect in an intramolecular 1-5 shift of hydrogen.

Rec. Trav. Chim. 84, 1305 (1965) CA 64, 3300b (1966)

1,3,6-Cyclooctatriene-5,8-d₂ as follows: Zn and NaOD added over 28 hrs. to cyclooctatraene, CuSO₄, and EtOD, the mixt. dild. with H₂O, extd. with Et₂O, the ext. distd., and the fraction b_{60} 67-8° subjected to preparative GLC; yield 20%.

66-175

THOMAS A. F., WILLHALM B.

Mass spectra and organic analysis. Part VII. The mass spectra of the menthols, carvomenthols, their acetates and related alcohols.

J. Chem. Soc. (B) 1966, 219.

2,2,4-d₃-Menthyl acetate, pyrolysis at 400° \rightarrow 2,4-d₂-menth-2-ene (52%, isotopic purity 92%) and 2,2-d₂-menth-3-ene (47%, isotopic purity 90%).

1,3,3-d₃-Carvomenthyl acetate, treated as above \rightarrow 47% of 3,3-d₂-menth-1-ene (19.5 d₃, 71% d₂, 9.5% d₁) and 53% of 1,3-d₂-menth-2-ene (91% d₂)

66-176

WEBER H., SEIBL J., ARIGONI D.

Die absolute Konfiguration von $1-{}^{2}H_{1}-$ Äthanol.

Helv. Chim. Acta 49, 741 (1966)

(-)-(2R,3S)-3-d₁-2-Butanol by asym. hydroboration of cis-butene with optically active diisopinocampheyl borane.

 (\pm) -threo- and (\pm) -erythro-3-d₁-Butan-2ol by redn. of the corresp. cis- and transepoxybutane with LiAlD₄.

66-177

WEINBERG D. S., DJERASSI C.

Mass spectrometry in structural and stereochemical problems. LXXXVIII. Rearrangements of simple terpenes on electron impact.

J. Org. Chem. 31, 115 (1966)

4-Methyl cyclohexanone + triphenylisopropylphosphonium bromide (I) in dimethyl-d₆ sulfoxide $\rightarrow \Delta^{4(8)}$ -menthene-3,3,5, 5-d₄, containing 70% d₄, 20% d₃, 5% d₂, 3% d₁ and 2% d₀.

 $\Delta^{4(8)}$ -Menthene-9,9,9,10,10,10-d₆ from I-d₆, 88% d₆, 12% d₅.

Camphor-3,3-d₂ by exchange in trifluorodeuterioacetic acid/D₂O, 130°, 9 days; 95% d₂, 5% d₁.

See also : 66-263, Methylketene-d

1.0.3 — AROMATIC COMPOUNDS

66-178

BALIGA B. T., BOURNS A. N.

Kinetic hydrogen isotope effects in aromatic bromodeprotonation.

Can. J. Chem. 44, 379 (1966)

Direct exchange of protons for prepn. of sodium p-methoxybenzenesulfonate-0,0'-d₂ was unsuccessful. Alternative method: Anisole + CH₃COOD \rightarrow anisole-2,4,6-d₃, + chlorosulfonic acid.

66-179

CRAWFORD R. J., WOO Ch.

Ortho participation in the conversion of syn-benzaldoxime esters to nitriles.

Can. J. Chem. 43, 3178 (1965)

o-lodo-, o-chloro-, o-methoxybenzaldehyde-d and o-methylthiobenzaldehyde-d by redn. of the corresp. N-methyl benzanilides with LiAlD₄ by the method of Weygand *et al.*

66-180

DI MARI S. J., SUPPLE J. H., RAPOPORT H.

Mass spectra of naphthoquinones. Vitamin $K_1(20)$.

J. Am. Chem. Soc. 88, 1226 (1966)

2-Methyl-d₃-1,4-naphthoquinone, 2-methyl-d₃-3-phytyl-1,4-naphthoquinone, starting with naphthoic acid and redn. with LiAlD₄. 2-Methyl-3-phytyl-1,4-naphthoquinone-5,6, 7,8-d₄ from 2-methylnaphthalene by exchange of ring protons with D₃PO₄.BF₃. 2 - Methyl - 3 - phytyl - α - d₂ - 1,4- naphthoquinone.

66-181

ITO Sho, TSUNETSUGU J., KANNO T., SUGIYAMA H., TAKESHITA H.

Syntheses and reactions of deuterated troponoids.

Tetrahedron Letters **1965**(41), 3659 CA **64**, 3412f (1966)

Catalytic deuteration of 3,5,7-tribromotropolone over Pd-C with D in D₂O-dioxane in the presence of NEt₃ \rightarrow 10% tropolone-3,5,7-d₃. The corresp. OMe deriv. similarly in the presence of NaOAc instead of NEt₃, and methylation.

66-182

PRYOR W. A., HENDERSON R. W., PATSIGA R. A., CARROLL N.

Hydrogen secondary isotope effects on the radical polymerization of styrene.

J. Am. Chem. Soc. 88, 1199 (1966)

The following substituted styrenes were prepd.: α -d, β -d₂, ring-d₅, α -t, and trans- β -t.

See also: 66-199, Phenols, labeling by exchange in alkaline soln.

1.0.4 — HETEROCYCLIC COMPOUNDS

66-183

BAK G., CHRISTENSEN C. H., CHRISTENSEN D., HANSEN T. S. PEDERSEN E. J., NIELSEN J. T.

Preparation of 1,3,4-thiadiazole and its (2-D), $(2,5-D_2)$, $(2^{-13}C)$, and $(3^{-15}N)$ isotopic species.

Acta Chem. Scand. 19, 2434 (1965)

Title compds. were prepared in high purity and sufficient quantities.

66-184

KORYTNYK W., PAUL B.

Pyridoxine chemistry. IX.1. Selectively deuterated pyridoxols and some aspects of N. M. R. spectroscopy of vitamin B_6 compounds. 2.

J. Heterocyclic Chem. 2, 481 (1965) CA 64, 8130c (1966)

Pyridoxol- α^4 , α^4 -d₂. HCl in 48% yield by acylation of 4-pyridoxic acid lactone with Ac₂O and treatment of the 3-O-acetyl-4pyridoxic acid lactone with LiAlD₄. Pyridoxol- α^5 , α^5 -d₂ by redn. of Me α^4 .3-O-isopropylidene-5-pyridoxate with LiAlD₄, followed by cleavage of α^4 ,3-O-isopropylidenepyridoxol- α^5 , α^5 -d₂ with HCl.

1.0.5 - CARBOHYDRATES

66-185

LEMIEUX R. U., STEVENS J. D.

The proton magnetic resonance spectra and tautomeric equilibria of aldoses in deuterium oxide.

Can. J. Chem. 44, 249 (1966)

6.6'-Dideuterio-1,2:5,6-di-O-isopropylidene - α -D-glucofuranose (I) by redn. of 1,2-Oisopropylidene- α -D-glucofuranurono-6,3lactone with LiAlD₄; yield 41.4% based on LiAlD₄.

2-Deuterio- β -D-arabinose (II) from 2-Obenzyl-D-arabinose and D₂O/NaOD, 25°, 7 days and subsequent hydrogenolysis. 2,5,5'-Trideuterio- β -D-arabinose starting from I, then as described for II.

66-186

PERLIN A. S.

Hydroxyl proton magnetic resonance in relation to ring size, substituent groups, and mutarotation of carbohydrates.

Can. J. Chem. 44, 539 (1966)

1,2-O- Isopropylidene - β - D - arabinofuranose-5,5'-d₂(I) by redn. of the corresp. uronic acid methyl ester with B₂D₆. Hydrolysis of I \rightarrow D-arabinose-5,5'-d₂.

1.0.6 — PEPTIDES, AMINO ACIDS, PROTEINS

66-187

BLOMQUIST A. T., HISCOCK B. F., HARPP D. N.

Deuterated amino acids. I. The synthesis of glycine-d₅ and related derivatives.

J. Org. Chem. 31, 338 (1966)

Diethyl acetamidomalonate heating in DCl-D₂O (from thionyl chloride and D₂O) \rightarrow glycine-d₅ deuteriochloride in 97% yield; \rightarrow glycine-d₅ (I) (97.1% isotopic purity) by treatment with triethylamine. Recrystallization of I from water \rightarrow glycine-d₂ with >99% deuteration on the α -carbon atom.

66-188

CALF G. E., GARNETT J. L., HALPERN B. H., TURNBULL K. Stereospecific catalytic labeling of amino acids and mandelic acid with isotopic hydrogen.

Nature 209, 502 (1966)

L(+)-Alanine (I) L(-)-phenylalanine (II) and mandelic acid (III), exchange with D_2O in the presence of hydrogen prereduced Pt. Labeling of II at 30° with retention of configuration, mainly in the phenyl group, at 130° labeling with inversion, with I only labeling at 130° with inversion.

1.0.7 — STEROIDS

66-189

DJERASSI C., TÖKES L.

Mass spectrometry in structural and stereochemical problems. XCIII. Further observations on the importance of interatomic distance in the McLafferty rearrangement. Synthesis and fragmentation behavior of deuterium-labeled 12-keto steroids.

J. Am. Chem. Soc. 88, 536 (1966)

20,20-d₂-5 α -Pregnan-12-one by redn. of the 20-tosylhydrazone of the 12 β -aceto-20ketone with NaBD₄ and reoxidation of the 12-hydroxyl group. Monodeuteration at C-20 from : 5 α -pregnan-12,20-dione, ketalization at C-12, LiAlD₄ redn., -H₂O, hydrogenation \rightarrow 5 α -pregnan-12-one-20-d₁. 5 α -Pregnan-12-one, + SeO₂ $\rightarrow \Delta^{9(11)}$ -5 α pregnan-12-one, + SeO₂ $\rightarrow \Delta^{9(11)}$ -5 α pregnan-12-one (1), catal. deuteration and back exchange with OH⁻ \rightarrow 9 α -d₁-5 α pregnan-12-one; base catalyzed exchange of 1 in MeOD, catal. hydrogenation and back exchange with OH⁻ \rightarrow 8 β -d₁-5 α pregnan-12-one.

66-190

KARLINER J., BUDZIKIEWICZ H., DJERASSI C.

Mass spectrometry in structural and stereochemical problems. XCl. The electron impact induced elimination of water from 3-hydroxy steroids.

J. Org. Chem. 31, 710 (1966)

 5α -Cholestan- 3β -ol, labeled with D in positions :

3 α ; 2,2,4,4; 1 α ; 5 α ; 1,1. 5 α -Cholestan-3 α -ol-1 α -d₁;-5 α -d₁;-1,1,3 β -d₃. 5 α -Cholestan-2 β -ol-1,1,3,3-d₄; Δ^2 -5 α -cholestene-1,1,3-d₃.

1.1 — Tritium compounds

1.1.1 - GENERAL

66-191

AVDONINA E. N., BARANOVSKII I. B., WUNG Hao-ming, NESMEYANOV An. N.

Reactions of tritium recoil atoms and ¹⁴C with heterocyclic amines.

Radiokhimiya, 7, 220 (1965) N. S. A. 20, 1921 (1966)

Radiation stability and radiochemical yields of pyridine and picoline are increased with increase of the possibility of energy dispersion in the system. In the presence of nickel compounds the introduction of tritium into the organic molecule increases because of the abrupt intensification of the isotope exchange with HT under exposure conditions.

66-192

CRAWFORD B. R., GARNETT J. L.

Wilzbach tritiation studies. II. Stereospecificity in the tritiation of alcohols.

Aust. J. Chem. 18, 1951 (1965)

Phthalic acid oct-2-yl monoester, resolved in its (+)- and (-)-form were labeled with T by gas exposure predominantly under retention of configuration, whereas the free alcohol racemizes to the extend of 80%.

66-193

ODELL A. L., PACKER J. E., WHITE G. R.

Labeled products from the internal radiolysis

of liquid cyclohexane saturated with tritium gas.

Nature **209**, 72 (1966) CA **64**, 6441b (1966)

No compds. other than the parent cyclohexane were detected with a 90 Sr- β -ionization mass detector, but numerous labeled products were identified with the radiation detectors.

1.1.2 — ALIPHATIC COMPOUNDS

66-194

ARIGONI D., LYNEN F., RETEY J.

Stereochemie der enzymatischen Carboxylierung von (2R)-2-³H-Propionyl-Coenzym A.

Helv. Chim. Acta **49**, 311 (1966) Diacetyl + LiAl³H₄, periodate cleavage \rightarrow acetaldehyde-1-³H, + germ-ADH + NADH, + tosyl chloride \rightarrow ethyl tosylate (6.6 × 10⁶ ipm/mmole), + KCN, sapon. \rightarrow (R)-2-³H-propionic acid (6.24 × 10⁶ ipm/mmole), transformation to the title compd.

66-195

KOEBRICH G., FROEHLICH H.

Zum Chemismus der Thermolyse von Salzen der α-Chlor-zimtsäure.

Ann. Chemie 691, 68 (1966)

PhLi + ¹⁴CH₂O \rightarrow benzylalcohol (I) \rightarrow benzaldehyde, + ethoxy-carbonyl-chloromethylene-triphenylphosphorane \rightarrow trans-2-chloro-3-phenyl-acrylic acid-3-¹⁴C, yield 23% from I, sp. act. 117 μ Ci/mole.

66-196

NISHIZAWA Y., CASIDA J. E.

Synthesis of d-trans-chrysanthemumic acid- 1^{-14} C and its antipode on a semimicro scale.

J. Agr. Food Chem. 13, 525 (1965) CA 64, 3608d (1966)

dl-trans-Chrysanthemumic acid-1-14C in

45% yield from 4 mmoles of ethyl glycinate-1-¹⁴C (I). Geometrical isomers were sepd. by column chrom, and optical isomers of the trans-acid were resolved as an 1- α methylbenzylamine salt for the d-isomer. Overall yield based on I (2.7 mCi/mmole), 7.0% pure d-isomer (sp. act. 1.3 to 2.7 mCi/mmole).

66-197

THOMAS R. C., IKEDA G. J.

Preparation of tritium-labeled compounds. I. Series of sulfonylurea hypoglycemic agents by exchange with tritium gas.

J. Pharm. Sci. 55, 112 (1966) CA 64, 6490e (1966)

Sodium salts of the sulfonylureas were found to incorporate stably bound tritium more effectively than did the corresponding free compds. Exposure to tritium gas in the presence of an electrical discharge was also found to be an effective method for prepg. tritium-labeled sulfonylureas.

1.1.3 — AROMATIC COMPOUNDS

66-198

BOHLMANN F., von KAP-HERR W.

Polyacetylenverbindungen, XCII. Zur Biogenese des Carlinaoxyds.

Chem. Ber. 99, 148 (1966).

Benzoic acid-³H \rightarrow phenylacetylene (2.6 \times 10⁸ ipm/mmole) + tetrahydropyranyl ether of cis-bromopentenynol, subsequent hydrolysis \rightarrow 60% cis-1-(phenyl-³H)-hepta-5-en-1,3-diyn-7-ol (2.6 \times 10⁸ ipm/mmole).

66-199

KIRBY G. W., OGUNKOYA L.

Deuterium and tritium exchange reactions of phenols and the synthesis of labeled 3,4dihydroxyphenylalanines.

J. Chem. Soc. 1965, 6914

Preparative procedures are outlined for the labeling of phenols with deuterium and tritium by exchange in alkaline solution.

Illustration by the synthesis of (\pm) -3,4-dihydroxyphenylalanine labeled spec. at each of the nuclear and side-chain positions.

1.1.4 — HETEROCYCLIC COMPOUNDS

66-200

ARGOUDELIS C. J., KUMMEROW F. A.

Synthesis of pyridoxine labeled with tritium at specific positions.

Biochemistry 5, 1 (1966)

Pyridoxine labeled with T at the 4- or 5-hydroxymethyl group by reducing the corresp. 4- or 5-pyridoxic acid lactone with tritiated LiAlH₄, yield 70-74% based on the lactones and 20-21% based on the radio-activity. Degradn. on the former showed that more than 96% of the radioactivity was at the 4-hydroxymethyl group.

66-201

BARZ W., GRISEBACH H.

Über die Bedeutung von 3,5,7,4'-Tetrahydroxyflavanon (Dihydrokaempferol) für die Biosynthese von Isoflavonen.

Z. Naturforschg. 21b, 47 (1966)

T-labeling of dihydrokaempferol (I) by a modified Wilzbach method on quartz powder, sp. act. 11.7 mCi/mmole. Dehydrogenation of labeled I with sodium bisulfite to Kaempferol, sp. act. 6.84 mCi/mmole.

66-202

SCHNEIDER W. C., FISCUS W. G., LAWLER Jo Ann B.

Enzymic preparation of labeled phosphoryl choline, phosphoryl ethanolamine, cytidine diphosphate choline, deoxycytidine diphosphate choline, cytidine diphosphate ethanolamine, and deoxycytidine diphosphate ethanolamine.

Anal. Biochem. 14, 121 (1966)

Title compds. labeled with either ^{14}C (in the aliph. moiety) or ^{3}H (in the hetero-

cyclic moiety), in yields ranging from 50 to 97%, by incubating CTP or dCTP with P-choline or P-ethanolamine with crude preparations obtained from rat liver, or by incubating choline or ethanolamine with ATP and similar rat liver preparations.

See also: 66-205, Actinomycins-³H of high sp. act.

1.1.5 — CARBOHYDRATES

66-203

BICHUL T. V., POCHIKOVSKAYA V. M., SAPOZHNIKOYA E. P., KOLOSOV M. A., KOZLOVA L. P.

D-Ribose.

U.S.S.R. 172. 741. July 7, 1965, Appl. March 31, 1964.

CA 64, 2152h (1966)

Redn. of D-ribono-1,4-lactone with NaBH₄- 3 H, isolation as the complex of N-phenyl- α -D-ribopyranosylamine-1- 3 H.

66-204

WARTBURG A. v., KALBERER F., RUTSCHMANN J.

Tritium-labeled cardiac glycosides. Digoxin- $(12\alpha$ -t).

Biochem. Pharmacol. 14, 1883 (1965) CA 64, 6739a (1966)

The partial synthesis of digoxin- $(12\alpha - t)$ with a sp. act. 50 mCi/mmole is described.

1.1.6 — PEPTIDES, AMINO ACIDS, PROTEINS

66-205

KATZ E., MAUGFR A. B., WEISSBACH H.

Biosynthesis of highly labeled actinomycins. Mol. Pharmacol. 1 107 (1965)

CA 64, 5707e (1966)

Actinomycins (80,000 cpm/ γ) by Streptomyces antibioticus during growth with L-methionine-(methyl-³H).

66-206

SIMONOV E. F., NESMEYANOV An. N.

Radiation protection of amino acids during a reaction with tritium recoil products.

Vestn. Mosk. Univ. Ser. II, Khim. 20 (5), 28 (1965)

CA 64, 5410a (1966)

The chem. transformations of L-glutamic acid (I), DL-methionine, and L-cysteine in the presence of Li_2CO_3 under the action of slow neutrons were studied.

The main decompn. products of I were glutaric, α - and γ -aminobutyric, and pyrrolidinonecarboxylic acids, and serine. When the system contained 35% Li₂CO₃, the max. amt. of I remained chem. unchanged.

See also: 66-264, Amino acids-³H

1.1.7 - STEROIDS

66-207

BJOERKHEM I., DANIELSSON H., ISSIDORIDES C., KALLNER A.

On the synthesis and metabolism of cholest-4-en- 7α -ol-3-one. Bile acids and steroids 156.

Acta Chem. Scand. 19, 2151 (1965)

Electrolytic coupling of chenodeoxycholic acid, labeled by exposure for 4 weeks to 2 Ci of T gas, with isovaleric acid \rightarrow 5 β cholestane-3 α ,7 α -diol (sp. act. 30 μ Ci/mg), oxidn. with Al-tert-butoxide \rightarrow 5 β -cholestan-7 α -ol-3-one (sp. act. 23 μ Ci/mg), + SeO₂ \rightarrow title compd. (sp. act. 11 μ Ci/mg).

66-208

BRODIE H. J., BABA S., GUT M., HAYANO M.

The catalytic reduction of 3β -hydroxyandrost-5-en-17-one with tritium. The distribution and orientation of label in the product. Steroids 6, 659 (1965) CA 64, 5161f (1966)

Redn. with carrier-free tritium \rightarrow mainly 3 β -hydroxy-5 α -androstan-17-one (I) \rightarrow androst-4-one-3,17-dione (II) with a loss of 43% of the label. 6 β -Bromination and 6 β -methoxylation on II with little loss of label, indicating the tritium at C-6 to be α -orientated. The distribution of tritium in I was 43% 5 α , 35% 6 α and 22% 7 α .

66-209

EDWARDS B. E., RAO P. N.

Synthesis of $(1\beta^{-3}H)$ testosterone.

Biochim. Biophys. Acta 115, 518 (1966)

Catal. redn. of 17 β -hydroxyandrost-1,4dien-3-one with ${}^{3}H_{2} \rightarrow$ testosterone-1,2- ${}^{3}H$, \rightarrow stereosp. redn. with Li/THF-NH₃, equilibration in methanolic KOH (labile T at C-2) and oxidn. with chromic acid \rightarrow 5 α -androstane-3,17-dione-1 β - ${}^{3}H$, incubn. with enzym extract from B. sphaericus ($\Delta^{1,2}$) redn. with LiAIH₄, oxidn. with DDO, + (Ac)₂O \rightarrow 17 β -acetoxy-5 α -androst-1-en-3-one-1- ${}^{3}H$, hydrogenation, and transformation to the title compd.by known methods (sp. act. 30 μ Ci/mg). Proof of the site of the label.

66-210

FISHMAN J.

Stereochemistry of enolization of 17-keto steroids.

J. Org. Chem. 31, 520 (1966)

 16β -³H-17 α -Estradiol benzoate (3.10 × 10^{6} cpm/mg), 16β -³H-estrone benzoate, 16α -³H-17 β -estradiol 3-benzoate (5.42 × 10^{6} cpm/mg), and 16α -³H-estrone benzoate were prepd. by the reaction sequence described in J. A. C. S. 87, 3455 (see abstr. 65-429).

66-211

KLEIN P. D., ERENRICH E. H.

Tritiated alumina as a reagent for selflabeling chromatographic analyses.

Anal. Chem. 38, 480 (1966)

Tritiated alumina by exchange of the surface hydroxyl groups with tritiated water,

excellent reproducibility and stoichiometry. Model compounds show incorporation of activity proportionate to sample size over a range from 3 μ g. to 10 mg.; tritium incor, bration also shows a good correlation with the structural features and the number of enolic hydrogens. Radiochemical visualization and separation of a mixture of three ketosteroids by a chromatographic column of tritiated alumina is presented as an illustration.

66-212

OKUDA K., DANIELSSON H.

Synthesis and metabolism of 5β -cholestane- 3α , 7α , 12α -TRIOL-26-al. Bile acids and steroids 161.

Acta Chem. Scand. 19, 2160 (1965)

Cholic acid of a sp. act. of 20 μ Ci lab. with T gas, 2 Ci, by exposure for 4 weeks, \rightarrow corresp. aldehyde, + (α -carbethoxy-ethylidene)-triphenyl-phosphorane $\rightarrow 3\alpha,7\alpha$, 12 α -trihydroxy-5 β -cholest-24-en-26-oic acid, Grundmann synthesis (28-homo-5 β cholestane-3 α , 7 α , 12 α , 27, 28-pentol) \rightarrow 5 β -cholestane-3 α , 7 α , 12 α -triol-26-al (sp. act. 15 μ Ci/mg over-all yield 5%).

See also: **66-204**, Digoxin-³H **66-247**, 3α- and 3β-³H-4-¹⁴C-Cholest-4-ene-3α, 7α, 12α-triol

1.2 — Carbon-14 compounds

1.2.1 - GENERAL

66-213

BARAKAT M. F., FIRSOVA L. P., NESMEYANOV An. N.

Reaction of ${}^{14}C$ recoil atoms in mixtures containing α -picoline.

Radiokhimiya, 7, 361 (1965) N. S. A. 20, 7167 (1966)

66-214

CACACE F., WOLF A. P.

Reactions of energetic carbon atoms with ammonia. II.

J. Am. Chem. Soc., 87, 5301 (1965)

Carbon atoms react with gaseous ammonia to give methane, methylamine, and methylenimine.

66-215

DZANTIEV B. G., Shevchenko A. P.

Formation of polymers labeled with ¹⁴C during ethylene-ammonia irradiated in nuclear reactor.

Radiokhimiya, 7, 368 (1965) N. S. A. 20, 1922 (1966)

Small additions (2 to 5%) of ethylene and ammonia lead to an abrupt increase of the fraction of recoil ¹⁴C held in the form of labeled polymers.

See also: 66-191, Recoil reaction of pyridine and picoline with C-14.

1.2.2 — ALIPATHIC COMPOUNDS

66-216

BOUTHILLIER L. P., PUSHPATHADAM J. J., BINETTE Y.

Study of the metabolism of 2-hydroxy-4aminobutyric acid, a product of γ -hydroxyglutamic acid decarboxylation.

Can. J. Biochem. 44, 171 (1966)

DL-2-Hydroxy-4-aminobutyric-4-¹⁴C acid (I) from K¹⁴CN (1 mCi) + ethyl 3-bromopropionate, hydrogenation in (Ac)₂O and subseqn. hydrolysis \rightarrow 4-aminobutyric acid, + N-carbethoxy phthalimide, bromination in 2-pos., hydrolysis first with CaCO₃ and then with HCl \rightarrow I, over-all yield of 23%, sp. act. 1.9 \times 10⁵ cpm/mg.

66-217

DOBBS H. E.

The preparation of carbon-14 labeled chloroform and methylene chloride.

Atompraxis 12, 83 (1966)

Chloroform-¹⁴C (sp. act. 2.3 mCi/mole) from acetone-1,3-¹⁴C and calcium hypochlorite. A refluxing solution of chloroform in dioxan is reduced to methylene chloride by addition of LiAlH₄ in dioxan. The active methylene chloride is removed from the system by distillation, yield 70%.

66-218

EL-MERZABANI M.M.

Synthesis of 3,3'-bis(mesyloxy)-N-methyl-¹⁴C-dipropylamine hydrochloride.

Chem. Pharm. Bull. (Tokyo) 13, 1362 (1965)

CA 64, 4926e (1966)

Addn. of ¹⁴CH₃-NH₂. HCl to Et-acrylate, redn. with LiAlH₄, + (MeSO₂)₂O \rightarrow title compd., sp. act. 1.8 × 10⁴ cpm/mg.

66-219

LEE C. C., FORMAN A. G.

Rearrangement studies with ${}^{14}C$. XXIV. Solvolyses of 2-(α -naphthyl)-1- ${}^{14}C$ -ethyl p-toluenesulfonate.

Can. J. Chem. 43, 3387 (1965)

Carbonation of the Grignard reagent with ¹⁴C-carbon dioxide $\rightarrow \alpha$ -naphthyl-1-¹⁴C-acetic acid, + LiAlH₄, $\rightarrow 2$ -(α -naphthyl)-1-¹⁴C-ethanol, \rightarrow title compd.

66-220

MERRILL E. J.

Solubility of pentaerythritol-1,2-¹⁴C tetranitrate in water and saline.

J. Pharm. Sci. 54, 1670 (1965) CA 64, 1901g (1966)

Acetaldehyde-1,2-¹⁴C, \rightarrow tetraacetate by Wiersma's method (W., et al., CA 58, 6169 d), --> tetranitrate by Berlow's method (B., et al., The Pentaerythritols, New York : Reinhold Pub. Corp., 1958, 317 pp.).

66-221

SCHUCHING S. L. von, FRYE G. H.

A new derivative of vitamin C and its application to the synthesis of labeled ascorbic acid.

Biochem. J. 98, 652 (1966)

Preparation of a mono-O-cyclohexylidene derivative of L-ascorbic acid shielding C-5 and C-6 of the ascorbic acid molecule. The double bond of the new derivative is more resistant to oxidation than its parent compound. Ascorbic acid is easily regenerated by mild acid hydrolysis. The new derivative facilitates the synthesis of ¹⁴C-labeled vitamin C.

66-222

WARD P. F. V., HUSKISSON N. S.

Small scale preparation of (1-¹⁴C)fluoroacetic acid.

Biochim. Biophys. Acta 115, 515 (1966)

(1-14C)Chloroacetic acid (6.9 mg; 0.5 mCi) + diazomethane, addn. to KF in molten acetamide.

Final purifn. by GLC. Yield : 60%, sp. act. 0.42 mCi/mmole. Description of the app.

1.2.3 — AROMATIC COMPOUNDS

66-223

BADGER G. M., JOLAD S. D., SPOTSWOOD T. M.

The formation of aromatic hydrocarbons at high temperatures. XXV. The pyrolysis of (3-14C) indene.

Aust. J. Chem. 19, 85 (1966)

Grignard reagent of β -phenylethylbromide + ¹⁴CO₂, Friedel-Crafts reaction, redn. to the carbinol, -H₂O \rightarrow title compd.

66-224

BADGER G. M., JOLAD S. D., SPOTSWOOD T. M.

The formation of aromatic hydrocarbons at high temperatures. XXVI. Pyrolysis of $(1-^{14}C)$ styrene.

Aust. J. Chem, 19, 95 (1966)

Friedel-Crafts reaction between benzene and $(1^{-14}C)$ -sodium acetate, redn. to 1-phenyl-ethanol-1-¹⁴C, + HCl concd. \rightarrow

1-chloro-1-phenylethane, $-HCl \rightarrow title compd.$

66-225

BUTOMO S. V., REIKHSFEL'D V. O., MAKOVETSKII K. L.

Synthesis of trimethylbenzenes for measuring natural radiocarbon by means of scintillation method.

Radiokhimiya, 7, 364 (1965). N. S. A. 20, 2062 (1966)

Mesitylene and pseudocumene by the scheme $C \rightarrow CaC_2 \rightarrow Mg_2C_3 \rightarrow CH_3-C \cong CH \rightarrow C_6H_3(CH_3)_3$ with a total carbon yield of 50%.

66-226

FISCHER E., HAFFERL W., SCHMIDL M.

Synthesis of ¹⁴C-labeled terphenyls.

EUR 2527.d (1965)

o-Terphenyl, and p-terphenyl either $U^{-14}C$ or $1^{-14}C$ labeled by reaction of aryl lithium compounds with cyclic ketons, yield (on the 10 to 25 mmole scale) between 40 and 60%, referred to radioactive starting material, sp. act. up to 0.25 mCi/mmole.

66-227

GRIFFITHS M. H., MOSS J. A., ROSE J. A., HATHWAY D. E.

The comparative metabolism of 2,6-dichlorothiobenzamide (Prefix) and 2,6-dichlorobenzonitrile in the dog and rat.

Biochem. J. 98, 770 (1966)

2,6-Dichlorobenzo(¹⁴C)nitrile (I) from 2,6dichloroiodobenzene + Cu¹⁴CN; sp. act. 9.1 μ Ci/mg. I + H₂S \rightarrow 2,6-dichlorothiobenz(¹⁴C)amide; sp. act. : 3.2 μ Ci/mg.

66-228

HAGOPIAN M.

Synthesis and metabolism of dopamine-¹⁴C.

Thesis (Clark Univ., Worcester, Mass.) Order No. 65-10,401; Dissertation Abstr. 26(4), 1894 (1965)

3,4-Dimethoxybenzaldehyde, catal. hydrogenation \rightarrow corresp. alcohol, + SOCl₂ \rightarrow corresp. chloride, $+ K^{14}CN + LiAlH_4/AlCl_3 \rightarrow 3,4$ -dimethoxyphenethylamine-¹⁴C, demethylation (HI), purifn. as its O,O,N-triacetyl deriv. hydrolysis \rightarrow dop amine¹⁴C,

66-229

KUWATSUKA Sh., CASIDA J. E.

Synthesis of methylene-¹⁴C-dioxyphenyl compounds. Radioactive safrole, dihydrosafrole, myristicin, piperonyl butoxide and diastereoisomers of sulfoxide.

J. Agr. Food Chem. 13, 528 (1965) CA 64, 3391g (1966)

Methylene-¹⁴C iodide, prepd. by redn. of iodoform-¹⁴C + appropriate catechol \rightarrow following methylene-¹⁴C-dioxyphenyl compounds with a sp. act. of 1.0 mCi/mmole : safrole, dihydrosafrole, myristicin, sulfoxide synergist (1,2-methylenedioxy-4-(2-(octylsulfinyl)propyl)benzene, and piperonyl butoxide(α -(2-(2-butoxyethoxy)ethoxy)-4,5-methylenedioxy-2-propyltoluene).

Yields from iodoform-¹⁴C were 31 to 55% on a 0.5-0.8-mmole scale.

66-230

McDOWELL L. L., RYAN M. E.

Laboratory production of diborane and activation of silica-alumina catalyst for conversion of ${}^{14}C_2H_2$ to ${}^{14}C_6H_6$: radiocarbon dating by liquid scintillation spectrometry.

Intern. J. Appl. Radiation Isotopes 17, 175 (1966)

Diborane from NaBH₄-boron trifluoride etherate to column containing about 300 g of silica-alumina. Each column will yield about 5 g of ${}^{14}C_6H_6$.

66-231

PACKTER N. M.

Studies on the biosynthesis of phenols in fungi.

Conversion of $({}^{14}C)$ orsellinic acid and $({}^{14}C)$ orcinol into fumigatol by Aspergillus fumigatus I.M.I. 89353.

Biochem. J. 98, 353 (1966)

(14C)Orsellinic acid was prepared biosyn-

thetically from Na(1-¹⁴C)acetate in a culture medium of P. barnense. Isolation after 7 days. Sp. act. 4030 cpm/ μ mole.

66-232

SCHWEER K.-H.

Die Synthese von 1-(p-Hydroxy-phenyl)-2-amino-äthanol-1-(1-14C)-hydrochlorid.

Atompraxis 12, 85 (1966)

p-Bromophenyl benzylether \rightarrow p-benzyloxybenzoic acid-(carbonyl-¹⁴C), + SOCl₂, + Cd(CH₃)₂ \rightarrow p-benzyloxy-acetophenone- α -¹⁴C (I), bromination, aminolysis with phthalimide-K, hydrolysis (II) and hydrogenation \rightarrow title compd., sp. act. 166 μ Ci/ mmole. Yield from I to II, 31%, and in the last step 73%.

66-233

SHAFER J., BARONOWSKY P., LAURSEN R., FINN F., WESTHEIMER F. H.

Products from the photolysis of diazoacetyl chymotrypsin.

J. Biol. Chem. 241, 421 (1966)

Phosgene-¹⁴C (1.0 mCi; 50 mg) + 80 mg of anhydrous sodium p-nitrophenylate, dilution with 222 mg of unlabeled p-nitrophenyl chloroformate \rightarrow 214 mg with about 0.47 mCi of ¹⁴C per mmole, + CH₂N₂ \rightarrow p-nitrophenyl diazo acetate-¹⁴C.

1.2.4 — HETEROCYCLIC COMPOUNDS

66-234

ACKER T. E., BRENNEISEN P. E., TANENBAUM S. W.

Isolation, structure, and radiochemical synthesis of 3,6-dimethyl-4-hydroxy-2-py-rone.

J. Am. Chem. Soc. 88, 834 (1966)

Condensation of acetoacetate and methylmalonic acid \rightarrow 5-carbethoxy-3,6-dimethyl-4-hydroxy-2-pyrone, hydrolysis, -CO₂ \rightarrow title compd. (I). Starting from malonic ester-2-¹⁴C (1 mCi/mmole) and after subsequent addns. of carrier there was obtained 5.4 mmoles of I-3-¹⁴C (sp. act. 23.4 μ Ci/mmole).

66-235

BUTLER T. C., DAVIDSON J. D.

Synthesis of 5,5-dimethyl-2,4-oxazolidine-dione-2-¹⁴C.

J. Pharm. Sci 52, 1110 (1963) CA 64, 2079c (1966)

Condensation of urea. ^{14}C with butyl 2methyllactate in the presence of sodium butylate in butanol.

66-236

KING L. J., PARKE D. V., WILLIAMS R. T.

The metabolism of (2-14C)indole in the rat.

Biochem. J. 98, 266 (1966)

(¹⁴C)-Formic acid (0.73 g., 0.57 mCi) + otoluidine $\rightarrow N(^{14}C)$ -formyl-o-toluidine, (1.57 g., 0.67 mCi), addn. to K-t-butoxide, pyrolysis (360°) $\rightarrow (2^{-14}C)$ indole (0.174 g., 97 μ Ci, equivalent to 19.4% of the theor. radiochem. yield).

66-237

NISHIZAWA Y., CASIDA J. E.

Synthesis of rotenone-6a-14C on a semimicro scale.

J. Agr. Food Chem. 13, 522 (1965)

CA 64, 3510 f (1966)

2 mmoles Methyl bromoacetate-1-¹⁴C with 3 mmoles derritol \rightarrow 6a, 12a-dehydrorotenone-6a-¹⁴C in approx. 50% yield. NaBH₄ redn. and subsequent Oppenauer oxidn. \rightarrow rotenone-6a-¹⁴C. Yields for conversion with material of 2.36 mCi/mmole 7.5%

66-238

SCHENK H.

Mercapto-thiocarbonyl-isocyanate und ihre Umlagerung zu Mercapto-carbonyl-senfölen.

Chem. Ber. 99, 1258 (1966)

242

Phenyl thiocyanate- ${}^{14}C$ + 0.0-diethyl dithiophosphate \rightarrow S-phenyl dithio- $({}^{14}C)$ -carbamide (80%), + oxalyl chloride \rightarrow S-phenylmercaptothiazoline -4,5 -dione-2 - ${}^{14}C$ (66%).

66-239

SHAW E., RAUGH C. M., KRUMDIECK C. L.

The chemical degradation of folic acid. Photolysis of 2,4,7-trihydroxypteridine.

J. Biol. Chem. 241, 379 (1966)

Isoxanthopterin-4a.¹⁴C via 2,4,5-triamino-6-hydroxypyrimidine-5-¹⁴C from ethyl cyanoacetate-2.¹⁴C by the method of Bennett (J. A. C. S. 74, 2420) followed by condensation with ethyl glyoxylate. Ethyl glyoxylate labeled in the carboxyl group from tartaric acid-1,4-¹⁴C, esterification, glycol cleavage with sodium bismuthate; condensation with 2,4,5-triamino-6-hydroxypyrimidine \rightarrow isoxanthopterin-7-¹⁴C.

- See also: **66-202**, Esters of choline- and 2amino-ethanol-1,2-¹⁴C with cytidine- and deoxycytidine pyrophosphate
 - 66-229, Methylene-¹⁴C-dioxyphenyl compounds.

1.2.5 — CARBOHYDRATES

66-240

BAYLY R. J., TURNER J. C.

The preparation of 2-deoxy-D-(1-¹⁴C)ribose.

J. Chem. Soc. (C), 1966, 704.

Prepn. of the title compd. starting from 1-deoxy-2,4-O-ethylidene-1-iodo-D-erythritol, + $K^{14}CN$, hydrolysis with dilute HCl and subsequent hydrogenation. Isolation by paper chrom. 18% Radiochemical yield based on $K^{14}CN$, 99% radiochem. pure.

66-241

FRUSH H. L., SNIEGOSKI L. T., HOLT N. B., ISBELL H. S.

Synthesis of D-glucose-3-14C and related compounds.

J. Res. Natl. Bur. Stand. 69 A, 535 (1965)

¹⁴C-Labeled cyanide to D-glyceraldehyde, hydrolysis, improved Rosenmund redn. \rightarrow Kiliani synthesis, D-tetroses-1-¹⁴C, hydrolysis, lactonization, chrom. sepn. of the four D-pentonic-1-¹⁴C acids, redn. of the fraction containing D-arabinono-2-¹⁴Cand D-xylono-2-¹⁴C-lactone to the corresponding sugars, and chrom. sepn. of these, conversion of D-arabinose-2-¹⁴C into Dglucose-3-¹⁴C and D-mannose-3-¹⁴C by a third Kiliani synthesis. Approx. 3 percent of the radioactivity in the form of Dglucose-3-¹⁴C (2800 µCi).

66-242

LUCCHINI G., PARISI B., COCUCCI S.

The biosynthesis of $U^{-14}C$ gibberellic acid and $3,4^{-14}C$ -glucose.

EUR 2539. i (Feb. 1966)

Glucose-3,4-¹⁴C by using castor bean endosperms and rat liver. In the first case, ¹⁴CO₂ has been supplied to the tissues in a closed atmosphere; in the second NaH¹⁴CO₃ was injected intra peritoneum to adult male rats. Sp. act. 0.035 and 0.057 μ Ci/ μ mole resp.

A new technique for the degradation of labeled glucose has been worked out, based on the use of purified enzyme. Biosynthesis of gibberellic acid of sp. act. of 1.05 μ Ci/ μ mole.

66-243

NEJEDLY Z., KOUTECKY Z., GRUENBERGER D.

Preparation of ribonucleoside 5'-monophosphates- 14 C of high specific activity from the algae Chlorella pyrenoidosa.

Coll. Czech. Chem. Commun. 30, 3361 (1965)

Photosynthesis in ${}^{14}CO_2$ atmosphere, from Ba ${}^{14}CO_3$ of high isotopic ratio (33 to 47%); enzymatic cleavage of the nucleic acids- ${}^{14}C$ with the phosphodiesterase from snake venom; chrom. on Dowex 1 \times 2 and on Whatman N° 3 paper; sp. act. up to 100 mCi/mmole.

66-244

PATSCHKE L., BARZ W., GRISEBACH H.

Stereospezifischer Einbau von (-)5.7.4'-Trihydroxyflavanon in Flavonoide und Isoflavone.

Z. Naturforschg. 21b, 201 (1966)

 $(\pm)5,7,4'$ -Trihydroxyflavanone-5-glucoside - $(2.^{14}C)$ was synthesized and the diastereomeric (+) and (-) glucosides were separated by paper chromatography.

66-245

PICHAT L., DUFAY P., LAMORRE Y. Méthode chimique simple de préparation des deux anomères α et β de la désoxy-2' adénosine marqués au ¹⁴C.

Bull. Soc. Chim. France 1966, 177.

2 Mmoles of 1-chloro-3,5-di-O-p-toluyl-2deoxy-D-ribose + 1 mmole of N₆-acetyladenine-8-¹⁴C \rightarrow after deacylation, 18% of the α -anomer and 9% of the β -anomer of 2'-deoxyadenosine-8-¹⁴C and 65% of adenine-8-¹⁴C.

1.2.6 — AMINO ACIDS, PEPTIDES, PROTEINS

66-246

NEUMANN D., SCHROETER H. B.

Syntheses of radioactive labeled compounds. XIV. Synthesis of α -N-methyl-¹⁴C-ornithine (I) and of δ -N-methyl-¹⁴C-ornithine (II)

Z. Chem. 5, 385 (1965) CA 64, 3675h (1966)

 $\label{eq:a-(p-Tolylsulfonyl)ornithine} + $^{14}CH_3I$ (2.5 mCi/mmole), sealed tube, + HCl <math display="inline">\rightarrow$ I (1.02 \times 10⁹ cpm/mmole).

α-Benzoylornithine + p-MeC₆H₄SO₂Cl, OH⁻, \rightarrow δ-(p-tolylsulfonyl)ornithine, \rightarrow (see above) \rightarrow II (9.4 \times 10⁸ cpm/mmole).

1.2.7 - STEROIDS

66-247

BJOERKHEM I., DANIELSSON H.

On the formation of cholic acid from cholest-4-ene- 3α , 7α , 12α -triol and cholest-4-ene- 3β , 7α , 12α -triol. Bile acids and steroids 166.

Acta Chem. Scand. 19, 2298 (1965)

 3β -³H-4-¹⁴C-Cholest-4-ene- 3α , 7α , 12 α -triol and 3α -³H-4-¹⁴C-cholest-4-ene- 3β , 7α , 12 α triol starting from cholic acid-4-¹⁴C. Introduction of T label by redn. of cholest-4-ene- 7α , 12 α -diol-3-one with NaBT₄ (sp. act. 2 μ Ci/mg).

66-248

DEAN P. D. G., WHITEHOUSE M. W.

The chemical synthesis and biological oxidation of 7α -hydroxy(26-¹⁴C)cholesterol, 7-dehydro(26-¹⁴C)cholesterol and 26-hy-droxy(26-¹⁴C)cholesterol.

Biochem. J. 98, 410 (1966)

25-Bromonorcholesterol (from the corresp. 25-oxo-compd. via the alcohol) + Na¹⁴CN, sapon. \rightarrow 3 β -hydroxycholest-5-en-25-oic acid-26-¹⁴C (30%), + CH₂N₂, + LiAlH₄ \rightarrow 26-hydroxycholesterol-26-¹⁴C.

 7α -Hydroxycholesterol-26-¹⁴C from lab. cholesterol by subsequent treatment with benzoyl chloride, t-butyl perbenzoate, LiAlH₄; 12-20% yields.

7-Dehydrocholesterol-26- 14 C from cholesterol-26- 14 C benzoate by treatment with 2,3-dibromo-5,5-dimethyl-hydantoin, yield 10%.

1.3 --- Halogen Labeled Compounds

66-249

KATSANOS N. A., VARVOGLIS A. G.

The influence of structure upon the retention of ⁸²Br in some neutron-irradiated organic compounds.

J. Inorg. Nucl. Chem. 27, 2445 (1965) N.S.A. 20, 7149 (1966)

66-250

KATO S., KURATA K.

Application of a new method to synthesis of radioactive sodium 3,5-diiodofluorescein-3,5-¹³¹I.

244

Chem. Pharm. Bull. (Tokyo) 13, 1252 (1965) CA 64, 6029d (1966)

In this method the produced radioisotope of inert form was converted into the active form by isotopic exchange reaction and was reused for the reaction. The radioactive yield was increased from 43% to 70%.

66-251

ABDEL-WAHAB M. F., MEGAHED Y. M.

Preparation of ¹³¹I-Tyrosines and ¹³¹I-Thyroxine.

Intern. J. Appl. Radiation Isotopes 17, 132 (1966).

(1-5)mCi K¹³¹I + diluted hydrogen peroxide, ether extract, addn. to tyrosine, or thyroxine. Paper chrom.

66-252

VERINGA H. A., KERKHOF M. F.

Labeling of certain milk proteins with ¹³¹I.

J. Dairy Res. **32**, 181 (1965) CA **64**, 3888g (1966)

1 g Casein dissolved in 50 ml. 0.01 M Na tetraborate buffer at pH 9.2 at 4° with a soln. contg. 30 mg. ¹³¹] \rightarrow 750 mg. of material with a sp. act. of 40 nCi/mg. Starchgel electrophoresis revealed no difference between the iodinated and non-iodinated casein.

1.4 — Phosphorus-32 Compounds

66-253

DZANTIEV B. G., KISELEVA N. N., SHISHKOV A. V.

Development of hot synthesis methods for ³⁵S labeled biologically active substances. III. Preparation of triethylenimine-thiophosphoramide with binary labeling with ³⁵S and ³²P.

Radiokhimiya 7, 366 (1965) N. S. A. 20, 5586 (1966)

Formation of hot atoms by the ${}^{35}Cl(n,p){}^{35}S$ and ${}^{35}Cl(n,\alpha){}^{32}P$ reactions from CCl4.High S and P activities in short irradiation periods, not exceeding 15 hours, thus preventing radiolysis of the thio TEP.

66-254

PROTSENKO L. D., NEGIEVICH L. A., BOGODIST Yu. I., KUZ'MENKO I. I., SKUL'SKAYA N. Ya.

N-Benzoyl-N',N',N'',N''-diethylenetriamide of phosphoric acid, tagged with ^{32}P .

Probl. Organ. Sinteza. Akad. Nauk. SSSR, Otd. Obhsch. i Tekhn. Khim. **1965**, 319

CA 64, 6597c (1966)

Prepn. of the title comp. in 26% yield and sp. act. of 11.56 mCi/g.

66-255

VANDERHEIDEN B. S., BOSZORMENYI-NAGY I.

Preparation of ³²P-labeled nucleotides.

Anal. Biochem. 13, 496 (1965)

Rapid isotope equilibrium exchange between ³²P-labeled orthophosphate, ATP, and added nucleotides in human erythrocyte hemolyzates. Varying yields, depending on the nucleotide added. Sp. act. varying from 0.2 to 0.7 μ Ci/ μ mole for the γ -phosphate, and 0.003 to 0.1 μ Ci/ μ mole for the β -phosphate starting with 10 μ Ci ³²Pi.

66-256

ZWAIG N., MILSTEIN C.

The phosphorylated intermediate in the phosphoglyceromutase reaction.

Biochem. J. 98, 360 (1966)

2,3-Di(³²P)phosphoglycerate by an enzymic method from 1 mCi ³²P. Up to 7% conversion. Purifn. by paper electrophoresis.

1.5 — Sulfur-35 Compounds

66-257

NAKABAYASHI T., KAWAMURA S., KITAO T., TSURUGI Ji.

Aralkyl hydrodisulfides. V. The reaction of ³⁵S-labeled aralkyl hydrodisulfides with triphenylphosphine.

J. Org. Chem. 31, 861 (1966)

Benzyl chloride addn. to sodium disulfide- ${}^{35}S \rightarrow 77\%$ dibenzyl disulfide (1). Redn. of 1 with LiAlH₄ $\rightarrow 84\%$ α -toluenethiol- ${}^{35}S$. Benzhydryl bromide and thiourea- ${}^{35}S$, heating for 3 hrs. $\rightarrow 75\%$ α -diphenylmethanethiol- ${}^{35}S$.

66-258

ORATZ M., BURKS A. L., ROTHSCHILD M. A.

The determination of free ε -amino groups in proteins.

Biochim. Biophys. Acta 115, 88 (1966)

Aniline + sulfuric acid-³⁵S (100 mCi) \rightarrow quantitatively sulfanilic acid-³⁵S, diazotation, + KI \rightarrow Na pipsylate, + PCl₅ \rightarrow p-iodobenzenesulfonyl chloride-³⁵S.

See also: 66-253, Triethylenethiophosphoramide.³⁵S and -³²P, by recoil reaction.

1.6 — Oxygen labeled compounds

See also: 66-263, Methylketene-¹⁸O

1.7 — Nitrogen-15 Compounds

66-259

CRANE C. W.

The incorporation of ¹⁵N into egg protein.

Clin. Chim. Acta 13, 67 (1966)

Incorporation into egg protein by feeding whole yeast protein and yeast protein hydrolyzate, enriched with ^{15}N , to laying hens. The av. isotope content of egg white from 4 eggs was sufficient to enable the digestion and absorption of the protein to be followed in one normal subject.

66-260

PUCHKOV V. A., PLINER S. A., KHOKHLOV A. S.

O-Methylisourea-¹⁵N₂. U. S. S. R. 173. 746. CA 64, 1972g (1966)

Urea- ${}^{15}N_2$ is treated with Me₂SO₄ with heating to 120°.

See also: 66-183, 1,3,4-Thiadiazole-3-15N

1.8 — Miscellaneous

66-261

ANGHILERI L. J., MARQUES R.O.

Biosynthetic Preparation of ⁷⁵Se-Methionine and ⁷⁵Se-Cystine.

NP-15594. C.N.E.A. R.154, Argentina. 1965.

N.S.A. 20, 3661 (1966).

Addn. of sodium selenite (⁷⁵Se) to Saccharomyces cerevisiae culture free of sulphur compounds, \rightarrow proteins, hydrolysation, sepn. by exchange resin.

66-262

CELANDER D. R., CELANDER E.

Utilization of inorganic radioselenium for biosynthetic labeling of tracer proteins.

Tex. Rep. Biol. Med., 23, 589 (1965) N. S. A. 20, 5262 (1966)

Plasma samples from animals injected with Na₂⁷⁵SeO₃ were subjected to dialysis at three different pH values, to precipitation with such protein precipitants as tungstic acid, trichloroacetic acid, and lead nitrate in an alkaline medium, and to electrophoresis. The results of all these procedures indicate the firm association of 75 Se with protein. Isolation of urokinase from the urine of 75 Se-treated animals gave a preparation containing about 1 μ Ci/mg crude enzyme protein.

1.9 — Carbon-13 compounds

66-263

BAK B., CHRISTIANSEN J., NIELSEN J. T.

Preparation of 300-500 mg quantities of isotopic methyl ketenes.

Acta Chem. Scand. 19, 2252 (1965)

Methods are described for the prepn. of methyl ketene labeled with C-13 at position

2. — RADIODECOMPOSITION, STABILITY, STORAGE

66-264

NOUVERTNE W.

Preparation of ³H labeled amino acids with high specific activity and studies of the storage time (Thesis).

Cologne, Univ. 1964. N. S. A. 20, 3978 (1966)

³H labeling of amino acids by decarboxylation and chain lengthening was studied. Methods of preparation and maximum possible storage times for various compounds are given. (See also 65-166, EUR 1828. d.) , 0174

and 3,3,3-d₃).

66-265 Rochlin P.

Self-decomposition of carbon-14-labeled organic compounds.

1, and 2-3, with O-18, with D (2-d, 2,3-d,

See also: 66-183, 1,3,4-Thiadiazole-2-13C

Chem. Rev. 65, 685 (1965) CA 64, 3297c (1966)

A review with 41 references.

3 – PURIFICATION, SEPARATION

66-266

COPAL N. G. S.

Control of the radiochemical purity of some organic radiopharmaceuticals labeled with ¹³¹I.

Intern. J. Appl. Radiation Isotopes 17, 75 (1966)

The two ion-exchange cellulose papers Whatman paper AE 30 and DE 20* both in the free-base form have been employed. Ascending chrom. and electrophoresis.

66-267

ROGINSKII S. Z., AL'TSHULER O.V., VINOGRADOVA O. M., YANOVSKII M. I., KRIVORUCHKO O. P.

New variations of the chromatographic production of high-purity gases and vapors.

Bull. Acad. Sciences USSR (div. chem. sc.) 2, 204 (1965)

The production of especially pure substances using new variations of gas chromatography — thermal displacement, quasi-displacement, and others — was described (for example, the synthesis of oxygen compounds, with a close to 100% content of O-18, the synthesis of organic compounds with a close to 100% content of C-14, etc.).

66-268

URAKUBO G., KIDO Ya., HASEGAWA A.

Studies on the quality and test method of radiopharmaceuticals. I. Paper chromatography of preparations labeled with 131 I and 125 I.

Radioisotopes (Tokyo), 14, 504 (1965) N.S.A. 20. 5515 (1966)

Among the solvents tested, the following were regarded as the most suitable for purity tests: for labeled sodium iodide, ethanol:water:benzene (65:35:1) and methanol:water (75:25); for radioactive triiodothyronine, n-butanol:dioxane (4:1) saturated with 2N ammonium carbonate; and for radioactive sodium o-iodohippurate, n-butanol:ethanol (4:1) saturated with 2N ammonium carbonate.

See also: 66-211, Ketosteroids-³H

4 — ANALYSIS

4.1 — Determination of activity

66-269

BOYD J. B., MITCHELL H. K.

Measurement of the radioactivity in carbon-14 and tritium-labeled proteins that have been separated by disk electrophoresis.

Anal. Biochem. 14, 441 (1966).

Counting with scintillation techniques after the water in a gel slice has been replaced with a toluene-based scintillation solution.

66-270

BRASELMANN H.

Microdetermination of sulfate content and of sulfate- 35 S activity of mucopolysaccharides.

Acta Biol. Med. Ger. 15, 173 (1965). C.A. 64, 8625d (1966).

A method is described for detg. $2-12\gamma SO_4^{-1}$ with an error of ± 0.2 .

The radioactivity of the sample can be detd. after oxidn. of the Na₂S with satd. Br water. At 2000 counts, the relative error of the activity detn. is $\pm 4\%$, and self-absorption is ~ 3%. Protein S does not interfere.

66-271

CORTI F.

Il dosaggio del tritio (rassegna). Parte I.

ISS-65/8. (1965).

N. S. A. 20, 3876 (1966).

Some methods used in preparing tritiated samples to be directly measured are reviewed.

110 references are cited.

66-272

DAVIES J. W., COCKING E. C.

Liquid scintillation counting of ¹⁴C and ³H samples using glass-fibre or filter -paper discs.

Biochim. Biophys. Acta 115, 511 (1966)

Routine analyses of amino acids, nucleosides and for incorporation studies of amino acids and bicarbonate into proteins by plant tissues. 66-273

MAHIN D. T.

A new way to reduce oxygen quenching in liquid scintillation samples.

Intern. J. Appl. Radiation Isotopes 17, 185 (1966)

Repeatedly freezing samples in liquid nitrogen is a more effective method of gas displacement than gas bubbling, particularly when volatile compounds are involved.

66-274

TRELSTAD R. L.

Double isotope autoradiography.

Exptl. Cell Res. 39, 318 (1965)

CA 64, 5438e (1966)

Two emulsions which differ in their sensitivity to beta-radiation. The top emulsions is sensitive to ³H beta-particles and insensitive to ¹⁴C. Specificity for ¹⁴C is accomplished by using a celloidin film which sep. the second ¹⁴C-sensitive emulsion from close contact with the section.

66-275

YAMAZAKI M., ISHIHAMA H., KASIDA Y.

Tritium measurement with a liquid scintillation counter. The application of the oxygen-flask combustion method to a strong coloured sample.

Intern. J. Appl. Radiation Isotopes 17, 134 (1966)

4.2 — Apparatus

66-276

BAGGIOLINI M., BICKEL M. H.

A new type of incubation apparatus for the determination of metabolically produced $^{14}CO_2$.

Anal. Biochem. 14, 290 (1966)

Open system under conditions of slightly

reduced pressure. The vessels for ${}^{14}CO_2$ absorption which are not contained inside the incubation flask are used directly for the measurement of radioactivity in a liquid scintillation counter.

66-277

CONWAY D. W., GRACE A. J., ROGERS J. E.

Simplification of oxygen-flask combustion procedure for preparation of samples for liquid scintillation counting.

Anal. Biochem. 14, 491 (1966).

Nichrome for the combustion baskets.

66-278

CRAMER W. A., HOUTMAN J. P. W., KOCH R. O., PIET G. J.

Measurement of radioactivity in effluents of a gas chromatograph.

The flame ionization detector used as a combustion chamber in combination with specially designed absorbers.

Intern. J. Appl. Radiation Isotopes 17, 97 (1966)

The CO₂ from a gas chromatographic column with a flame ionization detector is trapped in special absorbers which are connected with the detector. Total ¹⁴C activities of 10⁻¹¹ Ci/fraction can be determined with $\pm 15\%$ accuracy in 1 hr counting time.

66-279

FORYS M., ZLOTOWSKI J.

A device for precise measurements of ¹⁴C radioactivity in organic compounds.

Nukleonika, 10, 427 (1965) N. S. A. 20, 5511 (1966)

The construction and operation of a selfquenching G-M counter for measuring radioactivity of ¹⁴C in organic compounds, converted to CO₂, is described. The statistical error involved in measuring specific activities of the order of $5 \times 10^5 \,\mu\text{Ci/mg}$ was less than 1°_{\odot} .

66-280

MERCER N. J. H. HENDERSON J. F.

Selective elution of scintillation phosphors from chromatography paper following radioactivity measurements.

Anal. Biochem. 13, 559 (1965)

66-281

QUAZI A. H.

Influence of sample volume on weak β counting efficiency in liquid scintillation counting.

Naturwissenschaften **52**, 490 (1965) N. S. A. **20**, 5510 (1966)

The dependence was measured on tritiated toluene, 14 C-toluene, tritiated water, and 35 S-labeled urine. The maximum counting efficiency in all cases was obtained with samples between 7 and 15 ml and was independent of the type of scintillator solution.

66-282

SHARP R. A., ELLIS J. G.

System design in low background internal gas sample counting of ¹⁴C and tritium.

Gmelin, AED-CONF-65-158-11. N. S. A. 20, 2179 (1966)

From International ¹⁴C and ³H Dating Conference, Pullman, Wash.

66-283

WERNER G., WERNER H., BOSQUE P. G., QUEVEDO J. C.

Eine Methode zur autoradiographischen Darstellung hydrophiler Substanzen in biologischem Material.

Z. Naturforschg. 21b, 238 (1966)

A method is described for obtaining autoradiograms from hydrophilic T labeled compounds of low molecular weight in biological materials.

66-284

WHITE R. E., DAVIS H. G.

Detection of volatile ¹⁴C labeled compounds

by a modified gas chromatography-ionization chamber technique.

Anal. Chim. Acta 34, 105 (1966) N. S. A. 20, 3899 (1966)

Compds. are separated by preparative gas chromatography, trapped out as they elute from the column, and then are transferred to a static ionization chamber where entire separated fractions are counted. Advantages of the method are discussed.

4.3 — Determination of radiochemical pattern

66-285

BUTLER K.

Anisomycin. II. Biosynthesis of anisomycin.

J. Org. Chem. 31, 317 (1966)

Degradation of anisomycin after application of various 14 C labeled precursors. For a more detailed description see ibid., **30**, 2334 (1965)

66-286

CURTIS R. F., HARRIES P. C., HASSALL C. H., LEVI J. D., PHILLIPS D. M.

The biosynthesis of phenols. Part X. Mutation and radioactive tracer studies relating to the biosynthesis of sulochrin.

J. Chem. Soc. 1966 (C), 168

Degradation of sulochrin, derived either from acetic acid- 2^{-14} C or diethyl malonate- 2^{-14} C.

66-287

RAUSCHENBACH P.

Isotope studies of the biochemistry of fructose metabolism and gluconeogenesis in the liver (Thesis).

Munich, Tech. Univ., 1964, 107 p. N. S. A. 20, 3684 (1966)

Methods for the determination of ¹⁴C distributions in glucose are described. 66-288

VYKHOVANETS V. V., CHENETS V. V., KNUTOV V. I., KALECHITS I. V.

Method of determination of the labeled position in six-membered rings.

Izv. Vysshikh Uchebn. Zavedenii, Khim.i Khim. Tekhnol. 8, 432 (1965)CA 64, 4883h (1966)

An improved Steinberg-Sixma method of degradation of toluene-1-¹⁴C is described.

5. — Miscellaneous

66-289

McFARLANE A. S.

Turnover of labeled plasma proteins.

Bull. Schweiz. Akad. Med. Wiss. 21, 173 (1965)

N. S. A. 20, 6940 (1966)

Various problems associated with the use of labeled plasma proteins in metabolic studies are discussed, such as reutilization of labeled amino acids, in vitro and in vivo methods of synthesizing labeled proteins, self-radiation damage.

250