[CONTRIBUTION FOR THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

peri-Substituted Naphthalenes. III. Acid-induced Rearrangement of 8-Isopropyl-1-naphthoic Acid[1]

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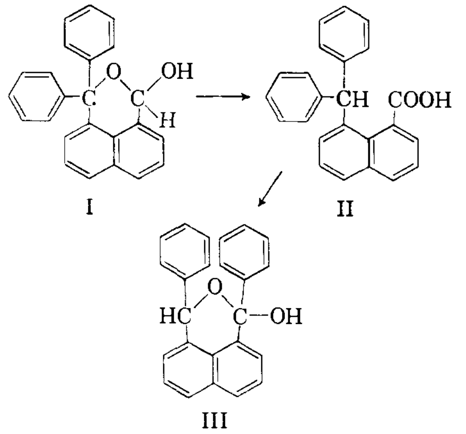
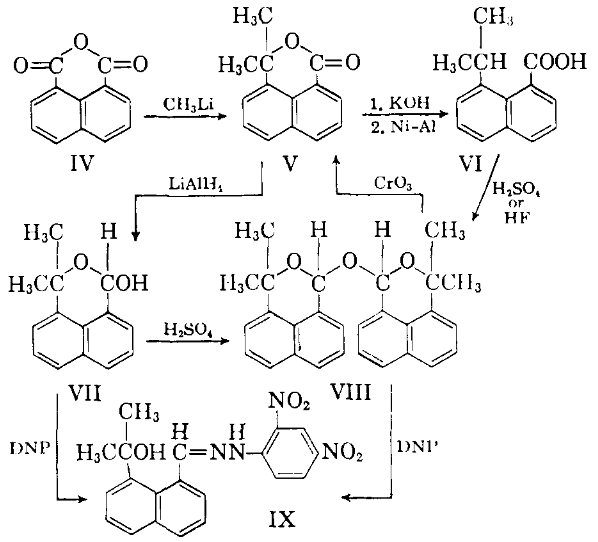
8-Isopropyl-1-naphthoic acid was synthesized from 1,8-naphthalic anhydride. In sulfuric acid or in hydrogen fluoride it rearranged with a transfer of hydrogen from the isopropyl group to the carbonyl group. There was no indication of a 1,5-methyl shift. The same aldal product (VIII) also was obtained by dehydration of 1-hydroxy-3,3-dimethyl-1H,3H-naphtho-[1,8-c,d]pyran with sulfuric acid.

In the previous papers[3] it was shown that hemiacetal I rearranged readily in formic acid solution to 8-benzhydryl-1-naphthoic acid (II), which in turn rearranged to ketal III in sulfuric acid. Both transformations could be accomplished in one operation by the action of concentrated sulfuric acid on I.



The effect of acid reagents on the analogous methyl compounds, VII and VI, is reported in this paper. An investigation of VI was of particular interest since, in view of the rearrangement of II, it would appear that the molecular geometry of this compound would be very favorable for a 1,5-methyl shift. Although many cases of rearrangements involving 1,2-methyl migrations are known, previous work has failed to reveal any unambiguous examples of acid-catalyzed intramolecular methyl migrations that occur between carbon atoms separated by one or more atoms (*i.e.*, 1,3-, 1,4-, 1,5-, etc. shifts).

1,8-Naphthalic anhydride (IV) was converted to 3,3-dimethyl-1,8-naphthalide (V), which was reduced to 8-isopropyl-1-naphthoic acid. Considerable experimentation was necessary to determine conditions for effecting both of these transformations. Although aryl magnesium halides yield diarylnaphthalides on reaction with IV,[4] we failed to isolate 3,3-dimethyl-1,8-naphthalide from any of several reactions involving methylmagnesium iodide and IV. However, yields of V of the order of 25% were obtained by addition of IV to two mole equivalents of methyllithium.



Lactone V proved to be remarkably unreactive. It was unchanged by 25% aqueous sodium hydroxide at 150° for 40 hours and by concentrated ammonium hydroxide at 100° for 45 hours. It was likewise unchanged by aqueous hydrogen iodide and phosphorus (65 hours at reflux) and by zinc amalgam in formic acid and hydrochloric acid (30 hours at reflux), although 1,8-naphthalide has been reduced by the Clemmensen procedure.[5] Saponification could be effected by heating V at 145° with excess potassium hydroxide in triethylene glycol for several hours. Reduction of the resulting salt with nickel-aluminum alloy[6] yielded 8-isopropyl-1-naphthoic acid. If the reduction was carried out without prior saponification of the lactone, a tetrahydrolactone rather than VI was produced.

Acidic reagents converted 8-isopropyl-1-naphthoic acid to a neutral, crystalline solid, VIII. The best yield, 67%, was obtained when liquid hydrogen fluoride was used as a solvent. Concentrated sulfuric acid was also an effective reagent for this transformation and furnished a 55% yield of VIII. The conditions which had been found to be most satisfactory for the isomerization of II to III (the action of stannic chloride on the acid chloride of II) were less suitable with VI; hydrolysis of the com-

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[1] Presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

[2] Sinclair Oil Co. Harvey Fellow, 1956–1957; Standard Oil Co. of Indiana Fellow, 1957–1958.

[3] R. L. Letsinger and P. T. Lansbury, THIS JOURNAL, **81**, 935 (1959); P. T. Lansbury and R. L. Letsinger, *ibid.*, **81**, 940 (1959).

[4] M. S. Kharasch and D. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954.

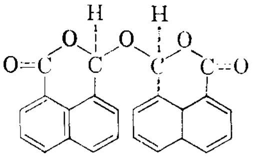
[5] R. C. Fuson and G. Munn, *ibid.*, **71**, 1870 (1949).

[6] For a survey of the use of nickel–aluminum alloy as a reducing agent see D. Papa, E. Schwenk and H. Breiger, *J. Org. Chem.*, **14**, 366 (1949), and previous papers in this series.

plex obtained by treating the acid chloride of VI with stannic chloride afforded only low yields of VIII (10% from a 2-hour reaction and 17% from a reaction of about 14 hours).

Compound VIII could be isolated in two crystalline modifications. One, m.p. 149.5–150.5°, was obtained by recrystallization from hexane, and the other, m.p. 130–131°, by recrystallization from ethyl alcohol. The two forms were readily interconvertible and gave identical infrared spectra in carbon disulfide solution.

An aldal structure[7] (see structural formula) corresponding to a bimolecular dehydration product of VII was assigned to VIII on the basis of the following data: (a) The combustion analysis of VIII was in agreement with that calculated for $C_{28}H_{26}O_3$; (b) no bands attributable to hydroxyl and carbonyl groups were found in the infrared spectrum; (c) VIII reacted with 2,4-dinitrophenylhydrazine to give an orange hydrazone, $C_{20}H_{18}O_5N_5$; and, finally, (d) neutral oxidation of VIII with N-bromosuccinimide and also acidic oxidation with chromium trioxide gave lactone V as a product. A closely related structure, X, has been proposed[8] for a pyrolysis product of 8-carboxy-1-naphthaldehyde.[9]



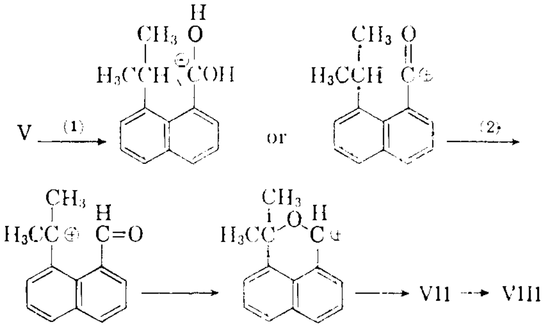
X

Support for the structure assigned to VIII was gained from hemiacetal VII, which was prepared by reduction of naphthalide V with lithium aluminum hydride. As expected, VII yielded a 2,4-dinitrophenylhydrazone which was identical with that obtained from VIII. Furthermore, VII was converted to VIII by concentrated sulfuric acid. Weaker acids such as formic acid and dilute hydrochloric acid transformed VII to a neutral oil which failed to crystallize. Under similar treatment the analogous phenyl compound (I) had rearranged to the naphthoic acid (II).

8-Isopropyl-1-naphthoic acid, therefore, rearranged with transfer of hydrogen from the isopropyl group to the carbonyl carbon in the presence of either sulfuric acid or hydrogen fluoride. No evidence for a methyl migration was found. The net result of this process is a reduction of the carboxyl group to the aldehyde stage of oxidation and an oxidation of the alkyl group to the alcohol stage. This change is the *reverse* of that in which 8-benzhydryl-1-naphthoic acid is formed from hemiacetal I, and it demonstrates in a striking manner the significant role played by the substituent groups (methyl and phenyl) in determining the course of these reactions.

Evidence that the reaction VI → VIII was not reversible was gained by subjecting aldal VIII to the action of concentrated sulfuric acid; 55% of the aldal was recovered from the reaction and no 8-isopropyl-1-naphthoic acid could be found. Two further pieces of evidence indicate that the rearrangement is an intramolecular one. (1) Cumene and benzoyl chloride did not react under conditions for which 8-isopropyl-1-naphthoic acid was converted, in part, to the aldal. On the basis of steric grounds, the reaction, if intermolecular, should occur more readily with cumene and benzoyl chloride than with the isopropylnaphthalene derivative. (2) A mixture of isopropyl-1-naphthoic acids, probably mainly the 5- and 6-isopropyl isomers, was prepared by an alkylation reaction. Sulfuric acid did not convert these acids, which are unfavorably constituted for an intramolecular reaction, to neutral products.

A feasible pathway for an intramolecular rearrangement of V is represented below. Step 1 is the conversion of a carboxylic acid to a dihydroxycarbonium ion or an acylium ion (for simplicity subsequent steps are formulated only for the latter ion),



and step 2 is a hydride transfer reaction. The abstraction of hydride by alkyl carbonium ions is a common reaction; however, a transfer of this type from an alkyl group to a dihydroxycarbonium ion or an acylium ion is unusual. Its occurrence in this case may be attributed to the proximity of the groups involved.

Experimental[10]

3,3-Dimethylnaphthalide (V).—Powdered 1,8-naphthalic anhydride (56 g., 0.282 mole) was added over a period of one hour to a refluxing ether solution of methyllithium (0.588 mole). Reflux and stirring were continued for two hours and the mixture was stirred overnight at room temperature, whereupon it was decomposed by pouring onto ice and hydrochloric acid. Concentration of the ether layer, after thorough washing with sodium hydroxide solution to remove acidic material, yielded 23 g. of a yellowish solid, m.p. 105–112°. The crude lactone was purified by dissolution in hot 10% ethanolic potassium hydroxide and reprecipitation by pouring into water. This procedure was repeated (generally one to three times were sufficient) until the colored impurity, believed to be 3-methylperinaphthindenone, had been largely removed. The last traces of color were removed by Darco treatment and recrystallization from petroleum hexane; yield of pure product, 16.2 g. (27%), m.p. 113.5–114°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.3; H, 5.6.

8-Isopropyl-1-naphthoic Acid (VI).—Lactone V (15 g.) was saponified by heating overnight at 145° in 450 g. of triethylene glycol containing 60 g. of potassium hydroxide. A solution of 48 g. of potassium hydroxide in 400 cc. of water was added; then, with the temperature at 78–82° and good

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[7] For the origin of the term "aldal" see C. D. Hurd and S. M. Cantor, This Journal, **60**, 2678 (1938). The aldal linkage is found in several disaccharides and it has been generated synthetically by C. D. Hurd and C. D. Kelso, *ibid.*, **70**, 1484 (1948).

[8] G. Errera and A. Cuffaro, *Gazz. chim. ital.*, **41**, II, 807 (1911); *C. A.*, **6**, 996 (1912).

[9] C. Graebe and E. Gfeller, *Ann.*, **276**, 14 (1893).

[10] All carbon and hydrogen analyses were made by Miss H. Beck.

stirring, 30 g. of lumpy nickel-aluminum alloy[11] was added portionwise. Small amounts of capryl alcohol were occasionally added to reduce foaming. After an additional hour of stirring the mixture was allowed to stand at room temperature overnight. It was then warmed and filtered, and the filtrate was cooled and poured into concd. hydrochloric acid. The resulting mixture was extracted with ether, and the ether layer was extracted with several portions of sodium carbonate solution. From the ether layer was isolated 4.5 g. of unreacted lactone. From the sodium carbonate solution was obtained by conventional procedures 6.5 g. of an acid mixture. Fractional crystallization from petroleum hexane yielded 3.5 g. (23%) of 8-isopropyl-1-naphthoic acid, m.p. 126–127°. The second crystalline crop, 1.5 g., melted at 86–95°, and the third fraction consisted of about 1 g. of oil.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.2; H, 6.5.

Rearrangement of 8-Isopropyl-1-naphthoic Acid. (a) **Hydrogen Fluoride.**—A solution of 0.400 g. of acid VI in 20 g. of liquid hydrogen fluoride was allowed to stand 45 minutes at 0°, then 45 minutes at room temperature. The solution was poured onto ice and extracted with benzene; and the combined benzene extracts were washed with dilute sodium hydroxide, then dried and evaporated. No carboxylic acid salts were present in the alkaline extracts. The neutral products, 0.380 g., partially crystallized on standing. Separation of the crystals and recrystallization from petroleum hexane yielded 0.235 g. of VIII, m.p. 149.5–150.5°. This material would not sublime. The infrared absorption spectrum showed strong absorption in the region for C–O–C at 9.25, 9.37, 9.80 and 9.95 μ and a very prominent band at 10.3 μ. There was no absorption attributed to O–H and C=O.

Anal. Calcd. for $C_{28}H_{26}O_3$: C, 81.92; H, 6.38; mol. wt., 410.5. Found: C, 81.5; H, 6.2; mol. wt. (Rast), 413.

The oily portion of the neutral product exhibited a very similar infrared spectrum. An additional quantity of VIII, 0.020 g., was isolated by dissolving the oil in cold sulfuric acid and then diluting the solution with water. The total quantity of pure, crystalline aldal VIII isolated was 0.255 g., 67% of theory.

The aldal reacted with 2,4-dinitrophenylhydrazine to give an orange derivative, m.p. 221.2–222°. Strong infrared bands were present at 2.96 (possibly O–H), 3.05 (N–H) and 6.15 μ (C=N). The dinitrophenylhydrazone derivative of naphthaldehyde showed bands at 3.02 and 6.18 μ. The similarity in color and infrared spectra of these compounds suggests that the DNP derivative of VIII may have a conventional hydrazone grouping ($—CH=\overset{H}{N}—$) rather than a cyclized structure (

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Anal. Calcd. for $C_{20}H_{18}O_5N_4$: C, 60.91; H, 4.60; N, 14.21. Found: C, 60.5; H, 4.6; N, 14.3.

(b) **Sulfuric Acid.**—8-Isopropyl-1-naphthoic acid (0.670 g.) was dissolved in 40 cc. of ice-cold concentrated sulfuric acid, giving an amber colored solution with a greenish fluorescence. After an hour at ice temperature and two hours at room temperature, the solution was poured onto ice. The white suspension was taken up in ether and the resulting solution extracted with base. Evaporation of the ether left an oil which solidified after treatment with hexane–ether; weight 0.30 g. (55%), m.p. 147–149°. A mixed melting point determination and the infrared spectrum showed this material to be the same as the aldal from the hydrogen fluoride reaction. 8-Isopropyl-1-naphthoic acid (0.1 g.) was recovered from the base extract.

(c) ***Via* the Acid Chloride.**—Compound VI (1.0 g.) was converted to the acid chloride by refluxing with thionyl chloride (9 cc.) and two drops of pyridine in ether (20 cc.). The solvent was removed under vacuum; then 5 cc. of benzene was added and boiled off and replaced with carbon disulfide (10 cc.). To this solution was added 2 cc. of stannic chloride in 10 cc. of carbon disulfide. A sticky, orange complex settled out though no heat was evolved. The mixture was heated at reflux temperature for two hours, then decomposed on a mixture of ice and dilute hydrochloric acid. Lumps of organic matter were crushed in order to effect dissolution in the carbon disulfide, after which the organic layer was removed and evaporated to dryness. The residue was taken up in ether and washed successively with dilute hydrochloric acid, water, dilute sodium hydroxide, and water. Acidification of the alkaline extract yielded 0.5 g. (50%) of the starting acid. Evaporation of the ether layer and recrystallization of the residue gave 0.10 g. (10%) of VIII, m.p. 117–125°. A subsequent recrystallization from petroleum hexane raised the melting point to 148–149°.

No rearrangement occurred in the absence of stannic chloride. Thus, conversion of 8-isopropyl-1-naphthoic acid to the acid chloride, hydrolysis of the acid chloride with water, and recrystallization of the product gave a 91% recovery of the acid. The infrared spectrum of the crude material before recrystallization showed none of the strong absorption at 10.3 μ which is characteristic of the aldal.

From another experiment which differed from the first in that the mixture of acid chloride and stannic chloride was refluxed overnight, there was obtained from 1.5 g. of 8-isopropyl-1-naphthoic acid 0.25 g. (17%) of the aldal, m.p. 147–148.3°; 0.5 g. of a reddish oil; and 0.25 g. of 3,3-dimethyl-1,8-naphthalide, identified by mixed melting point with an authentic sample and the infrared spectrum. Only a trace of the starting acid was recovered from this experiment.

Oxidation of Aldal VIII. (a) **N-Bromosuccinimide.**—To 0.100 g. of the aldal in carbon tetrachloride was added 0.86 g. of N-bromosuccinimide and a few crystals of benzoyl peroxide. After 30 minutes at reflux, the solution was allowed to stand overnight at room temperature. The solvent was removed under vacuum and the residue was boiled for three hours with a solution of 20 cc. of 10% aqueous sodium bicarbonate and 20 cc. of ethanol. The mixture was then diluted with water and extracted with ether. Evaporation of the ether left 0.70 g. (68%) of 3,3-dimethyl-1,8-naphthalide, m.p. 108–110°. After recrystallization from petroleum-hexane the sample melted at 113–113.5° and did not depress the melting point of an authentic sample of 3,3-dimethyl-1,8-naphthalide.

(b) **Chromium Trioxide.**—A solution of the aldal (0.05 g.) and excess chromium trioxide in 8 cc. of acetic acid was heated at 50–60° for 30 minutes and then poured into water. An ether extract of this solution was washed with sodium hydroxide solution and evaporated. The solid which remained melted at 113° and weighed 0.04 g. A mixed melting point with an authentic sample of lactone was not depressed, and the infrared spectrum of this product was identical with that of lactone V.

1-Hydroxy-3,3-dimethyl-1H,3H-naphthol[1,8-c,d]pyran (VII).—3,3-Dimethyl-1,8-naphthalide (0.500 g.) was added quickly to a suspension of 0.300 g. of lithium aluminum hydride in 35 cc. of refluxing tetrahydrofuran. The mixture was refluxed for an additional 100 minutes, then decomposed by dropwise addition of water; 10% sodium hydroxide solution (2 cc.) was added and the suspension was filtered by suction. The filtrate and ether washings of the filter cake were dried over magnesium sulfate and evaporated on the steam-bath, leaving a solid residue which was recrystallized from petroleum-hexane; weight of VII, 0.30 g. (60%), m.p. 97.5–98.5°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.5; H, 6.4.

In agreement with the hemiacetal structure, the infrared spectrum showed strong O–H absorption, but no bands in the carbonyl region. This compound reacted with dinitrophenylhydrazine to form a dinitrophenylhydrazone which melted at 221.2–222° and was identical with the derivative obtained from VIII.

A solution of 0.40 g. of the hemiacetal in 25 cc. of cold sulfuric acid was allowed to stand for 45 minutes in an ice-bath; then it was poured into water and extracted with ether. Evaporation of the ether layer (after it had been washed with dilute sodium hydroxide solution) yielded 0.225 g. (59%) of the aldal, m.p. 142–144°. Continued recrystallization raised the melting point to 149.5–150.7°. The infrared spectrum was identical with that of the aldal prepared from 8-isopropyl-1-naphthoic acid.

Effect of Sulfuric Acid on VIII.—The aldal (VIII) (0.200 g.) was dissolved in 20 cc. of cold, concentrated sulfuric acid. After standing 45 min. at 0° and another 30 min. at room temperature, the amber colored solution was poured onto ice. The white suspension was dissolved in ether and the ether solution extracted with dilute sodium hydrox-

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(11) Gilman Paint and Varnish Co., Chattanooga, Tenn.

ide. No carboxylic acid could be detected when the alkaline solution was acidified. From the ether layer was obtained 0.130 g. of solid which was shown to be aldal by its infrared spectrum. One recrystallization from hexane-ether yielded 0.110 g. (55%) of VIII, m.p. 147-148.5°. The remainder of the starting material had been converted to water-soluble products (probably sulfonic acids) by the sulfuric acid.

In another, similar experiment, the white suspension which resulted when the sulfuric acid solution was poured onto ice was filtered directly, instead of being taken up in ether and treated with sodium hydroxide solution. The solid melted at about 65°, was very hygroscopic, and yielded an acidic oil on standing. Dilute alkali converted the solid to VIII. It seems likely that the solid was an oxonium salt of VIII or a sulfate ester of VII.

x-Isopropyl-1-naphthoic Acid.—Ethyl 1-naphthoate was alkylated with isopropyl bromide in carbon disulfide in the presence of aluminum chloride by the procedure of Gilman and Calloway.[12] The alkyl ester, b.p. 96-110° (0.2 mm.), n_D 1.5772-1.5780, was saponified with sodium hydroxide. After chromatography and standing for three weeks, the oily acid crystallized. Recrystallization yielded a mixture of acids, probably the 5- and 6-isopropylnaphthoic acids, which melted at 95-105° (3% yield); neut. equiv., 215; calcd. for $C_{14}H_{14}O_2$, 214.

A 0.35-g. sample of the acid was dissolved in cold, concentrated sulfuric acid and allowed to stand at 0° for 30 minutes. The mixture was then poured onto ice and worked up in the usual way to give 0.20 g. (57%) recovery of the acid (m.p. 128-133°, the infrared spectrum was virtually identical with that of the starting material). Only a trace of a neutral material was obtained and this did not give a dinitrophenylhydrazine derivative. There was, therefore, no evidence that an aldal had formed.

Attempted Reaction of Cumene with Benzoyl Chloride.—A solution containing 1.2 g. of cumene, 1.4 g. of benzoyl chloride and 3.5 cc. of stannic chloride in carbon disulfide was refluxed for 7 hours. No observable reaction occurred. The pale yellow solution was poured onto ice and hydrochloric acid, and the organic matter was taken up in ether. This solution was extracted with sodium bicarbonate solution and then washed with water and tested for the presence of carbonyl compounds with 2,4-dinitrophenylhydrazine reagent. There was no indication that any aldehydes or ketones were present. The ether layer was then extracted with dilute potassium hydroxide solution. Acidification of the combined alkaline extracts yielded 1.10 g. (90%) of benzoic acid. Evaporation of the ether left an oil which was shown by its infrared spectrum to be cumene contaminated with a very small amount of benzoyl chloride.

EVANSTON, ILL.

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(12) H. Gilman and N. O. Calloway, THIS JOURNAL, **55**, 4205 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Terpenes. X.[1,2] The Constitution of Maaliol

BY G. BÜCHI, M. SCHACH V. WITTENAU AND DWAIN M. WHITE[3]

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The structure of maaliol, a tricyclic sesquiterpene alcohol, was shown to be LIII.

Maali resin is a soft elemi-like exudation from *Canarium samoense*, a tree endemic to the Samoan Islands. Chemical investigations on the resin were initiated by an anonymous chemist of Schimmel and Co.[4] who described a sesquiterpene alcohol, maaliol, m.p. 103-104°, and established the formula $C_{15}H_{26}O$. More recently, another substance of the same molecular composition, m.p. 102-103°, was isolated from *Valeriana officinalis L.* and the investigators suspected its identity with maaliol.[5] We have sent a sample of authentic maaliol to Dr. A. Hofmann, Sandoz A. G., Basel, and he has kindly informed us that the two specimens were indeed identical. The early researchers already established the presence of a tertiary hydroxyl group in maaliol by preparing a crystalline chromate ester $(C_{15}H_{25})_2CrO_4$. Furthermore, the natural product was reported to be stable to base, but on exposure to acids it was rapidly converted to a hydrocarbon $C_{15}H_{24}$. Some further relevant observations on the structure of maaliol are due to Hosking.[6] He found the compound to be stable to bromine and alkaline potassium permanganate and to be resistant to catalytic reduction over platinum in neutral solvents. Maaliol was not affected by prolonged exposure to ozone and thus exhibited properties typical of saturated molecules. Treatment with hot formic acid produced a hydrocarbon $C_{15}H_{24}$ which on catalytic hydrogenation absorbed almost *two* mole equivalents of hydrogen. Dehydrogenation of maaliol with selenium gave eudalene (VI) characterized by a picrate and a styphnate which were both compared with authentic samples. Hosking correctly concluded that this natural product is a saturated tricyclic sesquiterpene alcohol which may contain a cyclopropane ring.

We first eliminated the possibility that maaliol is identical with juniperol (macrocarpol)[7] ($C_{15}H_{26}O$), m.p. 108°. A comparison of the infrared spectra of the two substances demonstrated their non-identity which was confirmed by mixture melting point determination.[8] Hosking[6] had shown previously by mixture melting point determination that maaliol is not identical with ledol[9] ($C_{15}H_{26}O$), m.p. 105°.

In this paper it is shown that maaliol has structure I. In agreement with a previous finding[6] treatment of I with selenium gave eudalene (VI)

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(1) Part IX, G. Büchi and K. Biemann, *Croatica Chem. Acta*, **29**, 163 (1957).

(2) A part of this investigation was published in a Communication to the Editor, G. Büchi and D. M. White, THIS JOURNAL, **79**, 750 (1957).

(3) National Institutes of Health Predoctoral Fellow 1955-1956.

(4) *Schimmel Reports*, 137 (1908).

(5) A. Stoll, E. Seebeck and D. Stauffacher, *Helv. Chim. Acta*, **40**, 1205 (1957).

(6) J. R. Hosking, deceased Oct. 14, 1946. We are indebted to Mrs. Alida Hosking-Wind for making these findings available to us in the form of an unpublished manuscript by J. R. H.

(7) H. Erdtman and B. R. Thomas, *Chemistry & Industry*, 381 (1955).

(8) This comparison was kindly carried out by Dr. B. R. Thomas, Royal Institute of Technology, Stockholm.

(9) L. Dolejš, M. Soucek, M. Horák and F. Šorm, *Chemistry & Industry*, 491 (1958); N. P. Kiryalov, *J. Gen. Chem. U.S.S.R.*, **23**, 1617 (1953), and earlier papers cited.