

this solution excess of standard 0.01M EDTA was added and the excess back-titrated against standard 0.01M magnesium chloride.

The final filtrate containing the soluble molybdosilicate complex and the unreacted orthosilicate was treated with ~ 25 ml. of 10% ammonium molybdate, brought to the appropriate pH for the precipitation of quinoline molybdosilicate by the addition of hydrochloric acid (sp. gr. 1.18) till the solution turned distinctly red. The precipitation was brought about by the dropwise addition of ~ 2% quinoline accompanied by constant stirring. The presence of excess of quinoline and ammonium molybdate was confirmed by the absence of further precipitation from the supernatant liquid on the addition of a few more drops of these reagents. The precipitate was digested at ~ 70° C. for ~ 10 minutes. It was cooled in an ice-bath, filtered through a weighed 1G4 crucible, washed with 0.05% quinoline till it was free from molybdate ions, dried at 130° C. and weighed as the dihydrate.

Three representative sets of results with solutions of known concentrations of Ca^{2+} , PO_4^{3-} and SiO_4^{4-} are given in Table I. The method was found to be quick and accurate; successive determinations of the three ions from the same aliquot could thus be achieved.

The authors thank Prof. G. B. Singh, Head of the Chemistry Department, Banaras Hindu University, for providing facilities. Financial assistance given to one of us (R. P. S.) by CSIR is also gratefully acknowledged.

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February 10, 1970.

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NEW TETRACYCLIC TRITERPENES FROM *FOMES SENEX*: SENEXONOL, SENEXDIONE, OXIDOSENEXONE AND SENEXDIOLIC ACID

THE wood-rotting fungus *Fomes senex* Nees & Mont. has been chemically examined further.¹ Besides the known compounds pinicolic acid A (VIa) and trametenolic acid B (VI b), four

new compounds have been isolated: a tetracyclic triterpene acid, **senexdiolic acid** ($\text{C}_{30}\text{H}_{48}\text{O}_4$) and three neutral nor-triterpenes, **senexonol** ($\text{C}_{29}\text{H}_{46}\text{O}_2$), **senexdione** ($\text{C}_{29}\text{H}_{44}\text{O}_2$) and **oxidosenexone** ($\text{C}_{29}\text{H}_{46}\text{O}_2$). They are all interrelated. Senexonol is a ketoalcohol and senexdione the corresponding diketone. Acid treatment of senexonol gives rise to an isomeric compound in which the alcoholic function and an isopropylidene double bond in the side chain disappear simultaneously giving rise to a cyclic ether (a tetrahydrofuran derivative) which may be called 'oxidosenexone' and which is present as a minor compound in the fungus. Senexdiolic acid is a dihydroxy acid in which the acidic function is β - to one of the hydroxyls, since oxidation of this hydroxyl group to keto leads to decarboxylation. The nor-product obtained in this manner starting from the acid isomerisation product (V) of senexdiolic acid was identical with oxidosenexone. All the compounds contain an 8:9 double bond. A number of chemical transformations, taken together with U.V.,

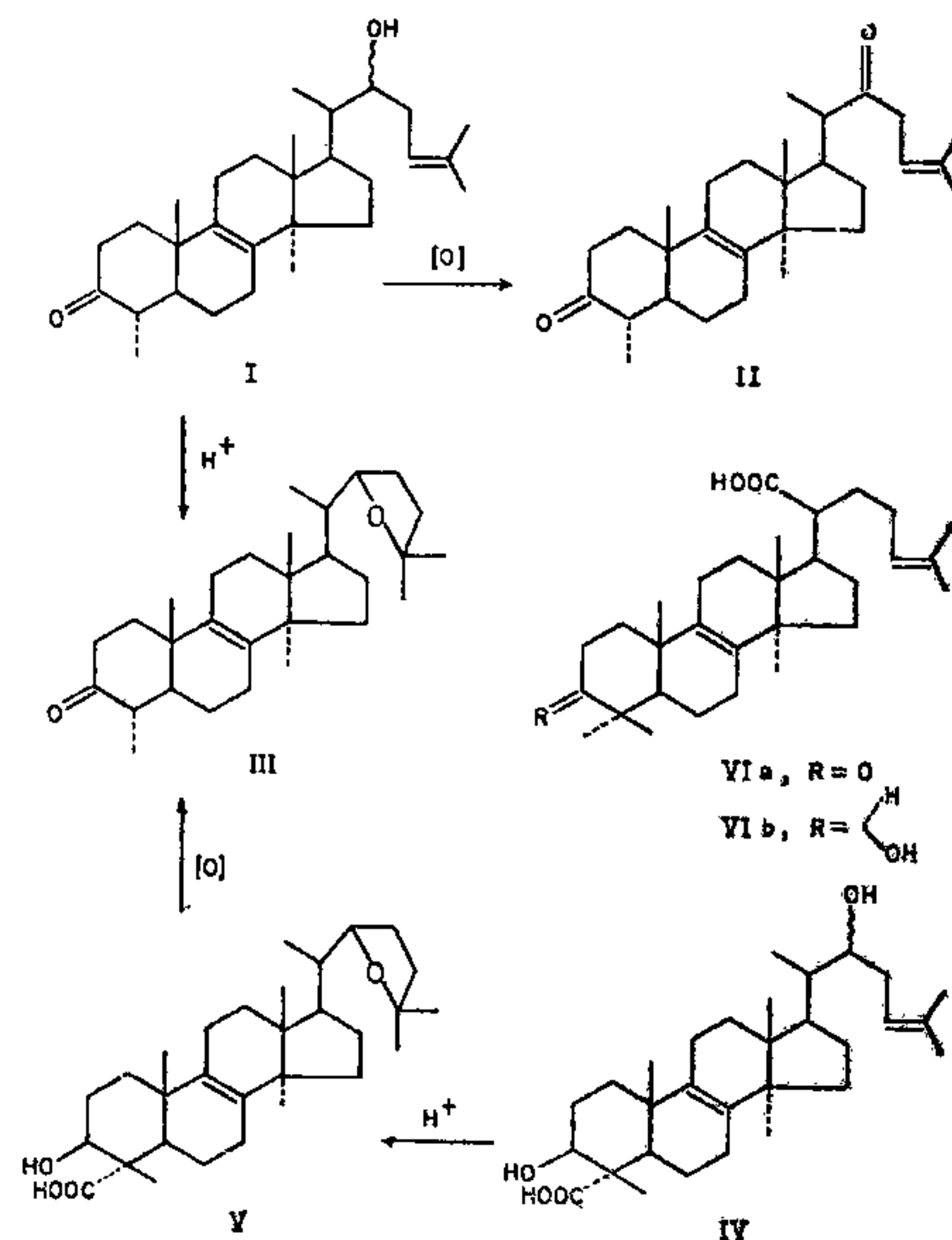


FIG. 1

I.R., N.M.R. and mass spectral data, and the correlation of senexdiolic acid with trametenolic acid B (VI b) lead to the structure, (I) for senexonol, (II) for senexdione, (III) for

oxidosenexone and (IV) for senexdiolic acid. The co-occurrence of (I) and (IV) is of interest in connection with the mode of formation of sterols from tetracyclic triterpenes.

The authors thank Prof. T. R. Seshadri for his kind interest.

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* This structure supersedes the one proposed earlier.

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SYNTHESES OF 4-(2'-THIENYL)- AND 4-(2'-FURYL)-THIAZOLES

2-METHYL- or 2-amino-4-alkyl or aryl thiazole derivatives which are of industrial and biological importance have been studied extensively. But relatively few compounds containing this ring with heterocyclic nuclei as substituents at position-4 are known and therefore it was considered of interest to synthesise a few 2-amino- and 2-methyl thiazoles with α -thienyl and α -furyl substituents at position-4.

EXPERIMENTAL

2-Methyl-4-(2'-thienyl)-thiazole methiodide

The intermediate bromomethyl-2-thienyl ketone required for the purpose was obtained by treating 2-acetyl thiophene¹ with calculated quantity of bromine in chloroform medium. The resulting bromo-ketone was then refluxed with thioacetamide, (1.2 mole) in absolute ethanol for 2 hours. Excess of alcohol was removed under reduced pressure and on adding very dilute ammonium hydroxide solution, a yellow oil separated out. The oil was extracted with ether, the ether extract was washed with water and then dried over anhydrous magnesium sulphate. After removing ether, the oil was heated with methyl-iodide (1.2 mole) in a sealed tube for 6 hours at 100° C. The solid methiodide, thus obtained, was recrystallised from absolute ethanol.

2-Methyl-4-(2'-furyl)-thiazole methiodide was prepared similarly from 2-acetyl furan.²

2-Amino- and 2-phenylamino derivatives of the above-mentioned thiazoles were obtained by condensation of the corresponding bromo-ketones with thiourea and phenyl thiourea respectively and the compounds were isolated in usual manner.

The analytical data and m.p., etc., of all these compounds are described in Table I.

TABLE I
4-(2'-Thienyl)- and 4-(2'-furyl) thiazole derivatives

Name of thiazole derivatives	MP °C.	Yield %	Percentage sulphur	
			Found	Calc.
4-(2'-Thienyl)-2-methyl-thiazole methiodide	189	70	19.63	19.81
4-(2'-Furyl)-2-methyl-thiazole methiodide	218(a)	65	10.27	10.43
4-(2'-Thienyl)-2-amino thiazole	128	70	35.01	35.16
4-(2'-Thienyl)-2-phenyl-aminothiazole	112	50	24.48	24.80
4-(2'-Furyl)-2-amino thiazole	117	60	18.82	19.27
4-(2'-Furyl)-2-phenyl-aminothiazole	107	45	12.81	13.22

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LEONHARDITE FROM A GRANITIC PEGMATITE IN NELLORE DISTRICT, ANDHRA PRADESH

DURING a systematic study of the mineralogy of the Nellore granitic pegmatites of Andhra Pradesh, leonhardite (a partly dehydrated variety of laumontite) is found to occur in cavities, measuring about 4 cm. in diameter, located in albite of a granitic pegmatite, situated at a distance of about 400 metres west of Nityakalyani mica mine in the Nellore District of Andhra Pradesh. The mineral is white in colour and is pulverulent. It shows good (010) and (110) cleavages. The sign of elongation of the mineral is both positive and negative. The mineral is analysed by an adaptation of the method of Shapiro and Brannock¹ and the chemical and optical data of the mineral are furnished in Table I.

From the chemical data, it is seen that the mineral is essentially a calcium end-member, with a small amount of alkalis. According to Coombs,² the solid solution between the calcium and sodium end-members of laumontite may be both of the plagioclase type, in which Na and Si atoms simultaneously act as proxy for Ca and Al atoms, and of the zeolitic type, in which two alkali atoms replace one of Ca. The chemical analysis suggests that the solid solution between the two end-members of the