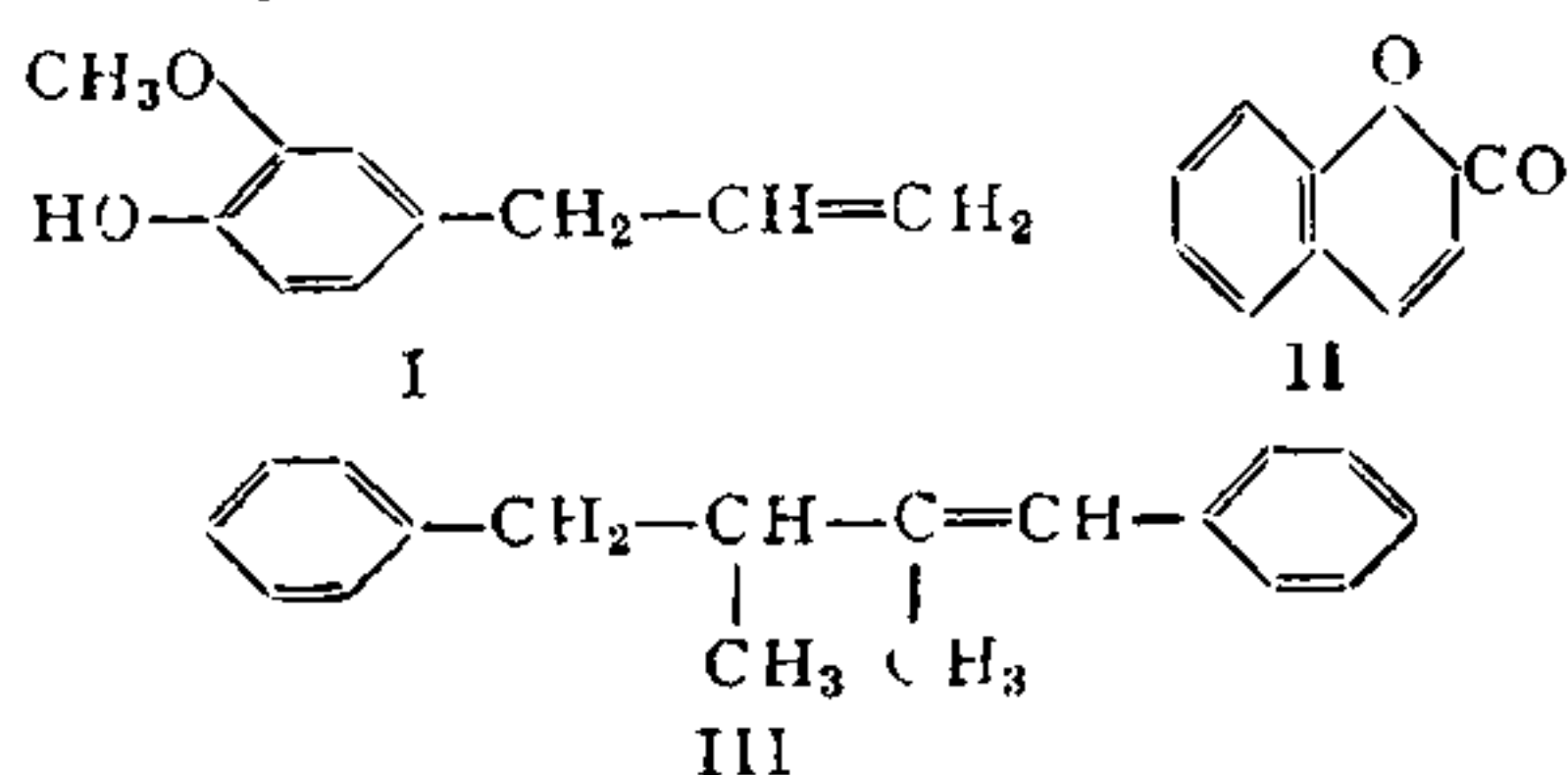


OCCURRENCE OF C₉ (FORKED) UNITS IN POLYPORIC AND PULVINIC ACID DERIVATIVES

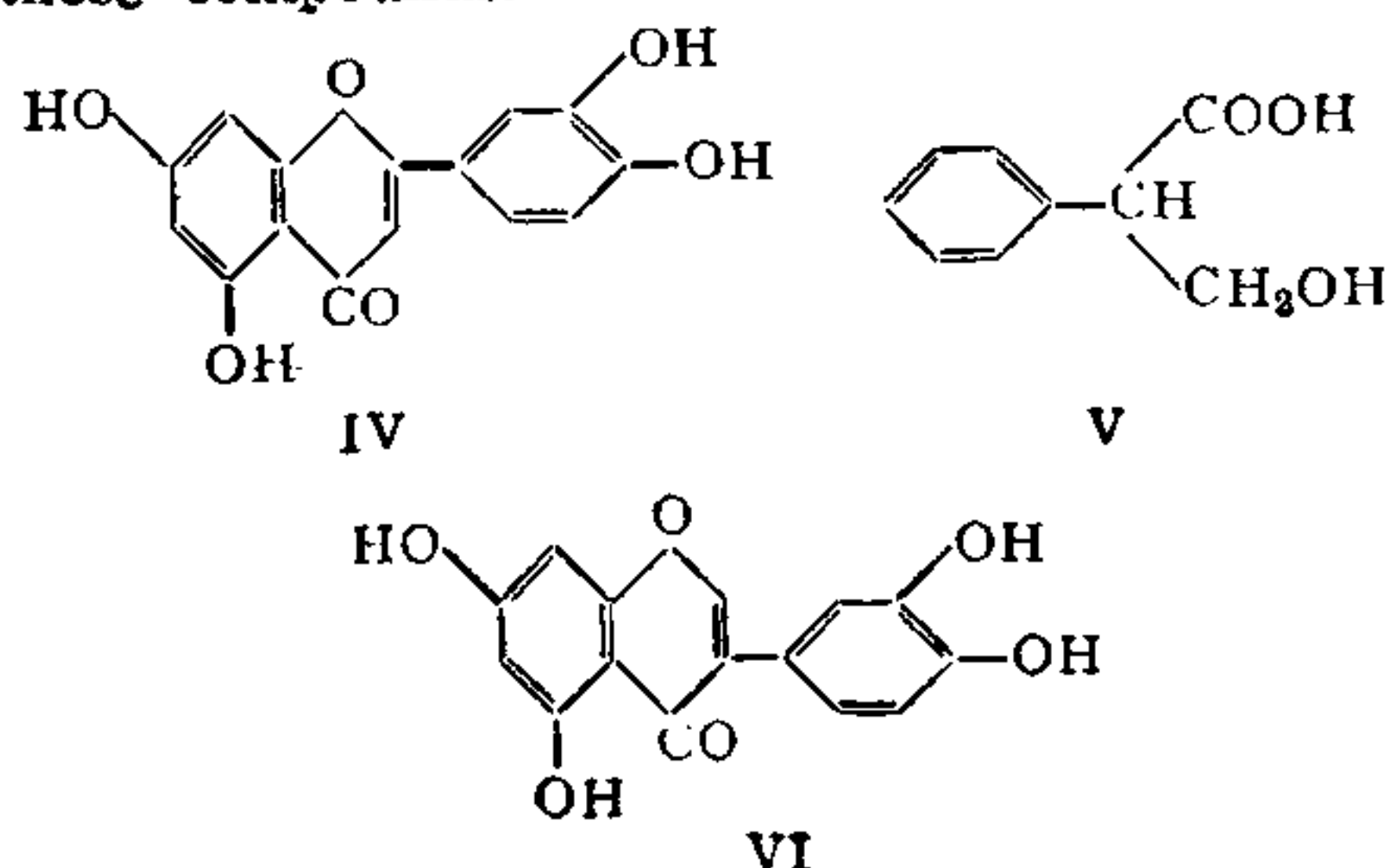
O. P. MITTAL AND T. R. SESHADRI

Dept. of Chemistry, Delhi University, Delhi-8

THE C₉ unit, also expressed as C₆-C₃ unit, is of common occurrence in nature and is found in several groups of compounds. Essential oils, probably, are the largest natural sources and members of the eugenol group (I) including cinnamyl alcohol and cinnamic acid are the most important and numerous. Lignin which is so widely distributed seems to be based on a skeleton, built of similar C₉ units. A small variation in the pattern leading to lactone ring closure yields coumarins (II) which are widely found in plants.



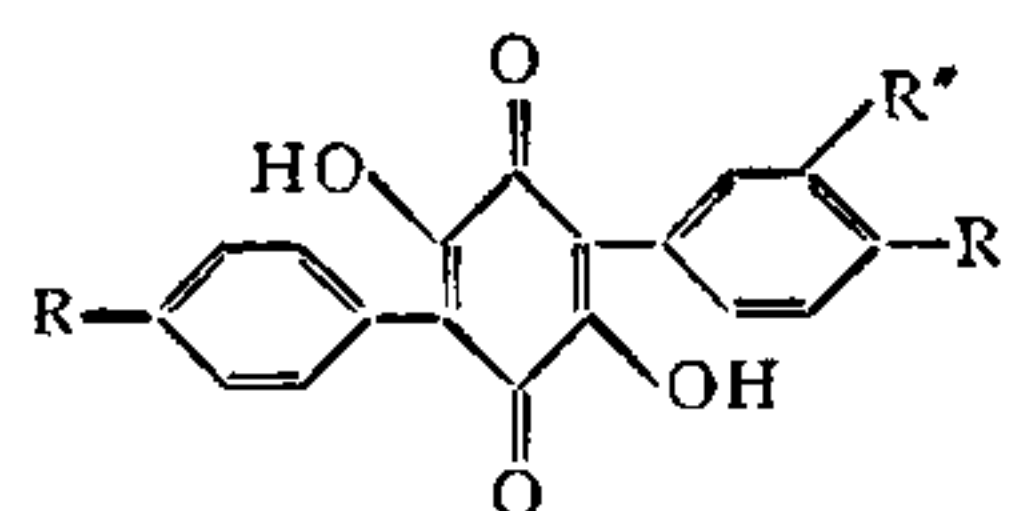
As representing compounds derived from two C₉ units may be mentioned, the lignan group, abundantly found in the heartwoods and overflow resins of plants belonging to the family 'Coniferae'. This group has been studied in great detail and a large number of compounds have been isolated and examined. Invariably the two units are linked at the β -positions (III), and subsequent variations lead to the production of five important sub-groups of these compounds.



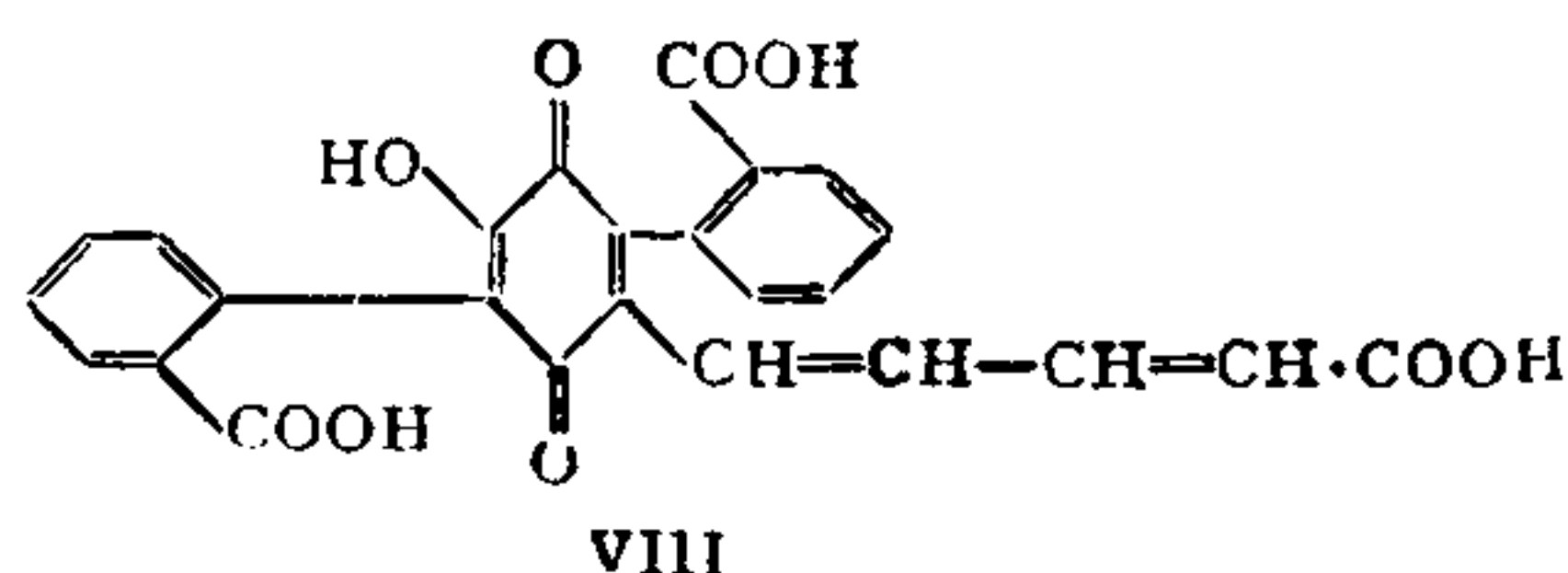
The C₉ unit of the above type showing a straight chain arrangement of three carbon atoms is considered to be present in the large number of compounds belonging to the group of flavonoids (IV). In these compounds this C₉ unit is condensed with a C₆ unit, most commonly phloroglucinol, and the variations in the bridge of three carbon atoms produce a large number of types (see Seshadri¹).

The forked arrangement represented by tropic acid (V) does not seem to be so common in simple members. It has been considered to be present in the make-up of the iso-flavonoids (VI) which have a phenyl ring in the 3 position (see Seshadri¹). C₁₈ compounds derived from the forked pattern of C₉ units seem to be represented by two groups most commonly found in fungal metabolites and in lichens and named polyporic acid derivatives (terphenyl quinones) and pulvinic acid derivatives.

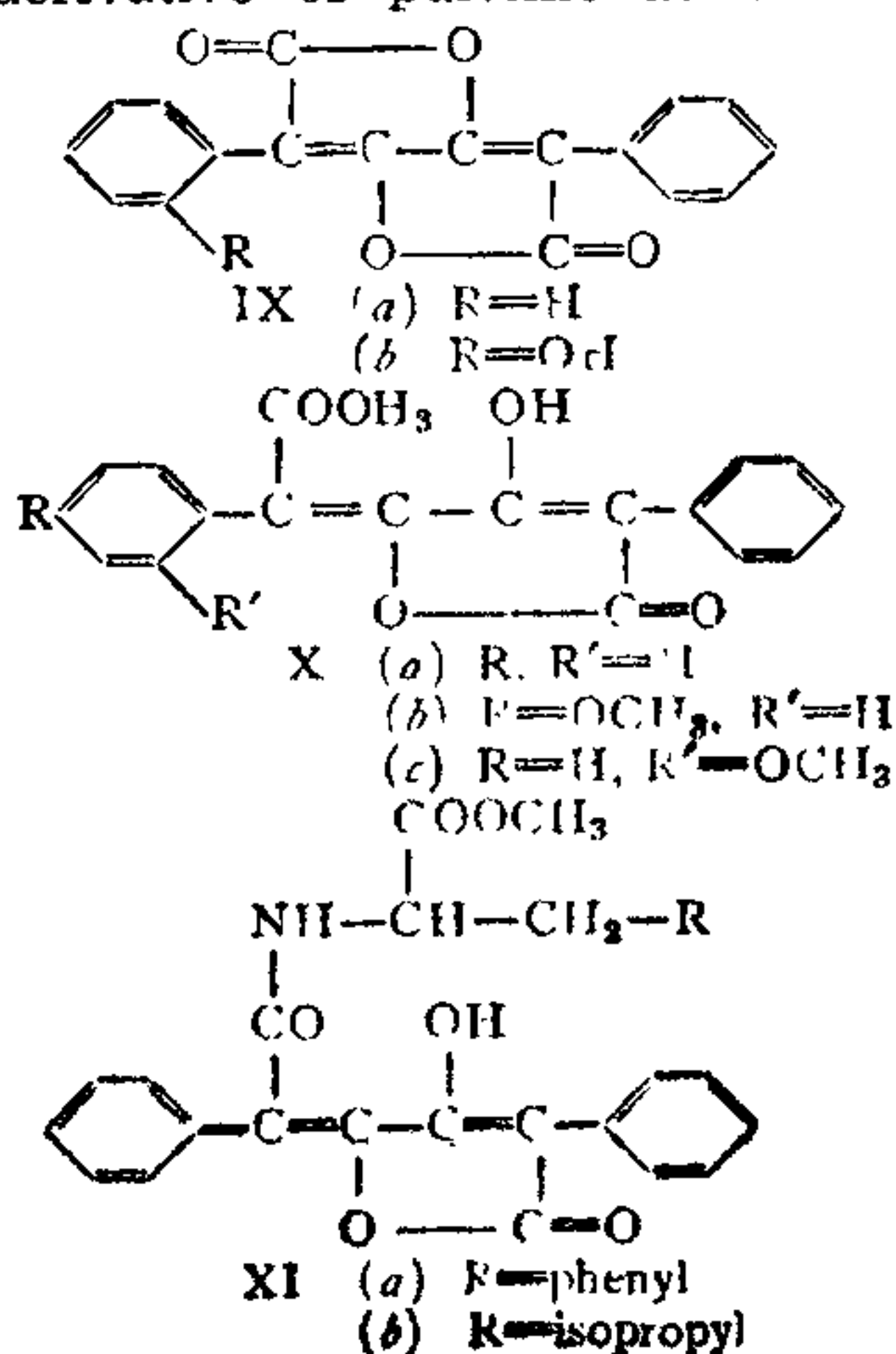
1. *Terphenyl quinones* (polyporic acid derivatives).—There are four compounds belonging to this group: (a) *Polyporic acid*² (C₁₈H₁₂O₄) (VIIa) has been isolated from the fungi, *Polyporus purpurascens* and *Polyporus nidulans* and also from the lichen *Sticta coronata* Mull. Its structure has been established as 3:6-dihydroxy-2:5-diphenyl-1:4-benzoquinone. (b) *Atromentin*³ (C₁₈H₁₂O₆) (VIIb) is present in *Paxillus atrotomentosus*, a fungus which frequently appears on old fir trees. It is dihydroxy polyporic acid having the extra hydroxyl groups in the 4 and 4' positions. (c) *Leucomelone*⁴ (C₁₈H₁₂O₇) (VIIc) has been isolated by Akagi and Hirose from *Polyporus leucomelas*, a black mushroom found in Japan. It contains one hydroxyl group more than atromentin and its structure has been established as 3' hydroxy atromentin. (d) *Muscarufin*⁵ (C₂₅H₁₆O₉) (VIII) is the colouring matter of the fly fungus (*Amanita muscaria*) and occurs probably as a glycoside. The constitution proposed for it by Kögl and Erxleben is more complex and unusual, being 2':2''-dicarboxy-6-hydroxy-3(α -carboxybutadiene)-1:4-benzoquinone.



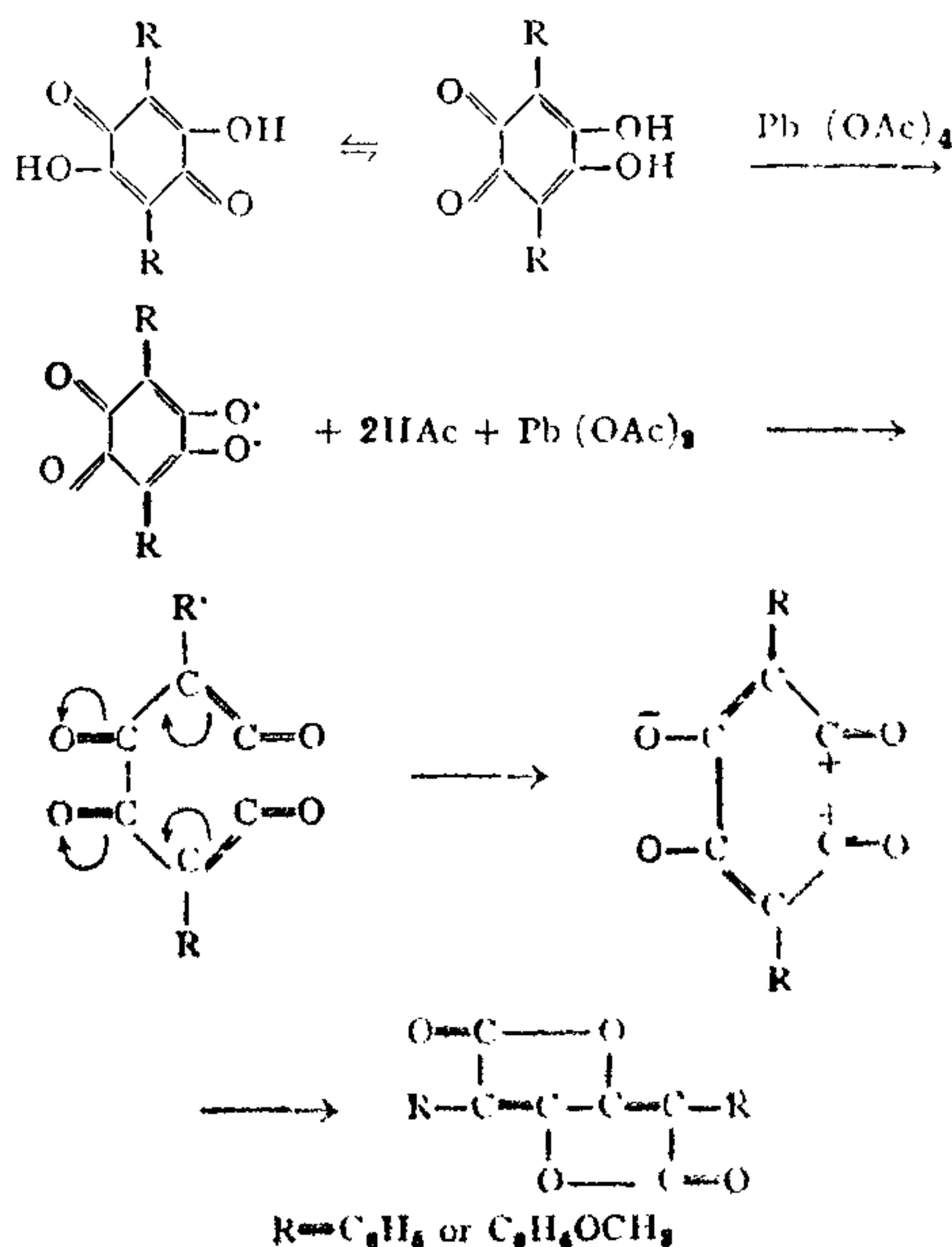
VII (a) R, R', R''=H
(b) R, R'=OH, R''=H
(c) R, R', R''=OH



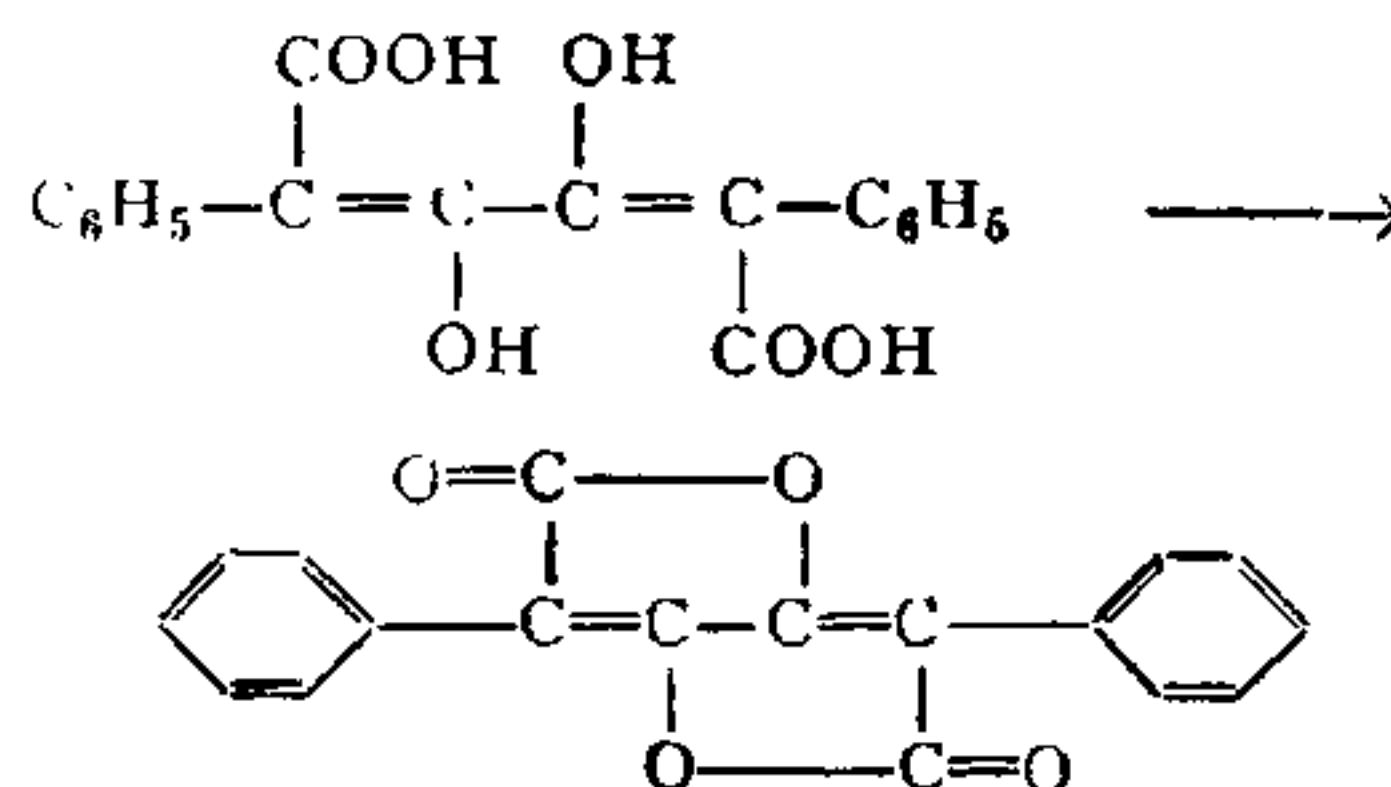
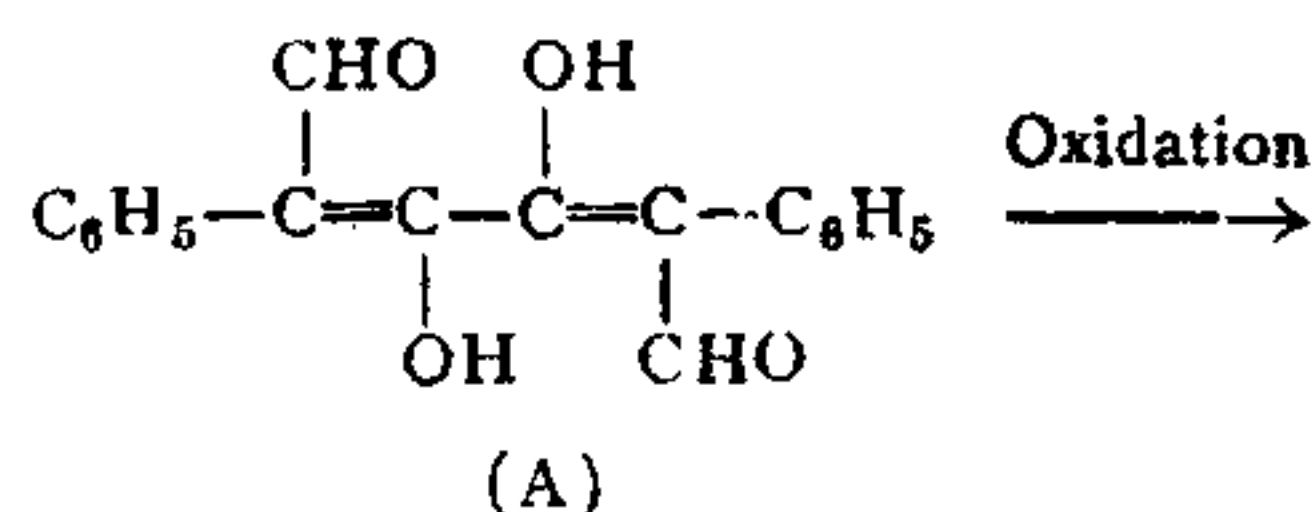
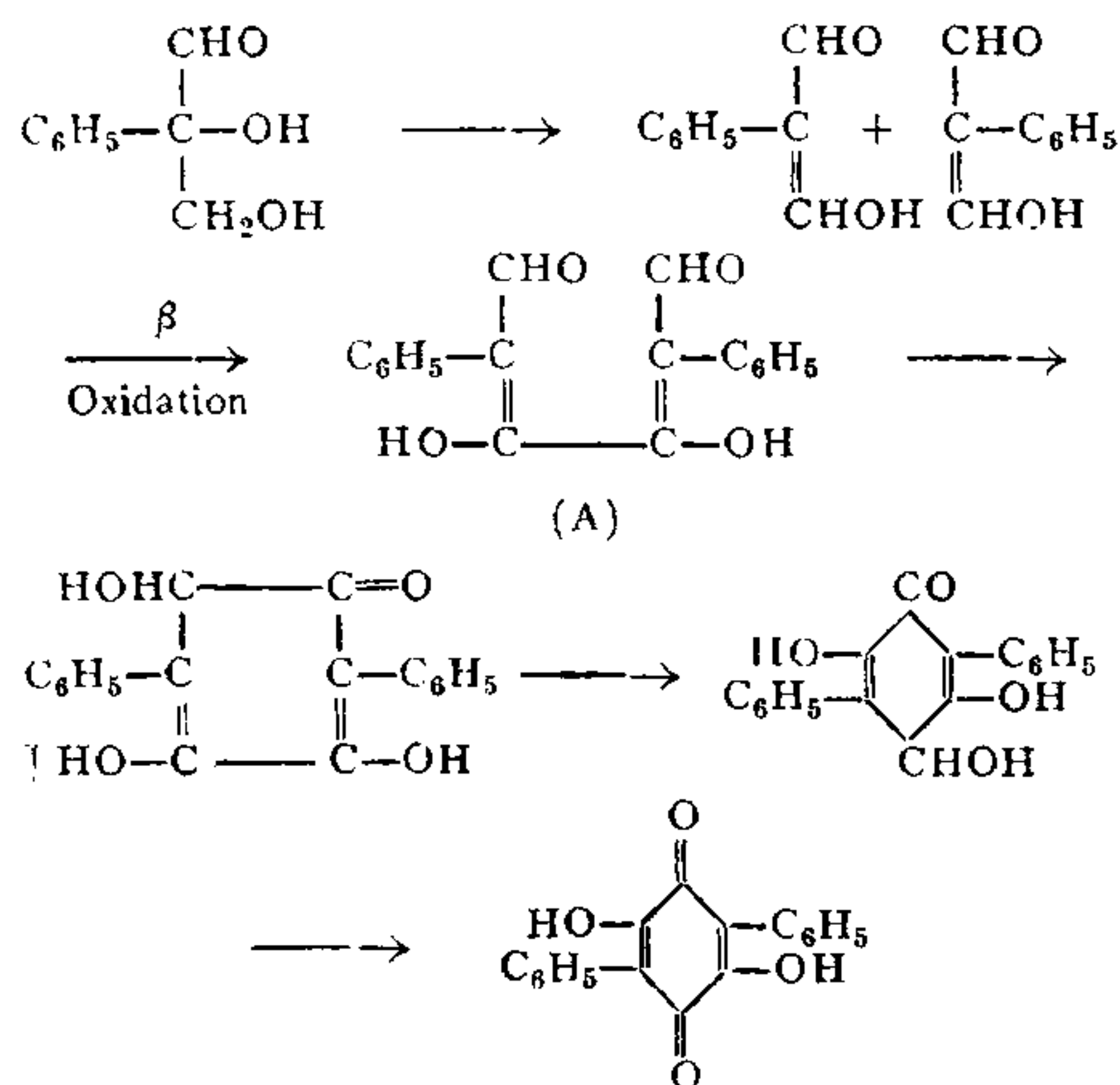
2. *Pulvinic acid derivatives*: (a) *Pulvinic dilactone*⁶ (C₁₈H₁₀O₄) (IX a) is the simplest compound of this group. It occurs in the lichen *Sticta aurata* and is accompanied by another compound of this series, calycin. (b) *Calycin* (C₁₈H₁₀O₅) (IX b) has been obtained from a number of *Calycium*, *Lepraria* and *Sticta* species. Its constitution has been shown to be *o*-hydroxy pulvinic dilactone. (c) *Vulpinic acid*⁷ (C₁₉H₁₄O₅) (X a) was first isolated from *Evernia vulpina* and it also occurs in a number of other lichens, viz., *Cyphelium chrysophalum*, *Calycium chlorinum*, *Cetraria juniperina*, *Cetraria pinastri*, *Lepra chlorina* and *Parmelia perlata*. Its structure was established as the methyl ester of pulvinic acid. On hydrolysis with baryta it yields pulvinic acid, which on heating alone or with acetic anhydride changes into pulvinic dilactone (IX a). (d) *Pinastric acid*⁶ (C₂₀H₁₆O₆) (X b) has been isolated from *Cetraria pinastri*, *C. tubulosa*, *C. juniperina* and also from *Lepraria flava*. Its structure has been established to be *p*-methoxy vulpinic acid. (e) *Lepra-pinic acid*⁸ (C₂₀H₁₆O₆) (X c) is an isomeric compound occurring in *Lepraria citrina*; and it has the methoxyl in the ortho position. (f) *Rhizocarpic acid* (C₂₈H₂₃O₆N) (XI a) is an optically active compound occurring in a number of lichens and was isolated by Zöpf from *Rhizocarpon geographicum*. Nolan and co-workers showed it to be a compound of pulvinic acid and phenyl alanine methyl ester which was confirmed by its synthesis by Frank, Cohen and Coker.⁹ (g) *Epanorin*⁹ (C₂₅H₂₅O₆N) (XI b) isolated by Zöpf from *Lecanora epanora* was found to be methyl leucine derivative of pulvinic acid.



Compounds of the polyporic acid group have been found to occur in higher fungi, though polyporic acid itself is present also in the lichen *Sticta coronata* Mull. Those belonging to the pulvinic acid group are found exclusively in lichens. However, there is reason to believe that they are products of the fungal half of the lichens. The similarity between the two groups is shown by the following: (1) formation of similar degradation products from both of them, (2) ready conversion of a terphenyl quinone, e.g., polyporic acid into a dilactone, e.g., pulvinic dilactone. Quite early it was noted by Kögl and Becker³ that the oxidation of atromentin with alkaline hydrogen peroxide yields *p*-hydroxy benzoic acid, but if the medium is acidic, then 4:4'-dihydroxypulvinic dilactone is formed as one of the oxidation products. Oxidation with lead tetra acetate in the cold is much better and gives excellent yields. Frank, Clark and Coker¹⁰ were the first to employ this reaction for converting polyporic acid into pulvinic dilactone. Atromentin dimethyl ether has now been found to undergo this change more satisfactorily to yield 4:4'-dimethoxy-pulvinic dilactone. Based on the findings of Criegee¹¹ on the specific action of lead tetra acetate on glycols, the above oxidation can be considered to proceed in the following manner (see also Waters¹²). The pulvinic acid type of compounds represent therefore a higher state of oxidation.



3. The pulvinic acid derivatives are obviously made up of two C_9 units of the forked type. Based on the principle of β -linking of C_9 units, the polyporic acid derivatives also should consist of two such units. Hence both the structures may be considered to be derived from the same precursor, viz., two units of β -phenyl glyceric aldehyde (see Seshadri¹) or structure A. Though no precise information is available on the details, the following tentative suggestion is made on the possible route of biosynthesis of the two types.



1. Seshadri, T. R., *Annual Review of Biochemistry*, 1951, **20**, 501.
2. Kögl, F. and Becker, H., *Ann.*, 1926, **447**, 78.
3. —, *Ibid.*, 1928, **465**, 211.
4. Akagi, M. and Hirose, K., *J. Pharm. Soc., Japan*, 1942, **62**, 191, 195, 199 (*C.A.*, 1951, **45**, 6169).
5. Kögl, F. and Erxleben, H., *Ann.*, 1930, **479**, 11.
6. Asano, M. and Kameda, Y., *Ber.*, 1935, **68**, 1565.
7. Hesse, O., *J. Pr. Chem.*, 1898, **57**, ii, 306, 316.
8. Mittal, O. P. and Seshadri, T. R., *J.C.S.*, 1955, 3053.
9. Frank, R. L., Cohen, S. M. and Coker, J. N., *J.A.C.S.*, 1950, **72**, 4454.
10. Frank, R. L., Clark, G. R. and Coker, J. N., *Ibid.*, 1950, **72**, 1824.
11. Criegee, R., *Ber.*, 1931, **64**, 260.
12. Waters, W. A., *Ann. Rep. Chem. Soc.*, 1945, 144.

DETECTION OF THE NEUTRINO

THE existence of the free neutrino has been experimentally established by a group of scientists led by Frederic Reines and Clyde Cowan, Jr., at the United States Atomic Energy Commission Laboratories.

Over 20 years ago, Fermi and Pauli theorized on the existence of such a particle in order to account for the mysterious disappearance of energy from beta decay. However, the neutrino has hitherto escaped the direct detection deemed necessary to prove its existence in the free state away from the radioactive atom from which it is emitted.

The neutrino interacts only very weakly with material, and could be expected to penetrate a distance of many light years through solid matter. Consequently, the detector used is of extraordinary design. In it more than 100 gal-

lons of ordinary water containing a dissolved cadmium salt served as a target for the neutrinos coming from the reactor. This target was "watched" by a scintillation system, which is in principle like the scintillation detector used by uranium prospectors but which contained over 1,000 gallons of sensitive liquid and 330 large photomultiplier tubes. Despite its huge size and the many billions of neutrinos from the reactor which passed through it each second, only a few neutrino captures were observed in the target water each hour.

During the experiment normally stable protons (hydrogen atoms in the water) were made to absorb a neutrino, emit a positive electron, and become neutrons, and the discovery marks the first time that man has knowingly caused a direct reversal of beta-decay.