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TERPENOIDS—XXV*

STRUCTURE OF SAUSSUREA LACTONE

A. SOMASEKAR RAO, A. PAUL, SADGOPAL† and S. C. BHATTACHARYYA
National Chemical Laboratory, Poona, India

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Abstract—Saussurea lactone is identical with the product of pyrolysis of dihydrocostunolide. On cyclisation in the presence of p-nitrobenzoic acid followed by hydrogenation it gives santanolide C. Hence structure (V) is assigned to saussurea lactone.

COSTUS root oil obtained from the plant *Saussurea lappa* C. B. Clarke has been well known for its lactonic constituents. Of these, dehydrocostus lactone,[1] costunolide (I)[2,3] and 12-methoxy-dihydrocostunolide(II)[4] have been completely characterized. From vacuum distilled (60–210°/11 mm) costus root oil Rao and Varma[5] isolated a crystalline lactone which they have named as saussurea lactone. In a subsequent communication Rao *et al.*[6] suggested a tentative bicyclic structure (III) for this lactone on the basis of degradative studies. The possibility of the santenolide type of structure (IV) was not entirely ruled out. According to them, the lactone has the molecular formula $C_{15}H_{22}O_2$ and contains one double bond of the type $=CH_2$. They obtained 1-methyl-7-ethyl naphthalene on selenium dehydrogenation.

Investigations described in the present communication show that saussurea lactone is to be represented by the structure (V).

At the initial stages of our investigations, it was felt that a comparison of fully hydrogenated product from saussurea lactone (V) with the various santanolides or alantolides would be of help in firmly establishing its structure and possibly in elucidating its stereochemistry, but this did not lead to any fruitful result, as fully hydrogenated saussurea lactone could not be identified with any of the santanolides or alantolides. It was therefore felt that the structure of saussurea lactone required a more critical examination.

Earlier authors[6] have described saussurea lactone as a monoethynoid compound, but more careful examination showed that saussurea lactone does not contain one double bond, but contains two double bonds and hence is a monocarbocyclic compound and not a bicyclic product as previously postulated. Consequently the previous structure (III) required revision.

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* Contribution No. 429 from the National Chemical Laboratory, Poona, India.

† Indian Standards Institution, Delhi.

[1] M. Romanuk, V. Herout and F. Sorm, *Coll. Czech. Chem. Comm.* **21**, 894 (1956) and references cited therein.

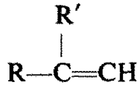
[2a] A. Somasekar Rao, G. R. Kelkar and S. C. Bhattacharyya, *Tetrahedron* **9**, 275 (1960); [b] *Chem. & Ind.* 1359 (1958); [c] *Chem & Ind.* 1069 (1959).

[3] V. Herout and F. Sorm, *Chem. & Ind.* 1067 (1959).

[4] Part XXIV: *Tetrahedron* **12**, 178 (1961).

[5] P.S. Rao and B. S. Varma, *J. Sci. Ind. Res.* **10B**, 166 (1951).

[6] P. S. Rao, B. S. Varma, N. R. Ghosh and P. C. Dutta, *J. Sci. Ind. Res.* **17B**, 228 (1958).



The I.R. spectrum of saussurea lactone (V) showed the presence of both types of methylenic double bonds (i) $R.CH{=}CH_2$ (909 cm^{-1}), (ii) $R\text{—}\overset{R'}{\overset{|}{C}}{=}CH_2$ (892 cm^{-1}). In view of this and the conversion of saussurea lactone (V) to 1-methyl-7-ethyl naphthalene it was suspected that saussurea lactone may have the elemane type of carbon skeleton. Rao and Varma[5] obtained saussurea lactone (V) from costus root oil distilled at high temperature. In connexion with our work,[7] involving large amounts of costus root oil isolated and processed under very mild conditions without employment of any thermal treatment and involving mostly column chromatography, we failed to isolate any saussurea lactone, but such oil contains large amounts of costunolide (I) and also appears to contain dihydrocostunolide (VI). Hence it was felt that saussurea lactone (V) was derived from the pyrolysis of the latter (VI).

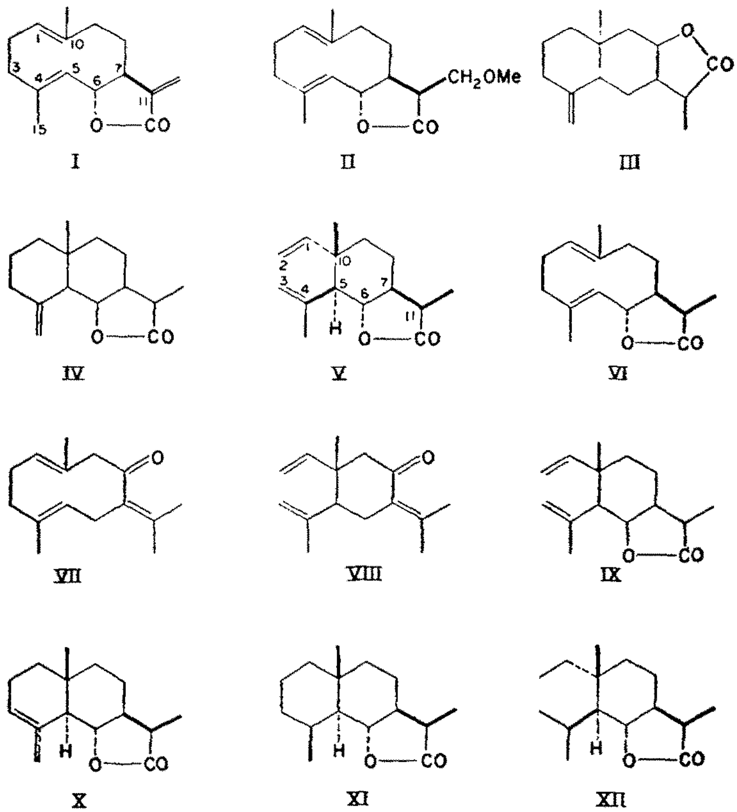


FIG. 1.

To prove the validity of this assumption pyrolysis of dihydrocostunolide (VI) prepared from costunolide (I) was carried out and the product was found to be identical with saussurea lactone (V). On the basis of the earlier work dealing with the

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[7] A. Paul, A. S. Bawdekar, R. S. Joshi, G. H. Kulkarni, A. Somasekar Rao, G. R. Kelkar and S. C. Bhattacharyya, *Perf. & Ess. Oil Rec.* **51**, 115 (1960).

pyrolysis of germacrone (VII) to pyrogermacrone (VIII)[8,9] the gross structure (IX) can be assigned to saussurea lactone. Such a structure is also consistent with its I.R. spectrum discussed earlier. In addition, this also establishes the absolute configuration of saussurea lactone at C_6, C_7 and C_{11} since the absolute configuration of dihydrocostunolide (VI) is known.[2,3]

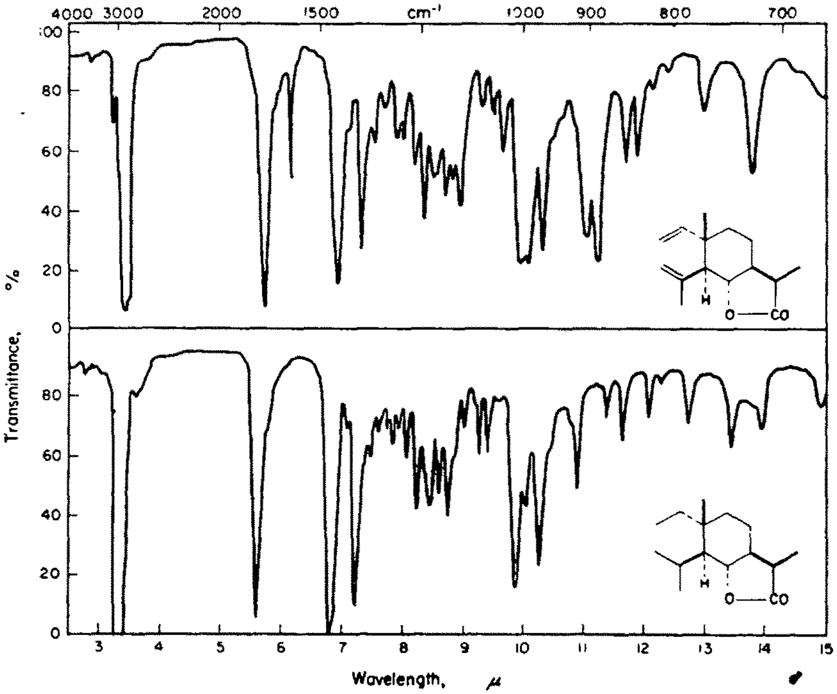

FIG. 2. I.R. spectra (in Nujol) of saussurea lactone and tetrahydrosaussurea lactone.

To determine the absolute configuration at the remaining asymmetric centres, C_{10} and C_5 saussurea lactone (V) was cyclized by heating with *p*-nitrobenzoic acid[10] to a monoethynoid bicyclic product. The exact position of the double bond in the cyclized product (X) has not been determined; but the U.V. and the I.R. spectra of the cyclized product excluded the presence of the Δ^4-isomer (tetrasubstituted double bond) and indicated that it was a mixture of Δ^3 and $\Delta^{4(15)}$ isomers in which the former predominated. This is supported by a comparison of the m.p. and rotation of the cyclized product with those of the Δ^3 isomer reported previously by Cocker and McMurry[11]. It became necessary to investigate this aspect as an unsaturated lactone with the double bond between carbon atoms C_4 and C_5 cannot be of much value in determining the absolute configuration at C_5. The cyclized product (X) on hydrogenation gave santanolide C.[2,3] This leads to the unambiguous assignment of the absolute configuration to saussurea lactone (V) at all the centres of asymmetry.

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[8] I. Ognjanov, V. Herout, A. Horak and F. Sorm, *Coll. Czech. Chem. Comm.* **24**, 2371 (1959).

[9] G. Ohloff, H. Farnow, W. Phillipp and G. Schade, *Liebigs Ann.* **625**, 206 (1959).

[10] W. Wicki, J. Kalvoda and O. Jeger. *Croatica Chem. Acta* **29**, 263 (1957); *Chem. Abstr.* **53**, 16197e (1959).

[11] W. Cocker, and T. B. H. McMurry, *J. Chem. Soc.* 4549 (1956).

It would appear that saussurea lactone (V) is not a natural constituent of costus root oil, but is an artefact formed by pyrolysis of dihydrocostunolide (VI).

EXPERIMENTAL

All melting points are uncorrected. Rotations were taken in chloroform. Ultra-violet spectra were determined in alcohol solution on Beckman DK-2 recording spectrophotometer. Infra-red spectra were determined with Grubb Parson spectrophotometer and Perkin-Elmer infracord spectrophotometer. Microanalyses were carried out by Mr. Pansare and colleagues.

Saussurea lactone (V)

The saussurea lactone used at the initial stages of the present work was obtained from the personal collection of samples of Dr. Sadgopal. It was crystallized repeatedly from methanol. m.p. 148–149°, $[\alpha]_D = +66°$, lit.[5,6] records for saussurea lactone m.p. 146–147°, $[\alpha]_D$ +57°, +62°. (Found: C, 76·9; H, 9·6. $C_{15}H_{22}O_2$ requires C, 76·88; H, 9·46%). U.V. spectrum: no peak in the region 210–340 mμ, ε_{210}, 1300.

I.R. spectrum (in Nujol): Bands at 1760, 1633, 1450, 1374, 1334, 1310, 1276, 1258, 1228, 1207, 1187, 1178, 1158, 1146, 1127, 1080, 1060, 1041, 1007, 996, 974, 943, 909, 892, 856, 840, 826, 812, 774 and 727 cm^{-1}.

Hydrogenation of saussurea lactone (V)

Saussurea lactone (0·814 g) was hydrogenated in acetic acid solution in the presence of platinum oxide (80 mg) catalyst. The amount of hydrogen taken up (180 ml at 27° and 710 mm) corresponded to the presence of two double bonds. The catalyst was filtered off. From the filtrate acetic acid was removed on steam bath with water pump. The residue was taken up in ether and washed with sodium carbonate solution. The solid left after removal of ether was crystallized three times from ethanol and sublimed to give the tetrahydrosaussurea lactone (XII), m.p. 123–125°, $[\alpha]_D^{27} = +42°$ (C, 7·0) (Found: C, 75·8; 75·8; H, 10·9; 11·2. $C_{15}H_{26}O_2$ requires C, 75·58; H, 11·00%).

I.R. spectrum (in Nujol): Bands at 1760, 1444, 1374, 1333, 1315, 1285, 1271, 1257, 1236, 1207, 1175, 1158, 1139, 1124, 1102, 1073, 1057, 1037, 1005, 991, 968, 914, 873, 853, 823, 811, 782, 742, 714 cm^{-1}.

Pyrolysis of dihydrocostunolide (VI)

Dihydrocostunolide (VI) was prepared from costunolide by following the procedure described earlier.[8a] It had m.p. 77–78°, $[\alpha]_D + 114°$.

Dihydrocostunolide (1 g) was taken in a sublimation apparatus and heated at 200–220° at 50 mm for 20 min. Subsequently the pressure was reduced and the sublimation completed. The process was repeated with the sublimed product once more. The material obtained after two sublimations was crystallized three times from ethanol and again sublimed (120°/0·5 mm) to give a solid (yield 0·4 g) m.p. 147–148°, mixed m.p. with saussurea lactone was undepressed. $[\alpha]_D = +66°$ (C, 3·0). (Found: C, 77·3; H, 9·7. $C_{15}H_{22}O_2$ requires C, 76·88; H, 9·46%). I.R. spectrum was identical with that of saussurea lactone.

Cyclization of saussurea lactone (V)

A mixture of saussurea lactone (0·75 g) and *p*-nitrobenzoic acid (0·5 g) was heated at 180–190° for 4 hr in nitrogen atmosphere. The reaction product was taken up in ether and washed with sodium carbonate solution to remove *p*-nitrobenzoic acid. Ether was evaporated from the neutral ether extract and the residue was sublimed (120°/0·5 mm). It was then crystallized three times from ethanol and again sublimed to give the cyclized product (X) (yield 0·31 g); m.p. 129–131°, $[\alpha]_D = +109°$ (C, 3·3), lit.[11] records for sant-3-enolide m.p. 136–137°, $[\alpha]_D = +91°$. (Found: C, 76·72; H, 9·45. $C_{15}H_{22}O_2$ requires C, 76·88; H, 9·46%); U.V. spectrum ε_{210} 2200; ε_{215} 1000; ε_{220}, 350.

Hydrogenation of the lactone (X)

The cyclized product (X) (0·20 g) from the above experiment was hydrogenated in acetic acid in the presence of platinum oxide (50 mg) catalyst at room temperature and atmospheric pressure and hydrogen approximately corresponding to one double bond was absorbed. The hydrogenation product was worked up in the usual way. It was crystallized twice from ethanol and sublimed to give 130 mg of a solid which was identified as santanolide C from its melting point and mixed m.p. with an authentic sample 151–153°, $[\alpha]_D = +56°$ and identity of its I.R. spectrum with that of santanolide C. (Found: C, 75·9; H, 10·0. $C_{15}H_{24}O_2$ requires C, 76·22; H, 10·24%), lit.[2a,3] records for santanolide C, m.p. 154–155°, 153–154°, $[\alpha]_D$ +55°.