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# COMPONENTS OF THE ROOT OF *LINDERA STRYCHNIFOLIA* VILL.—XI[1]

## CONFIGURATION OF THE CYCLOPROPANE-RING IN LINDERENE AND THE STRUCTURE OF ISODIHYDROLINDERENE

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**Abstract**—Linderene and its dihydro-derivatives were converted to the corresponding unsaturated enol lactones (III, IXa and XIIa) by the action of dichlorodicyanobenzoquinone. These unsaturated enol lactones (IXa and XIIa) gave the triene lactones (XVI and XVII). Configuration of the cyclopropane ring in linderene was assigned as $\beta$ from the results of the NMR spectra of XVI and XVII. The structure of isodihydrolinderene was also confirmed by comparison of the NMR spectra of XIIa and its acetate (XIIb).

THE structure of linderene, a sesquiterpenic component of the root of *Lindera strychnifolia* Vill., was recently revised by us[1] as I, from the results of the NMR and IR studies of its hydrogenated derivatives, i.e. dihydro-, hexahydro- and octahydrolinderene.

*Oxidation of linderene and its derivatives with dichlorodicyanobenzoquinone*

We now attempted oxidation of the allylic hydroxyl group in linderene by means of dichlorodicyanobenzoquinone,[2] which was used on other steroidal derivatives. Surprisingly, instead of the expected ketone (II) two new crystalline compounds were isolated from the neutral fraction of the reaction mixture when linderene was treated with 3·0 equivalent mole of dichlorodicyanobenzoquinone in dioxan at 50° for several minutes.

The main product $C_{15}H_{18}O_3$ (III, yeild 24%), m.p. 150–151°, $[\alpha]_D^{26\cdot0}$ +67·4°, $\nu_{max}^{nujol}$ 3440, 1788, 1668, 1642, 890 cm$^{-1}$, $\lambda_{max}^{alc}$ 280 m$\mu$ ($\epsilon$ 25,600), shows no Ehrlich colour reaction and is shown to possess an unsaturated lactonic group from the results of the IR and UV spectrum. The NMR spectrum shows a vinylproton at 3·75 $\tau$ as a singlet but there is no signal corresponding furan ring. The other product, $C_{15}H_{18}O_3$ (IV), m.p. 179–181°, the minor one (yield 16·5%), $\nu_{max}^{nujol}$ 3265, 1658, 1555, 893, 883 cm$^{-1}$, $[\alpha]_D^{24\cdot5}$ −25·9° shows a positive Ehrlich colour test (purple). The NMR spectrum of IV is very similar to that of the parent compound and the only difference is the presence of an additional proton signal attached to a carbon bearing hydroxyl group. From these results the structure is tentatively assigned as IV, but no further investigation was made due to the lack of material.

The optical properties of the former lactonic substance is very similar to that of the

[1] Part X. K. Takeda, M. Ikuta and M. Miyawaki, *Tetrahedron* **20**, 2991 (1964); see also K. Takeda and M. Ikuta, *Tetrahedron Letters* No. 6, 277 (1964).

[2] A. Bowers, P. G. Holten, E. Necoechea and F. A. Kincl, *J. Chem. Soc.* 4057 (1961); [3] D. Burn, V. Petrow and G. O. Weston, *Tetrahedron Letters* No. 19, 14 (1960).

unsaturated enol lactone (VII), which was obtained by Hikino *et al.*[3] from the oxylactone (VI), the auto-oxidation product of atractylone (V) by dehydration. This unsaturated enol lactone (VII) is obtained directly when atractylon is treated with dichlorodicyanobenzoquinone at room temperature in dioxan, as expected. The hydroxylated derivative of atractylon corresponding to IV is not isolated in this case. The assumed structure of the unsaturated lactone obtained from linderene, represented by III, is thus strongly supported by this result of the oxidation reaction of atractylon with dichlorodicyanobenzoquinone.

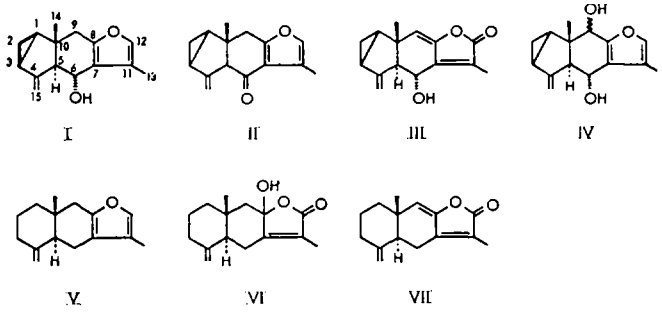


Chart 1

Dihydrolinderene (VIII), $C_{15}H_{20}O_2$, m.p. 125–127°, the reduction product of linderene, also undergoes this oxidation and gives an unsaturated enol lactone (IXa), m.p. 171–172·5°,* $C_{15}H_{18}O_3$, $\nu_{max}^{nujol}$ 3443, 1728, 1641, 1626 cm$^{-1}$, $\nu_{max}^{CCl_4}$ (3470), 1776, (1751), 1641 cm$^{-1}$, $\lambda_{max}^{alc}$ 284 m$\mu$ ($\epsilon$ 24,600), $[\alpha]_D^{26\cdot5}$ −50·0°, together with a small amount of the glycol (X), $C_{15}H_{20}O_3$, m.p. 202–203°: Ehrlich test: purple: $\nu_{max}^{nujol}$ 3241, 1550, 1041, 985 cm$^{-1}$, $[\alpha]_D^{26}$ −85·8°.

As reported earlier,[1] when linderene was catalytically reduced with Raney nickel there were obtained two isomeric dihydro derivatives in the ratio ca. 3:2, by careful separation through alumina chromatography. The structure of the predominant dihydro derivative, m.p. 125–127°, was already clarified as VIII but the structure of the minor isomer, $C_{15}H_{20}O_2$, m.p. 109–112°, $[\alpha]_D^{25\cdot6}$ −141·8°, $\nu_{max}^{CS_2}$ 3602, 1620, 1035 cm$^{-1}$, $\lambda_{max}^{heptane}$ 219·5 m$\mu$ ($\epsilon$ 7,400), remained unclear. Now the name "isodihydrolinderene" was given to this compound. The fact that isodihydrolinderene also does not have an exocyclic double bond was proven by the study of the NMR, IR and UV spectra. Therefore, the structure of isodihydrolinderene may be assumed to be a 15-epi-derivative (XI) of dihydrolinderene. But, as the step-wise reduction of isodihydrolinderene always gives impure oily hydrogenation products, no information about this structure was obtained. An attempt to acetylate isodihydrolinderene was unsuccessful as in the case of linderene or dihydrolinderene.

Similar treatment of isodihydrolinderene (XI) with dichlorodicyanobenzoquinone also gives an unsaturated enol lactone (XIIa), $C_{15}H_{18}O_3$, m.p. 172–173·5°, $[\alpha]_D^{26\cdot0}$ − 194·4°, $\nu_{max}^{nujol}$ 3466, 1754, 1645, 1633 cm$^{-1}$, $\lambda_{max}^{alc}$ 283–285 m$\mu$ ($\epsilon$ 21,700), and a glycol (XIII), m.p. 201–202°, $C_{15}H_{20}O_3$: Ehrlich colour test: purple: $\nu_{max}^{nujol}$ 3256, 1556, 1045, 983 cm$^{-1}$, $[\alpha]_D^{25\cdot5}$ −175·9°. Unsaturated enol lactone of the iso-derivative (XIIa) gives

* Dimorphism, m.p. 137–141°. $\nu_{max}^{nujol}$ 3520, 1758, 1661, 1636 cm$^{-1}$, is obtained in some lots.

[3] H. Hikino, Y. Hikino and I. Yosioka, *Chem. Pharm. Bull.* **12**, 755 (1964).

an acetate (XIIb), m.p. 83–89°, by the action of acetic anhydride in pyridine at room temperature.

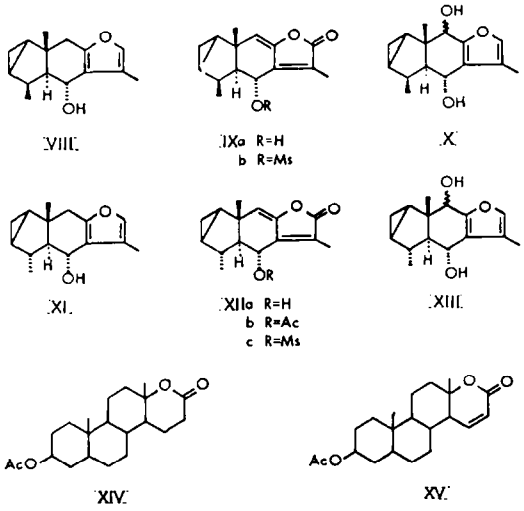



Chart 2

Although it was reported that the saturated lactone, such as XIV, underwent dehydrogenation with dichlorodicyanobenzoquinone and gave an unsaturated one (XV),[4] the fact that the furan ring converted directly to the unsaturated enol lactone as mentioned above by the same reagent is hitherto unknown and it seems to be very interesting reaction. This reaction may be initiated by the abstraction of the hydride ion at C-9 as in the case of the dehydrogenation reaction of $\Delta^4$-3-keto-steroid.[5,6] Further study of the mechanism of this oxidation reaction on the furan derivatives is now under investigation.

*NMR Study of the iso-dihydrolinderene derivatives*

The NMR spectral data on some examined compounds are listed in Table 1.

Singlet signals corresponding to the C-14 angular methyl groups of VIII and IXa appear at 9·20 and 9·00 $\tau$, respectively, whereas those signals in XI and XIIa are found at slightly higher fields, 9·29 and 9·12 $\tau$, respectively. However, the C-15 methyl group shows its signals as poor doublets at considerably lower fields, 8·66 and 8·67 $\tau$, for the cases of XI and XIIa, respectively, in contrast to the corresponding methyl signals of VIII and IXa, which appear at 9·04 and 8·98 $\tau$ as distinct doublets, respectively. These results suggest that the methyl group at C-15 in XI and XIIa has an $\alpha$-configuration, and accordingly, the methyl signal is affected by a non-bonded 1,3-interaction of the hydroxyl group at C-6 to suffer a downfield shift,[7] which turns the methyl signal into a poor doublet (the $A_3$-part of an $A_3B$ system).[8] In the alteration

[4] B. Berkoz, L. Cuéllar, R. Grezemkovsky, N. V. Avila and A. D. Cross, *Proc. Chem. Soc.* 215 (1964).

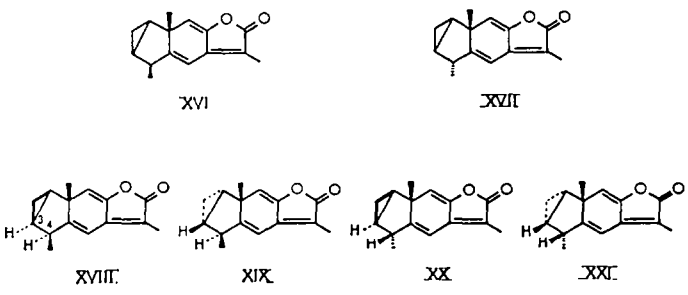
[5] H. J. Ringold and A. Turner, *Chem. & Ind.* 211 (1962).

[6] H. J. Brodie, M. Hayano and M. Gut, *J. Amer. Chem. Soc.* **84**, 3766 (1962).

[7] Y. Kawazoe, Y. Sato, M. Natsume, H. Hasegawa, T. Okamoto and K. Tsuda, *Chem. Pharm. Bull., Tokyo* **10**, 338 (1962).

[8] For example, see F. A. L. Anet, *Canad. J. Chem.* **39**, 2262 (1961).

in the signal pattern, an upfield shift of the C-4 proton (from $\alpha$- to $\beta$-configurations) by a shielding effect of the cyclopropane ring in these molecules might be implicated (*vide infra*).[9,10] The above suggestion was supported by comparison of the spectrum of XIIa with that of its acetate (XIIb). Together with other signals reasonably assigned as shown in Table 1, the subjected C-15 methyl signal in XIIb was found at 8·88 $\tau$ and turned into a distinct doublet and was shifted to a higher field in comparison with that of XIIa as anticipated.[7] Values of chemical shifts of the C-13 and C-14 methyl group and the C-6 proton of XIIb are also reasonable. Furthermore, the upfield shifts of the C-14 methyl signals in iso-series (XI and XIIa) can be explained by the disappearance of the 1,3-diaxial interaction between the C-14 and C-15 methyl groups.[11]



XVI XVII XVIII XIX XX XXI

Chart 3

*Configuration of the cyclopropane ring in linderene* (I)

Both unsaturated enol lactones (IXa and XIIa) were converted into the corresponding triene lactone (XVI), $C_{15}H_{16}O_2$, m.p. 102–104°, $\nu_{max}^{nujol}$ 1754, 1630 $cm^{-1}$, $\lambda_{max}^{alc}$ 300 m$\mu$ ($\epsilon$ 22,800), and an isomeric XVII, $C_{15}H_{16}O_2$, oil, $\nu_{max}^{film}$ 1765, 1637 $cm^{-1}$, $\lambda_{max}^{alc}$ 300 m$\mu$ ($\epsilon$ 27,700), *via* the mesylates (IXb), m.p. 112–114° and (XIIc), m.p. 160–161°, respectively.

Now we attempted to examine the NMR signal patterns of the C-4 proton in XVI and XVII in order to obtain information about the configuration of the cyclopropane ring in linderene (I).

As shown in Table 1, the C-4 proton signals in XVI and XVII appear at 6·85 and 7·35 $\tau$, respectively. The C-14 methyl signals of these two compounds are shifted to lower fields, as compared with those in IXa and XIIa, by introduction of the double bond between C-5 and C-6. Differences in the additional shift values of C-4 proton signals and the long-range spin–coupling between the C-6 and C-4 protons in XVI and XVII are also in accordance with the conclusion that these two compounds are isomers, differing only in the C-15 methyl configuration. An allylic long-range spin-coupling is known to be strongest when the dihedral angle between the $\pi$-orbital and an allylic methylene proton is 0° or 180°.[12]

The dihedral angle between the 3$\alpha$- and 4$\alpha$-hydrogens in XVIII is about 8–10° by

[9] For example, see K. Tori and K. Kitahonoki, *J. Amer. Chem. Soc.* **87**, 386 (1965).

[10] M. S. Bergqvist and T. Norin, *Ark. Kemi.* **22**, 137 (1964): K. Tori, *Chem. Pharm. Bull., Tokyo* **12**, 1439 (1964).

[11] For example, see G. Slomp and B. R. McGarvey, *J. Amer. Chem. Soc.* **81**, 2200 (1959).

[12] For a review, see S. Sternhell, *Rev. Pure. Appl. Chem.* **14**, 15 (1964); M. Barfield, *J. Chem. Phys.* **41**, 3825 (1964).

examination of Dreiding models and in the case of XIX the angle between the 3β- and 4α-hydrogens is about 76–78°. These facts imply that the coupling constant between the two protons at the positions 3 and 4 can be anticipated to be about 7–8 c/s in the former and to be almost 0 c/s in the latter case from the well-known Karplus equation.[13] Therefore, the signal pattern of the C-4 proton should be a quintet-like one or a quartet according to whether the configuration of the cyclopropane ring is

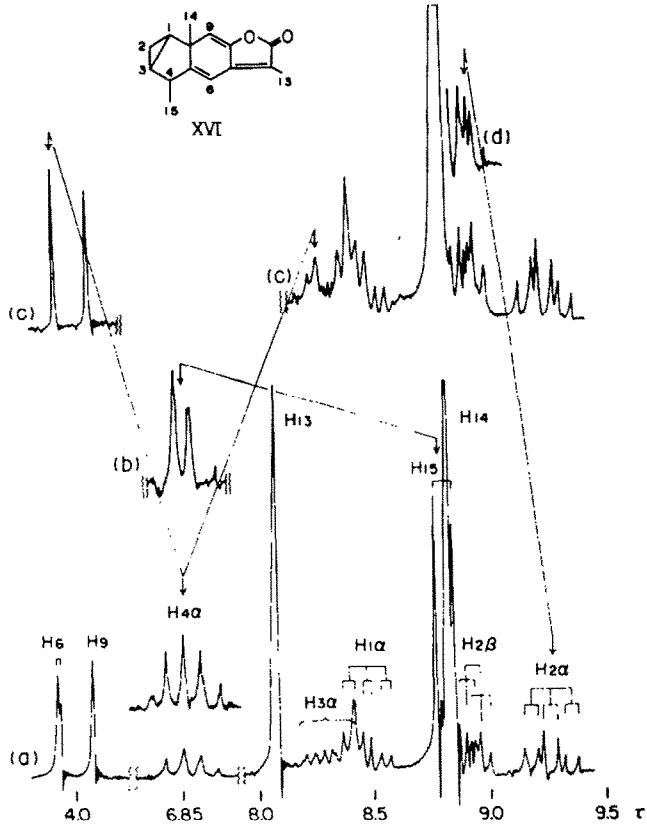



Fig. 1

β(XVIII) or α(XIX). Similarly in the iso-series, the coupling constant between the 3α- and 4β-protons in XX can be anticipated to be about 1–2 c/s (the angle = 110–112°) and that between the 3β- and 4β-protons in XXI to be about 4–5 c/s (the angle = 42–44°). In this case, the signal pattern of the C-4 proton should be nearly a quartet in XX and an octet-like one in XXI. The observed signal patterns in XVI and XVII actually agree well with those anticipated for XVIII and XX, although each peak is broadened by some long-range coupling effects.[12]

The above results obtained from 60 mc/s NMR spectra were further confirmed by proton spin-decoupling experiments at 100 mc/s field. The 100 mc/s spectra of XVI and XVII and some proton spin-decoupled patterns are shown in Figs. 1 and 2. As shown in Fig. 1(b), the slightly multipling quintet arising from C-4α proton

[13] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959).

collapsed to a slightly multipling doublet on double irradiation at the C-15 methyl proton frequency. This doublet (J = 7·0 c/s) results evidently from the coupling to the C-3 proton, as anticipated. Reverse double irradiation at the frequency of the C-4α proton caused the C-15 methyl proton doublet and the C-6 proton doublet due to the long-range spin coupling to degenerate to singlets [Fig. 1(c)]. Since this irradiation also altered the pattern around 8·2 ~ 8·4 τ, the signal at this region was

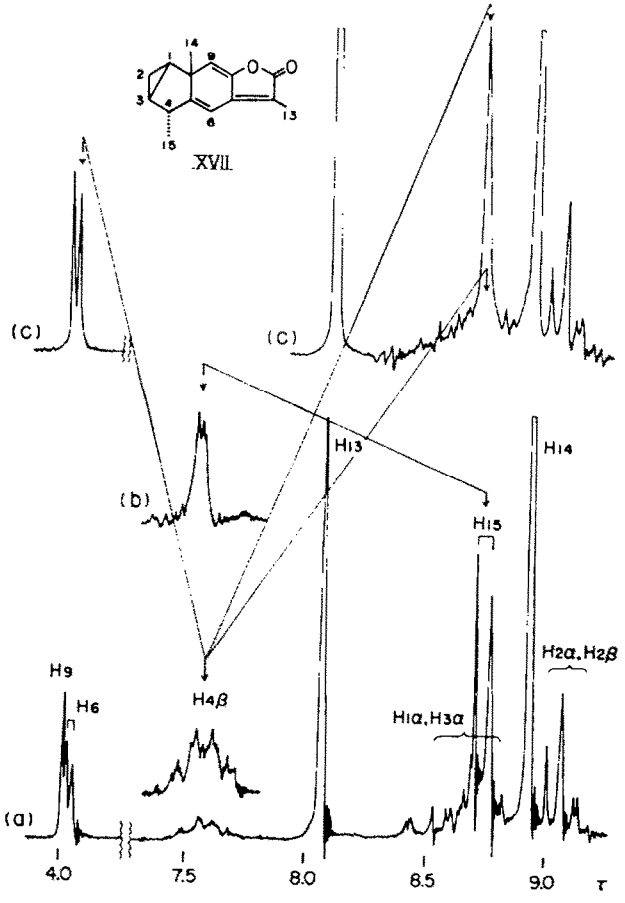



Fig. 2

revealed to arise from the cyclopropyl C-3α proton. Moreover, in this C-4α proton spin-decoupled pattern, a triplet of doublets (J = 4·2 and 6·0 c/s) appears obviously at 8·93 τ which can reasonably be ascribed to C-2β proton signal. This signal collapsed to a triplet (J = 4·2 c/s) on double irradiation at a cyclopropyl proton signal appearing as a triplet of doublets (J = 8·5 and 6·0 c/s) at 9·27 τ, [Fig. 1(d)]. This fact implies that this triplet of doublets arises from C-2α proton. Thus, similar triplet of doublets appearing at the highest field in the spectra of linderene (1) and its derivatives were revealed to arise from the C-2α proton (Table 1). On the other hand, the C-15 methyl proton spin-decoupled pattern of the C-4β proton signal is a slightly multipling doublet which results from the long-range spin-coupling to the C-6 proton, as shown

in Fig. 2(b). This fact was clarified by reverse double irradiation on the C-4$\beta$ proton [Fig. 2(c)]. Thus in this case, the coupling constant between the vicinal C-4$\beta$ and C-3 protons is nearly equal to zero, as anticipated earlier. Furthermore, in XVII cyclopropyl proton signals cannot strictly be assigned. The lower field shift of the C-2$\alpha$ proton signals in the iso-series would result from different anisotropic shielding effects of the C-15 methyl group. We might argue that the present application of the theoretically derived Karplus equation[13] to such highly strained ring systems as XVI and XVII is somewhat dangerous even in the absence of any heteroatoms in the systems because considerable attention to this subject has been provoked by several workers.[14] However, the above result in the configuration of the cyclopropane ring is not altered because the differences in the signal patterns anticipated from the molecular models are sufficient to reach the conclusion even though the matter would be treated in a more qualitative sense.

Furthermore, if the configuration of the cyclopropane ring would be $\alpha$, one of the proton signals due to this ring proton should move towards a very high field since the 2$\alpha$-cyclopropyl proton is situated within the shielding cone of the double bond between the positions 5 and 6, as shown in Fig. 3(b).[10] In reality, however, the proton signal due to a cyclopropyl proton is discernible at 9·28 $\tau$ in XVIII; this result might also support the $\beta$-configuration of the cyclopropane ring in linderene (1). The shielding effect of the cyclopropane ring[9] fused in $\beta$-configuration upon the C-14 methyl and C-4 protons also reasonably reflects their signal positions as described earlier.[10]

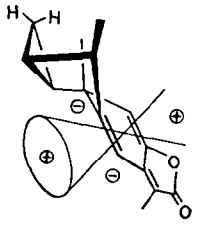


Fig. 3a

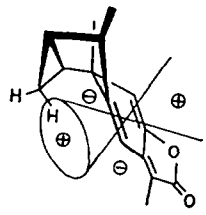


Fig. 3b

## EXPERIMENTAL

The NMR spectra were taken with a Varian A-60 spectrometer by using $CDCl_3$ solutions containing tetramethyl-silane (TMS) as an internal reference. Calibration of the spectrometer was checked by the usual side-band method. Accuracies of the measurements are within 0·02 $\tau$ for chemical shifts and 0·3 c/s for coupling constants. Proton spin-decoupling experiments at 100 mc/s. were made by using a Varian HA-100 spectrometer and a Hewlett-Packard HP 200ABR audio-oscillator in the TMS locked mode and frequency sweep operation. M.ps were taken on a Kofler block (Yanagimoto & Co.) and are uncorrected.

*Action of dicyclorodicyanobenzoquinone* (DDQ) *on linderene*

DDQ (196·4 mg) was added to a solution of linderene (65·3 mg) in dry dioxan (2 ml) was heated at 45° for 5 min. A large quantity of ether was added and the precipitated DDH filtered off. Ether solution was washed with 5% $K_2CO_3$ solution, $H_2O$, dried and evaporated. A residue was chromatographed on alumina (Woelm II, neutral) to give a crude lactone (III; 8·0 mg) from the benzene–ethyl

[14] M. Karplus, *J. Amer. Chem. Soc.* **85**, 2870 (1963); R. A. Wohl, *Chimia* **18**, 219 (1964); N. S. Bhacca and D. H. Williams, *Applications of NMR Spectroscopy in Organic Chemistry* Chap. 6. Holden-Day, San Francisco (1964).

acetate (9:1) eluate and a crude glycol (IV) (2·5 mg) from the benzene–ethyl acetate (8:2) fraction. The $K_2CO_3$-solution was acidified carefully and extracted with ether. The ether extract was purified as above and to give further 8·5 mg of III and 9·0 mg of IV. Pure lactone (III), m.p. 150–151°, colourless plated from ether–pet. ether (2:1), $[\alpha]_D^{26\cdot0}$ +67·4° (EtOH *c*, 0·975), IR $\nu_{max}^{nujol}$ 3440, 1788, 1668, 1642, 890 $cm^{-1}$, $\nu_{max}^{CHCl_3}$ (3500), (1770), 1760, 1665, 1645, 899 $cm^{-1}$: UV $\lambda_{max}^{alc}$ 280 m$\mu$ ($\epsilon$ 25,600): (Found: C, 73·86; H, 6·67. $C_{15}H_{16}O_3$ requires: C, 73·75; H, 6·60%). Pure glycol (IV), m.p. 179–181°, colourless needles (from ether), $[\alpha]_D^{24\cdot5}$ −25·9° (EtOH *c*, 0·746): IR $\nu_{max}^{nujol}$ 3265, (3210), 1658, 1555, (1495), 893, 883 $cm^{-1}$: (Found: 73·45; H, 7·31. $C_{15}H_{18}O_3$ requires: C, 73·14; H, 7·37%.) Ehrlich colour reaction: purple.

DDQ *oxidation of atractylon* (V)

Atractylon (52 mg) was treated with DDQ (219·6 mg) in dry dioxan (2 ml) at temp for 1 hr. Working up as above to give 17·5 mg of VII. Pure VII, m.p. 107–110°, colourless needles (from ether): IR $\nu_{max}^{KBr}$ 1772, 1667, 1649, 896 $cm^{-1}$: UV $\lambda_{max}^{alc}$ 275 m$\mu$ ($\epsilon$ 26,500): (Found: C, 78·59; H, 8·23. $C_{15}H_{16}O_2$ requires: C, 78·23; H, 7·85%.)

In this case no hydroxyl derivative corresponding X or XIII was detected.

DDQ *oxidation of dihydrolinderene* (VIII)

DDQ (2·818 g) was added to a solution of VIII (958·2 mg) in dry dioxan (13·5 ml) and was heated immediately at 50° on a water bath for 10 min. Ether (700 ml) was added and a supernatant was separated by decantation and the precipitated DDH was washed with ether. A combined etheral solution was treated as above and the oily ether residue (560·7 mg) was chromatographed on alumina to give a crude lactone (IXa; 231 mg) from the ether–benzene (1:9) eluated fraction and a crude glycol (X; 34·5 mg) from the ether–MeOH (9·7:0·3) eluated fraction. The $K_2CO_3$-solution was acidified with ice-cooled $H_2SO_4$ and extracted with ether. The etheral residue was chromatographed on alumina as above to give further 58·7 mg crude IXa and 43·3 mg crude X. Pure lactone (IXa), m.p. 171–172·5° (24%), colourless plates (from ether–pet. ether = 1:3), $[\alpha]_D^{26\cdot5}$ −50·0° (EtOH *c*, 1·054), IR $\nu_{max}^{nujol}$ 3443, 1728, 1641, 1626, 1063 $cm^{-1}$, $\nu_{max}^{CCl_4}$ (3470), 1776, (1751), 1641 $cm^{-1}$: UV $\lambda_{max}^{alc}$ 284 m$\mu$ ($\epsilon$ 24,600): (Found: C, 73·25; H, 7·44. $C_{15}H_{16}O_3$ requires: C, 73·14; H, 7·37%). Pure glycol (X) was obtained by preparative TLC (Kiesel gel GF) followed by recrystallization from ether–MeOH (9:1) as fine needles, m.p. 202–203° (5·7%), $[\alpha]_D^{26}$ −85·8° (EtOH *c*, 0·998): IR $\nu_{max}^{nujol}$ 3241, 1550, (1498), 1041, 985 $cm^{-1}$: (Found: C, 72·73; H, 8·03. $C_{15}H_{20}O_3$ requires: C, 72·55; H, 8·12%.) Ehrlich colour reaction: purple.

*Dimorph of* IXa

We obtained a crystalline product having a m.p. of 137–141°, colourless needles, instead of the lacton (IXa) in some lots. It's IR spectrum, $\nu_{max}^{nujol}$ 3520, 1758, 1661, 1636 $cm^{-1}$ in nujol mull, is slightly different from that of IXa but identical in $CCl_4$ solution. This was converted to the higher melting lacton (IXa) very easily by recrystallization using ether–pet. ether (5:1) as a solvent.

DDQ *oxidation of iso-dihydrolinderene* (XI)

Compound XI (657·3 mg) was oxidized with DDQ (1·935 g) in absolute dioxan as in the case of dihydrolinderene and afforded 145·4 mg (21·7%) of pure iso-lactone (XIIa) as colourless needles, from ether–MeOH (9:1), m.p. 172–173·5°, $[\alpha]_D^{26}$ −194·4° (EtOH *c*, 0·999): IR $\nu_{max}^{nujol}$ 3466, 1754, 1645, 1633, 1058 $cm^{-1}$, $\nu_{max}^{CCl_4}$ (3470), 1778, (1753), 1643 $cm^{-1}$: UV $\lambda_{max}^{alc}$ 283–285 m$\mu$ ($\epsilon$ 21,700): (Found: C, 72·95; H, 7·51. $C_{15}H_{18}O_3$ requires: C, 73·14; H, 7·37%), and 45·1 mg (6·7%) of pure glycol (XIII), m.p. 201–202°, fine needles (from ether), $[\alpha]_D^{26\cdot5}$ −175·9° (EtOH *c*, 1·055): IR $\nu_{max}^{nujol}$ 3256, 1556, (1513), 1045, 983 $cm^{-1}$: (Found: C, 72·51; H, 8·46. $C_{15}H_{20}O_3$ requires: C, 72·55; H, 8·12%.) Ehrlich colour reaction: purple.

*Mesylation of the lactones* (IXa) *and* (XIIa)

(a) Mesylchloride (173 mg) was added to a solution of IXa (106·2 mg) in pyridine (1·5 ml) at 0° and allowed to stand at 18° for 15 hr. Ice water (10 ml) was added and extracted with ether and the extract was washed and dried. Ether residue was purified through neutral $Al_2O_3$ followed by recrystallization from ether. Pure mesylate (IXb), plates, m.p. 112–114° (90%), IR $\nu_{max}^{nujol}$ 1764, (1722), 1644, 1359, 1170, (932) $cm^{-1}$: (Found: C, 59·52; H, 6·45. $C_{16}H_{20}O_5S$ requires: C, 59·25; H, 6·22%.)

(b) iso-Lactone (XIIa; 54·2 mg) was treated with mesylchloride (88 mg) as above and afforded pure mesylate (XIIc) as needles (from ether–pet. ether = 1:1), m.p. 160–161° (91%), IR $\nu_{max}^{nujol}$ 1761, 1639, 1367, 1179, (961, 949) $cm^{-1}$: (Found: C, 59·16; H, 6·17. $C_{16}H_{20}O_5S$ requires: C, 59·25; H, 6·22%.)

*Acetylation of the iso-lactone* (XIIa)

Compound XIIa (15 mg) was acetylated with acetic anhydride (0·2 ml) in pyridine (0·7 ml) at 24° for 17 hr. Working up in the usual manner and purified with preparative TLC (Kiesel gel GF). Pure sample was obtained by recrystallization from ether–pet. ether (1:2), XIIb, m.p. 83–89°, prisms, IR $\nu_{max}^{nujol}$ 1764, 1750, 1644, 1230, 1037 $cm^{-1}$: (Found: C, 69·32; H, 7·09. $C_{17}H_{20}O_4 \cdot \frac{1}{2}H_2O$ requires: C, 69·37; H, 7·08%.)

*Preparation of the triene* (XVI) *and* (XVII)

(a) Compound IXb (118·8 mg) was heated in pyridine (6 ml) in the oil bath at 175–185° for 8 hr. Ice water was added and extracted with ether and the ether extract was washed and dried. The ether residue was purified with Silica gel chromatography and the ether–pet. ether (1:9) eluate gave a crystalline triene-lactone (XVI; 45·3 mg). Pure XVI, m.p. 102–104°, colourless plates (from ether–pet. ether = 1:9), IR $\nu_{max}^{nujol}$ 1754, 1630 $cm^{-1}$: UV $\lambda_{max}^{alc}$ 300 m$\mu$ ($\epsilon$ 22,800): (Found: C, 78·72; H, 7·09 $C_{15}H_{16}O_2$ requires: C, 78·92; H, 7·06%.)

(b) Compound XIIc (75·2 mg) in pyridine was heated and treated as above to give an oily XVII, 30·5 mg. This was purified through preparative TLC. Pure XVII, colourless oil, IR $\nu_{max}^{film}$ 1765, 1637 $cm^{-1}$: UV $\lambda_{max}^{alc}$ 300 m$\mu$ ($\epsilon$ 27,700).

TABLE 1. NMR SPECTRAL DATA ON SOME EXAMINED COMPOUNDS IN DEUTERIOCHLOROFORM*

| Compound | Cyclopropyl (C-2a) | C-4 | C-5 | C-6 | C-9 | C-12 | C-13 | C-14 | C-15 | OAc |
|---|---|---|---|---|---|---|---|---|---|---|
| VIII | 9·47(t–d) | | 7·85(d–d) | 5·75(d–t) | 7·52(d), 7·35(d) | 2·98(qa) | 7·93(d) | 9·20(s) | 9·04(d) | — |
| | (8·6; 5·6) | | (10·0; 8·4) | (10·0; 1·7) | (~15; 1·7) | (1·2) | (1·2) | | (7·5) | |
| XI | | | | 5·67(d–m) | 7·38(d), 7·43(d) | 2·97(qa) | 7·94(d) | 9·29(s) | 8·66† | — |
| | | | | (8·0) | (~15) | (1·2) | (1·2) | | | |
| IXa | 9·18(t–d) | | | 5·32(d–m) | 3·83(s) | — | 7·92(d) | 9·00(s) | 8·98(d) | — |
| | (8·6; 6·4) | | | (~12) | | | (1·6) | | (7·0) | |
| XIIa | | | 7·86(t) | 5·30(d–qa) | 3·78(s) | — | 7·95(d) | 9·12(s) | 8·67† | — |
| | | | (11·0) | (11·0; ~1·5) | | | (1·8) | | | |
| XIIb | 9·27(t–d?) | | 7·72(t) | 3·98(d–qa) | 3·73(s) | — | 8·12(d) | 9·03(s) | 8·88(d) | 7·85(s) |
| | (~8; ~6) | | (11·5) | (11·5; 1·5) | | | (1·5) | | (6·8) | |
| XVI | 9·27(t–d) | 6·85(qi–m) | — | 3·93(d) | 4·07(s) | — | 8·07(s) | 8·82(s) | 8·80(d) | — |
| | (8·5; 6·0) | (7·5) | — | (1·02) | | | | | (7·5) | |
| XVII | | 7·53(qa–m) | — | 4·05(d) | 4·02(s) | — | 8·03(s) | 8·90(s) | 8·70(d) | — |
| | | (6·8) | | (2·2) | | | | | (6·8) | |

* Chemical shifts are expressed in $\tau$-values and apparent coupling constants (values in parentheses) in c/s. Peak multiplicities are represented by s (singlet), d (doublet), t (triplet), qa (quartet), qi (quintet), and m (multiplet). For example, d-t represents a doublet of triplets.

† The $A_2$ part of an $A_2B$ system.

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