Anal. Calcd for $C_{19}H_{23}NO_3$ (313.38): C, 72.82; H, 7.40; N, 4.47. Found: C, 73.04; H, 7.60; N, 4.44.

(−)-6,7-Dimethoxy-2-methyl-4(*S*)-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (10b).—Reductive N-methylation of 850 mg of **10a** as described in the previous experiment afforded 636 mg (71%) of **10b**, mp 83–85°, after crystallization from ether–petroleum ether. Recrystallization from the same solvent mixture gave 400 mg of analytically pure **10b**, mp 87–88°, after drying under reduced pressure at 40° for 4 days: $[\alpha]^{24.9}D$ −21.65° (*c* 0.965, MeOH); ORD (*c* 0.3134, MeOH), $[\alpha]_{294}$ −3960° (tr), $[\alpha]_{288}$ 0°, $[\alpha]_{279}$ +6760° (pk), $[\alpha]_{264}$ +2170° (tr), $[\alpha]_{244}$ +5750° (pk), $[\alpha]_{239}$ 0°, $[\alpha]_{232}$ −15,900° (tr), $[\alpha]_{222}$ 0°, $[\alpha]_{217}$ +4470° (pk), and $[\alpha]_{215}$ +2870°; CD $[\Theta]_{304}$ 0, $[\Theta]_{288}$ −24,090, $[\Theta]_{278}$ 0, $[\Theta]_{272}$ +5610, $[\Theta]_{267}$ +1980, $[\Theta]_{248}$ +14,850, $[\Theta]_{234}$ 0, $[\Theta]_{226}$ −68,640, $[\Theta]_{214}$ −5280, $[\Theta]_{205}$ −102,960, $[\Theta]_{200}$ 0, and $[\Theta]_{197}$ +58,080.

Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.77; H, 7.51; N, 4.49.

(+)-2-(4-Bromobenzoyl)-6,7-dimethoxy-4(*S*)-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (11).—To a stirred solution of 299 mg (1 mmol) of **10a** in 20 ml of benzene was added a solution of 300 mg (2.2 mmol) of potassium carbonate in 5 ml of water followed by the portionwise addition of 500 mg (2.3 mmol) of 4-bromobenzoyl chloride. After the addition was complete, stirring was continued for 2 hr. The benzene layer was separated and washed successively with 6 *N* sodium hydroxide, three portions of 2 *N* hydrochloric acid, and water. After drying (Na_2SO_4) and evaporation, the crystalline residue was washed with ether to give 323 mg (67%) of **11**, mp 158–160°. A sample was recrystallized from ether to afford analytically pure **11** as long needles: mp 159–161°; $[\alpha]^{24}D$ +120.3° (*c* 1.28, $CHCl_3$); ir ($CHCl_3$) 1630 (amide C=O), 1615 (sh), 1590, 1510, and 1460 (phenyl), and 1260 cm^{-1} (OCH_3); uv max (CH_3OH) 226 mμ (ε 35,500), 278 (6270), 283–284 (6060), and 291–292 (3800)(sh); nmr ($CDCl_3$) δ 3.72, 3.82, and 3.90 (s, 3 H each, OCH_3) 4.67 and 5.10 (cp, 2 H each, CH_2NCH_2), and 6.3–7.2 (cp, 10, aromatic H); ORD (*c* 0.482, methanol) $[\alpha]_{301}$ +1310° (pk), $[\alpha]_{291}$ +1240° (tr), $[\alpha]_{274}$ +26,000° (pk), $[\alpha]_{243}$ 0°, $[\alpha]_{225}$ −21,300° (tr), $[\alpha]_{218}$ −13,000° (sh), and $[\alpha]_{203}$ 0°; CD $[\Theta]_{300}$ 0, $[\Theta]_{288}$ −13,200, $[\Theta]_{271}$ 0, $[\Theta]_{238}$ +125,400, $[\Theta]_{228}$ 0, $[\Theta]_{208}$ −75,900, and $[\Theta]_{200}$ 0; mass spectrum (70 eV) *m/e* (rel intensity) 483 (30), 481 (30), 403 (5), 373 (5), 282 (20), 270 (45), 239 (100), 183 (30), and 121 (30).

Anal. Calcd for $C_{25}H_{24}BrNO_4$ (mol wt, 482.40): C, 62.25; H, 502; N, 2.90. Found: C, 62.25; H, 4.75; N, 3.20.

Registry No.—**3**·HCl, 23349-28-2; **4**·HCl, 23349-29-3; **5**, 23349-30-6; **5**·HCl, 23349-31-7; **6**·HCl, 23349-32-8; **7**, 23330-74-7; **9a**, 23330-75-8; **9b**, 23330-76-9; **10a**, 23330-77-0; **10b**, 23367-60-4; **11**, 23330-78-1; **12**, 23367-61-5; **12**·HCl, 23330-44-1.

Acknowledgment.—We are indebted to the Physical Chemistry Department, Hoffmann-La Roche Inc., Nutley, N. J., under the supervision of Dr. P. Bommer, for the analytical and spectral data. We are particularly grateful to Dr. V. Toome for the ORD and CD determinations.

Constituents of *Eurycoma longifolia* Jack

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Investigation of the constituents of *Eurycoma longifolia* Jack, obtained from several regions of Viet Nam, has resulted in the isolation of two steroids, namely β-sitosterol and campesterol, 2,6-dimethoxybenzoquinone, and a bitter principle called eurycomalactone (**1a**). Eurycomalactone is closely related to the other bitter principles previously encountered in the family *Simaroubaceae*. Eurycomalactone is the first compound of this series with a keto group at C-6 and a γ-lactone group between positions 14 and 7. The configuration is discussed. Dihydroeurycomalactone (**2a**) is also isolated from the bark of *Eurycoma longifolia* originated from Dinh-Quan.

Numerous plants of the *Simaroubaceae* are known in herbal medicine for their therapeutic activities, and several of them have been shown to be effective antiamebic agents.[2] Various studies on the bitter principles occurring in several genera of the family *Simaroubaceae* have shown that they belong to a group of structurally related compounds with close chemical and botanical relationships to each other.[3]

This work describes the investigation of the chemical constituents of *Eurycoma longifolia* Jack, a bush which is common in Viet Nam, especially around Bien-Hoa, Trang-Bom, and Dinh-Quan. Its local name is "cây bá binh" (tree which cures hundred of diseases), and its bark is used in the Vietnamese pharmacopaeia.

Chromatography of the bark afforded, besides β-sitosterol and campesterol, characterized as their acetates (see Experimental Section), eurycomalactone (**1a**) and 2,6-dimethoxybenzoquinone, which is a common chemical constituent of the Simaroubaceae family.[4]

Eurycomalactone (**1a**)[5] was also isolated from extracts of the leaves of *Eurycoma longifolia* (albeit in a much lower yield, *ca.* 10%) and analyzed for $C_{19}H_{24}O_6$. This was confirmed by its mass spectrum. Its infrared (ir) spectrum showed bands for hydroxyls, a saturated and an α,β-unsaturated ketone, and a γ-lactone grouping. The ultraviolet (uv) spectrum confirms the presence of a conjugated keto chromophore, which seemed to be homoconjugated with a saturated carbonyl. The nuclear magnetic resonance (nmr) spectrum showed resonances for four methyl groups, one secondary methyl, one vinylic methyl, and two tertiary methyls (see Experimental Section). A signal integrating for one vinylic proton appeared at 6.1 ppm, and a resonance for one proton situated on a carbon-bearing oxygen atom is observed at 4.8 ppm. Finally, eurycomalactone (**1a**) gives a mono- and a bis-2,4-dinitro-

(1) Taken in part from the D.Sc. Thesis of N.-N.-S. For a preliminary communication, see Le-Van-Thoi, Nguyen-Ngoc-Suong, and P. Crabbé, *Chem. Commun.*, 821 (1969).

(2) T. A. Geissman, *Ann. Rev. Pharmacol.*, **4**, 305 (1964).

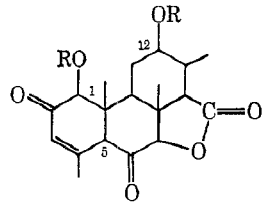
(3) For a review of the literature on simaroubaceous plants, see J. Polonsky, *Planta Med. Suppl.*, 107 (1966).

(4) See, among others, (a) J. Polonsky and E. Lederer, *Bull. Soc. Chim Fr.*, 1157 (1959); (b) W. Karrer, *Helv. Chim. Acta*, **13**, 1424 (1930); (c) D. J. Cosgrove, D. G. H. Daniels, E. N. Greer, J. B. Hutchinson, T. Moran, and J. K. Whitehead, *Nature*, **169**, 966 (1952); (d) D. J. Cosgrove, D. G. Daniels, K. J. Whitehead, and J. D. S. Goulden, *J. Chem. Soc.*, 4821 (1952).

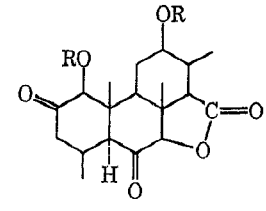
(5) Preliminary communications on the isolation of this substance have already appeared: (a) Le-Van-Thoi and Nguyen-Ngoc-Suong, *Ann. Fac. Sci. Saigon*, 89 (1962); (b) Le-Van-Thoi and Nguyen-Ngoc-Suong, International Symposium on the Chemistry of Natural Products, Kyoto, April 1964, Abstracts of Papers, p 51.

phenylhydrazone, thus confirming the presence of two keto groupings in the molecule.

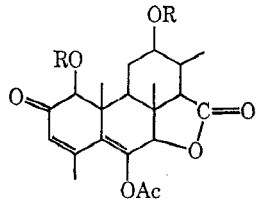
Catalytic hydrogenation of **1a** affords dihydroeurycomalactone (**2a**). Compound **2a** was also isolated from the bark of *Eurycoma longifolia* originated from Dinh-Quan. The dihydro derivative **2a** shows a weak uv band at 280 mμ and one strong saturated carbonyl band in the ir. A new signal (appearing as a doublet centered at 0.95 ppm) confirms the secondary nature of the methyl situated at C-4.



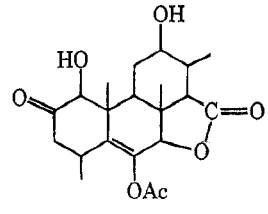
1a, 5α H, R = H
b, 5α H, R = Ac
c, 5β H, R = H



2a, R = H
b, R = Ac



3a, R = H
b, R = Ac



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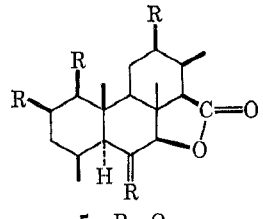
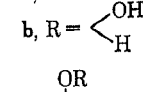
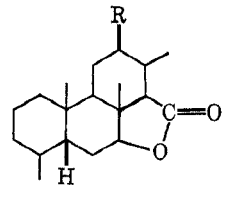
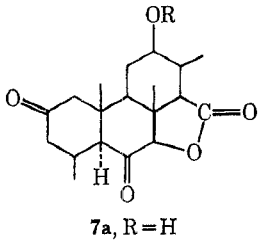


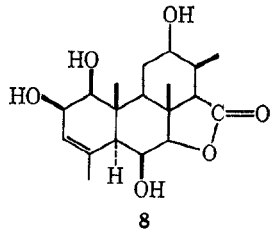
5a, R = O
b, R = 



6a, R = HOH
b, R = HOAc
c, R = O



7a, R = H
b, R = Ac



8

The saturated ketone in **1a** is located at position 6, since it is easily enolized in alkaline medium to give a conjugated enolate, typified by its uv absorption. The location of a ketone at C-6 is further confirmed by treatment of **1a** with acetic anhydride in pyridine at room temperature. An enol acetate (**3a**) resulted. Its ir still shows OH absorption (see Experimental Section) but, besides the γ-lactone band, there appeared a strong absorption corresponding to an enol acetate, also confirmed by uv (see Experimental Section).

When eurycomalactone (**1a**) is treated with acetic anhydride in pyridine solution at reflux temperature, the triacetate **3b** is obtained. However, reaction of **1a** with acetyl chloride gives exclusively the diacetate **1b**. Similarly, treatment of dihydroeurycomalactone (**2a**) with acetyl chloride furnished the diacetoxy derivative **2b**.

These results seem to indicate that the basicity of pyridine enolizes the 6-keto grouping, which is then more readily esterified than the hydroxyls at C-1 and C-12. Indeed, further acetylation of **3a** with acetic anhydride in pyridine for 9 hr on the steam bath affords the triacetate **3b**.

The presence of two secondary hydroxyl groups in eurycomalactone (**1a**) is also shown by chromic acid oxidation[6] of dihydroeurycomalactone (**2a**) which provided the tetraketolactone **5a**. The ir spectrum of **2a** is devoided of hydroxyl absorption.

Clemmensen reduction[7] of **2a** gives the monohydroxy derivative **6a**, which forms a monoacetate (**6b**). Oxidation of **6a** affords the ketolactone **6c**, which forms a 2,4-dinitrophenylhydrazone.

The presence of an α-ketol grouping in **1a** and **2a** is easily detected by ir spectroscopy.[8] Furthermore, the tetrol **5b**, obtained by reduction of **2a** with sodium borohydride, is readily oxidized with periodic acid, hence showing the presence of an α-glycol function in **5b**. Conversely, reaction of **1a** or **2a** with periodic acid is very slow.

When dihydroeurycomalactone (**2a**) is treated with zinc and acetic acid, the hydroxyl at C-1 is eliminated to afford the monohydroxy diketolactone **7a**, which is readily acetylated with acetyl chloride to give **7b**. Finally, Clemmensen reduction[7] of **7a** also provides the monohydroxy derivative **6a**.

The γ-lactone grouping of eurycomalactone (**1a**), easily identified by ir and nmr (*vide supra*), is quite stable, even under alkaline conditions.[9] However, the γ-lactone ring can be reduced with lithium aluminum hydride, as shown below.

The conjugated α-ketol shown to be present in eurycomalactone (**1a**) (*vide supra*) is common in simaroubolides, such as glaucarubinone,[10] chaparrinone,[10] ailanthone,[11] samaderine B,[12] and related compounds.[13] By similar reasoning the vinylic methyl group in **1a** is located at position C-4, thus explaining the uv of **1a**, which is in reasonable agreement with the calculated value.[14]

Since the α-ketol **2a** can be converted into the tetraketone **5a**, the hydroxyl at C-1, as well as all other hydroxyls present in the molecule, must be secondary. As indicated previously, on the basis of the easy formation of enol acetates (**3a**,**b**), as well as the facile isomer-

(6) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(7) See E. L. Martin, *Org. Reactions*, **1**, 155 (1942).

(8) L. Toris and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **90**, 4599 (1968).

(9) This observation has some precedent; *cf.* (a) Le-Van-Thoi and J. Ourgaud, *Bull. Soc. Chim. Fr.*, 761 (1955); (b) A. J. Birch, D. J. Collins, S. Muhammad, and J. P. Turnbull, *J. Chem. Soc.*, 2762 (1963); (c) J. Romo, L. Rodríguez-Hahn, P. Joseph-Nathan, M. Martínez, and P. Crabbé, *Bull. Soc. Chim. Fr.*, 1276 (1964).

(10) T. A. Geissman and K. R. Chandorkar, *J. Org. Chem.*, **26**, 1217 (1961).

(11) J. Polonsky and J. L. Fourrey, *Tetrahedron Lett.*, No. 52, 3983 (1964).

(12) (a) J. Polonsky, J. Zylber, and R. O. B. Wijesekera, *Bull. Soc. Chim. Fr.*, 1715 (1962); (b) J. Zylber, J. Polonsky, and C. Mitra, *ibid.*, 1322 (1963).

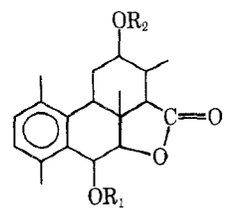
(13) (a) J. Polonsky and N. Bourguignon-Zylber, *ibid.*, 2793 (1965); (b) A. Gaudemer, J. L. Fourrey, and J. Polonsky, *ibid.*, 1676 (1967); (c) A. Gaudemer, *ibid.*, 406 (1967).

(14) (a) R. B. Woodward, *J. Amer. Chem. Soc.*, **64**, 76 (1942); (b) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Co., New York, N. Y., 1959, p 19.

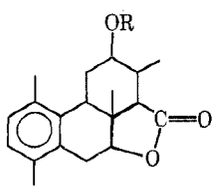
ization of the asymmetric center at C-5 (*vide infra*), the second ketone is located at position 6.

The hydroxylactone **6a** was obtained by two different routes, *i.e.*, either by Clemmensen reduction of dihydroeurycomalactone (**2a**) or from **7a** (*vide supra*). This indicates that the second OH group is somewhat hindered. Therefore, it is located at C-12 (*vide infra*).

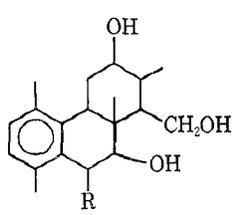
Sodium borohydride reduction of eurycomalactone (**1a**) affords a tetrol (**8**), which is noncrystalline, probably owing to a mixture of isomers at C-2, C-5, and C-6. Acid treatment of this tetrol gives the rearranged aromatic compound eurycomol (**9a**). Similar results are shown by other simaroubolides.[15]



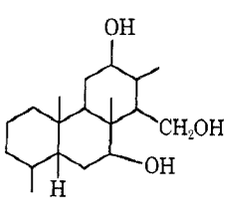
9a, $R_1 = R_2 = H$
b, $R_1 = Ac$; $R_2 = H$
c, $R_1 = R_2 = Ac$



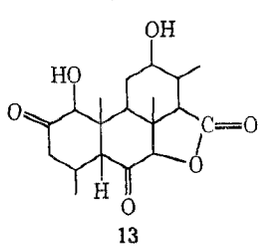
10a, R = H
b, R = Ac



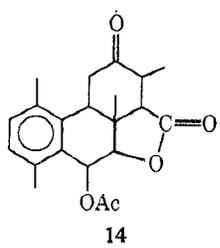
11a, R = OH
b, R = H



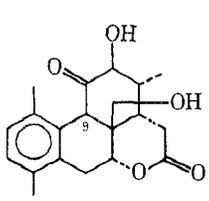
12



13



14



15a, 9α-H
b, 9β-H

The structure of eurycomol (**9a**) is supported by its uv and ir spectra (see Experimental Section). While acetylation of **9a** under vigorous conditions affords the corresponding diacetate **9b**, the monoacetate **9c** can be obtained under rather mild reaction conditions. The nmr spectra of **9b** and **9c** clearly indicate two aromatic methyls, besides the aromatic protons.

(15) (a) E. A. Ham, H. M. Schafer, R. G. Denkewalter, and N. G. Brink, *J. Amer. Chem. Soc.*, **76**, 6066 (1954); (b) J. Polonsky and A. Gaudemer, *Bull. Soc. Chim. Fr.*, 1432 (1961); (c) J. Polonsky, C. Fouquey, and A. Gaudemer, *ibid.*, 1255 (1962); 169 (1963); (d) T. A. Geissman and K. R. Chandorkar, *J. Org. Chem.*, **26**, 1217 (1961); (e) T. A. Geissman and G. A. Ellestad, *Tetrahedron Lett.*, No. 23, 1083 (1962); (f) T. A. Davidson, T. R. Hollands, and P. de Mayo, *ibid.*, No. 23, 1089 (1962); (g) T. A. Davidson, T. R. Hollands, P. de Mayo, and M. Nisbet, *Can. J. Chem.*, **43**, 2996 (1965).

Since eurycomol (**9a**) is unreactive toward periodic acid, in contrast to the high reactivity of tetrol **8**, one can conclude that at least one of the hydroxyls eliminated during conversion of **8** into **9a** belongs to the α-glycol group of ring A. Moreover, the methyl migration from C-10 to C-1 supports the hypothesis that one hydroxyl is located at position 1 in eurycomalactone (**1a**).

Treatment of eurycomol (**9a**) with platinum in acetic acid solution provides deoxyeurycomol (**10a**), which formed an acetate (**10b**). The elimination of one hydroxyl during the reaction indicates that this alcohol group must be benzylic, thus further confirming the presence of a ketone at C-6 in **1a**. Indeed, lithium aluminum hydride reduction of **10a** affords the triol **11b**, which does not react with periodic acid. The same applies to the triol **12** obtained by $LiAlH_4$ reduction of hydroxylactone **6a**.

Lithium aluminum reduction of eurycomol (**9a**) furnishes the tetrol **11a**. The tetrol **11a** reacts rapidly with periodic acid, thus showing the presence of an α-glycol group at C-6 and C-7. This also defines the position of the γ-lactone group in eurycomalactone (**1a**) and its derivatives.

The above experiments established the structure of rings A and B of eurycomalactone (**1a**). By analogy with other simaroubolides such as quassin,[16] simarolide,[16j,17] kalineanone,[18a] amarolide,[18] etc., the second tertiary methyl is situated at position 8. For similar reasons, supported by experimental evidence (*vide supra*), the γ-lactone function is located between positions 7 and 14.

A feature which is common to most simaroubaceous bitter principles is a methyl (or an equivalent oxidized entity) situated at C-13. Therefore, the secondary methyl in eurycomalactone (**1a**) is located at C-13.

Acetylation and reduction experiments performed on eurycomalactone (**1a**) and its derivatives indicate that the last secondary alcohol grouping is less reactive than the other hydroxyls present in the molecule. This may be attributed to steric hindrance, allowing the third alcohol group to be located at position C-12 (*vide infra*).

Eurycomalactone (**1a**) is easily isomerized by dilute acid to its 5β isomer, isoeurycomalactone (**1c**). When **1c** is treated with acetic anhydride in pyridine for several hours at 90°, compound **3b** is formed, clearly demonstrating that C-5 is the only asymmetric center involved in these transformations.

Catalytic reduction of isoeurycomalactone (**1c**) gives dihydroisoeurycomalactone (**13**), which is isomeric with **2a**. Enolization of the carbonyl at C-6 in dihydroiso-

(16) (a) E. P. Clark, *J. Amer. Chem. Soc.*, **59**, 927, 2511 (1937); (b) E. London, A. Robertson, and H. Worthington, *J. Chem. Soc.*, 3431 (1950); (c) R. J. S. Beer, D. B. G. Jaquiss, A. Robertson, and W. E. Savige, *ibid.*, 3672 (1954); (d) K. R. Hanson, D. B. G. Jaquiss, J. A. Lamberton, A. Robertson, and W. E. Savige, *ibid.*, 4238 (1954); (e) R. J. S. Beer, K. R. Hanson, and A. Robertson, *ibid.*, 3280 (1956); (f) R. J. S. Beer, B. G. Dutton, D. B. G. Jaquiss, A. Robertson, and W. E. Savige, *ibid.*, 4850 (1956); (g) Z. Valenta, S. Papadopoulos, and C. Podĕsva, *Tetrahedron*, **15**, 100 (1961); (h) Z. Valenta, A. H. Gray, D. E. Orr, S. Papadopoulos, and C. Podésva, *ibid.*, **18**, 1433 (1962); (i) R. M. Carman and D. A. Ward, *Tetrahedron Lett.*, No. 10. 317 (1961); (j) W. A. C. Brown and G. A. Sim, *Proc. Chem. Soc.*, 293 (1964).

(17) J. Polonsky, *ibid.*, 292 (1964); (b) J. Polonsky, *Bull. Soc. Chim. Fr.*, 1546 (1959); (c) S. C. Nyburg, G. L. Walford, and P. Yates, *Chem. Commun.*, No. 10, 203 (1965).

(18) C. G. Casinovi, V. Ballavita, G. Grandolini, and P. Ceccherelli, *Tetrahedron Lett.*, No. 27, 2273 (1963).

eurycomalactone (**13**) also occurs, affording an enol acetate (**4**) when treated with acetic anhydride in pyridine solution at room temperature. Clemmensen reduction of **13** affords **6a**, thus indicating the 5β configuration in **6a** and its derivatives **6b** and **6c**.

The circular dichroism (CD) curve of eurycomalactone (**1a**) exhibits a negative maximum[19] at *ca.* 400 mμ and a positive maximum[19] at *ca.* 370 mμ. This resembles the Cotton effect curve of chaparrinone[20] in this spectral region, and a marked negative Cotton effect at *ca.* 300 mμ, indicative of the homoconjugation existing between the unsaturated and the saturated keto chromophores. In isoeurycomalactone (**1c**) the negative Cotton effect at *ca.* 400 mμ is substantially decreased.

Dihydroeurycomalactone (**2a**) shows a "double humped" CD curve, with a negative maximum at 304 mμ and a positive maximum at 275 mμ (see Experimental Section). This Cotton effect strongly supports the 5α configuration in **2a**, since the 5β isomer would be expected to exhibit a very intense negative Cotton effect[19] in the 300-mμ region (summation of 2 ketone and 6 ketone in a 5β compound).

Oxidation of the acetoxy alcohol **9b** affords the acetoxy ketone **14**, which exhibits a negative Cotton effect in the 300-mμ region.

It has been shown earlier in the chaparrin series[20] that treatment of chaparrol (**15a**) with pyridine affords neochaparrol (**15b**) and that the inversion of configuration at C-9 is accompanied by a change in sign of the Cotton effect. Compound **15b** shows a very intense positive rotatory dispersion (RD) curve (a = +250).[19] In the 9β compound **15b** the nonbonded interactions between the 1-methyl group and the 11 ketone are substantially reduced, when compared with those in the 9α isomer **15a**, thus explaining the ease of isomerization.[21]

When the acetoxy ketone **14** was refluxed in pyridine, the starting material was recovered unchanged. This excludes the location of the keto group at C-11 in **14**; hence the secondary alcohol has to be situated at C-12 in eurycomalactone (**1a**) and its derivatives.

Further work will be performed in order to establish firmly the complete stereochemistry of eurycomalactone, when conditions will allow us to collect more starting material.

Experimental Section[22]

Extraction of the Bark of *Eurycoma longifolia*.—Dried bark (8 kg) was extracted with petroleum ether for a period of 7 days. After concentration *in vacuo*, 12 g of oily material were obtained. Petroleum ether (100 ml) was added, and the insoluble material was dissolved in benzene–hexane (1:1) and chromatographed over neutral alumina.

Elution with petroleum ether afforded 2.3 g of an oil which crystallized with methanol. Further recrystallizations from methanol gave 800 mg of β-sitosterol: mp 140°; $[\alpha]_D$ −36°; ν_{max}^{KBr} 3570 and 1650 cm^{-1}.

Anal. Calcd for $C_{29}H_{50}O$: C, 83.98; H, 12.15. Found: C, 83.88; H, 12.10.

Acetylation of 100 mg of β-sitosterol with 2 ml of acetic anhydride in pyridine gave the corresponding acetate, which was recrystallized from methanol: mp 129°; $[\alpha]_D$ −40°; ν_{max} 1724 and 1242 cm^{-1}.

Anal. Calcd for $C_{31}H_{52}O_2$: C, 81.51; H, 11.47. Found: C, 81.41; H, 11.40.

Further elution of the column gave 920 mg of a white substance which was purified further by crystallization from acetone to furnish pure campesterol: mp 157°; $[\alpha]_D$ −35°; ν_{max}^{KBr} 3571 and 1652 cm^{-1}.

Anal. Calcd for $C_{28}H_{48}O$: C, 83.93; H, 12.07. Found: C, 83.87; O, 12.12.

Acetylation as above provided the corresponding acetate, which was recrystallized from ethanol: mp 139°; $[\alpha]_D$ −38°; ν_{max}^{KBr} 1730 and 1259 cm^{-1}.

Anal. Calcd for $C_{30}H_{50}O_2$: C, 81.38; H, 11.38. Found: C, 81.28; H, 11.28.

2,6-Dimethoxybenzoquinone.—After extraction with petroleum ether, the bark was dried in the open air and then extracted with boiling water for 48 hr. This extraction was repeated until the water extracts did not show any bitterness. The water extracts were treated with lead acetate (30% water solution). The solution was filtered and the filtrate was treated with carbon. The bitter principles were adsorbed. The carbon was filtered and dried. The aqueous extracts were chromatographed on 400 g of magnesium silicate and Celite. Elution with chloroform afforded 2.04 g of an oily product which crystallized from methanol. Recrystallizations furnished a pure sample of 2,6-dimethoxybenzoquinone: mp 250–252° (in sealed tube); ν_{max}^{KBr} 1701, 1645, 1623, and 1592 cm^{-1}; λ_{max}^{EtOH} 287 mμ (log ϵ 4.29) and 380 (2.78).

Eurycomalactone (**1a**).—The carbon recovered from the previous extraction was dried in the open air for 3 days, and then for several hours at 50–60°. It was then extracted with chloroform. The chloroform extracts were concentrated under reduced pressure to afford 20 g of a bitter product. Chromatography on 400 g of magnesium silicate–Celite (2:1) gave 3 g of material by elution with benzene. Recrystallizations from methanol furnished 2 g of pure eurycomalactone (**1a**): mp 268–270°; $[\alpha]_D$ +100° ($CHCl_3$), +75° (MeOH), −4° (pyridine); CD (c 0.002, dioxane) $[\theta]_{398-404}$ −1710°; $[\theta]_{375-377}$ +700°, $[\theta]_{366}$ +815°, $[\theta]_{292-307}$ −17,750°; ν_{max}^{KBr} 3571, 3509, 1770, 1709, 1679, and 1621 cm^{-1}; $\nu_{max}^{CHCl_3}$ 3571, 3497, 1773, 1712, 1667, and 1629 cm^{-1}. ν_{max}^{Nujol} 3571, 3509, 1764, 1712, 1667, and 1618 cm^{-1}; λ_{max}^{MeOH} 241 mμ (log ϵ 3.85) and 290 (2.24); nmr 1.16 (d, J = 7 cps, 13-CH_3), 1.25, 1.55 (8-CH_3, 10-CH_3), 1.94 (4-CH_3), 6.1 (vinylic H), 3.10–3.20 and 4.30–4.40 (OH), and 4.80 ppm (HCO); mass spectrum m/e 348 (M^+).

Compound **1a** can exist at least partially in the enol form. The CD is solvent and concentration dependent; its uv absorption in alkaline medium is at λ_{max} 288 mμ (log ϵ 3.65), reminiscent of the uv of **3a** and **3b** (*vide infra*).

Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.43; H, 6.88.

The mono-2,4-dinitrophenylhydrazone derivative was obtained as yellow crystals, mp 125°, λ_{max}^{EtOH} 358 mμ (log ϵ 4.62).

Anal. Calcd for $C_{25}H_{28}O_9N_4$: N, 10.60. Found: N, 10.15.

The bis-2,4-dinitrophenylhydrazone derivative was obtained as red crystals, mp 150°, λ_{max}^{EtOH} 368 mμ (log ϵ 4.51).

Anal. Calcd for $C_{31}H_{32}O_{12}N_8$: N, 15.80. Found: N, 15.42.

Isoeurycomalactone (**1c**).—Treatment of 100 mg of eurycomalactone (**1a**) with 40 ml of a 1 N solution of H_2SO_4 at reflux temperature for 3 hr is followed by the usual extraction procedure. Chromatography over magnesium silicate–Celite (2:1) afforded 10 mg of recovered starting material. Elution with $CHCl_3$ gave 50 mg of isoeurycomalactone (**1c**): mp 255–258° (from ethanol–water); $[\alpha]_D$ ±0°; CD (c 0.009, dioxane) $[\theta]_{394-404}$ −726°; ν_{max}^{KBr} 3509, 3378, 1754, 1724, 1683, and 1629 cm^{-1}; λ_{max}^{EtOH} 232 mμ (log ϵ 3.92), 290 (3.20), and 334 (3.03); nmr (DMSO-d_6) 1.03 (d, J = 6 cps, 13-CH_3), 1.20, 1.36 (8-CH_3, 10-CH_3), and 1.48 (4-CH_3).

(19) P. Crabbé, "Applications de la dispersion rotatoire optique et du dichroisme circulaire optique en chimie organique," Gauthier-Villars, Paris, 1968.

(20) T. R. Hollands, P. de Mayo, M. Nisbet, and P. Crabbé, *Can. J. Chem.*, **43**, 3008 (1965).

(21) See also P. Crabbé and A. Bowers, *J. Org. Chem.*, **32**, 2921 (1967).

(22) Melting points were taken with a Maquenne block. Optical rotations were determined in chloroform solution with a Hilger M 412 polarimeter. Infrared spectra were determined with a Perkin-Elmer Model 137 spectrometer. Ultraviolet spectra were measured with a Beckman DK-2 spectrophotometer. The optical rotatory dispersion (RD) curves were obtained with a Jasco UV/5 spectropolarimeter. The circular dichroism curves were measured with a Jouan Dichrograph in the Laboratory of Professor G. Ourisson (University of Strasbourg). Unless otherwise stated, the nuclear magnetic resonance spectra were taken in deuteriochloroform solution (*ca.* 10% w/v) with a tetramethylsilane internal reference using a Varian A-60 spectrometer.

Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 64.99; H, 6.92.

Compound 1c was also obtained by treatment of 1a with hydrogen chloride or with concentrated formic acid.

Dihydroeurycomalactone (2a).—A solution of 100 mg of 1a in 20 ml of methanol was stirred in a hydrogen atmosphere in the presence of 100 mg of 10% Pd–C. After 1 equiv of hydrogen was taken up, the reaction mixture was filtered to give 98 mg of dihydroeurycomalactone (2a). Crystallization from methanol provided an analytical sample: mp 247–248°; $[\alpha]_D$ +23°; CD (*c* 0.001, dioxane) $[\theta]_{309-313}$ −2.600°, $[\theta]_{304}$ −2.780°, and $[\theta]_{278-278}$ +2.450°, ν_{max}^{KBr} 3571, 3448, 1783, and 1706 cm^{-1}; λ_{max}^{EtOH} 280 mμ (log ε 1.83); nmr 0.95 ppm (d, *J* = 7 cps, 4-CH_3).

Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.12; H, 7.47. Found: C, 65.00; H, 7.52.

The 2,4-dinitrophenylhydrazone derivative was obtained, mp 251°, λ_{max}^{EtOH} 355 mμ (log ε 4.54).

Anal. Calcd for $C_{31}H_{34}O_{12}N_8$: N, 15.70. Found: N, 14.93.

Enol Acetate 3a.—A solution containing 200 mg of 1a and 5 ml of acetic anhydride in 3 ml of pyridine was left at room temperature for 15 hr. After work-up, followed by chromatography, 170 mg of 3a was obtained: mp 272–273° (from benzene); $[\alpha]_D$ −98°; ν_{max}^{KBr} 3546, 1779, 1754, 1672, and 1681 cm^{-1}; λ_{max}^{EtOH} 285 mμ (log ε 4.66); mass spectrum *m/e* 388 (M^+).

Anal. Calcd for $C_{21}H_{28}O_7 \cdot {}^1/_2H_2O$: C, 63.01; H, 6.80. Found: C, 62.78; H, 6.50.

The same substance (3a) was obtained by treatment of 1a with acetic anhydride in presence of sodium acetate.

Triacetate 3b.—When a pyridine solution of 1a was heated for 9 hr at 90° in the presence of acetic anhydride (same proportions as above), a small amount of 3a was isolated, but the major compound was the triacetate 3b. Recrystallization from methanol furnished an analytical sample: mp 248°; $[\alpha]_D$ −95°; ν_{max}^{KBr} 1792, 1742, 1672, 1613, and 1285 cm^{-1}; λ_{max}^{EtOH} 285 mμ (log ε 4.37).

Anal. Calcd for $C_{25}H_{30}O_9$: C, 63.28; H, 6.37. Found: C, 63.68; H, 6.27.

Eurycomalactone Diacetate (1b).—A mixture of 200 mg of eurycomalactone 1a in 10 ml of acetyl chloride was heated under reflux for 3 hr. The residue (170 mg) obtained at the end of the reaction was chromatographed to afford the diacetate 1b: mp 267° (from ethanol); $[\alpha]_D$ +32°; ν_{max}^{KBr} 1786, 1739, 1721, 1678, and 1629 cm^{-1}; λ_{max}^{EtOH} 238 mμ (log ε 3.51) and 285 (2.53).

Anal. Calcd for $C_{23}H_{28}O_8$: C, 63.80; H, 6.52. Found: C, 63.63; H, 6.64.

Enol Acetate of Dihydroeurycomalactone (4).—Acetylation of 2a with acetic anhydride in pyridine solution, followed by the usual work-up, gave a 90% yield of enol acetate 4: mp 290° dec (from benzene); $[\alpha]_D$ −30°; ν_{max}^{KBr} 3597, 3333, 1779, 1742, 1712, and 1628 cm^{-1}; λ_{max}^{EtOH} 285 mμ (log ε 2.55).

Anal. Calcd for $C_{21}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 64.38; H, 7.12.

Dihydroeurycomalactone Diacetate (2b).—A mixture of 200 mg of 2a and 10 ml of acetyl chloride was heated on the steam bath for 10 hr. The reaction mixture was evaporated to dryness and the residue (195 mg) was chromatographed over 4 g of magnesium silicate–Celite (2:1). Elution with petroleum ether furnished the diacetate 2b: mp *ca.* 275–280° dec (from ethanol); $[\alpha]_D$ −36°; ν_{max}^{KBr} 1786, 1739, 1718, and 1277 cm^{-1}; λ_{max}^{EtOH} 285 mμ (log ε 2.52).

Anal. Calcd for $C_{23}H_{30}O_8$: C, 63.58; H, 6.95. Found: C, 63.40; H, 7.01.

Tetraketolactone 5a.—Chromic acid oxidation[6] of 100 mg of 2a at room temperature was followed by usual work-up to provide 75 mg of tetraketone 5a: mp 275° (from ethanol); $[\alpha]_D$ −57°; ν_{max}^{KBr} 1779, 1724, and 1718 cm^{-1}; λ_{max} 292 mμ (log ε 2.03).

Anal. Calcd for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.70; H, 6.30.

Preparation of the Monohydroxylactone 6a and Its Acetate 6b.—A solution containing 100 mg of 6a, 500 mg of zinc amalgam, 1 ml of hydrochloric acid, 3 ml of water, and 10 ml of toluene was heated under reflux for 80 hr. The reaction mixture was cooled to room temperature, the organic layer separated, and the aqueous layer extracted with chloroform. The organic extracts were washed with sodium bicarbonate and water, dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. This gave 90 mg of a product which was purified by chromatography. Elution with petroleum ether–benzene (1:1) furnished the hydroxylactone 6a: mp 220° (from petroleum ether–benzene); $[\alpha]_D$ +40°; ν_{max}^{KBr} 3448 and 1745 cm^{-1}; mass spectrum *m/e* 306 (M^+).

Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.46; H, 9.86. Found: C, 74.31; H, 9.70.

Acetylation of 6a by the usual techniques gave the corresponding acetate 6b: mp 135° (from ethanol); $[\alpha]_D$ +30°; ν_{max}^{KBr} 1779, 1739, and 1228 cm^{-1}.

Anal. Calcd for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.41; H, 9.19.

Ketolactone 6c.—To a solution of 100 mg of 6a in 5 ml of 90% acetic acid, a solution of 100 mg of chromic anhydride in 3 ml of 90% acetic acid was added dropwise. The reaction was allowed to stand at room temperature for 2 hr. Water was added, and the organic compound was extracted with chloroform. The organic layer was washed, dried, filtered, and evaporated to dryness, furnishing 90 mg of ketolactone 6c: mp 198–200° (from ethanol); $[\alpha]_D$ −75°; ν_{max}^{KBr} 1786 and 1721 cm^{-1}; λ_{max}^{EtOH} 300 mμ (log ε 1.76).

Anal. Calcd for $C_{19}H_{28}O_3$: C, 74.96; H, 9.30. Found: C, 74.59; H, 9.43.

The 2,4-dinitrophenylhydrazone derivative was obtained as yellow-orange crystals, mp 135°, λ_{max}^{EtOH} 358 mμ (log ε 3.85).

Anal. Calcd for $C_{25}H_{32}O_8N_4$: N, 11.56. Found: N, 11.04.

Tetrahydroxylactone 5b.—Sodium borohydride (200 mg) was added in small portions to 100 mg of 2a in 10 ml of methanol. Stirring was continued for 3 hr. Water was added, and the solution was neutralized with dilute sulfuric acid. Extraction with chloroform afforded 60 mg of noncrystalline tetrol 5b, which showed no keto band in the ir.

Treatment of 100 mg of 5b in dioxane solution with 10 ml of 0.25 *M* periodic acid showed that the cleavage of α-glycol is complete after 4 hr.

Hydroxydiketolactone 7a and Its Acetate 7b.—To a solution of 100 mg of 2a in 10 ml of glacial acetic acid, 300 mg of zinc powder and 2 ml of concentrated hydrochloric acid were added. The reaction mixture was gently refluxed for 6 hr, 1 ml of concentrated hydrogen chloride being added after 3 hr. The solution was cooled, extracted with chloroform, washed, dried, filtered, and concentrated *in vacuo*. The hydroxydiketolactone 7a (90 mg) was recrystallized from ethanol: mp 262°; $[\alpha]_D$ +11°; ν_{max}^{KBr} 3424, 1779, and 1706 cm^{-1}; λ_{max}^{EtOH} 282 mμ (log ε 1.84).

Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.83. Found: C, 68.50; H, 7.97.

Acetylation of 7a with acetyl chloride under the conditions described previously provided the corresponding acetate 7b: mp 135–140° (from ethanol); $[\alpha]_D$ −11°; ν_{max}^{KBr} 1779, 1745, 1715, and 1231 cm^{-1}; λ_{max}^{EtOH} 280 mμ (log ε 2.61).

Anal. Calcd for $C_{21}H_{28}O_6$: C, 67.00; H, 7.49. Found: C, 67.32; H, 7.60.

Clemmensen Reduction of 7a.—A solution of 100 mg of 7a, 10 ml of toluene, 1 ml of concentrated hydrochloric acid, 3 ml of water, and 500 mg of zinc amalgam was heated under reflux for 80 hr. After the usual work-up, there was obtained 90 mg of hydroxylactone 6a: mp 220°; $[\alpha]_D$ +40°; identical in all aspects with the compound obtained above.

Eurycomol (9a).—600 mg of sodium borohydride was slowly added, with stirring, to a solution of 300 mg of 1a in 40 ml of methanol containing 600 mg of boric acid. Stirring was continued for 2 hr after addition was finished. Water was added, and the solution was neutralized with dilute sulfuric acid. Extraction with chloroform furnished 150 mg of noncrystalline 8: $[\alpha]_D$ −25°; ν_{max}^{KBr} 3462, 3360, 1752, 1650, and 1625 cm^{-1}.

This material was used as such for the rearrangement reaction, which was performed as follows. 8 (200 mg) was treated with 40 ml of 10% sulfuric acid at reflux temperature for 3 hr. The reaction mixture was cooled, water was added, and the compound was extracted with chloroform. The organic layer was washed, dried, filtered, and evaporated, thus affording 150 mg of a yellow compound which was chromatographed over 3 g of magnesium silicate–Celite (2:1).

Elution with 200 ml of benzene gave eurycomol (9a), which was recrystallized from ethyl alcohol: mp 265°; $[\alpha]_D$ +14°; RD (*c* 0.001, dioxane) $[\Phi]_{600}$ +244°, $[\Phi]_{350}$ +367°, $[\Phi]_{296}$ +215°, $[\Phi]_{291}$ ±0°, $[\Phi]_{282}$ −380°, $[\Phi]_{273}$ −123°, $[\Phi]_{240}$ −5460°, and $[\Phi]_{232}$ −3240°; ν_{max}^{KBr} 3571, 3424, 1754, 1655, and 1628 cm^{-1}; λ_{max}^{EtOH} 224 mμ (log ε 4.08), 270 (2.68), 279 (2.57), and 308 (1.55).

Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.64. Found: C, 72.00; H, 7.50.

Eurycomol Monoacetate (9b) and Diacetate (9c).—A solution containing 200 mg of 9a, 3 ml of pyridine, and 4 ml of acetic anhydride was heated on the steam bath for 10 hr. The reaction mixture was then evaporated to dryness *in vacuo*. The

residue (190 mg) was chromatographed over 4 g of magnesium silicate–Celite (2:1).

Elution with petroleum ether–benzene (1:1) afforded the diacetate **9c**: mp 235–240° (from ethyl alcohol); $[\alpha]D$ +20°; ν_{max}^{KBr} 1764, 1724, and 1234 cm^{-1}; λ_{max}^{EtOH} 223 mμ (log ε 3.48), 270 (2.72), 274 (2.68), and 279 (2.71).

Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.04. Found: C, 68.68; H, 7.00.

Further elution with benzene furnished the monoacetate **9b**: mp 255–260° (from ethyl alcohol); $[\alpha]D$ +40°; ν_{max}^{KBr} 3472, 1754, 1724, 1650, 1625, and 1234 cm^{-1}; λ_{max}^{EtOH} 223 mμ (log ε 3.44), 270, (2.27), 274, (2.22), and 279 (2.24); nmr 0.95 (8-CH_3), 1.35 (d, J = 6 cps, 13-CH_3), 2.05 (6-OAc), 2.31 (1-CH_3), 2.67 (4-CH_3), and 6.98 ppm (2 aromatic H).

Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.36; H, 7.31. Found: C, 70.10; H, 7.14.

Reduction of Eurycomol (9a) with Lithium Aluminum Hydride.—To a solution of 1 g of $LiAlH_4$ in 40 ml of anhydrous tetrahydrofuran, cooled at 0°, 100 mg of **9a** in tetrahydrofuran was slowly added. The reaction mixture was stirred for 3 hr. Ethyl acetate was then slowly added. After filtration and extraction with chloroform, an amorphous material was obtained: ν_{max}^{KBr} 3570, 1656, and 1626 cm^{-1}; λ_{max}^{EtOH} 248 mμ (log ε 2.74), 254 (2.77), 260 (2.79), 269 (2.82), and 279 (2.76).

When compound **11a** was treated with periodic acid under the conditions described above for the tetrahydroxylactone **5b**, the cleavage of the α glycol was achieved in less than 5 hr.

Deoxyeurycomol (10a) and Its Acetate (10b).—A solution of 80 mg of eurycomol (**9a**) in 20 ml of acetic acid was treated in a hydrogen atmosphere with 80 mg of prereduced platinum oxide. After taking up 1 mol of hydrogen, the catalyst was filtered, water was added, and the product was extracted with chloroform. The organic layer was washed, dried, filtered, and concentrated under reduced pressure to give deoxyeurycomol (**10a**): mp 215° (chloroform); $[\alpha]D$ +25°; ν_{max}^{KBr} 3424, 1754, 1658, and 1628 cm^{-1}; λ_{max}^{EtOH} 224 mμ (log ε 4.10), 261 (2.38), 270, (2.42), and 279 (2.36).

Anal. Calcd for $C_{19}H_{24}O_3$: C, 75.96; H, 8.05. Found: C, 76.01; H, 8.15.

Acetylation of **10a** under usual conditions furnished the corresponding acetate **10b**: mp 110°; $[\alpha]D$ +27°; ν_{max}^{KBr} 1779, 1742, 1634, 1618, and 1231 cm^{-1}; λ_{max}^{EtOH} 224 mμ (log ε 4.05), 270 (2.09), and 279 (2.04).

Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.65; H, 7.65. Found: C, 73.38; H, 7.50.

Preparation of Triol 11b.—A solution of 100 mg of **10a** in 20 ml of anhydrous tetrahydrofuran was reduced with 1 g of $LiAlH_4$ in 20 ml of the same solvent. At the end of the reaction, the excess of reagent was decomposed by careful addition of ethyl acetate. Addition of water and then 20% sulfuric acid was followed by extraction with chloroform. After washing and drying, evaporation of the solvents afforded 85 mg of triol **11b**: mp 190° (from chloroform); ν_{max}^{KBr} 3333 and 1484 cm^{-1}.

Anal. Calcd for $C_{19}H_{34}O_3$: C, 73.50; H, 11.03. Found: C, 73.14; H, 11.09.

Preparation of Triacetate 3b.—A solution containing 200 mg of isoeurycomalactone (**1c**), 4 ml of acetic anhydride, and 3 ml of pyridine was heated on the steam bath for 8 hr. The reaction mixture was then evaporated to dryness *in vacuo*. The amorphous residue was chromatographed to afford 120 mg of triacetate **3b**: mp 245° (from ethyl alcohol); $[\alpha]D$ −95°; ν_{max}^{KBr} 1792, 1742, 1672, 1613, 1285, and 1227 cm^{-1}; λ_{max}^{EtOH} 285 mμ (log ε 4.35).

Anal. Calcd for $C_{25}H_{30}O_9$: C, 63.28; H, 6.37. Found: C, 63.55; H, 6.24.

Dihydroisoeurycomalactone (13).—Catalytic reduction of **1c** (90 mg) with 180 mg of palladium on carbon (10%) in 10 ml of methanol in a hydrogen atmosphere furnished the saturated compound **13**: mp 230° (from methanol); $[\alpha]D$ +20°; ν_{max}^{KBr} 3521, 3448, 1757, and 1712 cm^{-1}; λ_{max}^{EtOH} 278 mμ (log ε 2.22).

Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.12; H, 7.47. Found: C, 65.10; H, 7.51.

Hydroxylactone 6a.—When dihydroisoeurycomalactone (**1c**) was reduced under the Clemmensen reaction conditions described above, the hydroxylactone **6a** was isolated. Recrystallization from petroleum ether afforded the analytical sample: mp 220°; $[\alpha]D$ +40°; ν_{max}^{KBr} 3496, 1754, and 1458 cm^{-1}. This compound was shown to be identical with the substance obtained from **2a**. The melting points and $[\alpha]D$ values were identical, and the ir curves were superimposable.

Preparation of the Acetoxy Ketone 14.—Oxidation of the acetoxy alcohol **9b** with chromic acid in the usual manner[16] afforded the acetoxy ketone **14**: mp 225° (from ethanol); CD (*c* 0.0014, dioxane) $[\Theta]_{298-301}$ −3800°; $[\Theta]_{294-296}$ −3930°.

When **14** was dissolved in pyridine and the solution was heated to reflux, no change was observed. The starting material was recovered.

Registry No.—**1a**, 23062-24-0; **1a** bis-2,4-dinitrophenylhydrazone, 23102-76-3; **1b**, 23062-25-1; **1c**, 23062-26-2; **2a**, 23042-48-0; **2a** 2,4-dinitrophenylhydrazone, 23042-49-1; **2b**, 23102-77-4; **3a**, 23042-50-4; **3b**, 23042-51-5; **4**, 23042-52-6; **5a**, 23042-53-7; **6a**, 23042-54-8; **6b**, 23042-55-9; **6c**, 23042-56-0; **6c** 2,4-dinitrophenylhydrazone, 23042-57-1; **7a**, 23042-58-2; **7b**, 23042-59-3; **8**, 23042-60-6; **9a**, 23102-78-5; **9b**, 23042-61-7; **9c**, 23042-62-8; **10a**, 23042-63-9; **10b**, 23102-79-6; **11a**, 23042-64-0; **11b**, 23042-65-1; **13**, 23042-48-0; **14**, 23042-67-3; β-sitosterol, 83-46-5; β-sitosterol acetate, 915-05-9; campesterol, 474-62-4; campesterol acetate, 3037-45-4; 2,6-dimethoxybenzoquinone, 530-55-2.

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